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TECHNICAL ARTICLE

Iron Removal by a Passive System Treating Alkaline Coal Mine Drainage

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Abstract The Marchand passive treatment system was constructed in 2006 for a 6,000 L/min discharge from an abandoned underground bituminous coal mine located in western Pennsylvania, USA. The system consists of six serially connected ponds followed by a large constructed wetland. Treatment performance was monitored between December 2006 and 2007. The system inflow was alkaline with pH 6.2, 337 mg/L $CaCO_3$ alkalinity, 74 mg/L Fe, 1 mg/L Mn, and <1 mg/L Al. The final discharge averaged pH 7.5, 214 mg/L $CaCO_3$ alkalinity, and 0.8 mg/L Fe. The settling ponds removed 84% of the Fe at an average rate of 26 g Fe m^{-2} day^{-1}. The constructed wetland removed residual Fe at a rate of 4 g Fe m^{-2} day^{-1}. Analyses of dissolved and particulate Fe fractions indicated that Fe removal was limited in the ponds by the rate of iron oxidation and in the wetland by the rate of particulate iron settling. The treatment effectiveness of the system did not substantially degrade during cold weather or at high flows. The system cost \$1.3 million (2006) or \$207 (US) per L/min of average flow. Annual maintenance and sampling costs are projected at \$10,000 per year. The 25-year present value cost estimate (4% discount rate) is \$1.45 million or \$0.018 per 1,000 L of treated flow.

Keywords Iron oxidation · Mine drainage · Passive treatment

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Introduction

Effective passive treatment is generally the most economical technology for treating polluted coalmine drainage. A properly designed and constructed passive system achieves effluent targets without any chemical or energy inputs and substantially smaller manpower requirements than conventional technologies. Passive treatment is particularly reliable for alkaline waters where Fe can be precipitated as iron oxyhydroxide solids while the pH is maintained between 6 and 8 by bicarbonate buffering (Hedin et al. 1994a). The alkalinity can be natural or generated through pre-treatment with limestone (Hedin et al. 1994b). Dozens of passive treatment systems are successfully treating alkaline Fe-contaminated waters (Brodie 1990; Dempsey et al. 2001; Hedin et al. 1994a; Hellier et al. 1994; Nuttall 2002; Stark et al. 1994; Younger 2000; Younger et al. 2002).

Flooded underground coalmines with calcareous overburdens commonly produce large flows of alkaline Fe-contaminated water (Hedin et al. 1994a; Lambert et al. 2004; Wood et al. 1999; Younger et al. 2002). In southwestern Pennsylvania (USA) alone, the author is aware of 26 mines that each discharge at least 3,800 L/min (1,000 gpm) of alkaline, Fe-contaminated water. Fifteen of the flows are treated with conventional chemical and mechanical procedures, at great expense. The remaining discharges are untreated and severely degrade their receiving streams. Passive treatment of most of these discharges has been considered but not implemented for several reasons. There is uncertainty about scaling the successes realized with moderate flows to large flows without sacrificing treatment effectiveness. The performance of large passive systems under variable contaminant loading conditions and in cold weather has been questioned. The management of sludge produced by large systems is considered problematic. Lastly, large passive systems are expensive because they handle very large flows and Fe loadings.

In 2006, the Sewickley Creek Watershed Association (SCWA) constructed a passive treatment system for a 6,000 L/min (1,600 gpm) discharge of alkaline Fe-contaminated water flowing from the abandoned Marchand mine. It is one of the largest passive treatment systems constructed to date in the United States. The system has produced a high quality effluent with minimal operational requirements. This paper presents the first year of performance and explores the iron removal processes that are providing the effective treatment.

Background

The Marchand mine is located in southwestern Pennsylvania (USA) in Westmoreland county. The mine was an underground room and pillar operation in the Pittsburgh coal seam that operated between 1902 and 1938. The mine is below local drainage and flooded when it was closed. A large contaminated discharge has flowed continuously since the 1940s from the primary slope entry (Pullman Swindell 1977). The discharge flows into Sewickley Creek, which is a major tributary of the Youghiogheny River in the Ohio River basin.

The discharge and treatment system are located on a 8 ha (20 acre) flat site that formerly contained railroad tracks, coke ovens, coal refuse, a steam plant, and mine buildings. The site location is 40″15′0.50N, 99″45′52.00W. The property was purchased by the SCWA in 1998 for the purpose of installing a treatment system. Initial site investigations determined that the discharge elevation was too low for reliable passive treatment at the site. A berm was constructed around the slope entry and the flow was redirected through a water level control structure. The discharge was raised 2 m without a measurable loss of flow or the creation of new discharges locally. By raising the discharge, it became feasible to construct a gravity-driven treatment system at the site.

The system was constructed in 2005 and 2006. Mine water began flowing through the system in November 2006. The wetlands were planted in the fall of 2006, but did not grow in until summer 2007. The wetlands were devoid of vegetation in the winter of 2006/2007 when most of the cold-weather monitoring described in this paper occurred.

Design

The system's design follows the general guidance of Hedin et al. (1994a), with modifications that follow a patent on the production of iron oxide from mine water (Hedin 1999). The flow and chemical characteristics of the Marchand discharge were determined by regular sampling between 2001 and 2005 (Table 1). The Marchand discharge is naturally net alkaline and the only metal of concern is Fe. The system was designed to oxidize Fe and retain iron oxyhydroxide solids in six serially connected settling ponds, each of which is about 3,500 m^2. The redundant pond design was used so that the system would continue to function when one or two ponds were removed from service for maintenance. The ponds were constructed with trough influent and effluent structures and features that facilitate sludge recovery. It is anticipated that iron sludge will be removed every 5–7 years and processed to a marketable iron product (Hedin 2003, 2006). The ponds were followed by a 28,000 m^2 constructed wetland that was intended to remove residual Fe and provide ecological values. The final 5,000 m^2 of the constructed wetland was designated as mitigation for pre-existing wetlands impacted by the project and was constructed with variable water depths and a variety of native herbaceous and woody wetland species.

Table 1 Characteristics of the Marchand mine discharge, 2001–2007

	Flow (L/min)	pH	Alk (mg/L)	Fe (mg/L)	Mn (mg/L)	Al (mg/L)	Sulfate (mg/L)	Fe (kg d^{-1})
Pre-system (January 01–November 05)								
Average	6,046	6.2	338	63.1	1.1	<0.5	1,117	531
Count	64	26	32	37	36	36	37	35
System (December 06–07)								
Average	6,275	6.2	337	74.4	1.2	<0.5	1,085	671
Median	6,238	6.2	338	75.9	1.2	<0.5	1,070	723
Standard deviation	1,026	0.1	19	8.6	0.1	na	40	117
Minimum	4,731	6.1	310	56.6	1.0	<0.5	1,029	391
Maximum	8,444	6.4	386	88.4	1.5	<0.5	1,154	799
Count	13	14	20	31	13	13	10	13

Methods

Sampling stations were established at the influent of each pond, the treatment wetland (“Wet-in”), the mitigation wetland (“Mit-in”), and at the final effluent. Measurements of pH and temperature were made in the field with a Hanna 9023 pH meter. Alkalinity was measured in the field by titration to pH 4.5 with 1.6 N sulfuric acid. Samples were collected for laboratory analyses by G&C Laboratories, Summerville, PA and the Pennsylvania State Laboratory, Harrisburg, PA. Raw samples were analyzed for acidity, sulfate, and total suspended solids (TSS). Acidified samples (50% HNO_3) were analyzed for total concentrations of Fe, Mn, and Al by inductively coupled plasma spectrophotometry. Methodologies for both laboratories followed standard protocols (APHA 1999).

Carbon dioxide partial pressures were calculated from the pH and alkalinity by the following equation:

$$CO_2 = [H^+]\left[HCO_3^-\right]/(K_H K_{a1})$$

where CO_2 was in atmospheres, HCO_3^- was estimated from the alkalinity, and the constants were each adjusted for temperature (13°C) and ionic strength (0.1), so that K_H was $10^{-1.31}$ and K_{a1} was $10^{-6.24}$ (Butler 1991).

On three occasions, an extra set of filtered samples (Cameo 0.22 µm acetate syringe filter) were collected, immediately acidified, and analyzed by the laboratory for Fe. Filtered Fe concentrations were assumed to represent dissolved iron (FeD), which at pH 6–8, is predominantly ferrous iron. Particulate Fe concentrations (FeP) were calculated from the difference of the unfiltered and filtered samples and were assumed to represent ferric oxyhydroxide solids. These assumptions may be violated by colloidal ferric solids that pass through the 0.22-µm filter and by ferrous iron adsorbed to the solids removed by the filter. The significance of these errors was considered negligible for the analyses presented in this paper.

Sampling occurred between 5 December 2006 and 15 December 2007. Samples were collected from all stations approximately monthly and analyzed for all field and laboratory parameters. Samples were collected more frequently from the system influent and final effluent and analyzed for total Fe.

The final discharge flows through a 1.8 m (6-foot) wide rectangular wooden structure that impounds water behind it and acts as a weir. The depth of water through the structure was measured and flow was estimated with the following equation:

$$Q = 1492(w - 0.2\mathrm{d})d^{1.5}$$

where Q is the flow rate in g/m, w is the width of the weir (6 feet), and d is the depth of water above the weir (measured in feet).

In March 2007, an infestation of muskgrass (*Chara vulgaris*) clogged the final effluent station, eliminating the stilling conditions necessary for accurate flow estimation. Subsequent modifications to the station made its use as a weir impractical. In August 2007, the system flow rate was measured by the cross-sectional velocity method using a flow velocity meter.

Results

Discharge Characteristics

Table 1 shows the characteristics of the system influent (Marchand mine discharge) before and after the installation. The inflow to the treatment system was consistent with pre-system monitoring and with the assumptions used for the design. The flow was strongly net alkaline and contaminated with 57–88 mg/L Fe. The concentrations of Mn were 1–2 mg/L and the concentrations of Al were less than 0.5 mg/L.

The flow rate averaged 6,275 L/min (1,658 gpm) and ranged as high as 8,444 L/min (2,231 gpm). The last flow rate measured before the muskgrass infestation made the weir inoperable (March 2007) was the highest flow measured. Flows were sustained at a high level well into spring 2007. If the weir had been operational through the spring of 2007, the average flow rate would likely have been higher.

Treatment System Performance

Table 2 shows the average chemical characteristics of the sampling stations. As water flowed through the system, the pH rose while concentrations of alkalinity and Fe fell. The decrease in alkalinity is due to the neutralization of acidity produced by iron oxidation and hydrolysis.

$$Fe^{2+} + 2HCO_3^- + {}^1\!/\!_4O_2 \rightarrow FeOOH(s) + {}^3\!/\!_2H_2O + 2CO_2.$$

The decrease in alkalinity, 123 mg/L, is generally consistent with the 132 mg/L acidity calculated to have been produced by iron oxidation and hydrolysis.

Increased pH is a common feature for passive systems with net alkaline water and is attributed to exsolution of CO_2 (Cravotta 2007; Younger et al. 2002). The discharge from the mine had an average CO_2 partial pressure of $10^{-0.82}$. This value greatly exceeds the atmospheric CO_2 partial pressure ($\approx 10^{-3.5}$), causing CO_2 to exsolve.

$$HCO_3^- \rightarrow CO_2(g) + OH^-.$$

The exsolution decreased dissolved CO_2, and exchanged HCO_3^- for OH^-, which increased pH but did not affect alkalinity.

Table 2 Average chemistry at Marchand system stations

Station	pH	Alk (mg/L)	Fe (mg/L)	Mn (mg/L)	SO_4 (mg/L)	TSS (mg/L)	pCO_2 (atm)
Pond A in	6.2	337	74.4	1.2	1,085	26	0.82
Pond B in	6.4	302					1.07
Pond C in	6.5	283	51.2	1.2	1,097	76	1.20
Pond D in	6.6	255					1.34
Pond E in	6.7	243	26.2	1.2	1,098	49	1.46
Pond F in	6.9	232					1.68
Wet in	7.0	223	12.1	1.2	1,126	22	1.79
Mit in	7.5	220	1.8	0.8	1,139	10	2.30
Final	7.5	214	0.8	0.5	1,124	<5	2.31

Al was <0.5 mg/L at all stations

Fe concentrations decreased on average from 74 mg/L to less than 1 mg/L. Figure 1a shows influent and final effluent concentrations. Figure 1b shows the effluent data on an expanded scale. The highest effluent Fe concentration, 2.4 mg/L, is considered a sampling or laboratory error. The upstream sample on this day (influent to the mitigation wetland) contained 2.1 mg/L iron. Samples collected from the same final effluent station 6 days earlier and three days later contained 0.7 and 0.8 mg/L, respectively.

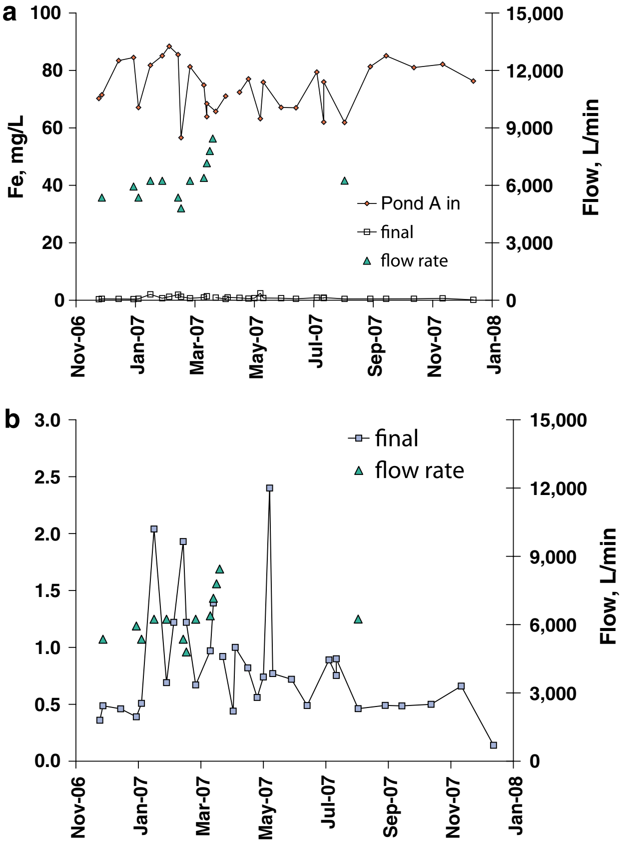

Fig. 1 **a** Influent (Pond A in) and final effluent concentrations of Fe and flow rate at the Marchand passive treatment system. **b** Final effluent concentrations of Fe and flow rate at the Marchand passive treatment system

Table 3 shows area-adjusted Fe removal rates for components of the treatment system. The rates were calculated from the average change in Fe chemistry and the average flow rate. The first two pairs of ponds removed 23–25 mg/L Fe at a common rate of 33 g m^{-2} day^{-1}. The third pair of ponds removed 14 mg/L Fe at a rate of 16 g m^{-2} day^{-1}. The whole series of settling ponds removed 62 mg/L Fe at a rate of 26 g m^{-2} day^{-1}. The treatment wetland removed 10 mg/L Fe at a rate of 4 g m^{-2} day^{-1}. Overall, the whole system removed iron at an average rate of 13 g m^{-2} day^{-1}.

The production of iron oxyhydroxide resulted in highly turbid orange water in the ponds. The wetland effectively removed these solids. The final discharge was typically clear with total suspended solids less than 5 mg/L (Table 2).

Fe Removal Processes

The Marchand system was designed for the oxidative removal of iron. No organic matter was incorporated into

Table 3 Iron removal by the Marchand system

	Surface area (m^2)	Fe in (mg/L)	Fe removal (mg/L)	Fe in (g $m^{-2}d^{-1}$)	Fe removal (g $m^{-2}d^{-1}$)
Ponds A and B	6,378	74	23	105.4	32.9
Ponds C and D	6,888	51	25	67.2	32.8
Ponds E and F	7,949	26	14	29.8	16.0
Treatment wetland	23,424	12	10	4.7	4.0
Mitigation wetland	5,206	2	1	3.1	1.7
Entire system	49,845	74	73	13.5	13.3

All loading calculations assume a flow rate of 6,275 L/min the treatment system that would promote reducing conditions. The wetlands were constructed with existing soils, which were generally mineralized in nature.

The oxidative removal of iron from alkaline water occurs through its oxidation to ferric iron, hydrolysis to a suspended (ss) iron oxyhydroxide solid, and precipitation (p) of the iron solid.

Oxidation	$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$
Hydrolysis	$Fe^{3+} + 2H_2O \rightarrow FeOOH(ss) + 3H^+$
Settling	$FeOOH(ss) \rightarrow FeOOH(p)$

Under alkaline conditions where the pH is maintained between 6 and 8, the hydrolysis step is rapid and the limiting processes are oxidation and solids settling.

The oxidation step is generally considered rate limiting for mine water treatment systems (Hustwit et al. 1992) and has received the most attention by AMD researchers. Above pH 5, the reaction is dominated by abiotic processes (Hedin et al. 1994a; Kirby et al. 1999). Two abiotic oxidation mechanisms have been identified: a homogeneous reaction involving oxidation of dissolved Fe^{2+}, and a heterogeneous reaction involving oxidation of Fe^{2+} sorbed onto ferric oxyhydroxide solids. Rate reactions for the two reactions are provided below where ferric oxyhydroxide solids are represented as Fe(III).

Homogeneous oxidation	$d[Fe(II)]/dt = k_1[Fe^{2+}][O_2]/[H^+]^2$
Heterogeneous oxidation	$d[Fe(II)]/dt = k_2[Fe(III)][Fe^{2+}][O_2]/[H^+]$

Both mechanisms are first order with respect to Fe^{2+} and dissolved oxygen. The heterogeneous mechanism is also first order with respect to Fe(III) and pH. The homogeneous reaction is second order with respect to pH. The relative importance of the mechanisms varies with pH and concentrations of Fe(III). At high pH values, such as those created in chemical treatment systems, the homogeneous reaction dominates. At lower pH, the heterogeneous reaction can dominate, but the amount of Fe(III) available is limited by its initial formation via the homogeneous mechanism and the loss of Fe(III) solids from the water column through settling.

The relative importance of oxidation and solids settling processes was evaluated by comparing dissolved Fe (FeD) and particulate Fe (FeP) on 3 days when filtered samples were collected. Table 4 shows the summary data and Fig. 2 plots average concentrations of FeD and FeP through the Marchand system. Because of the very low solubility of ferric iron at pH 6–8, FeD approximates dissolved ferrous iron. The discharge from mine was always clear water with negligible particulate Fe. Solids were visible in pond A within 0.5 m of the influent trough. Solids accumulated in the water column in ponds A and B, reaching 11–21 mg/L FeP. Particulate iron decreased gradually with flow through the rest of the system.

In the ponds, the iron content was dominated by ferrous iron (FeD). The situation was reversed in the wetlands, where

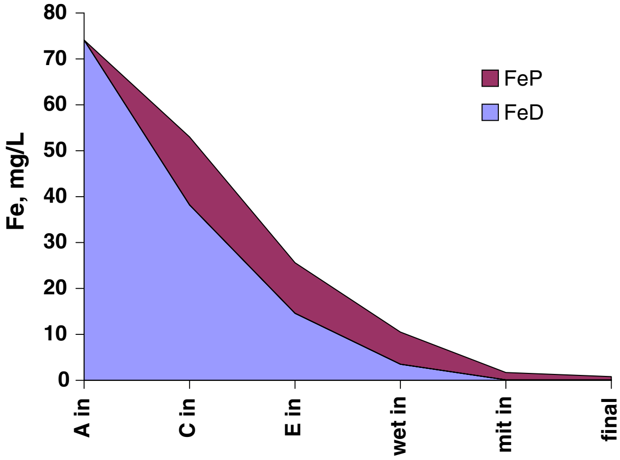

Fig. 2 Changes in dissolved (Fe^D) and particulate (Fe^P) iron in the Marchand system; the average of three measurements is shown

Table 4 Average iron oxidation and settling in the Marchand ponds and wetlands (Wet)

	FeT^{in} (mg/L)	FeD^{in} (mg/L)	FeP^{in} (mg/L)	Fe Ox (mg/L)	FeP^{tot} (mg/L)	Fe set (mg/L)	Oxidized ($g\ m^{-2}d^{-1}$)	Settled ($g\ m^{-2}d^{-1}$)
Ponds A and B	69.0	69.0	0.0	30.8	30.8	16.0	42.6	22.6
Ponds C and D	53.0	38.2	14.8	23.6	38.4	27.4	39.9	33.9
Ponds E and F	25.6	14.6	11.0	11.1	22.1	15.1	18.2	17.4
Treatment wet	10.5	3.5	7.0	>3.5	10.5	11.3	>1.4	4.6
Mitigation wet	1.6	<0.1	1.6	<0.1	1.6	1.2	<0.1	2.3
Final	0.8	<0.1	0.7		0.8			

FePin = FeTin − FeDin, Fe Ox = FeDin − FeDout, FePtot = FePin + Fe Ox, Fe Set = $FeT^{in} - FeT^{out}$

particulate iron (FeP) dominated. The quality of the final discharge was determined by the efficiency of FeP settling.

Iron oxidation and particulate settling rates were calculated for the treatment units (Table 4). The amount of oxidation (FeOx) within a unit was estimated from the change in ferrous iron (FeD) between a unit's influent and effluent station. Oxidation was assumed to generate iron oxyhydroxide solids. The amount of particulate Fe available within a unit for settling, FeP^{tot} was estimated from the sum of the influent FeP and the oxidation within the unit (FeOx). The amount of settling (Fe Set) was calculated from the change in FeT between the unit's influent and effluent stations. Area-adjusted oxidation and settling rates were calculated from the changes in concentrations, the flow rate, and the unit's surface area.

Figure 3a, b shows the individual oxidation and settling rate calculations plotted against the total Fe available in the unit for each process. Rate calculations were included only if there was more than 1 mg/L Fe at the downstream station. The inclusion of rates where the reactant is exhausted is not useful in rate capacity evaluations (Hedin et al. 1994a). This screen eliminated oxidation rates at low concentrations because all of the FeD measurements within the wetland were <1 mg/L. Least squares equations were calculated for each. For the oxidation data, an exponential function provided the best fit. For the settling data, a linear function provided the best fit.

Figure 3c plots the oxidation and settling functions on a common Fe axis. The plot shows the concentration-dependent nature of the iron removal process. Both oxidation and settling processes are directly affected by the concentrations of available Fe reactants. At higher Fe concentrations, the oxidation rate is slower and limits the treatment performance of the system. At lower Fe concentrations, the settling rate is slower and limits the performance of the system.

Cold Weather

The kinetics of chemical reactions varies directly with temperature, approximately doubling with each 10°C change. Moderate declines in Fe removal during cold weather have been observed by the author at several passive treatment systems in Pennsylvania. The treatment effectiveness of the Marchand system, however, did not substantially decline in cold weather. For 6 weeks between mid-January and March 2007, the wetlands were largely frozen with several inches of ice, and the final discharge was less than 4°C. Despite these extreme cold-weather conditions, the final discharge was good quality (Fig. 1b). Effluent concentrations while the wetland was frozen were 0.7–2.0 mg/L and averaged 1.3 mg/L, only 0.8 mg/L higher than during warm weather conditions.

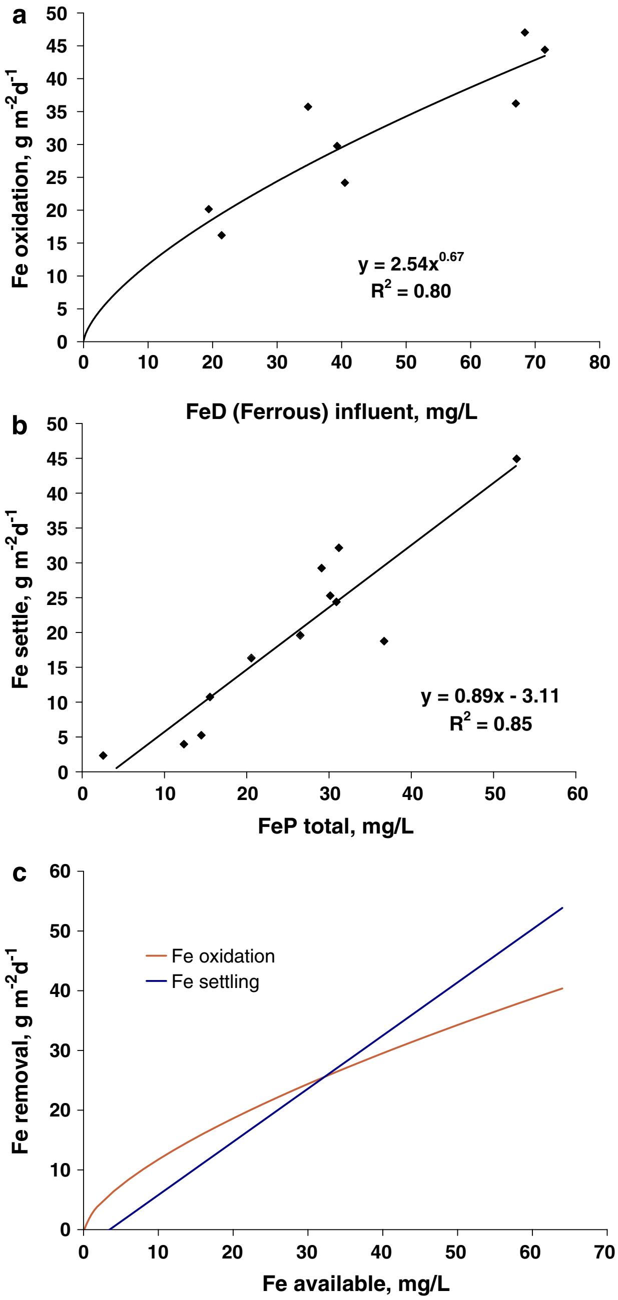

Fig. 3 **a** The relationship between the measured ferrous iron oxidation rate and the concentration of ferrous iron available in the treatment unit. **b** The relationship between the iron settling rate and the total concentration of particulate iron in the treatment unit. **c** Iron oxidation and settling rates plotted as a function of Fe available for each process

The small impact of cold temperature on the Marchand system's Fe removal was attributable to several factors. First, temperature variation was not as substantial as might be inferred from measurements at the final effluent. Table 5 shows average water temperatures within the Marchand system in winter and summer months. In winter, final discharge temperatures were 22°C less than in summer.

Table 5 Average (avg) water temperature and pH in winter (Win) and summer (Sum); only data from the 11 days when all stations were sampled is included

	Temp (°C)			pH		
	Win	Sum	Avg	Win	Sum	Avg
Pond A in	13.2	14.6	13.8	6.2	6.2	6.2
Pond B in	12.1	16.2	13.8	6.4	6.3	6.4
Pond C in	10.9	17.2	13.6	6.6	6.4	6.5
Pond D in	9.0	19.0	13.4	6.8	6.5	6.6
Pond E in	8.0	20.1	13.4	6.9	6.6	6.7
Pond F in	7.2	20.9	13.4	7.1	6.6	6.9
Wet in	6.6	22.1	13.6	7.3	6.8	7.0
Final	3.8	26.3	13.9	7.9	7.5	7.6
Ponds, avg	9.6	18.6	13.6	6.8	6.5	6.6
Wetland, avg	5.2	24.2	13.7	7.6	7.1	7.3

Winter (Win): four dates in December 06, January 07, February 07, December 07, Summer (Sum): four dates in June 07, July 07, August 07, September 07

However, little iron oxidation occurred in the wetlands because ferrous iron concentrations were low (Fig. 2). Most of the iron oxidation occurred in the ponds where winter temperatures were only 9°C colder in winter than summer. This temperature difference could slow chemical reactions in cold weather to about 50% of the warm weather rates.

The negative impact of lower temperatures on the reaction kinetics in the Marchand system appears to be offset by temperature-related chemical variation. Iron oxidation is directly related to dissolved oxygen (DO), whose solubility is inversely related to temperature. The change in solubility should increase gas transfer at lower temperature, increasing the rate of iron oxidation. The solubility of DO is 25% higher at 9°C than 19°C, and if the oxygen transfer into the water increases proportionally, the oxidation rate will increase 25%.

A second factor that influences iron oxidation in the Marchand system in cold weather is an inverse relationship between water temperature and field pH (Table 5). Figure 4 shows the relationship for the Wet-in station. Laboratory pH measurements also varied inversely with field temperature (not shown), indicating that the relationship was not due to a temperature-related problem with the field pH measurements. Overall, the average pH of the ponds during cold weather was 0.3 units higher than in warm weather. If the heterogeneous iron oxidation mechanism dominates under these conditions, then the higher pH could increase the oxidation rate by 1.9 times over lower pH, warm weather conditions. In the final pond, where the cold weather difference was 0.5 pH units, the oxidation reaction was potentially increased by 3.2 times.

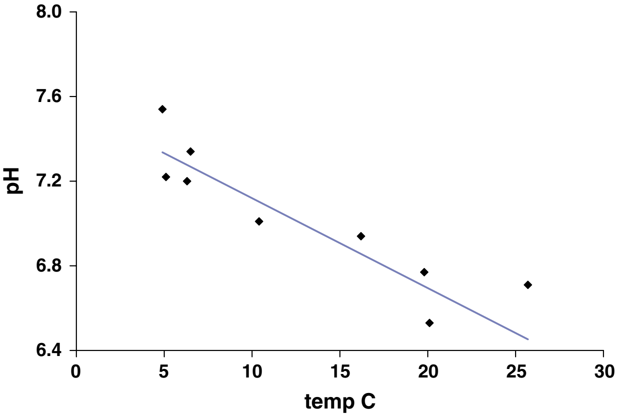

Fig. 4 Relationship between pH and water temperature at the effluent of the last settling pond (influent to the treatment wetland). The least squares regression equation is: pH = −0.043 temperature +7.54, $R^2 = 0.82$

The inverse relationship between pH and water temperature was not expected and the cause is currently under investigation. Similar analyses of pH and temperature at common sampling stations have not been reported, so it is unknown whether this is a common phenomena or a unique result of the Marchand system water chemistry and design.

The inverse relationship between temperature and both dissolved oxygen and pH is more than sufficient to offset the direct relationship between temperature and reaction kinetics for iron oxidation. The effect of temperature variation on the settling rate of iron oxyhydroxide is not known. It is possible that lesser Fe removal by some passive systems in winter is due to slower or less efficient solids settling rates, not slower ferrous iron oxidation.

High Flow Performance

Flow variation affects retention time. Between December 2006 and March 2006, flow increased from 5,300 L/min (1,400 gpm) to 8,400 L/min (2,200 gpm), decreasing the system's theoretical retention time from 106 to 68 h. This 35% decrease in retention did not result in a proportional decrease in Fe removal. The decrease in effluent quality during high flow conditions was only 1–2 mg/L Fe. The small absolute difference in effluent quality at high flow can be explained with a simple iron oxidation model. Figure 5a shows iron concentrations for a model that assumes first order removal of Fe from the Marchand system inflow, while holding other variables constant. The initial value, 74 mg/L is the average Marchand influent concentration. The kinetic constant was set by trial and error at 0.049 mg/L/h so that the final discharge after 90 h (average theoretical retention time) was 0.8 mg/L (average final effluent). Under these conditions, the half-life of Fe is 14 h.

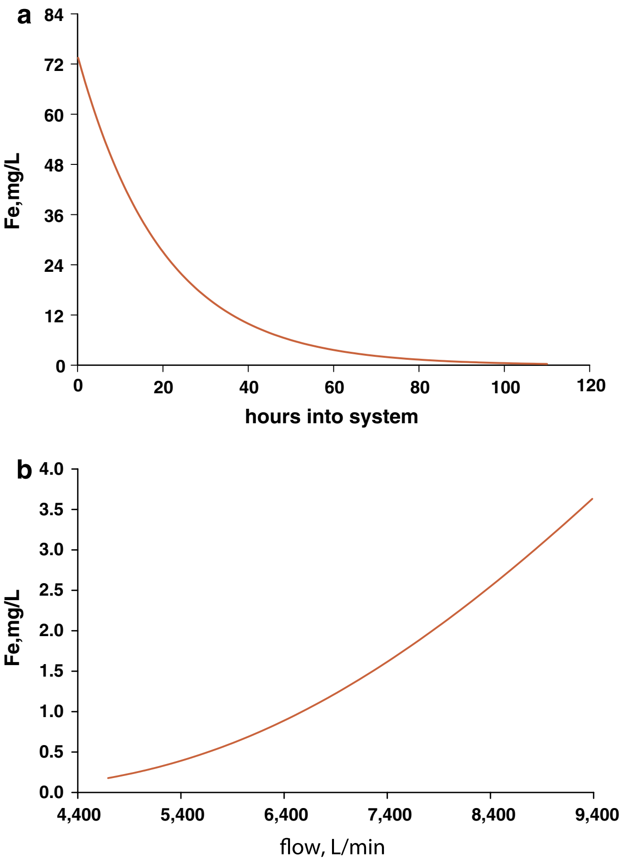

Fig. 5 **a** Time-dependent removal of Fe assuming first order Fe removal. **b** Relationship between flow rate and final effluent Fe concentration assuming first order Fe removal for scenario shown in 5a

The modeled system discharges less than 6 mg/L Fe whenever the retention times are at least 50 h. Figure 5b relates the system flow rate to the modeled final effluent Fe concentrations. At 8,400 L/min (2,200 gpm), a final effluent with 2.5 mg/L Fe is predicted. The observed final effluent under high flows was better than predicted by the model. In spring 2007, when flows were high, the final effluent averaged 1 mg/L (Fig. 2b).

Effluent Quality

The Marchand system produced an effluent in its first year of operation that was compliant with standard mine discharge permit limits. Table 6 compares the Marchand final discharge to the limits generally applied for permitted mine water discharges in Pennsylvania [Pa Code, Chapter 87.102 (a)]. The Marchand system effluent has never exceeded any of the discharge limits.

Table 6 Typical NPDES limits for coal mine treatment systems in the US and pertinent values from the Marchand passive system (from Pa Code, Chapter 87.102)

	Final discharge limits		Marchand system, 2007	
	Monthly average	Maximum	Monthly average	Maximum
Fe	3.0 mg/L	7.0 mg/L	0.3–1.3 mg/L	2.4 mg/L
Mn	2.0 mg/L	5.0 mg/L	0.1–0.8 mg/L	1.0 mg/L
TSS	30 mg/L	90 mg/L	<3–12 mg/L	12 mg/L
pH	6.0–9.0 at all times		7.1–8.1	
Alk	Net alkaline at all times		151–215 mg/L net alkalinity	

Pennsylvania has special effluent criteria for passive mine water treatment systems that require a final effluent with pH 6–9, net alkalinity, and Fe concentrations at least 90% less than the influent concentrations [Pa Code, Chapter 87.102 (c)(3)]. If these standards were imposed on the Marchand system, the effluent Fe limit would be 7 mg/L. The system consistently met this limit.

The earth disturbance and wetland encroachment permits included an effluent limit for the inflow to the mitigation wetland of 7 mg/L Fe. The mitigation wetland influent averaged 1.8 mg/L Fe (Table 2) and the highest value measured was 4.0 mg/L Fe.

Long-term Treatment Performance

The long-term performance of any treatment system requires that the conditions that promote contaminant removal be maintained. The Marchand system operates through oxidation and settling, both of which require adequate retention in the ponds and wetlands. In the short-term, retention is maximized by maintaining the flow distribution system. The troughs and pipes connecting the settling ponds must be cleaned monthly at a cost of approximately 12 man-h per month. Sampling and system inspections require 4 man-h per month. A contingency of 50 man-h per year is recommended for unexpected problems. The total requirement for routine operational maintenance of the Marchand system is approximately 250 man-h per year. Because these duties are simple and non-hazardous, they can be accomplished by trained volunteers. Alternatively, the operation and maintenance (O&M) can be contracted which, at $40/h, is estimated to cost approximately $10,000 (US) per year.

The system's retention time decays with iron sludge accumulation. The Marchand system was designed to produce a clean iron oxide sludge that could be easily removed and processed into a saleable iron pigment product (Hedin 1999; Hedin 2003). The first recovery of the iron will occur when sludge depths exceed 25 cm, which is expected in 2012 or 2013. The revenue from iron recovery is projected to offset sludge management costs. If the sludge revenues can also offset annual operational costs, the system will be self-sustaining.

Cost Analysis

The Marchand system was designed, permitted, and constructed for a total cost of $1.3 million (US) (2006). In its first full year of operation, it treated, on average, 6,275 L/min (1,658 gpm) of flow and 671 kg/day (1,476 lb/day) of Fe to a condition continuously compliant with standard effluent permits in the eastern United States. Assuming these flows and loadings, the capital cost was $207 per L/min average flow ($784 per gpm) or $1,937 per kg per day average Fe loading ($881 per lb per day Fe). This design treated flows 35% higher than average conditions to a high quality condition (<2 mg/L Fe).

The O&M cost is estimated at $10,000 per year which, when related to the average conditions, is equivalent to $0.003 per 1,000 L of flow ($0.011 per 1,000 g) or $0.041 per kg Fe treated ($0.019 per lb Fe). If long-term sludge management costs are offset by iron recovery, then the total capital and operational costs for 25 years are estimated at $1,550,000 (US). This cost stream, discounted at 4%, has a 2007 present value of $1,456,000. Over the 25-year period, the system is projected to treat water at a cost of $0.018 per 1,000 L ($0.067 per 1,000 g) or $0.238 per kg Fe ($0.108 per lb Fe). These costs are substantially less than conventional lime plants treating alkaline Fe-contaminated mine water. In the US, capital costs for plant construction are generally $250–500 per L/min of installed capacity ($1,000–2,000 per gpm). Annual operational costs are generally $0.05–$0.10 per 1,000 L of flow ($0.20–0.40 per 1,000 g). Assuming average cost estimates and a 4% discount rate, over a 25-year period, a lime plant would be expected to treat alkaline Fe-contaminated mine water at a cost of about $0.075 per 1,000 L of flow ($0.285 per 1,000 g).

Summary

During its first year of operation, the Marchand passive treatment system continuously treated a 4,700–8,400 L/min flow containing an average of 74 mg/L Fe to a final discharge that averaged <1 mg/L Fe and was fully compliant with standard Pennsylvania and US discharge permit criteria. The iron was precipitated in ponds designed to produce a clean iron sludge that can be recovered and processed to a marketable iron oxide. Analysis of total and dissolved iron concentrations provided insights into the iron removal processes. The ponds removed 85% of the iron loading at rates that were primarily controlled by ferrous iron oxidation. The removal of the remaining 15% of iron occurred in the constructed wetland where the process was controlled by the settling of iron solids. The quality of the final discharge is controlled by solids settling, not iron oxidation.

A common criticism of passive treatment is that systems are unreliable in cold weather and at high flow rates. During the first year of operation, a month of sub-freezing temperatures created extensive ice cover in the wetland, and high spring flows decreased the theoretical retention from 90 to 68 h. The discharge degradation during these periods was only 1 mg/L Fe. The kinetic penalties of cold temperatures were offset by increased dissolved oxygen solubility and also by an unexpected cold-weather increase in pH. The good performance under higher flows is consistent with first order removal of iron by the system. A simple empirical model indicated that 90% of the Fe should be removed after 50 h of retention and predicted that the final effluent at 68 h of retention should be ≈2.5 mg/L.

The Marchand system has low operational costs because it is passive and sludge management costs are offset by iron oxide production. The anticipated long-term costs are approximately 25% of the costs of a conventional lime plant.

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