MECHANISMS OF HETEROGENEOUS FE(II) OXIDATION IN ACID MINE DRAINAGE[1]

Byungtae Park and Brian A. Dempsey[2]

Abstract. The objective of the study was to investigate the sorption and abiotic oxidation of ferrous iron at ferric oxide surfaces at pH 6.8 and 7.0, and to identify changes in ferric oxide phase during the sorption and oxidation processes. Our group previously reported on mechanisms for sorption and heterogeneous oxidation at pH less than 6.5 and on the characteristics of ferric oxide sludge. We have also reported on transformations from amorphous to crystalline ferric oxides as a function of pH and solution composition. Sorption experiments were conducted at room temperature in an anaerobic chamber with 97% N_2 and 3% H_2. An additional oxygen trap was used to ensure an anoxic environment. The Fe(II)/Fe(III) ratio and pH were varied. The rate and extent of sorption of Fe(II) were monitored. Changes in solid phases were monitored using ^{57}Fe-Mössbauer Spectroscopy. Subsequent to sorption, oxidation rate constants and mechanisms were evaluated after exposure to very low partial pressures of O_2. The results showed that oxidation processes that occurred with high Fe(III) to Fe(II) ratios were more complicated in the neutral pH range compared to pH < 6.5, due to phase transformations that resulted in short-term sorption anomalies, such as decreased sorption after conversion from amorphous ferric oxide to goethite or precipitation of mixed Fe(II)/Fe(III) phases that slowly became inert to oxidation. These results are important in the context of treatment processes for AMD that depend on the presence of a ferric oxide phase, that is for high-density sludge processes that result in heterogeneous oxidation of Fe(II) and that are conducted at slightly acid to alkaline pH values.

Additional Key Words: HFO, iron oxide, phase transformation, sorption

_____

[2]Byungtae Park is a Graduate Student, Department of Civil & Environmental Engineering, The Pennsylvania State University, University Park, PA 16802. Brian A. Dempsey is Professor, Department of Civil & Environmental Engineering, The Pennsylvania State University, University Park, PA 16802.

Introduction

Treatment of AMD often involves addition of alkalinity followed by oxidation of Fe(II) to form ferric hydroxide. The abiotic oxidation of Fe(II) is very slow at pH 2 to 3.5. The rate of abiotic oxidation increases exponentially when the pH is above 5, so that the half time for abiotic oxidation of dissolved Fe(II) in the presence of ambient dissolved oxygen concentrations is just a few minutes at pH 7 (Sung and Morgan, 1980).

The rate of oxidation of Fe(II) in AMD can be increased significantly in the presence of ferric oxides (Dietz and Dempsey, 2001). Heterogeneous oxidation has been described by several researchers, and it has been presumed that the process involves sorption of dissolved Fe(II) onto ferric oxide followed by oxidation of the sorbed Fe(II) in the presence of oxygen to form new ferric oxide (Tamura et al., 1976; Sung and Morgan, 1980; Dempsey et al., 2001; Dempsey et al., 2002). Tamura et al. (1976) and Sung & Morgan (1980) reported that the rate of heterogeneous oxidation of Fe(II) decreased linearly with $[H^+]$ while homogeneous oxidation of Fe(II) decreased with $[H^+]^2$.

$$Homogeneous \ rate = -k_{ho} \ [Fe^{2+}][O_2][OH^-]^2 \tag{1}$$

$$Heterogeneous \ rate = -k_{he} \ [Fe(III)][Fe^{2+}][O_2][OH^-] \tag{2}$$

Dempsey et al. (2001, 2002) used the Tamura model to describe oxidation of Fe(II) in passive abiotic systems for treatment of AMD. They reported that heterogeneous oxidation dominated in these systems. Heterogeneous oxidation rate constants were evaluated and were similar to those reported by Tamura et al. (1976) and by Sung and Morgan (1980). Subsequently Dietz and Dempsey (2001) described a treatment process for AMD in which ferric

oxides were recycled to increase the rate of heterogeneous oxidation. They also found heterogeneous rate constants that were similar to the values that had been previously reported.

Dzombak and Morel (1990) reported on the sorption of metals and ligands onto hydrous ferric oxide (HFO), although they did not report on sorption of Fe(II) because of the lack of literature on this subject. Dzombak and Morel found that they had to invoke strong and weak sorption sites to describe experimental results for sorption edges and sorption isotherms, and they reported 0.005 and 0.200 mol sorption sites per mol of Fe(III) for strong and weak sites, respectively. Jeon et al. (2001) studied sorption of Fe(II) onto hematite and onto HFO, and reported sorption at both strong and weak sorption sites, with similar relative concentrations as reported by Dzombak and Morel.

Dietz (2003) studied the sorption and oxidation of Fe(II) in the presence of ferric oxides that formed during treatment of AMD at slightly acidic pH values, as in passive treatment systems. Dietz (2003) proposed a sorption model that was similar to that used by Dzombak and Morel for other metals, i.e. multi-site (strong and weak) and sorption at a limited number of sites.

$$S_x = \equiv[Fe(III)] \times \Gamma_x \times \theta_x \tag{3}$$

where, S_x = sorbed Fe(II),

$[\equiv Fe(III)]$ = Fe(III) concentration, mol/L

Γ_x = sorption site density, mol sites/mol Fe(III)

θ_x = fractional coverage of surface sites = $\dfrac{K_x[Fe(II)_{diss}]}{1 + K_x[Fe(II)_{diss}]}$

$[Fe(II)_{diss}]$ = equilibrium concentration of sorbed Fe(II)

K_x = partition coefficient = $K_x^{app}\{H^+\}^{-x}$

Dietz (2003) found that sorption was accurately described by assuming two mechanisms for sorption (strong and weak sites) and therefore two mechanisms for heterogeneous oxidation, as described by the following equations.

Strong sorption $\equiv Fe(III)O^sH + Fe^{2+} \leftrightarrow \equiv Fe(III)O^sFe(II)^+ + H^+$ (5)

Oxidation $\equiv Fe(III)O^sFe(II)^+ + 1/4\ O_2 \leftrightarrow new \equiv Fe(III)OH + H^+$ (6)

Weak sorption $\equiv Fe(III)O^wH + Fe^{2+} \leftrightarrow \equiv Fe(III)O^wFe(II)OH + 2H^+$ (7)

Oxidation $\equiv Fe(III)O^wFe(II)OH + 1/4\ O_2 \leftrightarrow new \equiv Fe(III)OH$ (8)
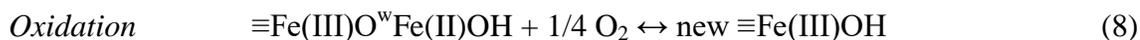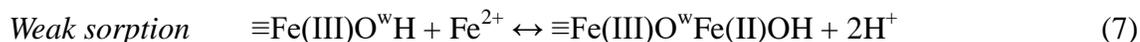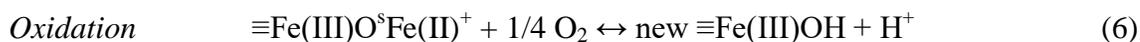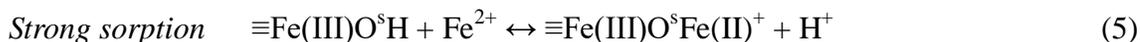
Dietz (2003) indicated that the rate of Fe(II) oxidation was first-order with respect to Fe(III) over the experimental pH range of 5.2 to 6.8 and for Fe(III) concentration from 0 to 2400 mg/L. But {H^+} dependence for heterogeneous oxidation varied from 1.5 to 2.5. He developed a deterministic heterogeneous Fe(II) oxidation model to estimate the total heterogeneous ferrous iron oxidation rate (R_{total}) in M s^{-1} based on two separate oxidation (R_1 and R_2) and sorption (S_1 and S_2) mechanisms.

$$-\frac{\partial[Fe(II)]}{\partial t} = R_{total} = \left(k_{He1} \times [DO] \times S_1\right) + \left(k_{He2} \times [DO] \times S_2\right)$$ (9)

Oxidation of Fe(II) at pH 6.3 to 6.8 occurred dominantly by the heterogeneous oxidation (Dempsey et al., 2002). Dietz (2003) confirmed that the heterogeneous Fe(II) oxidation dominates over homogeneous oxidation at slightly acidic pH values.

Transformation of hydrous ferric oxide into more stable phases was observed (Jang et al., 2003) at pH 6.5 and 8.5 in the presence of divalent transition metals. Solids from the Fe(II)-HFO experiment were identified as goethite with a possible presence of hematite (Jeon et al.,

2003a).   Other investigators also reported that sorption of Fe(II) onto HFO catalyzed dissolution of HFO and precipitation to a more stable phase at pH 8-11 (Tronc et al.,1992; Jolivet et al.,1992).

The objective of this study was to investigate the sorption and abiotic oxidation of ferrous iron at ferric oxide surfaces at neutral pH, and to identify changes in ferric oxide phases during the sorption and oxidation processes.

Materials and Methods

Temperature and pH were measured with an Orion Model 290A meter and calibrated with 4.01 and 7.00 buffers prior to use on a daily bases. Fe(II) was measured colorimetrically by modified 1,10-phenathroline (APHA, 1995; Tamura et al., 1974) to minimize interference of dissolved Fe(III).   After each set of experiments, the samples were reacted for color development inside the chamber and analyzed with a UV/VIS Spectrophotometer.   Dissolved ferrous iron was measured after filtration using a syringe and 0.2 μm filter cartridge.   Adsorbed Fe(II) was defined as the difference between Fe(II) recovered after 20 hr extraction in 0.5N HCl and dissolved Fe(II) recovered after filtration through a 0.2 μm membrane filter.

Distilled, de-ionized water (DI) was used for preparation of all solutions and suspensions. Glassware and plastic bottles were soaked in 10% nitric acid and rinsed with DI, and then dried before use.   Solutions and samples containing Fe(II) were prepared in the chamber.

All experiments of Fe(II) adsorption and oxidation were conducted in an inert atmosphere with 97% N_2 and 3% H_2 at room temperature inside an anaerobic chamber equipped with a palladium catalyst to remove oxygen traces (Coy Lab Products, Inc.).   An additional oxygen trap (Jeon et al., 2003b) was used to obtain a strict anoxic environment for sorption experiment.

A stock solution of 0.250 M Fe(II) was prepared in an anaerobic chamber by dissolving 12.4 g of $FeCl_2 \cdot 4H_2O$ in 250 mL of acidified (pH < 1.0) DI water and preserved in a dark container. The Fe(II) stock solution was calibrated by titration of primary standard $K_2Cr_2O_7$ to the ferroin end point (APHA, 1995). HFO was prepared in the anaerobic chamber by dissolving 0.676 g of $FeCl_3 \cdot 6H_2O$ in 500 mL DI followed by precipitation at pH 6.8-7.0 by slow addition of NaOH for 4 hr, and 500 mL of 0.02 M Na-piperazine N,N'-bis 2-ethane sulfonic acid (Na-PIPES) was added to produce final suspension of 2.5 mM Fe(III).

For the experimental run, the HFO suspension was dispensed into a 1 L glass reactor that contained buffer solution. The reactor was connected to the oxygen trap and the HFO was aged for 24 hours prior to the addition of Fe(II). Subsequently, a syringe was used to insert Fe(II) solution to produce 0.125 mM Fe(II). After 25 min or 24 hr of pre-equilibration of Fe(II) with the HFO suspension, the mixture was transferred to a 1L beaker and contacted with very low partial pressure of oxygen by introducing one interlock volume of air into the chamber. A fine bubble diffuser was used to accelerate the oxygen transfer from the air phase to the liquid suspension. Aliquots of test solution were withdrawn after appropriate time interval for analysis of Fe(II). At the end of each experiment, the Fe(II)-HFO solids were filtered and then dried in the anaerobic chamber for analysis by Mössbauer Spectroscopy to monitor the phase changes of the iron oxides.

Results and Discussion

Results of the oxidation of 0.125 mM Fe(II) in the presence of HFO (2.5 mM Fe(III)) are presented in Figure 1 for four different experimental conditions.
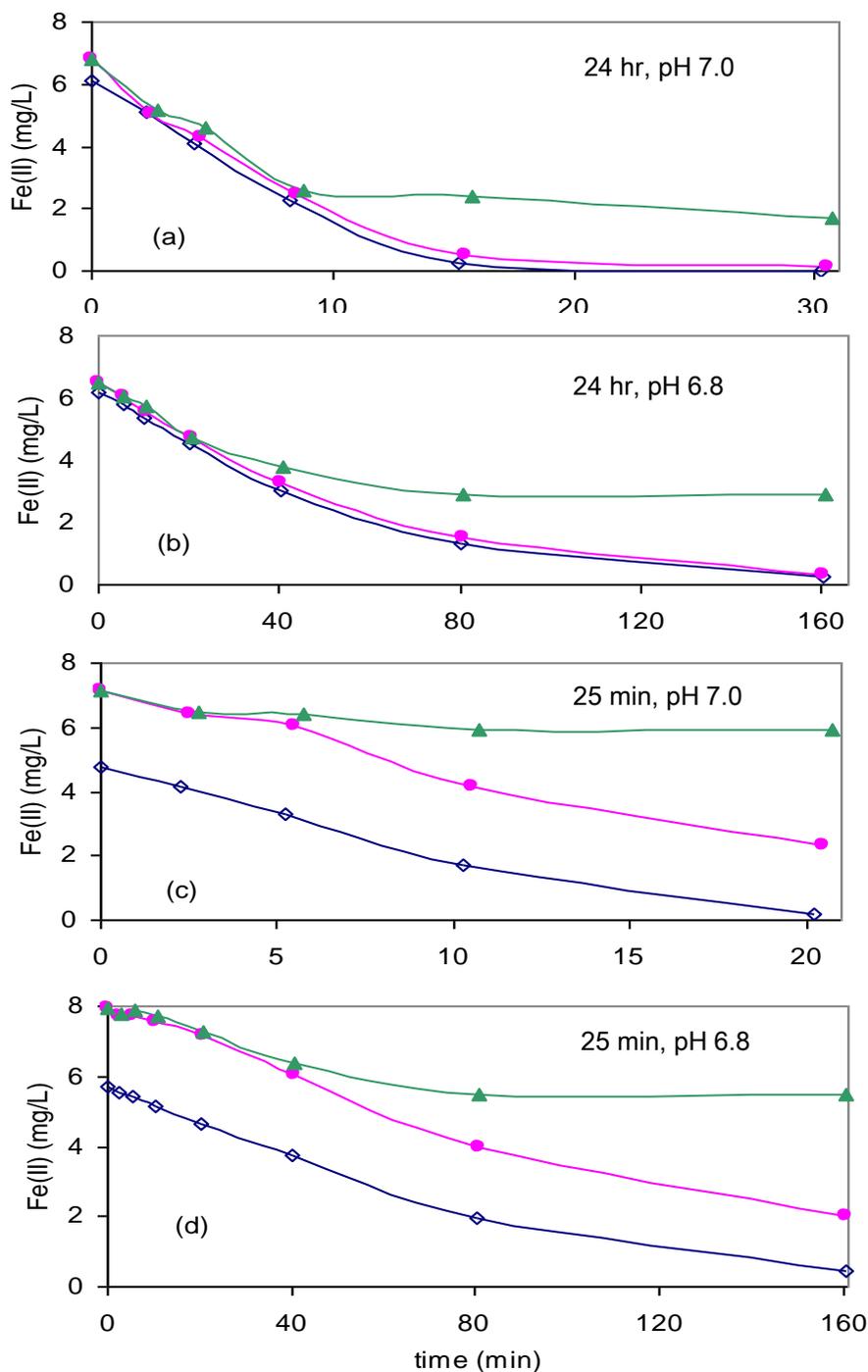
Figure 1. Sorption and oxidation results of 0.125 mM Fe(II) on 2.5 mM HFO: ◊ Dissolved Fe(II), ● 0.5 N HCl extractable Fe(II), ▲ 3 N HCl extractable Fe(II): (a) 24 hr equilibration at pH 7.0, P_{O2} =1894 ppm; (b) 24 hr equilibration at pH 6.8, P_{O2} =1115 ppm; (c) 25 min equilibration at pH 7.0, P_{O2} =1890 ppm; (d) 25 min equilibration at 6.8, P_{O2} =371 ppm

Sorption of Fe(II) and Transformation of HFO to Goethite and Other Phases

Adsorbed Fe(II) is represented by the difference between the two lower lines in Fig. 1, i.e. the difference between 0.5 N HCl extractable Fe(II) and dissolved Fe(II). More sorption was observed for the tests that had been equilibrated for a shorter time. Fig. 2 shows that the initial extent of sorption with 25 minutes of contact between Fe(II) and HFO prior to exposure to O_2 was between 28 and 33%, which is consistent with early reports (Jeon et al., 2003a) for cases where goethite did not form. The extent of sorption after 24 hours of contact between Fe(II) and HFO prior to exposure to O_2 was less than 10%, possibly due to transformation of HFO to more stable phases.
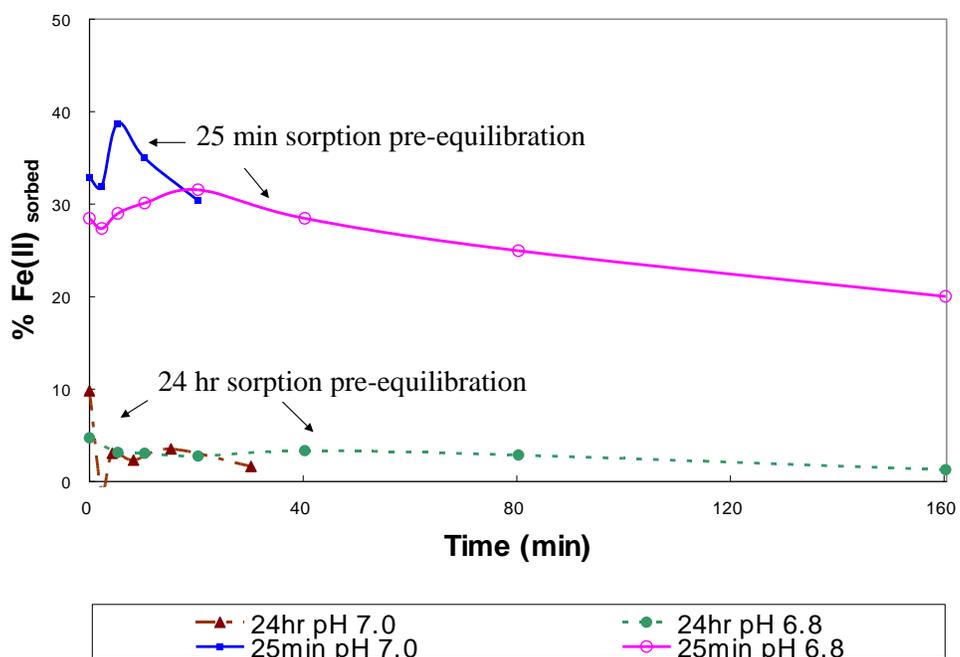
Figure 2.   Extent of Fe(II) sorption (%) compared to the initial 0.5 N HCl extractable Fe(II) for each experimental condition.

When the Fe(II)-HFO suspension was aged 24 hours, the color of the mixture changed from dark brown to yellow. The solids from the batch tests were collected and examined by Mössbauer spectroscopy to monitor the phase transformations (Fig. 3).
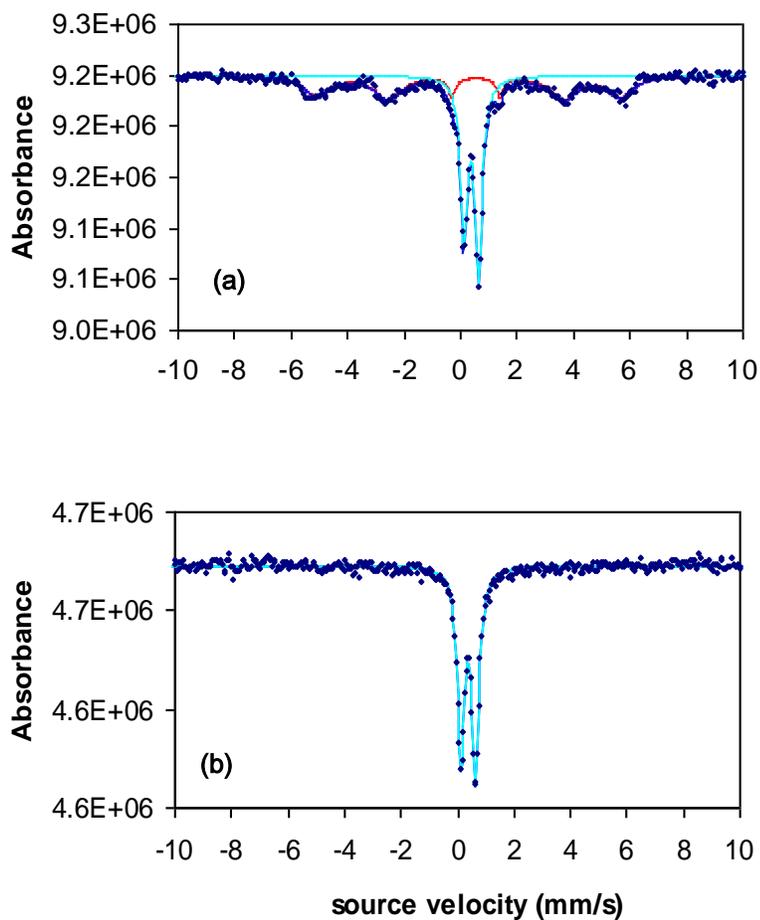
Figure 3. Mössbauer velocity distributions after Fe(II) oxidation; [Fe(II)]=0.125 mM, [HFO]=2.5 mM: (a) 24 hr pre-equilibration at pH 6.8; (b) 25 min pre-equilibration at pH 6.8.

The solid phase from 24 hours pre-equilibration with Fe(II) on HFO at pH 6.8 was identified as goethite, which is consistent with the results reported by previous researchers (Jeon et al., 2003a; Jang et al., 2003) at a similar ratio of Fe(II) to Fe(III). This transformation of iron oxide

from HFO to the more stable goethite may have changed the reactivity of the surface, resulting in the decrease of the Fe(II) sorption. The solids after 25 minutes equilibration at pH 6.8 were identified as ferrihydrite, which is the air dried form of HFO.

Fe(II) was also incorporated in an inert solid phase that could not be extracted using 0.5 N HCl. The fraction of Fe(II) in the inert solid phase is shown by the difference between the two top lines in the plots in Fig. 1. Based on the reported extraction efficiencies of the extraction for 0.5 N and 3 N HCl, it is presumed that the inert solid phase was a mixed Fe(II)/Fe(III) precipitate.

Oxidation of Fe(II) in the Presence of HFO and Other Phases

The rates of Fe(II) oxidation (-d[Fe(II)]/dt) were obtained using the equations described earlier, i.e. equation (1) for homogenous rate, (2) for Tamura et al. and (9) for Dietz heterogeneous. The initial rates were much faster than predicted by previous oxidation models. This is illustrated in Fig. 4.

The rate of Fe(II) oxidation was much lower during the second half of the experiments, when most of the Fe(II) was sorbed rather than dissolved. In addition, the rate constants were much lower during the second phase of the reaction. This was a surprising result, because oxidation in these processes was obviously catalyzed by the ferric oxide and therefore heterogeneous (i.e. compare the observed rate of oxidation compared to the modeled rate of homogeneous) oxidation, but the initial decrease in Fe(II) occurred predominantly from the dissolved fraction of Fe(II). This result was in qualitative (but not quantitative) agreement with Dietz (2003), who found that the rate of oxidation for weakly sorbed Fe(II) was much greater than for strongly sorbed Fe(II). During the second half of these reactions, when most of the Fe(II) was sorbed,

the rates of reaction were slower than the initial rates and were closer to values that would be

predicted by the Tamura and Dietz models for heterogeneous oxidation.
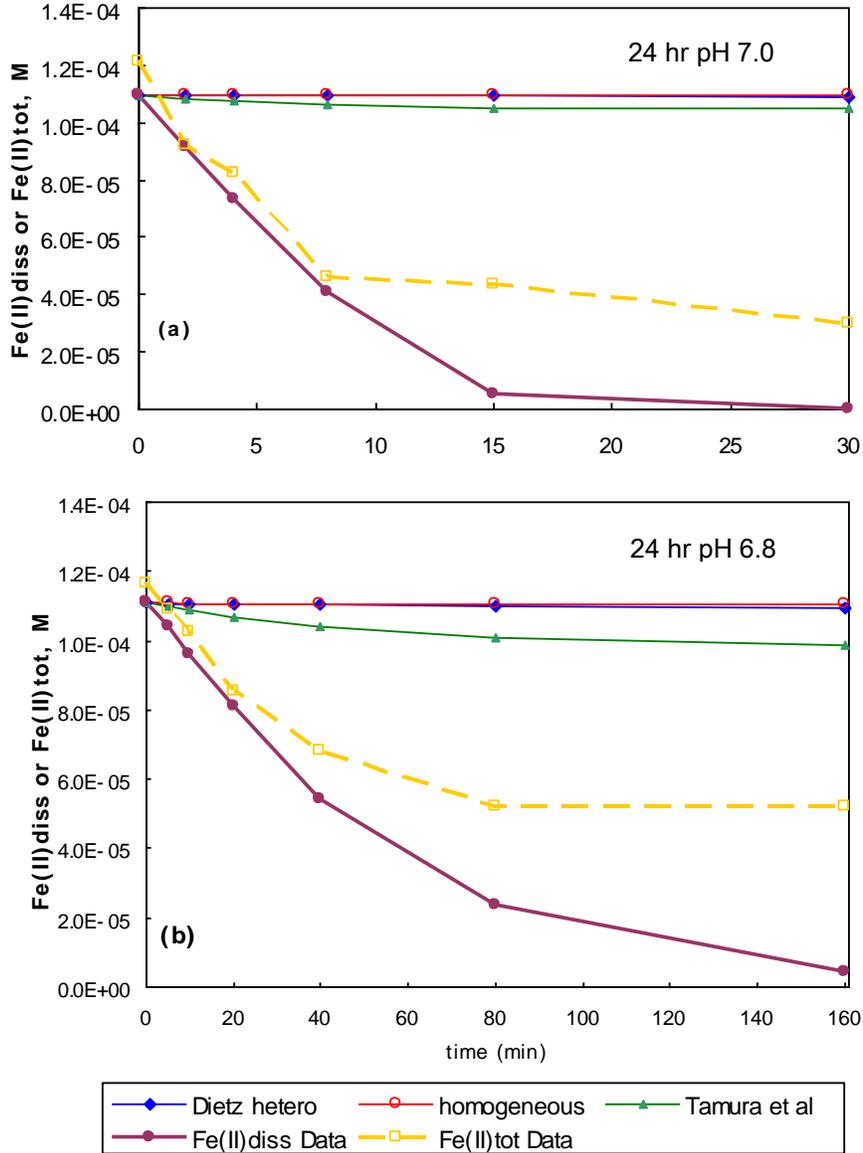
Figure 4. Fe(II) oxidation rates compared to previous models: (a) 24 hr pre-equilibration at pH 7.0, P_{O2} =1894 ppm; (b) 24 hr pre-equilibration at pH 6.8, P_{O2} =1115 ppm.

Fe(II) that was incorporated within an inert phase (relative to extraction by HCl) also appeared to be relatively inert to oxidation. The oxidation of Fe(II) in the inert phase will be studied in greater detail.
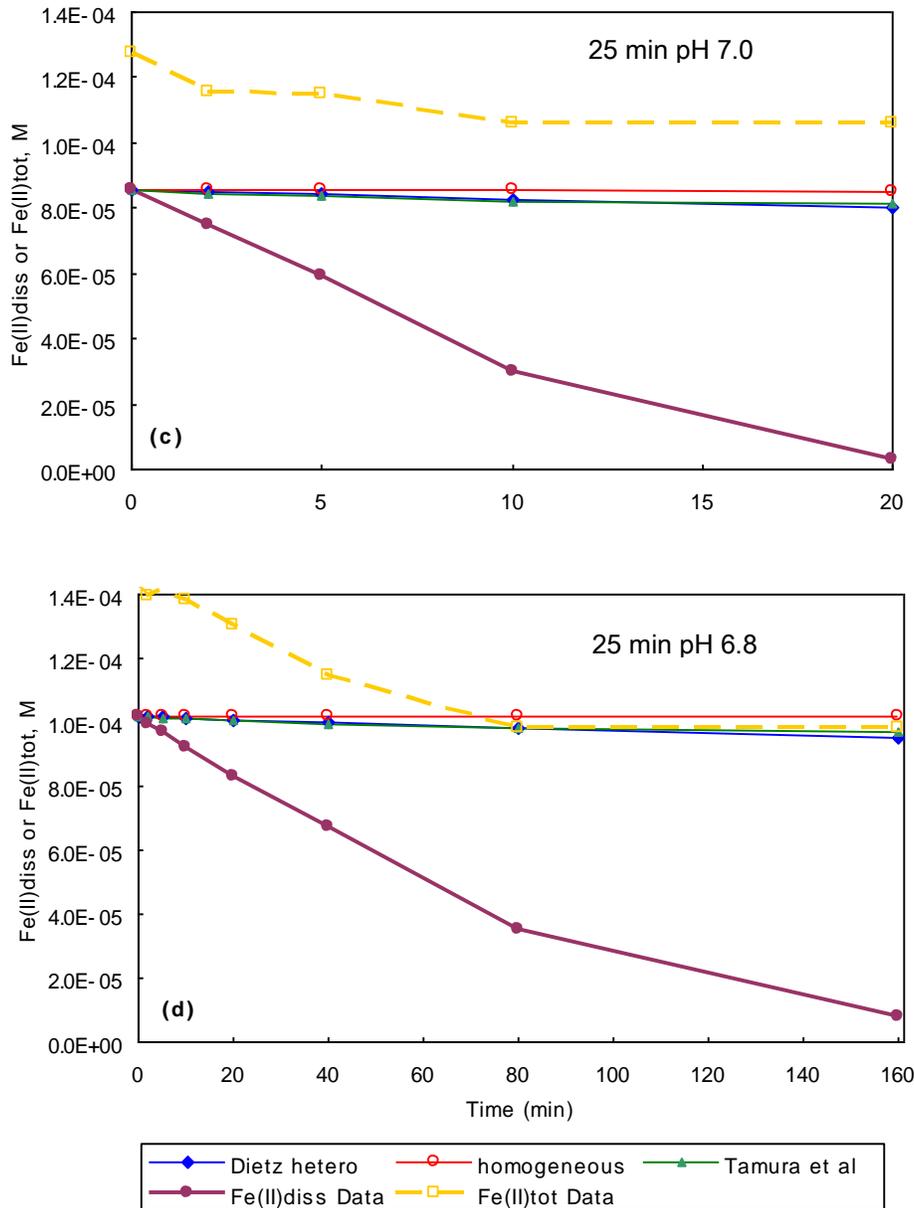
Figure 4 (cont). Fe(II) oxidation rates compared to previous models: (c) 25 min pre-equilibration at pH 7.0, P_{O2} = 1890 ppm; (d) 25 min pre-equilibration at 6.8, P_{O2} = 371 ppm.

Implications for Treatment of Acid Mine Drainage

Abiotic oxidation of Fe(II) at neutral pH in the presence of ferric oxides and low partial pressure of O_2 was much faster than previously reported. This could result in decreased tank size and improved designs for active treatment systems that are operated at pH 6 to 7 (Dietz and Dempsey, 2001). Phase transformations were observed that could be used to explain and control the formation of dense precipitates during passive or active treatments for AMD. There is increasing interest in reuse of ferric oxides from treatment of AMD, and control of the solid phase could be used to increase the value of these precipitates. The incorporation of Fe(II) into the solid phase reduces the immediate O_2 demand and could explain apparent anomalies in consumption of alkalinity in passive treatment systems for AMD, i.e. less consumption of alkalinity than predicted by removal of Fe(II)..

Conclusion

Sorption of ferrous iron on hydrous ferric oxide (HFO) was conducted in an anaerobic chamber at room temperature. The pH was kept constant at either 6.8 or 7.0, HFO was 2.5 mM as Fe(III), and initial Fe(II) was 0.125 mM. Either 25 minutes or 24 hours were provided for pre-equilibration of Fe(II) with HFO. Subsequent abiotic oxidation of Fe(II) was conducted at room temperature and with low dissolved oxygen concentrations that were in equilibrium with 0.0004 to 0.0019 atm of O_2(g).

The extent of sorption after 25 minute pre-equilibration was consistently higher than after 24 hour pre-equilibration, indicating formation of new phases. The Fe(II)-HFO solid after 24 hour sorption was examined by [57]Fe-Mössbauer spectroscopy, and was identified as goethite plus HFO, which is consistent with previous reports.

The apparent rate of Fe(II) oxidation at pH 6.8-7.0 and low partial pressure of oxygen (371-1894 ppm) was much faster than predicted by previous models for heterogeneous oxidation. Oxidation of sorbed Fe(II) was similar to previously reported rates for heterogeneous oxidation.

Fe(II) was also incorporated into a phase that could not be extracted using 0.5 N HCl for 20 hours, but was extracted in 3 N HCl after 24 hours. The nature of the new phase is currently under investigation. Earlier studies have not used more severe extraction and the existence of a new phase might have not been detected in those studies.

The results showed that sorption and oxidation processes at neutral pH were more complicated than previously reported. Phase transformations resulted in decreased sorption due to conversion from amorphous ferric oxide to goethite, and slow precipitation of mixed Fe(II)/Fe(III) phases resulted in a solid phase that was less reactive with respect to oxidation.

Acknowledgements

Literature Citations

APHA (American Public Health Association). 1995. Standard Methods for the Examination of Water and Wastewater. APHA, Washington, D.C. pp 5.7-5.8.

Dempsey, B.A., H.C. Roscoe, R. Ames, R. Hedin, & B.-H. Jeon. 2001. "Ferrous Oxidation Chemistry in Passive Abiotic Systems for Treatment of Mine Drainage". Geochemistry: Exploration, Environment, Analysis, 1(1): 81-88. http://dx.doi.org/10.1144/geochem.1.1.81.

Dempsey, B.A., J. Dietz, B.-H. Jeon, H.C. Roscoe, and R. Ames. 2002. Heterogeneous oxidation of ferrous iron for treatment of mine drainage. Proc. of 2002 National Meeting of ASMR, Lexington, KY, June 9-13. `For some unknown reason, it was not possible to find the doi link to this article.`
`10.21000/JASMR02010487`

Dietz, J.M. 2003. Abiotic heterogeneous ferrous iron oxidation in mine drainage: Modeling and treatment processes. Ph.D Thesis, Pennsylvania State University.

Dietz, J.M., and B.A. Dempsey. 2001. Treatment of Mine Drainage Using Recirculated Iron Oxides in a Complete Mix Reactor. Proc. of 2001 National Association of Abandoned Mine Lands Annual Conference, Athens, OH, August 19-22.

Dzombak, D.A. and F.M. Morel. 1990. Surface Complexation Modeling: Hydrous Ferric Oxide, John Wiley & Sons, New York.

Jang, J-H, B.A. Dempsey, G.L. Catchen, and W.D. Burgos. 2003. Effects of Zn(II), Cu(II), Mn(II), Fe(II), NO3-, or SO42- at pH 6.5 and 8.5 on transformation of hydrous ferric oxide (HFO) as evidenced by Mössbauer spectroscopy. Colloids and Surfaces A: Physicochem. Eng. Aspects 00, 1-14. http://dx.doi.org/10.1016/s0927-7757(03)00134-1.

Jeon, B.-H., B.A. Dempsey, W.D. Burgos, and R.A. Royer. 2001. Reactions of ferrous iron with hematite. Colloids and Surfaces, 191: 41-55. http://dx.doi.org/10.1016/S0927-7757(01)00762-2.

Jeon, B.-H., B.A Dempsey, R.A. Royer, and W.D. Burgos. 2003. Kinetics and mechanisms for reactions of Fe(II) with iron(III) oxides. Environ. Sci. & Technol. 37: 3309-3315

Jeon, B.-H., B.A Dempsey, R.A. Royer, and W.D. Burgos. 2003. Kinetics and mechanisms for reactions of Fe(II) with iron(III) oxides. Environ. Sci. & Technol. 37: 3309-3315 http://dx.doi.org/10.1021/es025900p

PMid:12966975.

Jolivet, J.P., P. Belleville, E. Tronc, and J. Livage. 1992. Influence of Fe (II) on the Formation of

the Spines Iron Oxide in Alkaline Medium. Clays Clay Miner. 40: 531-539. http://dx.doi.org/10.1346/CCMN.1992.0400506.

Sung, W. and Morgan, J.J. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. Environ. Sci. Technol., 14: 561-68. http://dx.doi.org/10.1021/es60165a006.

Tamura, H., K. Goto, T. Yotsuyanagi, and M. Nagayama. 1974. Spectrophotometric determination of iron(II) with 1,10-phenanthroline in the presence of large amount of iron(III). Talanta. 21: 314-318. http://dx.doi.org/10.1016/0039-9140(74)80012-3.

Tamura, H., K. Goto, and M. Nagayama. 1976. The effect of ferric hydroxide on the oxygenation of ferrous iron in neutral solutions. Corrosion Science, 16, 197-207. http://dx.doi.org/10.1016/0010-938X(76)90046-9.

Tronc, E., P. Belleville, J.P. Joivet, and J. Livage. 1992. Transformation of ferric hydroxide into spinel by FeII adsorption. Langmuir, 8: 313-319. http://dx.doi.org/10.1021/la00037a057.