

Laboratory and Field-scale Evaluation of Low-pH Fe(II) Oxidation at Hughes Borehole, Portage, Pennsylvania

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Abstract The Hughes Borehole is located in the bituminous coal region of south-central Pennsylvania and drains an underground mine complex of ca. 2,950 ha. The borehole discharge averages approximately 63 L/s of acidic (pH 4, 230 mg/L acidity) mine drainage that contains elevated concentrations of Fe(II) (100 mg/L). Long-term monitoring of the site showed that biological Fe(II) oxidation occurred without human intervention and, over previous decades, has produced a 0.6 ha iron mound up to 2 m deep. On-mound channel reactors along with laboratory-scale gutter reactors were constructed to determine conditions that can exploit biological Fe(II) oxidation for passive treatment. Dissolved Fe(II) was much more efficiently oxidized from gutter reactors that contained iron mound sediment than ones without any sediment. Close to 100% of the dissolved influent Fe(II) was oxidized in 5–10 h and 75% of the total dissolved Fe was removed. In addition, the reactors performed better as the sediment aged, so that shorter residence times of 1–2 h were also capable of oxidizing substantial amounts of the influent Fe(II). The addition of surface area to the on-mound reactors improved Fe(II) oxidation at residence times of 30 min or less. The results of this study can be used to help design and build treatment systems for low-pH acid mine drainage (AMD) discharges.

Keywords Acid mine drainage · Fe(II) oxidation · Metal oxidation

Introduction

The northern Appalachian Plateau of the eastern United States contains more than 8,000 km of streams that are affected by drainage from abandoned coal mines (Boyer and Sarnoski 1995). Many of these streams are located in Pennsylvania, where approximately half of the discharges have a pH < 5 (Brady et al. 1998). The anthracite coal fields in northeast Pennsylvania and bituminous coal fields in western Pennsylvania impact 45 of the state's 67 counties, including at least 3,900 km of streams and 1,000 km² of land.

Cost effective treatment technology is needed. In Appalachia, the removal of iron is probably the most important aspect of AMD treatment. Biological low-pH Fe(II) oxidation may be able to improve the performance of conventional passive limestone treatment systems. Limestone dissolution neutralizes acidic water and promotes the precipitation of Fe(III) (hydr)oxides (Cravotta and Trahan 1999; PA DEP 1999). Unfortunately, these Fe(III) precipitates chemically coat limestone surfaces (commonly called armoring), limiting further limestone dissolution and neutralization, and, more importantly, hydraulically clog the limestone bed (PA DEP 1999; Rose et al. 2004; Weaver et al. 2004).

To limit armoring and clogging, dissolved Fe may be removed from AMD before waters are neutralized with limestone. In the pH range typical of acidic Appalachian mine drainage (2.5–4.5) (Cravotta et al. 1999), the abiotic oxidation of Fe(II) is kinetically limited, but hydrolysis and precipitation of Fe(III) will still occur (Stumm and Morgan

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1996). Under such conditions, acidophilic Fe(II)-oxidizing bacteria (Fe(II)OB) catalyze Fe(II) oxidation, allowing for the oxidative precipitation of Fe from AMD discharges at low pH (Johnson and Hallberg 2003; Kirby et al. 1999; Nengovhela et al. 2004; Nicormat et al. 2006; Williamson et al. 2006). This water may then be neutralized using limestone before it is released into nearby streams. While this process will not remove all of the dissolved iron, and no aluminum or manganese, the decreased iron load should minimize armoring and clogging of downstream limestone beds. The spatial separation of iron oxidation and precipitation from alkalinity addition could improve the operation and maintenance of limestone beds and reduce the associated costs.

Site Description

The Stonycreek-Conemaugh watershed, located in south-central Pennsylvania, is highly affected by AMD. In 1994, the U.S. Geological Survey identified 270 abandoned coal mine discharges in this 1210 km² watershed, with the majority exceeding effluent standards for total iron and manganese (Zink et al. 2005). A subdivision of this watershed includes the Little Conemaugh watershed, in which a state-funded study found 197 coal mine discharge points, with seven major discharges that contribute over 73% of the metal load to the watershed (Zink et al. 2005). One of these seven large discharges is the Hughes Borehole.

The Hughes Borehole is an artesian AMD discharge located in Cambria County, PA, near Portage, PA. It is approximately 30 m from the Little Conemaugh River; however, most of the flow from Hughes Borehole enters the Little Conemaugh River about 1 km downstream of the emergence. The flow rate ranges from 19 to 126 L/s throughout the year, with a yearly average of approximately 63 L/s. The emergent discharge has an average pH of 4.0 and dissolved concentrations of iron(II), aluminum, and manganese of 100, 8, and 2 mg/L, respectively (Table 1). A 1.5 acre 'iron mound' (an area of iron hydroxide deposition) surrounds the borehole at depths up to 2 m.

Hughes Borehole drains a mine complex consisting of three interconnected underground mines located along the Lower Kittanning bituminous coal seam (GAI 2007). Together, these mines comprise an area of 2,955 ha, with Hughes mine being the largest at 1,480 ha. Operations at Hughes started before 1923 and continued until the mine was closed in 1954. Hughes Borehole was drilled sometime during the 1920s to facilitate drainage of the mine. The other three mines, which are all hydrologically up-gradient

Table 1 Water chemistry at the fence and toe locations at Hughes Borehole from June 2008 to July 2009; values are presented as mean \pm one standard deviation for *N* samples

	Fence (near emergence)	Toe (bottom of iron mound)
pH	3.96 \pm 0.25 (<i>N</i> = 29)	3.52 \pm 0.33 (<i>N</i> = 22)
Temperature (°C)	12.7 \pm 0.6 (<i>N</i> = 30)	16.0 \pm 3.8 (<i>N</i> = 21)
Dissolved oxygen (mg/L)	1.10 \pm 0.80 (<i>N</i> = 21)	9.99 \pm 1.22 (<i>N</i> = 16)
Conductivity (μ S/cm)	1080 \pm 99 (<i>N</i> = 23)	1140 \pm 126 (<i>N</i> = 17)
Fe(II) (mg/L)	100 \pm 17.2 (<i>N</i> = 25)	66.7 \pm 23.0 (<i>N</i> = 21)
Fe(III) (mg/L)	0.50 \pm 2.31 (<i>N</i> = 15)	14.6 \pm 11.7 (<i>N</i> = 14)
Fe (mg/L)*	88.5 \pm 3.3 (<i>N</i> = 7)	66.6 \pm 16.2 (<i>N</i> = 7)
Acidity (mg CaCO ₃ /L)	228 \pm 4.9 (<i>N</i> = 7)	200 \pm 21.2 (<i>N</i> = 7)
Sulfate (mg/L)	573 \pm 63 (<i>N</i> = 5)	572 \pm 53 (<i>N</i> = 5)
Al (mg/L)*	8.19 \pm 0.39 (<i>N</i> = 7)	8.25 \pm 0.44 (<i>N</i> = 7)
Mn (mg/L)*	2.42 \pm 0.02 (<i>N</i> = 7)	2.48 \pm 0.03 (<i>N</i> = 7)
Ca (mg/L)*	113 \pm 4.0 (<i>N</i> = 7)	113 \pm 3.0 (<i>N</i> = 7)
K (mg/L)*	6.23 \pm 0.17 (<i>N</i> = 7)	6.23 \pm 0.23 (<i>N</i> = 7)
Mg (mg/L)*	41.5 \pm 0.95 (<i>N</i> = 7)	41.9 \pm 0.87 (<i>N</i> = 7)
Na (mg/L)*	8.53 \pm 1.33 (<i>N</i> = 7)	8.21 \pm 0.28 (<i>N</i> = 7)
TOC (mg/L)	0.87 \pm 0.22 (<i>N</i> = 3)	NA
TN (mg/L)	1.00 \pm 0.14 (<i>N</i> = 3)	NA
Phosphate (mg/L)	0.59 \pm 0.30 (<i>N</i> = 3)	NA

N = number of samples

* Measured by ICP-AES

of the Hughes Mine, were deliberately connected to allow for gravity drainage into the Hughes Mine; the combined flows emerge at Hughes Borehole. Hughes Borehole was capped in the 1950s, but blew out in the 1970s and has been discharging ever since (Zink et al. 2005).

Objectives

The overarching goal of our studies of low-pH Fe(II) oxidation has been to better understand the biogeochemistry of these systems so that this naturally occurring process can be exploited for passive treatment of AMD (DeSa 2009; Lucas 2008; Senko et al. 2008). The specific objectives of this research were to conduct laboratory experiments in flow-through, open channel, 'gutter' reactors using iron mound sediments and water from Hughes Borehole to evaluate the effect of residence time on low-pH Fe(II) oxidation and Fe removal, to conduct similar field experiments in open channels constructed on the Hughes Borehole iron mound, and to monitor the effective removal of Fe across the whole iron mound for 1 year.

Materials and Methods

Field Sampling

The emergence of Hughes Borehole (40° 24' 31.7'' N; 78° 39' 17.2'' W) is surrounded by a chain link fence (Fig. 1a). The water flows under the fence (2.5 m downstream of the borehole), through a rectangular weir, across the existing iron mound (essentially uncontrolled), and discharges off the 'toe' of the iron mound (60 m downstream of the borehole) into a small tributary before flowing into the Little Conemaugh River (0.61 km downstream of the borehole). The Susquehanna River Basin Commission (SRBC) installed the weir with a pressure transducer in 2006 to record daily flow measurements. The channel downstream of the weir is relatively deep (ca. 0.60 m) with fast moving water and captures most of the flow from the borehole. A smaller portion of the water is conveyed as shallow (ca. 1 cm) sheet flow across the iron mound surface (Fig. 1b). The deep channelized flow likely has a

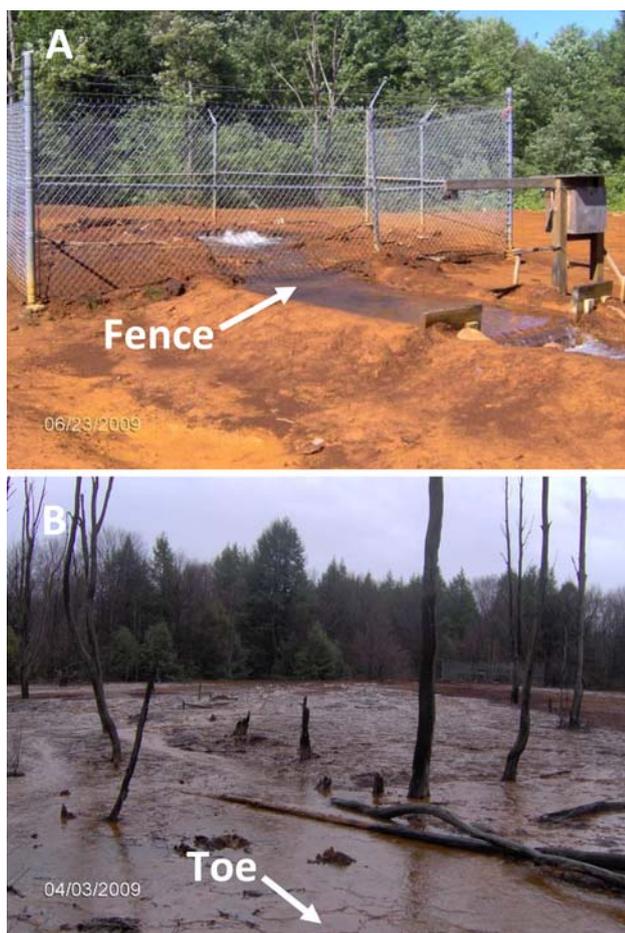


Fig. 1 Photos of the Hughes Borehole showing the **a** fence and **b** toe sampling locations. The fence can also be seen in **b** and is ca. 60 m from the toe

much shorter hydraulic residence time across the mound (minutes to travel to toe) s compared to the sheet flow regions (tens of minutes).

The fence and toe locations were chosen for long-term monitoring of geochemical changes across the iron mound (July 2008–2009). Field measurements included electrical conductivity (conductivity cell; Oakton 400 series), dissolved oxygen (galvanic probe; Oakton 300 series), and pH and temperature (combination electrode; Beckmann Φ 200) using portable meters. Water samples were filtered (0.2- μ m) into sterilized, acid washed centrifuge tubes and chemically preserved in the field with HCl (for Fe(II) and Fe(III)), or HNO₃ (for metals by ICP-AES), or H₂SO₄ (for total organic carbon analysis). Samples for sulfate were neither acidified nor filtered. Water samples were transported to the laboratory on ice and refrigerated at 4°C until analyzed. Sediment samples were collected from the top 2 cm of the iron mound at several locations with sterile spatulas and placed into sterile whirl-pak bags.

On-Mound Channel Reactors

On-mound channel reactors were constructed on the Hughes Borehole iron mound in June 2008 (Fig. 2a). The system included a splitter box (1.2 × 2.4 × 1.2 m, w × l × h) dug into the mound, and eight 12 m channels on top of the mound. A 0.61 m high weir was placed along the center of the splitter box to evenly distribute the influent AMD into the eight channels. The influent pipe to the splitter box was connected to the main channel flowing from the Hughes Borehole approximately 3 m downstream of the SRBC weir. The box was placed down-gradient of the influent pipe intake structure to promote gravity flow.

The eight channels were made with pressure-treated 5 cm × 20 cm × 2.4 m boards. The boards were placed on the existing mound surface and then sediment from the top 0.3–0.6 m of the mound was shoveled into the channels. The final sediment depth within the channels was 7–10 cm, leaving 10–13 cm of freeboard. An average slope of 0.46/12 m (0.038) allowed for gravity flow. The channels were labeled A–H (from left to right looking upstream). Channels G and H were 'control channels' and received no modifications besides the initial construction. Influent samples were taken from the splitter box, and effluent samples were taken from the downstream end of the channels. A Baski cutthroat flume was used to measure the effluent discharge of the individual channels.

In August 2008, wooden blocks were added as small steps to the six 'treatment channels' (A–F) to increase the residence time in each. Each channel modification was conducted in duplicate in adjacent channels. In October 2008, plastic media (Brentwood cross flow media, CF 1900) was added to the treatment channels to further



Fig. 2 **a** Photo of the channel reactors built on the Hughes Borehole iron mound. **b** Picture of laboratory-scale gutter reactors showing the feed tank in the background and the four open-channel, flow-through reactors in the foreground

increase the residence time and the surface area in the channels. The media (25 cm × 30 cm × 12 cm, w × l × h) were pushed 1.3–2.5 cm into the top layer of sediment. In June 2009, half the media (every other piece) was removed in channels A and B, and all the media was removed from channels C–F. Coconut (i.e. coir) erosion control netting (Rolanka BioD-Mat® 70; Stockbridge, GA) was laid in two layers on top of the sediments in channels C and D, and coir mats (Rolanka) were placed on top of the sediment in channels E and F.

Salt tracer slug tests were conducted during the four different test periods (I—June–August 2008; II—August–October 2008; III—October 2008–June 2009; IV—June–July 2009) to determine hydraulic residence times of the on-mound channel reactors. 50 g of NaCl was mixed with 1 L of Hughes AMD and poured into the influent end of the channels approximately 0.3 m downstream of the splitter box. An Oakton 400 series conductivity meter was placed at the effluent end of each channel and the conductivity was

recorded at intervals of 10–30 s. The values were corrected to account for background concentrations.

Laboratory Gutter Reactors

Flow-through, open channel, laboratory-scale ‘gutter reactors’ were constructed with iron mound sediments from Hughes Borehole in square PVC tubes (2.5 × 2.5 × 91 cm; w × h × l) (Fig. 2b). ‘Sediment reactors’ contained 100 g of air dried sediment evenly packed along the bottom of the tubes, while ‘control reactors’ contained no sediment. Inlet weirs were designed to maintain a 0.64 cm water column height in each reactor. The gutter reactors had a slope of 1.3/91 cm (0.014) to allow for gravity flow. A 19 L glass feed tank containing water from the Hughes Borehole (fence location, unfiltered) was sealed with a rubber stopper and constantly purged with N₂ gas to minimize any Fe(II) oxidation. A peristaltic pump (Masterflex #7519-25) was used to convey water from the feed tank to the four inlet weirs, and to collect the channel effluents into waste containers. Samples were collected from the influent and effluent ends of the gutter reactors.

Experiments conducted in the gutter reactors allowed longer residence times than were possible with the on-mound channel reactors. Experiments were conducted sequentially at residence times of 10, 5, 2, and 1 h, starting at the longest residence time and finishing at the shortest residence time. The flow rates in each reactor for these residence times were 0.207, 0.415, 1.04, and 2.08 mL/min, respectively and were verified by gravimetric analysis. The flow rates were set to achieve the selected residence times based on the assumed water volume in the gutter reactor.

Coir landscaping mats (Rolanka) were added to the gutter reactors during the course of the experiment. About 10 g of coir mat was added to each sediment reactor. The coir mat was cut to 2 cm wide and 0.64 cm in depth, to fit within the constraints of the reactors and was placed on top of the sediment.

Analytical Methods

Dissolved ferrous iron, Fe(II), was measured by the ferrozine assay (Stookey 1970) after centrifugation (2 min at 13,400 rpm). Dissolved total iron was also measured by the ferrozine assay after all of the iron was reduced by hydroxylamine-HCl (Luu et al. 2003). Fe(II) concentrations were measured by absorbance at 562 nm using a Shimadzu – UV-1601 spectrophotometer. Dissolved ferric iron, Fe(III), was calculated as the difference between total Fe and Fe(II). The pH was measured in the supernatant using a Thermo Orion 550A benchtop pH meter with a semi-micro pH probe. Dissolved oxygen (DO) was measured directly in the gutters using a Cole-Parmer benchtop

DO meter. Metals were measured using a Perkin-Elmer Optima inductively coupled plasma atomic emission spectrometer (ICP-AES). Acidity was calculated indirectly based on pH and measured concentrations of dissolved Fe(II), Fe(III), Mn, and Al according to Kirby and Cravotta (2005). Sulfate was measured by the HACH SulfaVer 4 method using a HACH DR/2800 spectrophotometer. Total organic carbon (TOC) and total nitrogen (TN) samples were analyzed using a Shimadzu TOC-VCSN total organic carbon analyzer and Shimadzu TNM-1 total nitrogen measuring unit, respectively. Lithium metaborate fusion was used to dissolve solid sediment samples, then ICP-AES was used to measure elemental content. Sediment samples were air dried, mixed with lithium metaborate, heated to 1,000°C for 30 min, and then diluted with nitric acid prior to ICP-AES analysis. Metal oxide percentages were based on the original weight of sample.

Results and Discussion

Low-pH Fe(II) Oxidation in Laboratory Reactors

The hydraulic residence time of AMD across an iron mound is extremely important with respect to the extent of Fe(II) oxidation and Fe removal (Senko et al. 2008). Therefore, we conducted a single continuous experiment where we incrementally decreased the hydraulic residence time to determine what minimum residence time was required for an acceptable level of treatment. We started with a 10 h residence time and continued until a pseudo-steady state condition had been reached with respect to the effluent Fe(II) concentration (Fig. 3). The residence times were then sequentially decreased to 5, 2, and 1 h.

When operated at a 10 h residence time, the pseudo-steady state $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ ratio dropped to 0.03 (i.e. 97% of the influent Fe(II) was oxidized). The influent dissolved Fe(II) concentration ranged from about 60 to 100 mg/L due to varying Fe(II) concentrations in the water collected from Hughes Borehole used to refill the feed tank. Normalized ratios of $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ are presented to account for this fluctuation. Compared to the control reactors, the effluent pH (Fig. 3b) was always significantly lower and the effluent DO (Fig. 3c) was slightly lower in the sediment reactors. The consumption of Fe(II) and DO, and the drop in pH are consistent with biological oxidation of Fe(II) followed by the precipitation of $\text{Fe(OH)}_3(\text{s})$. While no sterile controls were run in parallel with the gutter reactors, the $[\text{Fe(II)}]_{\text{final}}/[\text{Fe(II)}]_{\text{initial}}$ ratio measured in batch sediment reactors amended with 1% (vol/vol) formaldehyde was 0.88 after 2 h, and 0.85 after 24 h (Supp. Info. Fig. S1).

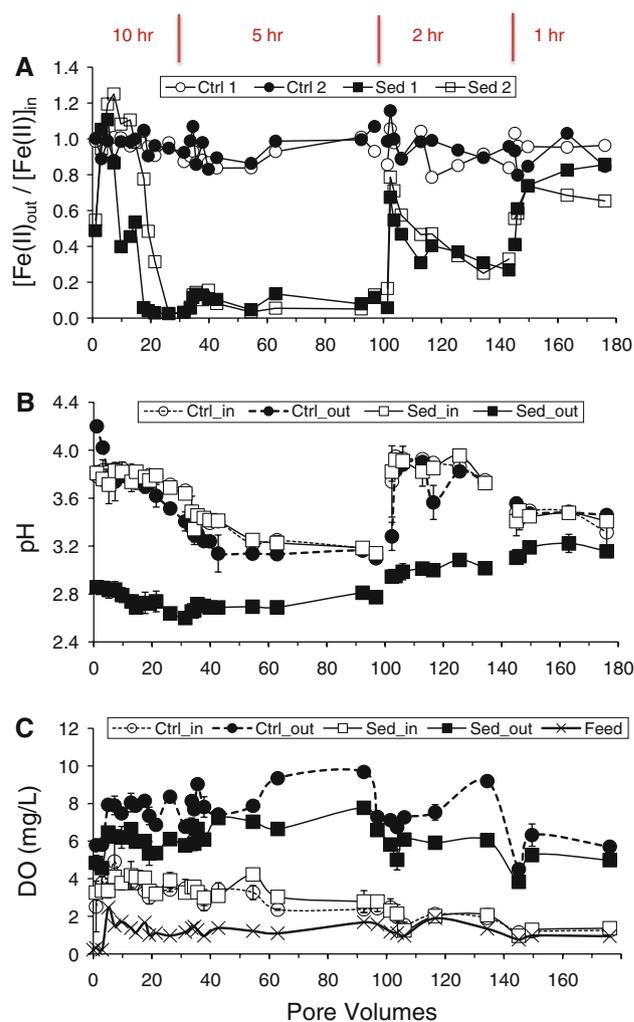


Fig. 3 Low-pH Fe(II) oxidation in laboratory gutter reactors operated at variable hydraulic residence times. Experiment began at a 10 h residence time that was incrementally reduced to 5, 2, and 1 h (delineated in a). Sediment reactors (Sed) contained sediment from Hughes Borehole and Control reactors (Ctrl) contained no sediment. For the normalized results in a, influent Fe(II) concentrations ranged from 60 to 100 mg/L. Results are shown for each duplicate reactor in a and averaged in b and c

When the gutter reactors were switched to a higher flow rate to achieve a shorter residence time, effluent Fe(II) concentrations were non-steady for a period of time before the next pseudo-steady state condition was attained. When operated at a 5 h residence time, the pseudo-steady state $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ ratio increased to 0.10. When operated at 2 and 1 h residence times, the pseudo-steady state $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ ratios increased further, to 0.31 and 0.76, respectively. At these shortest residence times, the effluent pH also increased from previous conditions, consistent with less precipitation of $\text{Fe(OH)}_3(\text{s})$. These data suggest that a hydraulic residence time across the iron mound of at least 5 h would be required for iron oxidation and precipitation.

While a high efficiency of Fe(II) oxidation can be achieved in the gutter reactors, soluble Fe as both $\text{Fe}^{2+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$ were still present in the reactor effluent (Fig. 4). When operated at 10 and 5 h residence times, 20–30% of the total influent Fe remained in solution, with the majority in the ferric form (Table 2). In the presence of 600 mg/L SO_4^{2-} (Table 1) and in the pH range of our measurements (pH 2.5–4.5), schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{4.5}(\text{SO}_4)_{1.75(\text{s})}$) is less soluble than ferrihydrite ($\text{Fe}(\text{OH})_{3(\text{s})}$) (Supp. Info. Fig. S2). For our paired measurements of pH and $\text{Fe}^{3+}(\text{aq})$, from both the Hughes Borehole and from our gutter reactors, it appears the water was supersaturated with respect to both of these minerals. However, based on X-ray diffraction patterns (Supp. Info. Figure S3), the predominant mineral in the iron mound appeared to be schwertmannite. Our interpretation of these results is that schwertmannite solubility controls the $\text{Fe}^{3+}(\text{aq})$ concentration in this system and that schwertmannite precipitation is the predominant mechanism of total Fe removal in this low-pH system.

Experiments were also conducted to determine if the addition of coir mats would enhance Fe(II) oxidation. These experiments were performed only at 1 h residence

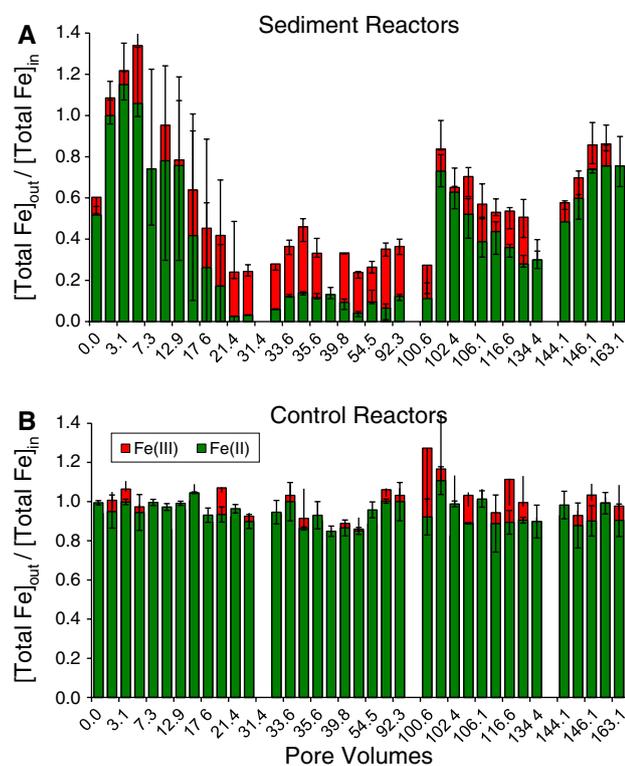


Fig. 4 Speciation of Fe(II/III) in laboratory gutter reactors operated at variable hydraulic residence times. Experiment began at a 10 h residence time (0–31.4 pore volumes (PV)) that was incrementally reduced to 5 h (31.4–92.3 PV), 2 h (92.3–134.4 PV), and 1 h (134.4–163.1 PV). Sediment Reactors contained sediment from Hughes Borehole and Control Reactors contained no sediment

Table 2 Average effluent Fe concentrations and pH values maintained during the pseudo-steady state period at each hydraulic residence time in the laboratory gutter reactors

Residence time (h)	Steady state effluent [Fe(II)] (mg/L)	Steady state effluent [Fe(III)] (mg/L)	Steady state effluent pH
10	2.91 ± 0.39	21.6 ± 2.4	2.62 ± 0.03
5	8.86 ± 3.6	22.1 ± 7.2	2.76 ± 0.06
2	28.4 ± 3.4	24.5 ± 4.9	3.05 ± 0.05
1	68.8 ± 9.9	11.9 ± 7.1	3.19 ± 0.06

times to better reveal any enhancement. We found that Fe(II) oxidation was greatly improved by the coir; the $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ decreased from 0.48 (before coir addition) to 0.03 (Fig. 5), a level of treatment previously only measured at a residence time of 10 h. Compared to the influent, effluent concentrations of TOC and TN did not significantly change due to coir addition (Supp. Info. Fig. S4). We believe the physical addition of surface area as compared to the chemical addition of nutrients was the primary mechanism by which coir promoted Fe(II) oxidation. This finding is consistent with Kirby and Kostak (2002), who showed that acidophilic iron-oxidizing bacteria preferentially attached to the surface of ferric minerals and that this, in turn, accelerated the rate of low-pH Fe(II) oxidation. This finding is also important because it indicates how simple, low-cost, physical modifications to existing iron mounds that increase surface roughness and/or surface area may significantly improve treatment potential.

Over the course of the 100 days in which we conducted the variable-residence and coir addition experiments, we re-established select experimental conditions in order to document any changes in sediment/reactor behavior. For the most part, we found all our experiments repeatable;

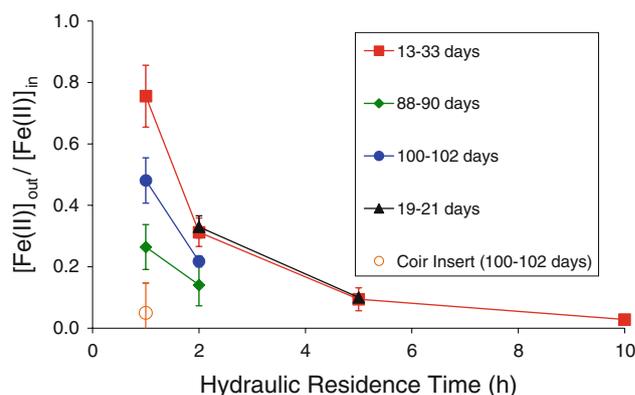


Fig. 5 $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ ratios maintained during pseudo-steady conditions in the laboratory gutter reactors versus hydraulic residence time. Reactors were operated in a semi-continuous manner for over 100 days, and results are grouped based on the ‘age’ of the sediment in the reactor. Result is also shown for the addition of coir mat to the sediment reactors

however, we found that Fe(II) oxidation improved over time. We believe that the sediments aged or ‘ripened’ over prolonged, semi-continuous use such that the microbial communities became more capable of oxidizing Fe(II) (Fig. 5). Filter ripening in sand filters used for drinking water treatment is a process where microbes grow together on the surface of the sand grains (Jellison et al. 2000). As filtration progresses, biofilms develop, which tends to enhance particle adsorption and biodegradation of soluble organic compounds.

We calculated the removal of total Fe in our laboratory reactors in terms of grams of iron removed per day per m² of active surface area (gdm):

$$\text{gdm}(\text{g Fe/d/m}^2) = (([\text{Fe}_T]_{\text{in}} - [\text{Fe}_T]_{\text{out}}(\text{mg/L})) \cdot Q (\text{mL/min}))/230 \text{ cm}^2 \cdot \text{conversion factors}$$

where the 230 cm² represented the sediment surface area in the gutter reactor. We found values ranging from 0.10 to 1.0 (g Fe/d/m²) for all of our laboratory experiments, with the highest rate from the coir-amended experiment. In comparison, design guidelines for iron removal from net-acid coal mine drainage using aerobic wetlands range from 2 to 5 gdm (Hedin and Nairn 1992). This comparison shows that, from a land area perspective, natural iron mounds are not exceptionally efficient. However, these mounds may still be advantageous because they provide essentially free treatment that improves the operation and maintenance of downstream limestone beds.

Low-pH Fe(II) Oxidation in Field Reactors

The on-mound channel reactors were constructed in June 2008. On average, the channels were sampled every other week from July 2008 to 2009 through four different test periods. Initially, no modifications were made to the channels (period I), wooden steps were then added to the treatment channels (period II), plastic trickling filter media was then added to the treatment channels (period III), and then the trickling filter media was removed and replaced with coir mats or coir erosion-control netting (period IV). There was no significant decrease in dissolved Fe(II) effluent concentrations for any of the channels until mid-November 2008, over a month after the plastic media was added (Fig. 6). A significant amount of fresh precipitates accumulated on the media during this ‘filter ripening’ period. The May 6, 2009 sampling event occurred directly after the removal of the plastic media and a clear increase in effluent Fe(II) was evident. Like the addition of plastic media, the addition of coir netting increased Fe(II) oxidation in the channel reactors.

Compared to the laboratory reactors, control of the hydraulic residence time in the on-mound channel reactors

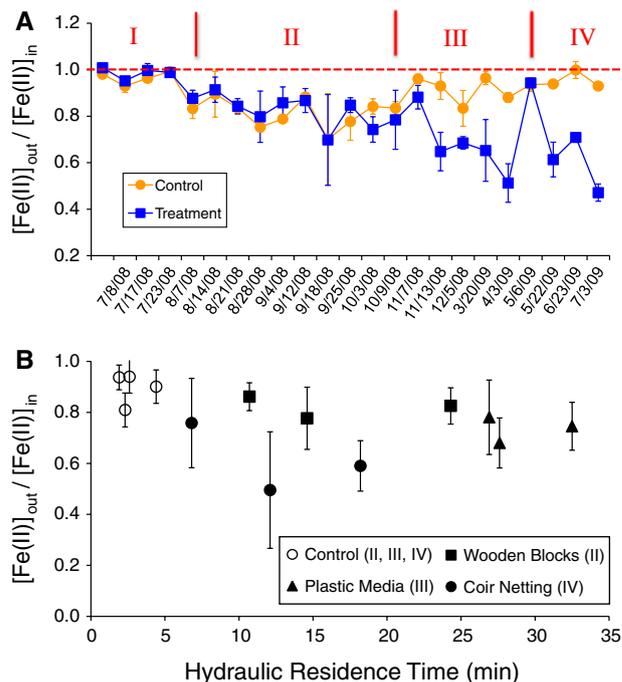


Fig. 6 Low-pH Fe(II) oxidation in on-mound channel operated from July 2008–2009. In **a**, I refers to no channel modification, II refers to the addition of wooden steps, III refers to the addition of plastic trickling filter media, and IV refers to the removal of the plastic media and replacement with coir netting. **b** $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ ratios maintained during operation of the channel reactors versus hydraulic residence time. For these normalized results, influent Fe(II) concentrations ranged from 60 to 130 mg/L

was far more difficult. The diameter of the influent pipe intake structure, the slope of the mound, and the channel lengths allowed only a narrow range of relatively short residence times (2–33 min). Because of this, the $[\text{Fe(II)}]_{\text{out}}/[\text{Fe(II)}]_{\text{in}}$ ratio was not well correlated to residence time (Fig. 6b). However, even at residence times of only 10–30 min, 20–50% of the influent Fe(II) (ranging from 60 to 100 mg/L during the test period) was oxidized.

Low-pH Fe(II) Oxidation across Iron Mound

Three comprehensive sampling campaigns were conducted to measure geochemical changes as a function of distance across the Hughes Borehole iron mound (August 2007, December 2007, May 2009). In general, dissolved Fe(II) and pH decreased with distance, DO increased with distance (until saturation), and EC remained constant. These results are consistent with geochemical changes expected due to low-pH biological Fe(II) oxidation (Senko et al. 2008). However, even though the Hughes Borehole has produced a 0.61 ha iron mound that is up to 2 m deep, Fe removal across the mound was relatively limited during these sampling events. The flow at Hughes ranged from

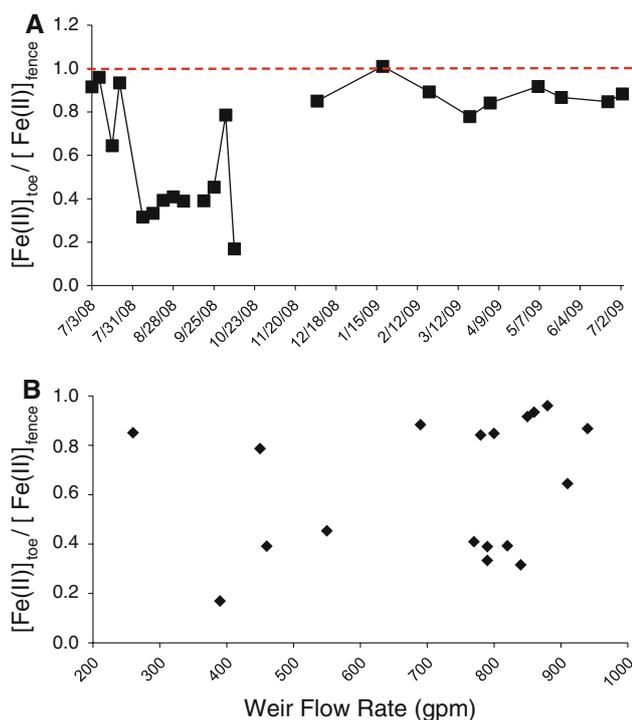


Fig. 7 a Low-pH Fe(II) oxidation measured across the Hughes Borehole iron mound from July 2008–2009. For these normalized results, Fe(II) concentrations at the fence ranged from 60 to 120 mg/L. **B**) $[\text{Fe(II)}]_{\text{toe}}/[\text{Fe(II)}]_{\text{fence}}$ ratios versus borehole flow rate for dates when both water chemistry and flow were measured

approximately 19–126 L/s since 2006. During the study period, the flow ranged from 19 to 63 L/s.

Water samples were collected from June 2008 to July 2009 at the fence and toe locations on the iron mound to collect long-term data (Fig. 7a). Every sampling event showed a decrease in dissolved Fe(II) at the toe location, compared to the fence. In August and September 2008, there was 40–50% oxidation of Fe(II) across the mound. Little Fe(II) oxidation occurred during all other times of the year. An average residence time for water traveling from the fence to the toe of the iron mound is difficult to calculate. Instead, we plotted the $[\text{Fe(II)}]_{\text{fence}}/[\text{Fe(II)}]_{\text{toe}}$ ratio versus the gauged flow rate (as a proxy for residence time) for all dates sampled (Fig. 7b). As with the on-mound channel reactors, the extent of Fe(II) oxidation was not well correlated to flow rate. However, it appears that the warm months of July–September 2008 may have provided seasonal enhancement.

Despite the removal of total Fe across the mound, all other aqueous trace metal cations showed no reduction in concentration across the mound (Supp. Info. Fig. S5). The concentrations of dissolved Al and Mn actually increased slightly at the toe location. Iron oxide, Fe_2O_3 , was the most abundant metal oxide by weight percent in the iron mound sediment for both the fence and toe locations at 66.7 and

67.0%, respectively (Supp. Info. Table S1). The second most abundant metal oxide was Al_2O_3 , at 0.39 and 1.28%, for the fence and toe, respectively. All other metal oxides were either not detected or present at very low concentrations.

Conclusions

Low-pH Fe(II) oxidation can be exploited for passive treatment of AMD. A hydraulic residence time of 5–10 h of shallow sheet flow across an existing iron mound could oxidize >95% of influent Fe(II), and remove >70% of total Fe. Physical modifications of the iron mound to increase surface area for microbial growth and/or Fe precipitation could further enhance performance. The precipitates found on these iron mounds were essentially pure iron with little to no metal cation incorporation. These minerals could prove valuable for industrial reuse applications.

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