BIOTIC AND ABIOTIC IRON OXIDATION KINETICS IN NET ALKALINE MINE DRAINAGE[1]

by

Denae Athay, Robert W. Nairn and Keith A. Strevett[2]

Abstract. Mine discharge waters at the Tar Creek Superfund Site in Oklahoma contain substantial alkalinity and have circumneutral pH but elevated concentrations of Fe, Zn, Cd and Pb. An understanding of Fe oxidation kinetics is necessary to design effective remediation strategies (most likely treatment wetlands) for these waters. In summer and fall 2000, we measured biotic and abiotic rates of iron oxidation in microcosms at a volunteer wetland receiving polluted mine waters from two abandoned boreholes. Water was pumped from each borehole and from the middle of the wetland directly into control microcosms (biotic + abiotic) and through both 5 μM and 0.2 μm filters into separate experimental microcosms (abiotic). All microcosms (0.425 m^3) were sampled at predetermined time intervals. Field parameters (pH, temperature, and alkalinity) and ferrous iron were determined. Changes in ferrous iron concentrations indicated no significant difference in rates of iron oxidation between control (abiotic + biotic) and experimental microcosms (abiotic). The control reaction resulted in decreases in ferrous iron at the rate of -1.4567 mg $Fe^{+2} \cdot L^{-1} \cdot hr^{-1}$ whereas the experimental reaction had a rate of -1.2250 mg $Fe^{+2} \cdot L^{-1} \cdot hr^{-1}$. Bacterial analyses indicated the presence of iron-related bacteria, but chemical results indicated that they are not significantly active in this system. Abiotic oxidation from exposure to air was the dominant form of iron oxidation in these circumneutral waters. Adequate aeration of the water will remove iron from solution. However, settling of the iron particulates may require substantial surface area in any proposed treatment scenario.

Additional Key Words: treatment wetlands, Superfund, design, Tar Creek, ecological engineering

Background

Decades of lead and zinc mining form the legacy for Tar Creek, a forty square mile Superfund site in northeast Oklahoma. It is part of the Tri-State Mining District (OK, KS, MO), which comprised the largest

[2]Denae Athay, Undergraduate Research Assistant, Robert W. Nairn and Keith A. Strevett, Assistant Professors, School of Civil Engineering and Environmental Science, University of Oklahoma, 202 W. Boyd Street, Room 334, Norman, OK 73019. Denae@ou.edu, Nairn@ou.edu, Strevett@ou.edu

lead and zinc producing area in the world. Zinc and lead sulfides, sphalerite and galena, were mined from the Boone Formation, composed of fossiliferous limestone and nodular chert (Luza 1983). Significant quantities of lead and zinc were produced from about 1900 through the 1960s with peak production occurring in the early 1920s when the mines accounted for over 55% of total U.S. zinc production (McKnight and Fischer 1970). During World War II, tailings were reprocessed two or three times to facilitate zinc recovery. Ore production through the early 1960s was over 7 million tons of zinc and slightly less than 2 million tons of lead (McKnight and Fischer 1970). Mining ceased by the early 1970s. Approximately 1,000 hectares (2,500 acres) are underlain by mine workings in the Picher Field, the Oklahoma portion of the Tri-State District (Luza 1983). During mining, large capacity dewatering operations pumped approximately 50,000 cubic meters (over 13 million gallons) of water per day (Reed et al.
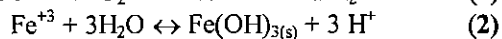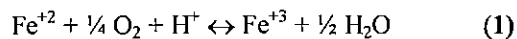
1955) from the workings. Upon cessation of mining, groundwater began to accumulate in the mine voids and approximately 94 million cubic meters (76,000 acre-feet) of contaminated water exist in underground voids today. In late 1979, metal-rich waters began to discharge into Tar Creek from springs, bore holes and abandoned mine shafts. Water quality of the discharges was originally characterized as follows: pH 3.6-5.7, 80 μg Pb/L, 154,000 μg Zn/L, 80 μg Cd/L and 331,000 μg Fe/L (EPA, 1999).

Active chemical treatment technologies for mine waters are laborious and cost-intensive and are not viable options for abandoned mines. Passive treatment technologies, i.e. treatment wetlands, rely on natural biogeochemical and microbiological processes to ameliorate mine drainage problems. The most common passive treatment systems for net alkaline mine drainage are aerobic wetlands. These low-maintenance and relatively inexpensive natural systems are often the only viable option for abandoned mine drainage treatment (Nairn and Hedin 1992; Hedin et al. 1994).

For this study, a site receiving net alkaline mine waters in the Tar Creek Superfund site, known as Mayer Ranch, was chosen. This was the location of the first known discharges from the mines after the voids filled with water, mine water discharges from two abandoned boreholes. Although the land was originally a horse pasture, twenty-one years later, it is dominated by a volunteer *Typha spp.* (cattail) wetland. In addition to the borehole discharges, the wetland receives substantial road runoff. Due to dissolution of carbonate strata, waters discharging from the boreholes are supersaturated with carbon dioxide, and have alkalinity values of approximately 450 mg/L as $CaCO_3$ and pH of 6.5 ± 0.5. Metal concentrations and flows from the boreholes vary seasonally.

Iron rich mine drainages are characterized by orange staining resulting from the oxidation and hydrolysis of iron. The reactions of interest are as follows:

$$Fe^{+2} + \tfrac{1}{4} O_2 + H^+ \leftrightarrow Fe^{+3} + \tfrac{1}{2} H_2O \qquad (1)$$
$$Fe^{+3} + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3 H^+ \qquad (2)$$

Copious volumes of iron oxyhydroxide precipitates characterize the Mayer Ranch wetland. The kinetics of the iron oxidation process was the focus of this study. The biotic iron oxidation process is catalyzed by the activity of various bacteria such as *Thiobacillus ferrooxidans* (Singer and Stumm 1970) and *Metallogium sp.* (Walsh and Mitchell 1972). These bacteria favor lower pH conditions of 3.5-4.5 for *Metallogium spp.* and a pH < 3.5 for *Thiobacillus ferrooxidans* (Walsh and Mitchell 1972) and is a major contributor to low pH conditions in acid mine drainage. The initial bacterial oxidation of iron is very rapid. The abiotic oxidation process occurs rapidly at a pH above 5.0.

Oxidation (reaction 1) is the limiting step (Singer and Stumm, 1970; Kirby and Brady 1998) and the hydrolysis occurs almost immediately at pH >2.8 to produce the iron oxyhydroxide solid. Oxidation can be catalyzed through a bacterial process and hydrolysis occurs rapidly. At neutral pH conditions, dissolved ferric (Fe^{+3}) concentrations are negligible (Singer and Stumm, 1970).

Little is known about the quality and quantity of mine waters at Mayer Ranch, although the discharges are often cited as major contributors to the degradation of Tar Creek. For purposes of remediation design, an understanding of iron oxidation kinetics and processes was needed. This experiment was designed to determine whether iron oxidation was occurring by biotic or abiotic means and further to determine which process could be maximized for effective iron removal. The biotic process is traditionally associated with acid mine drainage, but due to the relatively high alkalinity in this system, Mayer Ranch waters are well buffered and the pH is circumneutral throughout the wetland. Therefore the conditions may not be ideal for bacterially catalyzed iron oxidation to occur. It was suspected that the iron oxidizing bacteria, if present, were not significantly active in this system due to near neutral pH conditions.

Methods

Our experimental design utilized microcosms filled with mine water from the boreholes and the wetland water column. Bacteria were filtered in one set and rates of iron oxidation were compared to the controls which did not have the bacteria filtered. Two site visits occurred in July and October 2000. In July 2000, all experimental work was performed at the site. The microcosms were 0.425 m^3 acid washed polyethylene containers. For control microcosms, approximately 10 liters of mine water were pumped into the container through a 5 μm filter to remove particulates. The experimental microcosm setup varied from the control only in that water was pumped through a 0.2 μm filter to remove bacteria as well. The containers were loosely capped to prevent contamination from debris but still allow for free flow

of air. All microcosms were then floated in the wetland so that the temperature mimicked the natural conditions. Three sites were chosen for this experiment at Mayer Ranch: at each of the boreholes (Seep A and B) and W1, which is approximately 50 m from the boreholes (Figure 1).
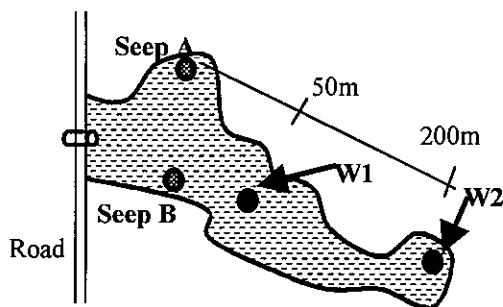

Figure 1. Map of Mayer Ranch and sample locations.

W1 was chosen because we theorized that there might be differences in bacterial composition and activity in the wetland compared to waters discharging directly from the mines. A sample was taken from each microcosm when pumping was initiated and then regular sampling intervals were set once the microcosms were placed into the wetland. Samples were obtained by slowly pumping the water from the microcosms. The water was collected in 250 mL HDPE bottles as well as in separate containers for *in situ* measurements. Pumping allowed measurements to be taken without the risk of transferring bacteria between microcosms. Field parameters (pH, dissolved oxygen and temperature) were measured with a calibrated Orion 1230 Multimeter. Alkalinity was determined using the Hach Digital Titrator Method 8203. Samples were acidified to pH<2 with HCl to fix the ratio of Fe^{+3}:Fe^{+2} and returned to the laboratory for subsequent analysis. Ferrous iron concentrations were determined utilizing a modified potassium dichromate redox titration method from the former U.S. Bureau of Mines (Mark Wesolowski, personal communication). The Hach Biological Activity Reaction Test (BART) for iron related bacteria was performed for all microcosms.

The experimental procedure was slightly modified for the second visit in October 2000, to allow for temporal sampling of the microcosms to be performed under controlled laboratory conditions. The mine water was pumped through a 5 μm filter and into 3.785-L polyethylene Cubitainers™. Cubitainers™ were immediately placed in coolers of ice water to minimize diffusion of oxygen across the plastic and any biological activity that may result. Mine water was

again pumped from the two boreholes. However, there was not sufficient flow at W1, so samples were obtained at site W2, 200 m from the boreholes (Figure 1). The Cubitainers™ were brought back to the lab and carefully pumped into acid-washed microcosms similar to those used in July. Similar to the first visit, experimental microcosms received water additionally pumped through a 0.2 μm filter. Samples were obtained by adapting the microcosms with a valve. Valves were placed so that samples could be obtained without pumping and minimize introduction of iron particulates that may have settled. Sampling at regular intervals as well as various *in situ* measurements was performed similar to the first visit.

Results and Discussion

Results of the BARTs for both visits indicated the presence/activity of bacteria in the control microcosms. Seep B and W1 experimental microcosms did not indicate the presence/activity of bacteria, demonstrating that iron bacteria had been successfully removed. However Seep A did indicate there had been contamination of the experimental microcosms, therefore the results of this seep will not be presented.

In situ measurements of pH indicated that pH did not decrease during the duration of the experiments; pH was maintained at 6.5 ± 0.5. This system was sufficiently buffered by bicarbonate alkalinity such that pH remains circumneutral throughout (Table 1).

Table 1. Mean initial water quality measurements for Mayer Ranch for samples taken prior to beginning iron oxidation experiments, data for Seep B and W1 in July 2000; W2 in October 2000 (na=not analyzed).

	Seep B	W1	W2
pH	6.2	6.3	6.2
Temperature °C	24	24	24
Dissolved Oxygen	0.3	0.2	0.4
Alkalinity (mg/L as CaCO3)	410	180	202

* Acidity calculated per Hedin et all, 1994

Dissolved oxygen (DO) measurements from the second experiment were consistently low at 2.58 ± 1.35 mg/L, but DO measurements from the first visit, 6.2 ± 2.8 mg /L, were higher and fluctuated due to the pump collection of the sample. It is notable that the DO throughout the wetland is 1 mg /L or less.

Concentrations of ferrous iron versus elapsed time were plotted for each set of microcosms and the

slope of a linear regression line was used to determine the rate of reaction in mg $Fe^{+2} \bullet L^{-1} \bullet hr^{-1}$ (figures 2 - 5).
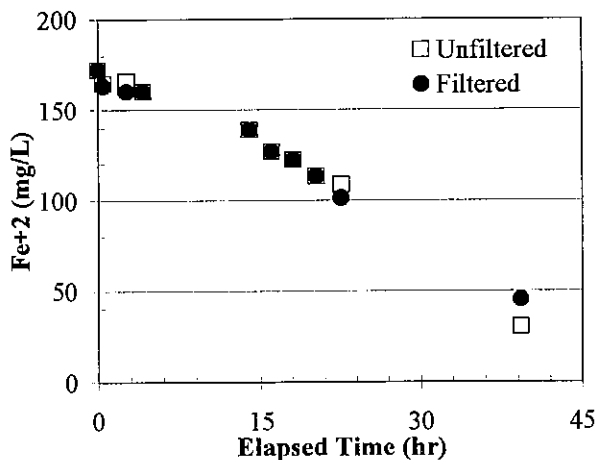

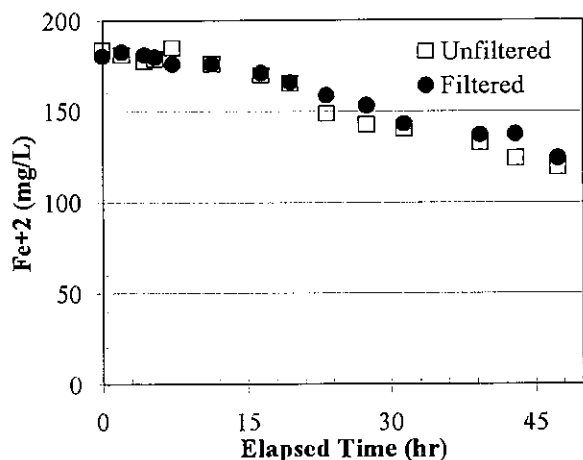Figure 2. Ferrous Iron concentrations for Seep B during July 2000 (visit 1) sampling event.

Figure 3. Ferrous Iron concentrations for Seep B during October 2000 (visit 2) sampling event.
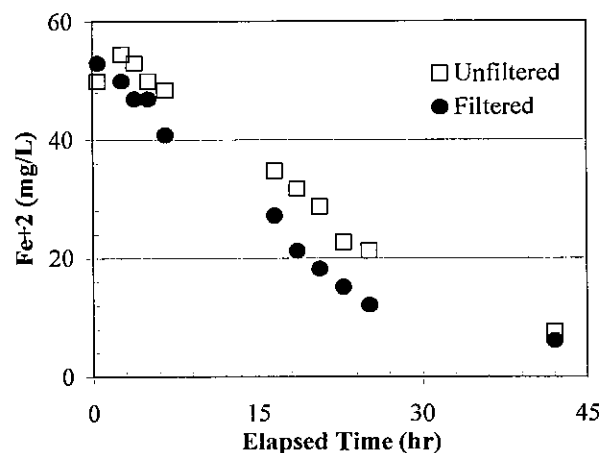

Figure 4. Ferrous Iron concentrations for W1 during July 2000 (visit 1) sampling event.
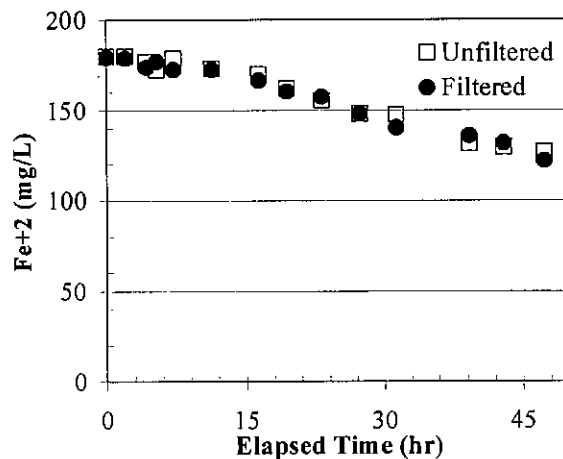

Figure 5. Ferrous Iron concentrations for W2 during October 2000 (visit 2) sampling event

A comparison of the rate of reaction for each sample location and visit shows there to be no significant difference between the biotic and abiotic ferrous iron oxidation rates (Table 2).

Table 2. Iron oxidation rates (mg $Fe^{+2} \bullet L^{-1} \bullet hr^{-1}$) for control and experimental microcosms.

	Visit 1 Seep B	Visit 2 Seep B	Visit 1 W1	Visit 2 W2
Unfiltered/ Biotic	-3.350	-1.457	-1.212	-1.222
Filtered/ Abiotic	-3.054	-1.225	-1.294	-1.211

The rate of iron oxidation for Seep B was much lower in October compared to July; this may be due to using a pump to extract sample from the vessel during the first visit, thus potentially introducing oxygen into the sample. The concentration of dissolved oxygen in the samples can have a significant impact on the rate of iron oxidation and dissolved oxygen concentrations were significantly higher in the samples during visit 1 than visit 2, thus leading to an increased reaction rate. Iron oxidation rates were slower for W1, compared to Seep B during the same trip, due to a lower initial concentration of Fe^{+2} in the wetland (55 mg Fe^{+2}/L), compared to that of the seep (180 mg Fe^{+2}/L). At W2, higher concentrations of ferrous iron (180 mg Fe^{+2}/L) were found, although W2 is further away from the boreholes. Although seasonal variations may have played a role, a major difference in the two visits were flow rates of water through the wetland. Mayer Ranch receives a significant amount of storm water runoff during rain events. A large rain event prior to the first

visit resulted in substantial amounts of runoff entering the Mayer Ranch wetland. This may have resulted in dilution of mine water from the boreholes, leading to a lower concentrations of ferrous iron during the first visit compared to concentrations found during the second visit, in which there was no visible runoff coming into the Mayer Ranch wetland.

Conclusions

Ferrous iron analyses indicated that although there was iron related bacteria present in the mine waters at Mayer Ranch, the bacterial iron oxidation process is neither dominant nor important to overall rates of iron removal. Comparison of the ferrous iron oxidation rates between microcosms that contain iron-related bacteria and those that did not show that there was little difference. It may be that the bacteria that are present are not active. The dominant iron oxidation process is abiotic for these alkaline mine waters. Iron oxidation appears to be limited by the diffusion of atmospheric oxygen into the water column. This is clearly demonstrated by the low dissolved oxygen concentrations found throughout the wetland as well as the effect of increased DO on reaction rates. In order to effectively remove iron from the water in the oxyhydroxide form, sufficient oxygen must be provided to the system.

Treatment wetlands have been recently proposed as a remediation alternative at Mayer Ranch. Information from this experiment can be used to assist in design of effective treatment wetlands to ameliorate mine waters before they enter the receiving waters. For purposes of iron removal, an aerobic wetland to promote oxygen diffusion, possibly with a windmill, would provide the oxygen needed to drive oxidation reactions and subsequent hydrolysis and precipitation of iron. Sufficient surface area will also be needed to allow for settling of the colloidal iron particulates.

Acknowledgments

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