HETEROGENEOUS OXIDATION OF FERROUS IRON FOR TREATMENT OF MINE DRAINAGE [1]

Brian A. Dempsey[2], Jon Dietz, Byong-Hun Jeon, Heath C. Roscoe, and Ryan Ames

Abstract. Heterogeneous oxidation of ferrous iron in AMD was studied at bench-top in the laboratory, at two passive abiotic treatment systems for AMD, in an aerated ditch to which ferric oxide sludge had been added, and in batch and recirculated sludge systems that were designed for abiotic heterogeneous oxidation of AMD at pH between 5 and 6.8. Heterogeneous oxidation accounted for between 60 and 99% of total oxidation of Fe(II) for the conditions that were tested. In bench-scale lab tests, the heterogeneous rate constant was $k_2 = 3.1 \times 10^{-8}$ $(mg/L)^{-1}sec^{-1}$ for 19.3 to 23.5°C using synthetic mine drainage solutions and E_{act} was 180 kJ/mol for k_2 (Ames 1998). In field tests at passive treatment facilities, average k_2 was 2.2×10^{-8} $(mg/L)^{-1}sec^{-1}$ for 11.7 to 19.2°C (Roscoe 1999). In large-scale tests with recirculated ferric oxide sludge, ferrous iron removal rates were above 1000 $g/m^2/d$ for pH as low as 5.4 and k_2 was 1.7×10^{-8} $(mg/L)^{-1}s^{-1}$ at 15°C (Dietz & Dempsey, 2001). The k_2 values were consistent with values previously reported by Tamura & Nagayama (1976) and by Sung and Morgan (1980), but both of those studies were conducted at higher pH and for low ferric oxide and sulfate concentrations. Sung & Morgan concluded that heterogeneous oxidation became more important as the pH rose above 7, but this was due to their dependence on fresh precipitation of a relatively low concentration of ferric oxide. Our work showed that heterogeneous oxidation is particularly useful for AMD treatment at pH 5 to 6.8. Heterogeneous oxidation at moderately acidic pH also resulted in relatively dense sludge. These kinetic parameters and mass transfer constants for O_2 and for CO_2 provide a basis for design of treatment processes that can operate at high areal capacity (greater than 1000 $g/m^2/d$) for net alkaline AMD waters while producing sludge that exceeds 15% (w/w) after settling.

Additional Key Words: auto-catalysis, passive treatment, oxidation rate

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Background

Heterogeneous oxidation of Fe(II) is generally accepted as one mechanism for the oxidation of Fe(II), but the relevance of heterogeneous oxidation to treatment of acid mine drainage (AMD) has not been widely accepted. Tamura et al (1976) studied heterogeneous oxidation of adsorbed Fe(II) for pH 6.2 to 6.6 and total Fe(III) up to 30 mg/L. Sung & Morgan (1980) did similar work but at pH 7.2 and total Fe(III) up to 3 mg/L. Both reported heterogeneous oxidation rate constants (k_2) of 2.6×10^{-8} mg/L/s at 25°C. These data were also cited in Stumm and Morgan (1996). Sung & Morgan reported that heterogeneous oxidation of Fe(II) increased linearly with $\{H^+\}$ while homogeneous oxidation of Fe(II) increased with $\{H^+\}^2$. These investigators reported the following rate equations for the homogeneous for pH > 5 and for the heterogeneous reactions.

$$\text{Homogeneous rate} = k_1 [Fe^{2+}]\{O_2\}\{H^+\}^{-2} \qquad \textbf{(1)}$$

$$\text{Heterogeneous rate} = k_2\, [Fe(III)][Fe^{2+}]\{O_2\}/\{H^+\} \qquad \textbf{(2)}$$

Sung & Morgan (1980) were clear that the rate of heterogeneous oxidation of Fe(II) was directly proportional to the concentration of ferric oxide, as described in equation (2). For a fixed concentration of ferric hydroxide, equations (1) and (2) indicate that the heterogeneous oxidation process should become increasingly important relative to homogeneous oxidation with decreasing pH. Some investigators have suggested that that ratio of heterogeneous to homogeneous oxidation should increase with pH, based on the Sung & Morgan statement that "autocatalysis is noticeable only for pH around 7 and above." Autocatalysis requires initial formation of ferric oxide by means of homogeneous oxidation, which increases with $\{H\}^2$. This paper focuses on catalysis of heterogeneous oxidation by addition of ferric oxide, rather than on autocatalysis.

Tüfecki & Sarikaya (1996) were the first to study catalytic effects of higher concentrations of ferric oxides. At pH 6.7, they reported that ferric oxides increased the rate of Fe(II) oxidation up to about 300 mg/L Fe(III). They did not observe increased rates at higher concentrations of ferric oxide. However, their initial concentration of Fe(II) was low, so that almost all of the Fe(II) was adsorbed at pH 6.7. Their failure to observe an increased rate of oxidation of Fe(II) with ferric oxide above 300 mg/L was in apparent disagreement with equation (2).Heterogeneous oxidation of Fe(II) is important in many environments. Wehrli (1990), Stumm & Sulzberger (1992), and others have shown that adsorbed Fe(II) is a stronger reducing agent than dissolved Fe(II), which is equivalent to saying that adsorbed Fe(II) is more easily oxidized than dissolved Fe(II). Adsorbed Fe(II) has been implicated in the reduction of U(VI), Cr(VI), and nitro-aromatics. Grenthe *et al*. (1992) showed that the Fe_2O_3/Fe(II) couple controlled the reduction potential in anoxic systems.

Problem Statement

Sung & Morgan (1980) concluded that heterogeneous oxidation became more important as the pH rose above 7. Tüfecki & Sarikaya (1996) showed that increasing concentration of ferric oxide increased the rate of oxidation of Fe(II), but only up to 300 mg/L of ferric oxide. These observations are in apparent conflict with published rate equations for the heterogeneous oxidation of Fe(II).

Objective

The objective of this paper was to investigate and quantify the heterogeneous oxidation of Fe(II) for conditions that might exist during treatment of AMD. The long-term goal of this research was to apply heterogeneous oxidation for optimization of abiotic treatment processes for AMD.

Methods

Samples for measurement of total Fe(II) were collected in acid-cleaned polyethylene bottles, H_2SO_4 was added to $pH<2$, and samples were analyzed within 72 hours using 1,10-phenanthroline (APHA 1989; Standard Methods 3500-Fe(D)). Samples for dissolved Fe(II) were analyzed using 1,10-phenanthroline immediately after filtration through 0.2 μm membrane filters. Temperature and pH were measured in the field with a VWR Scientific 2000 pH meter equipped with combination pH and temperature probes, or with various systems in the laboratory. DO was measured with a YSI 54a meter. DO probes measure activity and therefore DO is expressed as $\{O_2\}$.

Rate constants were determined in a variety of laboratory and field experiments. Experimental conditions for the laboratory studies were described by Ames (1998). Field sites included two passive treatment systems in Jefferson County, PA. That have been described by Roscoe (1999) and by Dempsey et al. (2001): the Howe Bridge system is conventional passive, with an anoxic limestone drain, abiotic ponds, and wetlands; the C&K coal system included anoxic limestone drain, a small waterfall, and a shallow channel. Field tests were also run using discharge from Bird Mine pool (Johnstown, PA). Ferric oxide from a passive abiotic pond was dumped into a ditch that received discharge from Bird Mine. In other tests at Bird Mine, water was passed through an anoxic limestone drain prior to entering a 400 gal reactor and then a 400 gal sedimentation tank. The system was run in either batch or continuous-mixed reactor (CMR) mode. For CMR experiments, sludge was settled in the sedimentation tank and then re-circulated to the reactor, and the homogeneous rate constant (k_1) and the heterogeneous rate constant (k_2) were calculated using equation (3).

$$\{\Delta[\mathrm{Fe(II)}]\{\mathrm{H}^+\}^2_{\mathrm{avg}}\} / \{\tau\,[\mathrm{Fe(II)}]_{\mathrm{avg}}\,\{\mathrm{O}_2\}_{\mathrm{avg}}\} = k_1 + k_2\{\mathrm{H}^+\}_{\mathrm{avg}}[\mathrm{Fe(III)}]_{\mathrm{avg}} \qquad \mathbf{(3)}$$

Values for $\Delta[\mathrm{Fe(II)}]$, $\{\mathrm{H}^+\}_{\mathrm{avg}}$, $\{\mathrm{O}_2\}_{\mathrm{avg}}$, and $[\mathrm{Fe(III)}]_{\mathrm{avg}}$ were derived from measurements. The hydraulic residence time (τ) was calculated based on pumped flow and tank volume. The rate constants k_1 and k_2 were obtained from least-squares linear regression of the left-hand side of equation (3) against $\{\mathrm{H}^+\}_{\mathrm{avg}}[\mathrm{Fe(III)}]_{\mathrm{avg}}$.

Results

The effect of ferric oxide solids on the oxidation of Fe(II) was demonstrated by addition of ferric oxide sludge to a channel that also received AMD. The sludge had been produced by slow abiotic oxidation of Fe(II) at pH~6.5. The rate of oxidation of Fe(II) was increased by the presence of ferric oxide solids, as shown in Figure 1. The effect was negligible 300 feet (2.3 min of travel time) from the addition point, and the effect increased with travel time as shown by data at 1600 ft (12 min) and at 2600 ft (16 min) sample locations. The increase in oxidation occurred in spite of the observation that pH was significantly lower during passage of the slug.

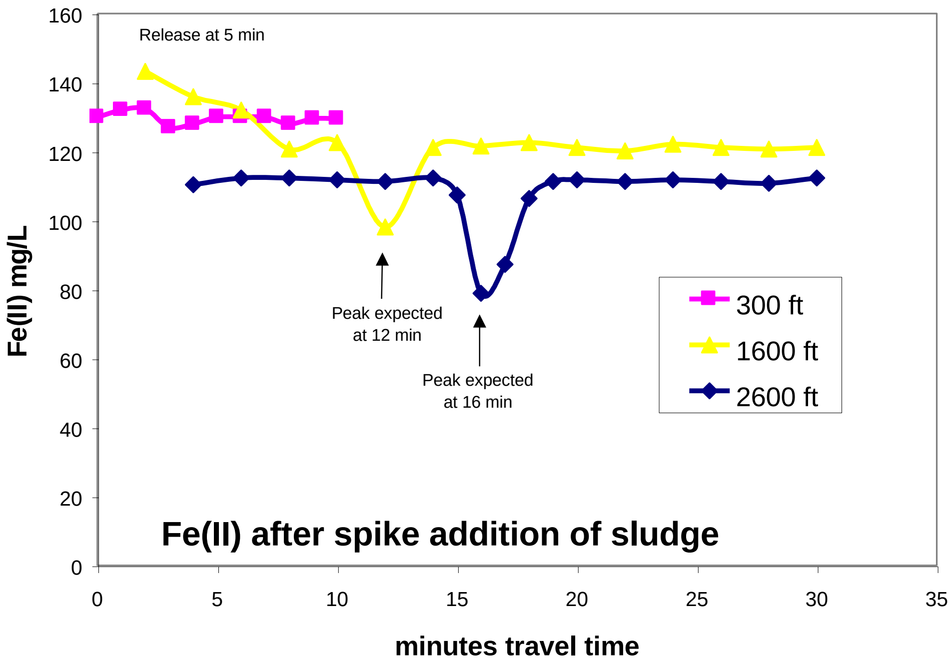

Figure 1. Effect of a slug addition of ferric oxide solids on the Fe(II) in a ditch..

The effect of ferric oxide solids on the rate of oxidation of Fe(II) has been shown in several other experimental venues. For example, results that are shown in Figure 2 were obtained from pilot batch tests on mine-pool water that had been passed through an anoxic limestone drain in order to produce net alkalinity, i.e. initial alkalinity greater than the acidity created by complete oxidation of Fe(II) and Mn(II). Ferric oxide solids were re-circulated into a 400 gal oxidation reactor, in a process analogous to conventional activated sludge for treatment of sanitary wastewaters. These results demonstrated that the rate of oxidation of Fe(II) was directly proportional to the concentration of ferric oxide solids, for fixed pH, [Fe(II)], and $\{O_2\}$. When initial Fe(III) was very low (top two lines in Figure 2), then the rate of Fe(II) oxidation increased with time, due to autocatalytic effects that were reported by Sung & Morgan (1980), and consistent with equation (3). For high initial Fe(III), oxidation was most rapid at the start of the experiment, when [Fe(II)] was highest.

Results from pilot CMR experiments (Dietz & Dempsey, 2001) are shown in Figure 3, where $K_{total} = \Delta[Fe(II)] / \{\tau\ [Fe(II)]_{avg}\}$ and the overall expression on the y-axis is identical to the left-hand side of Equation (3). The slope of the linear regression is k_2 and the intercept is k_1. Data in Figure 3 are from pilot-scale recirculation tests.

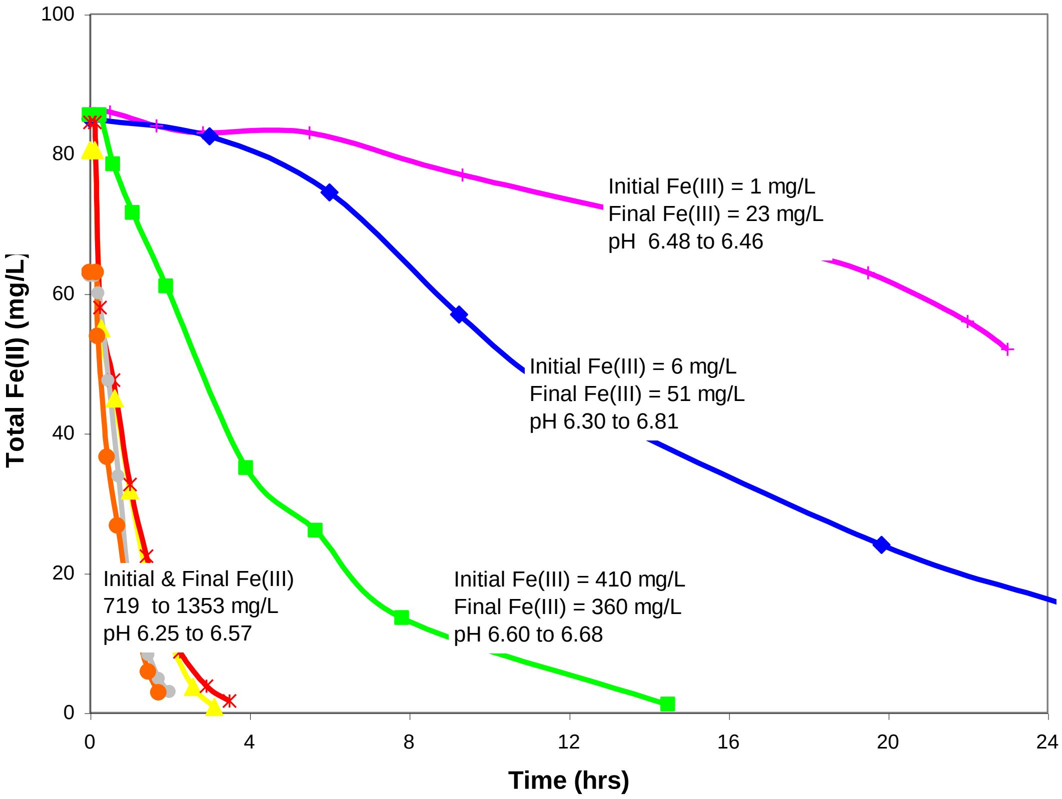

Figure 2. Pilot-scale batch tests showed that the rate of oxidation of Fe(II) increased with the concentration of ferric oxide solids, even at very high ferric oxide concentration.

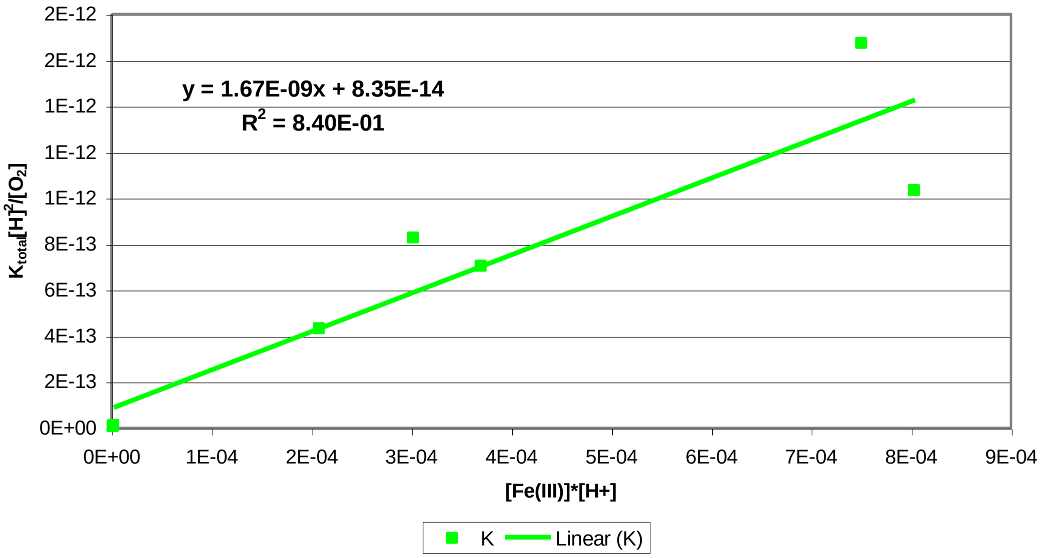

Figure 3. Determination of k_2 from the slope and k_1 from the intercept, using Eqn (3). Data in this plot are from recirculated sludge CMR experiments.

Table 1 summarizes k_1 and k_2 values from the literature and from a number of our studies with AMD systems. Ames (1998) measured $k_2 = 3.1\text{x}10^{-8}$ $(\text{mg/L})^{-1}\text{sec}^{-1}$ for 19.3 to 23.5°C and E_{act} of 180 kJ/mol for k_2 in bench-scale tests, using synthetic AMD solutions with chemistry similar to field sites. Roscoe (1999) measured average k_2 of $2.2\text{x}10^{-8}$ $(\text{mg/L})^{-1}\text{sec}^{-1}$ for 11.7 to 19.2°C in field studies at AMD passive treatment sites. Dietz and Dempsey (2001) measured ferrous iron removal rates greater than 1000 $\text{g/m}^2\text{/d}$ in large-scale field-tests for pH as low as 5.4 and k_2 was $1.7 \text{ x } 10^{-8}$ $(\text{mg/L})^{-1}\text{s}^{-1}$ at 15°C.

Table 1. Rate Constants for the homogeneous (k_1) and heterogeneous (k_2) oxidation of Fe(II).

Researcher(s)	*Temp (°C)*	*Fe(III) mg/L*	*k_1 (mol/L/s)*	*k_2 (L/mg/s)*
Ames (1998)	19.3-23.5	<100	$9.3\text{x}10^{-14}$	$3.1\text{x}10^{-8}$
Tamara et al (1976)	25	<30	$2.0\text{x}10^{-14}$	$2.6\text{x}10^{-8}$
Sung & Morgan (1980)	25	<3	$3.3\text{x}10^{-14}$	$2.6\text{x}10^{-8}$
Stumm & Morgan (1996)	25	n.a.	$9\ 10^{-14}$	
Millero et al (1987) & Liang et al (1993)	25	n.a.	10^{-14} to 10^{-12}	
Dempsey et al (2001)	17	<100		$6.0\text{x}10^{-9}$
Dietz & Dempsey (2001)	15	10 to 2,000	$8.4\text{x}10^{-14}$	$1.7\text{x}10^{-8}$

Heterogeneous oxidation accounted for between 60 and 99% of the oxidation of Fe(II) in these AMD systems. The k_2 values were consistent with values that were previously reported by Tamura & Nagayama (1976) and by Sung and Morgan (1980), both at higher pH and for low ferric oxide and sulfate concentrations.

Heterogeneous oxidation provides additional benefits. Dempsey and Jeon (2001) reported that settled sludge from heterogeneous oxidation was dewatered more easily, was less compressible, had lower reduced viscosity and much lower specific resistance to filtration than sludge that was generated by homogeneous oxidation.

Summary

Sung & Morgan (1980) concluded that heterogeneous oxidation became more important as the pH rose above 7, but this was due to the low initial concentrations of ferric oxide in their experiments. The system that they studied was an autocatalytic system, with oxidation rate increasing as the concentration of ferric oxide increased. Our work showed that the rate equations published by Tamura et al (1976) and by Sung & Morgan (1980) were correct and are applicable to chemical conditions typical for AMD.

Our experiments showed that the heterogeneous rate was directly proportional to the concentration of Fe(III) over the entire experimental range (12 to 1900 mg/L). This result was in contradiction to results published by Tüfecki & Sarikaya (1996), but consistent with the published rate equations for heterogeneous oxidation of Fe(II).

Our work showed that heterogeneous oxidation was particularly useful for AMD treatment at pH 5 to 6.8, and could produce Fe(II) oxidation rates greater than 1000 g/m^2/day, compared to about 20 g/m^2/day for typical abiotic ponds. In addition, Dempsey & Jeon (2001) also showed that ferric solids from treatment of AMD were denser and easier to thicken and dewater when heterogeneous oxidation processes dominated.

These kinetic parameters (k_1 and k_2) and mass transfer constants for O_2 and for CO_2 (reported by Dempsey et al, 2001) should permit the rational design of processes for treatment of AMD.

Citations

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