

EFFECTIVE PASSIVE TREATMENT OF A LARGE FLOW OF ALKALINE FE-CONTAMINATED MINE WATER¹

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Abstract: The Marchand passive treatment system was constructed in 2006 for a 6,000 L/min (1,650 gpm) 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 December 2007. The system inflow was net alkaline with pH 6.2 and 74 mg/L Fe, 1 mg/L Mn, and <1 mg/L Al. The final discharge averaged pH 7.5, 214 mg/L CaCO₃ alkalinity, and 0.8 mg/L Fe. The settling ponds removed 84% of the Fe at an average rate of 26 gFe m⁻²day⁻¹. The constructed wetland removed residual Fe at a rate of 4 gFe m⁻²day⁻¹. Analyses of dissolved and particulate Fe fractions indicated that Fe removal was limited in the ponds by iron oxidation and in the wetland by 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 \$153 per L/min (\$580 per gpm) installed capacity. Annual maintenance and sampling costs are projected at \$10,000/yr. The 25 year present value cost estimate (4% discount rate) is \$1.45 million or \$0.018 per 1,000 L (\$0.067 per 1000 gal) of treated flow.

Additional Key Words: mine drainage, passive treatment, iron oxidation

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Introduction

Effective passive treatment is the most economical technology for treating contaminated coal mine drainage. A properly designed and constructed passive system achieves effluent targets without any external 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 oxide solids while the pH is maintained between 6 and 8 by bicarbonate buffering (Hedin, et al. 1994a). The alkalinity can be derived naturally 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; Stark et al. 1994, Hedin et al. 1994a; Hellier, et al. 1994; Younger, 2000; Dempsey, et al. 2001; Nuttall, 2002; Younger, et al. 2002).

Flooded underground coal mines with calcareous overburdens commonly produce large flows of alkaline Fe-contaminated water (Hedin et al. 1994a; Wood et al. 1999; Younger et al. 2002; Lambert et al. 2004). In southwestern PA alone, the author is aware of 26 mine discharges of alkaline Fe-contaminated water that each flow at least 3,800 L/min (1,000 gpm). 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 have high capital costs because they handle very large flows and Fe loadings.

In 2006 the Sewickley Creek Watershed Association 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 discusses the reasons for the effective treatment.

Background

The Marchand Mine is located in southwestern Pennsylvania 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 1940's from the primary slope entry (Pullman Swindell 1977). The discharge resulted in the pollution of Sewickley Creek, a major tributary of the Youghiogheny River in the Ohio River Basin.

The discharge and treatment system are located on a 20 acre site that is relatively flat and formerly contained railroad tracks, coke ovens, coal refuse, a steam plant, and mine buildings. The site location is 40° 15' 0.50" N, 99° 45' 52.00" W. The property was purchased by Sewickley Creek Watershed Association (SCWA) in the 1990's for the purpose of installing a treatment system. Initial site investigations determined that the discharge was too low in elevation 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 5 ft without a measurable loss of flow or the creation of new discharges locally. By elevating 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 little growth occurred until summer 2007. Thus, the wetlands were devoid of actively growing vegetation in the winter of 2006/07 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 Marchand discharge is naturally net alkaline and the primary concern is Fe. The system was designed to oxidize Fe and retain iron oxide solids in six serially-connected settling ponds, each of which is about 3,500 m² (0.9 acre). 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). The ponds were followed by a 28,600 m² (7.0 acre) constructed wetland that was intended to remove

residual Fe and provide ecological values. The final 5,200 m² (1.3 acre) 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.

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 H₂SO₄. Samples were collected for laboratory analyses (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% HNO₃) were analyzed for total concentrations of Fe, Mn, and Al by inductively coupled plasma spectrophotometry. Methodologies for both laboratories followed standard protocols (APHA 1999).

On three occasions an extra set of filtered samples (0.45 µm) were collected and analyzed for dissolved metals. Particulate Fe was calculated from the difference of filtered and unfiltered samples.

Sampling occurred between December 5, 2006 and December 15, 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 6-ft wide rectangular wooden structure that impounds water behind it and acts as a weir. The depth of water through the effluent structure was measured from a gauge installed in the effluent pool and this value was used to estimate flow with the following equation.

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

Where Q is flow rate in gpm, w is the width of the weir (6 ft), 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) since the system was installed. The flow was strongly net alkaline and contaminated with 57-88 mg/L Fe. Concentrations of Mn were 1-2 mg/L and 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.

Table 1. Characteristics of the Marchand Mine discharge, Dec 2006 – Dec 2007.

	Flow	pH	Alk	Fe	Mn	Al	Sulfate	Fe
	L min ⁻¹		-----mg/L-----					kg d ⁻¹
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
St dev	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

Treatment System Performance

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



where each mg/L Fe removed neutralizes 1.8 mg/L of alkalinity as CaCO₃. The decrease in alkalinity, 123 mg/L, was 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 CO₂ (Younger, et al. 2002; Cravotta, 2007). Carbon dioxide partial pressures (Table 2) were calculated from the pH and alkalinity by the following equation:

$$\text{CO}_2 = [\text{H}^+] [\text{HCO}_3^-] / (\text{K}_\text{H} \text{K}_\text{a1})$$

Where CO₂ is atmospheres, HCO₃⁻ was estimated from 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).

Table 2. Average chemistry at Marchand System stations.

Station	pH	Alk	Fe	Mn	SO ₄	TSS	pCO ₂	
		-----mg/L-----						atm
Pond A in	6.2	337	74. 4	1.2	1,085	26	0.82	
Pond B in	6.4	302	na	na	na	na	1.07	
Pond C in	6.5	283	51. 2	1.2	1,097	76	1.20	
Pond D in	6.6	255	na	na	na	na	1.34	
Pond E in	6.7	243	26. 2	1.2	1,098	49	1.46	
Pond F in	6.9	232	na	na	na	na	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 < 0.5mg/L at all stations; na indicates data not available

The discharge from the mine had an average CO₂ partial pressure of 10^{-0.82}. This value greatly exceeds atmospheric CO₂ partial pressure (~10^{-3.5}), causing CO₂ to exsolve.



The exsolution decreases dissolved CO_2 with flow through the system. The exsolution exchanges HCO_3^- for OH^- , which increases pH but does not affect alkalinity.

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. During this sampling event, the upstream sample (influent to the mitigation wetland) contained 2.1 mg/L Fe. Samples collected from the same final effluent station six days earlier and three days later contained 0.7 and 0.8 mg/L, respectively.

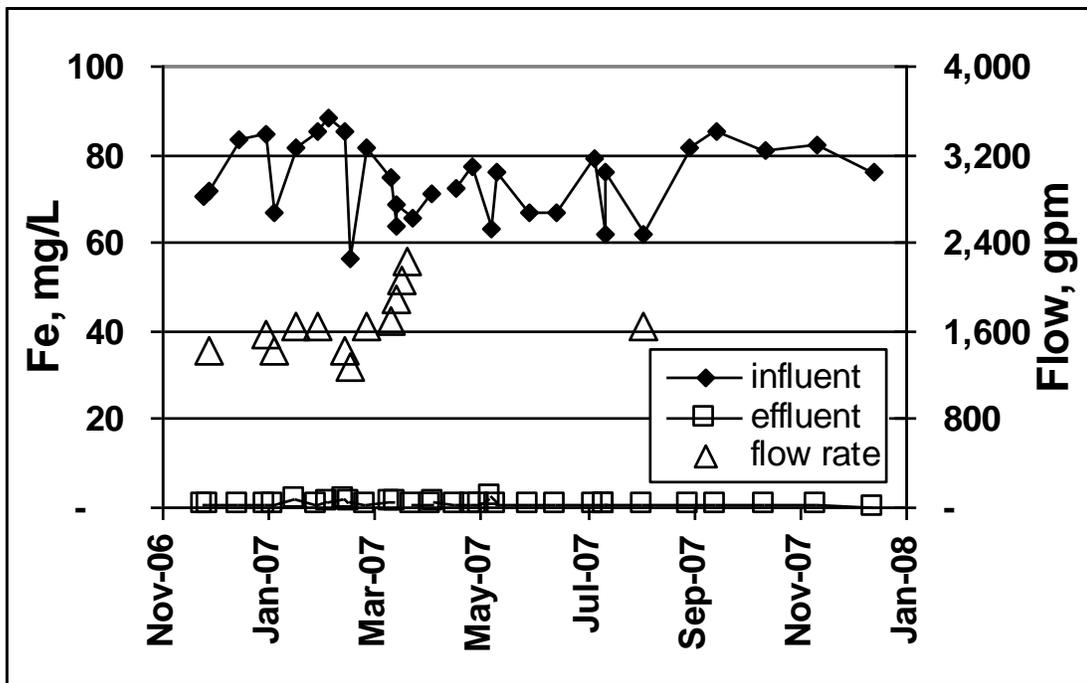


Figure 1a. Influent and Effluent concentrations of Fe at the Marchand passive treatment system.

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 $33 \text{ g m}^{-2}\text{d}^{-1}$. The third pair of ponds removed 14 mg/L Fe at a rate of $16 \text{ g m}^{-2}\text{d}^{-1}$. The whole series of settling ponds removed 62 mg/L Fe at a rate of $26 \text{ g m}^{-2}\text{d}^{-1}$. The treatment wetland removed 10 mg/L Fe at a rate of $4 \text{ g m}^{-2}\text{d}^{-1}$. Overall, the whole system removed iron at an average rate of $13 \text{ g m}^{-2}\text{d}^{-1}$.

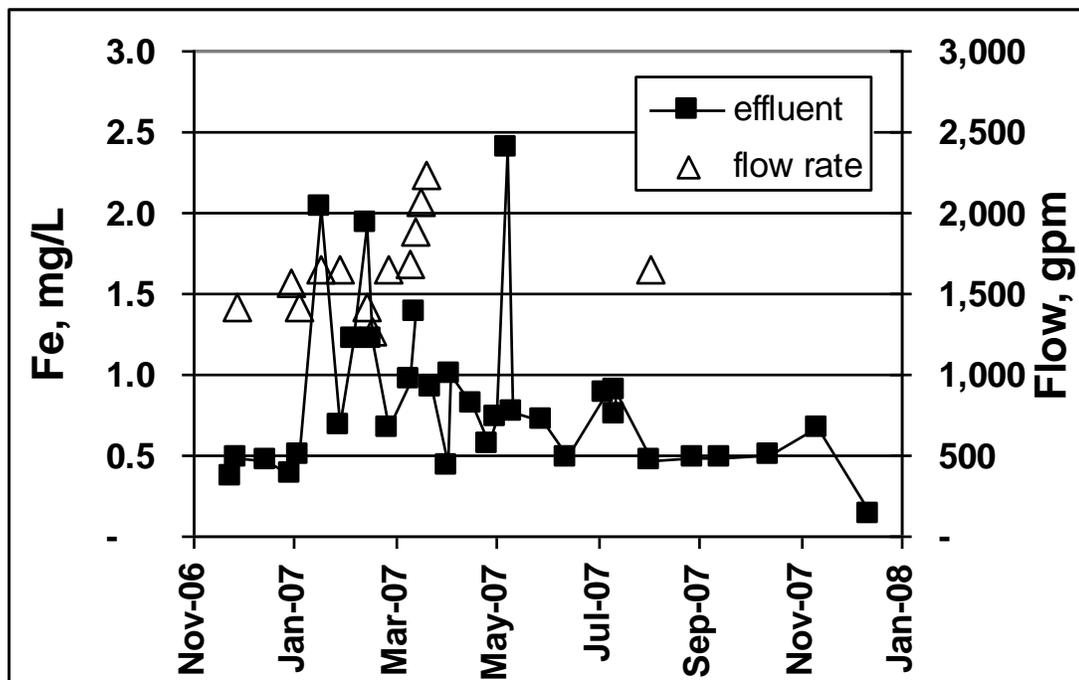


Figure 1b. Effluent concentrations of Fe at the Marchand passive treatment systems.

Table 3. Iron removal by the Marchand system.

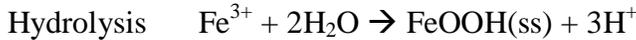
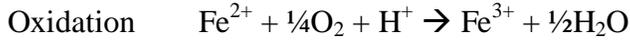
	Surface area, m ²	Fe in, mg/L	Fe removal mg/L	Fe in, g d ⁻¹ m ⁻²	Fe removal g d ⁻¹ m ⁻²
Ponds A&B	6,378	74	23	105.4	32.9
Ponds C&D	6,888	51	25	67.2	32.8
Ponds E&F	7,949	26	14	29.8	16.0
Treat Wetland	23,424	12	10	4.7	4.0
Mit Wetland	5,206	2	1	3.1	1.7
Entire System	49,845	74	73	13.5	13.3

All loading calculations assume a flow rate of 6,275 L/min.

Fe Removal Processes

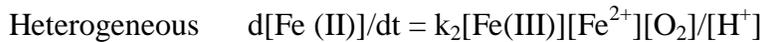
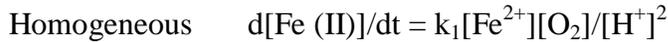
The Marchand system was designed for the oxidative removal of iron. No organic matter was incorporated into the treatment system that would promote reducing conditions. The wetlands were constructed with existing soils which were generally mineral in nature.

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



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 (Dempsey et al., 2001) Rate reactions for the two reactions are provided below, where Fe(III) represents ferric oxyhydroxide solids.



Both mechanisms are first order with respect to Fe^{2+} and dissolved oxygen. The heterogeneous mechanism is also first order with respect to $\text{Fe}^{(\text{III})}$ and pH. The homogeneous reaction is second order with respect to pH. The relative importance of the mechanisms varies with pH and concentrations of $\text{Fe}^{(\text{III})}$. 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 $\text{Fe}^{(\text{III})}$ available is limited by its initial formation via the homogeneous mechanism and the loss of $\text{Fe}^{(\text{III})}$ 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 three 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 clear 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&B reaching 11 – 21 mg/L FeP. Particulate iron decreased gradually with flow through the rest of the system.

Table 4. Average iron oxidation and settling in the Marchand ponds and wetlands

	FeTⁱⁿ	FeDⁱⁿ	FePⁱⁿ	Fe Ox	FeP^{tot}	Fe Set	Oxidize	Settle
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	g d⁻¹m⁻²	g d⁻¹m⁻²
A&B	69.0	69.0	0.0	30.8	30.8	16.0	42.6	22.6
C&D	53.0	38.2	14.8	23.6	38.4	27.4	39.9	33.9
E&F	25.6	14.6	11.0	11.1	22.1	15.1	18.2	17.4
T-wet	10.5	3.5	7.0	>3.5	10.5	11.3	>1.4	4.6
M-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			

$$\text{FeP}^{\text{in}} = \text{FeT}^{\text{in}} - \text{FeD}^{\text{in}}; \text{Fe Ox} = \text{FeD}^{\text{in}} - \text{FeD}^{\text{out}}; \text{FeP}^{\text{tot}} = \text{FeP}^{\text{in}} + \text{Fe Ox};$$

$$\text{Fe Set} = \text{FeT}^{\text{in}} - \text{FeT}^{\text{out}}$$

In the ponds, the iron content was dominated by ferrous iron (FeD). The situation was reversed in the wetlands, where particulate Fe 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 (Fe Ox) 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 oxide 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 (Fe Ox). 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, g d⁻¹ m⁻², were calculated from the changes in concentrations, the flow rate, and the unit's surface area.

Figures 3a and 3b show 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.

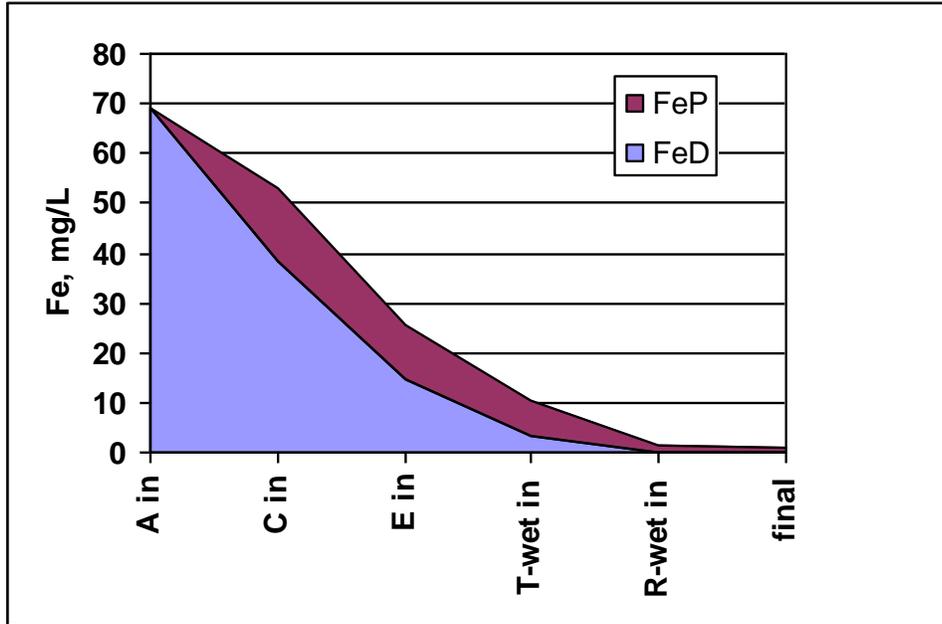


Figure 2. Changes in dissolved (Fe^{D}) and particulate (Fe^{P}) iron in the Marchand System. The average of three measurements is shown.

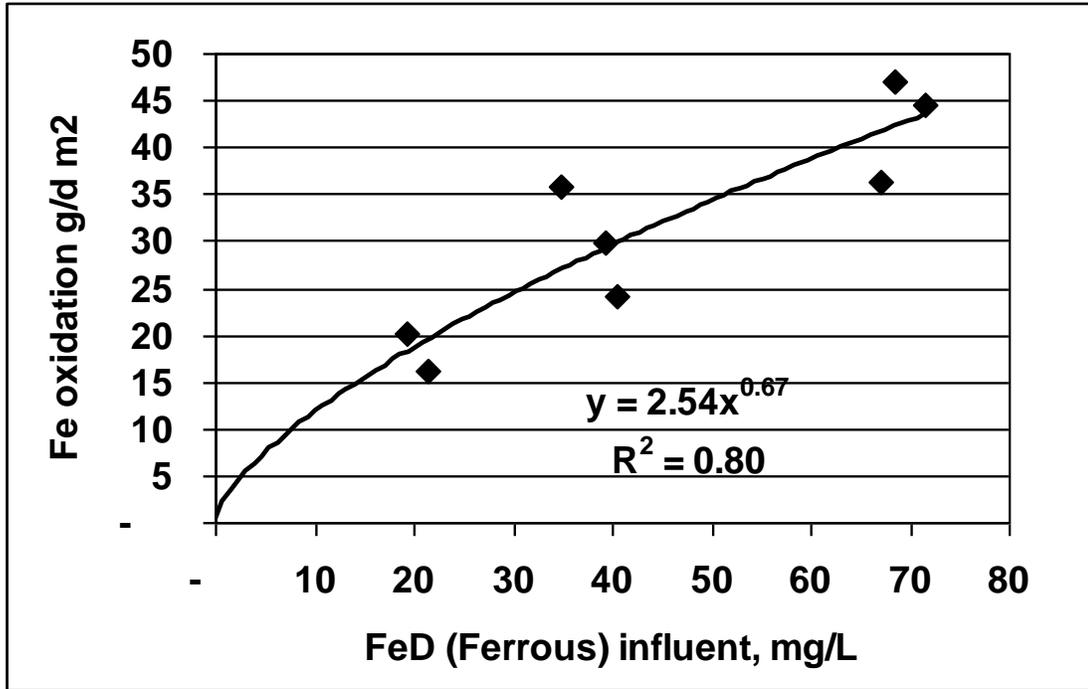


Figure 3a. The relationship between the measured ferrous iron oxidation rate and the concentration of ferrous iron available in the treatment unit.

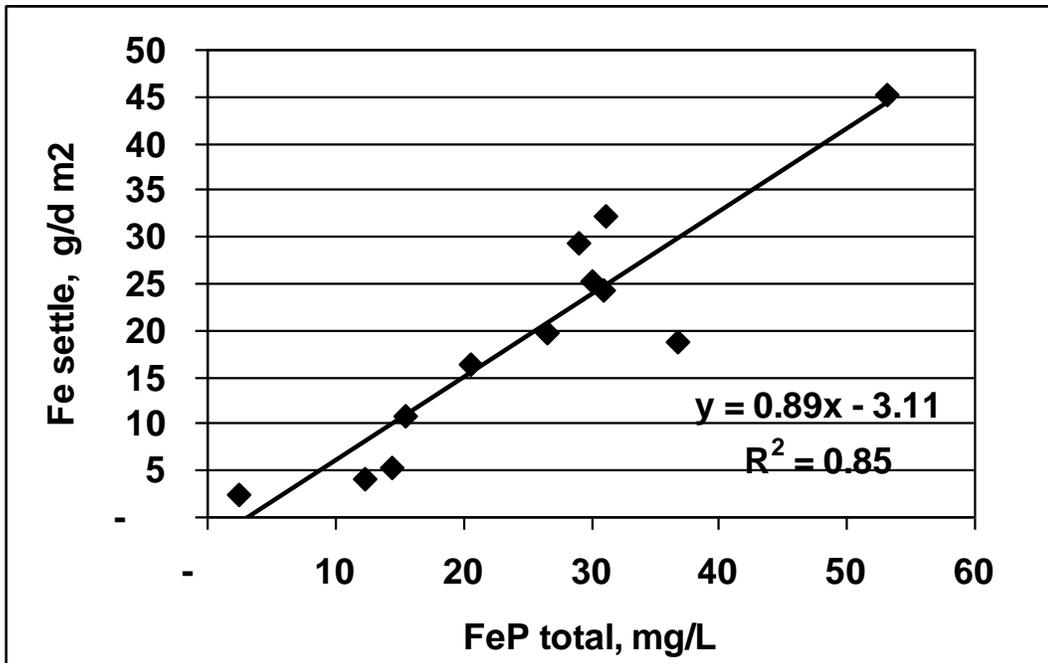


Figure 3b. The relationship between the iron settling rate and the total concentration of particulate iron in the treatment unit.

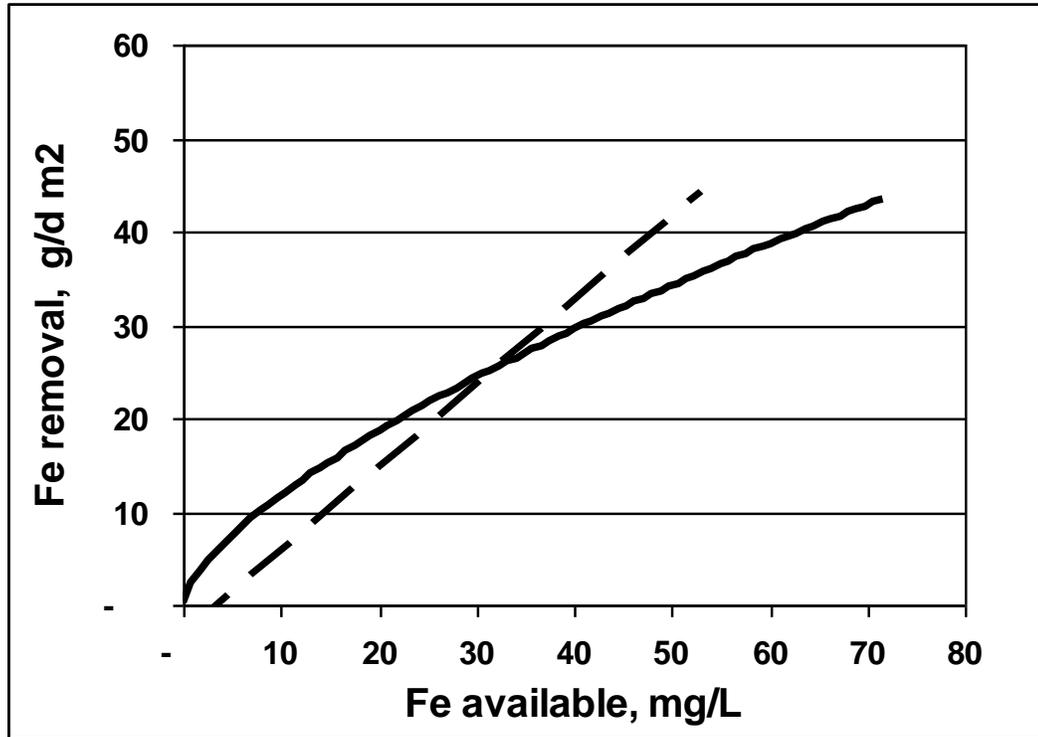


Figure 3c. Iron oxidation (solid line) and settling (dashed line) rates plotted as a function of Fe available for each process.

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. However, the treatment effectiveness of the Marchand system did not substantially decline during cold weather. For six 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 quality of the final discharge was good (Fig. 1b). Effluent concentrations while the wetland was frozen were 0.7 – 2.0 mg/L and averaged 1.3 mg/L, which was only 0.8 mg/L higher than warm weather conditions.

The small impact of cold temperature of the Marchand system's Fe removal is due to several factors. First, temperature variation is 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 average conditions. However, little iron oxidation actually occurs in the wetlands (Fig. 2). Most of the

iron oxidation occurs in the ponds where winter temperatures are only 9°C colder in winter than summer. This temperature difference could slow chemical reactions in cold weather to about 50% 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 variations. 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 temperatures, increasing the rate of iron oxidation. The solubility of DO is 25% higher at 9°C than 19°C, and if the DO transfer increases proportionally, the oxidation rate will increase 25%.

Table 5. Average water temperature and pH in winter (Win) and summer (Sum).

	Temp, C			pH		
	Win	Sum	Ave	Win	Sum	Ave
A in	13.2	14.6	13.8	6.2	6.2	6.2
B in	12.1	16.2	13.8	6.4	6.3	6.4
C in	10.9	17.2	13.6	6.6	6.4	6.5
D in	9.0	19.0	13.4	6.8	6.5	6.6
E in	8.0	20.1	13.4	6.9	6.6	6.7
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, average	9.6	18.6	13.6	6.8	6.5	6.6
Wetland, average	5.2	24.2	13.7	7.6	7.1	7.3

Only data on 11 days when all stations were sampled is included.

Winter (Win): four dates in Dec 06, Jan 07, Feb 07, Dec 07

Summer (Sum): four dates in Jun 07, Jul 07, Aug 07, Sep 07

Dissolved oxygen was not measured at the Marchand system. Dempsey et al. (2001) measured temperature and DO in a passive treatment pond containing alkaline water and Fe concentrations greater than 150 mg/L. DO varied with temperature as:

$$\text{DO (mg/L)} = -0.34 * \text{Temperature (C)} + 9.2, r^2 = 0.69$$

Using this relationship and the range in temperatures in the Marchand ponds, the estimated DO values at 9.6°C and 18.6°C are 5.9 mg/L and 2.9 mg/L, respectively. If iron oxidation is limited by DO, winter rates would be approximately double the summer rates. This increase, alone, is sufficient to offset the kinetic penalty of lower water temperatures.

A second factor that influences iron oxidation in the Marchand system in cold weather is an inverse relationship between water temperature and pH (Table 5). Figure 4 shows the relationship for the Wet-in station (effluent of the last settling pond). Overall, the average pH of the ponds during cold weather was 0.3 units higher than warm weather conditions. 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 is 0.5 pH units, the oxidation reaction is potentially increased by 3.2 times.

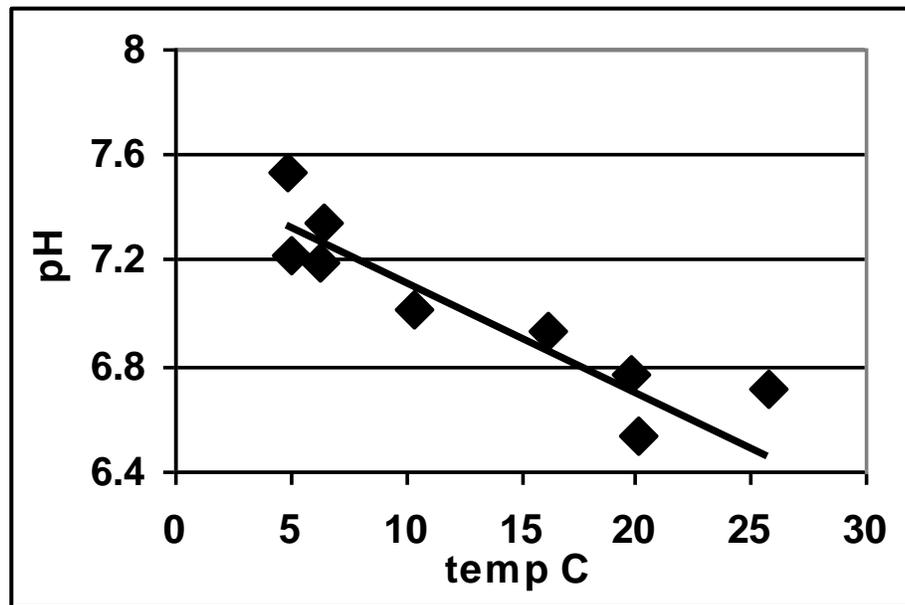


Figure 4. Relationship between pH and water temperature at “Wet in”. The least squares regression equation is: $\text{pH} = -0.043 \text{ Temp} + 7.54$, $r^2 = 0.82$

The inverse relationship between pH and water temperature was not expected and the cause is currently under investigation. Similar measurements of pH at varying temperature have not been reported; thus it is unknown whether this is a common phenomenon or it is 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 oxide solids 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 hours to 68 hours. 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 1st 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 per hr so that the final discharge after 90 hours (average theoretical retention time) was 0.8 mg/L (average final effluent). Under these conditions, the half-life of Fe is 14 hours.

The modeled system discharges less than 6 mg/L Fe whenever the retention times are at least 50 hours. Figure 5b relates the system flow rate to the modeled final effluent Fe concentrations. At 8,400 L/m (2,200 gpm) a final effluent with 2.5 mg/L Fe is predicted. The observed final effluent under high flows was better quality than predicted by the model. In March and April, when flows were high, the final effluent averaged 1 mg/L and rose on several occasions to 1.5 – 2.4 mg/L (Fig. 2b).

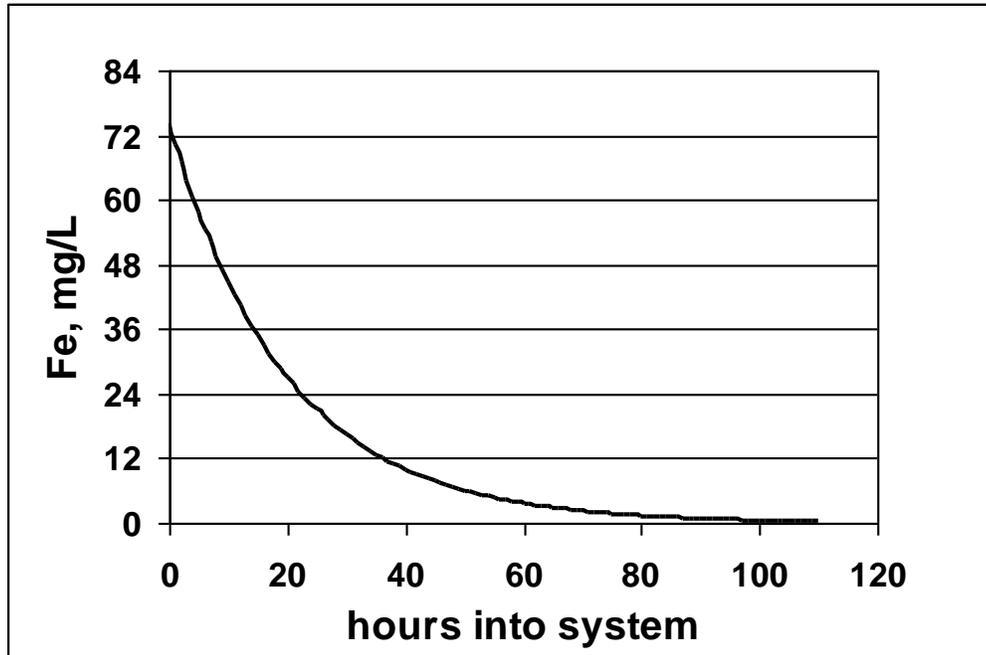


Figure 5a. Theoretical time-dependent removal of Fe assuming 1st order Fe removal.

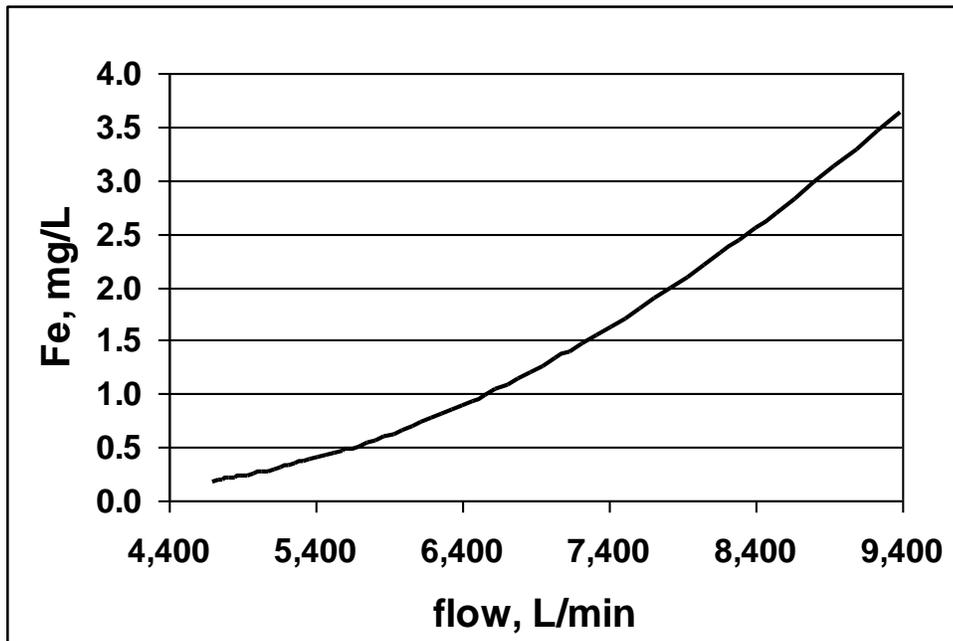


Figure 5b. Theoretical relationship between flow rate and final effluent Fe concentration assuming 1st order Fe removal for scenario shown in 4a.

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 PA (Pa Code, Chapter 87.102 (a)). The Marchand system effluent has never exceeded any of the discharge limits.

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 Marchand system has never exceeded this limit.

The terms of the earth disturbance and wetland encroachment permits include a limit on the influent 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.

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

	Final Discharge Limits		Marchand System, 2007	
	Monthly average	Instantaneous maximum	Monthly average, range	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	

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-hours

per month. Sampling and system inspections require 4 man-hours per month. A contingency of 50 man-hours per year is recommended for unexpected problems, such as the musk grass infestation of 2007. The total requirement for routine operational maintenance of the Marchand system is approximately 250 man-hours per year. Because these duties are simple and non-hazardous, they can be accomplished by trained volunteers. Alternatively, the O&M can be contracted which, at \$40/hr, is estimated to cost approximately \$10,000/yr.

The system's retention time decays with iron sludge accumulation. The Marchand system was designed to produce a clean iron oxide sludge that is easily removed and can be processed to a saleable iron oxide (Hedin 1999; Hedin 2003). The first recovery of the iron oxide product will occur in 2012 or 2013. The revenue from iron recovery is expected 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 (2006). In its first full year of operation it treated up to 8,444 L/min (2,231 gpm) of flow and 799 kg/day (1,758 lb/day) Fe to a quality compliant with standard effluent permits in the eastern United States. Assuming these flows and loadings, the capital cost was \$154 per L/min (\$583 per gpm) of installed capacity or \$6.27 per kg/day (\$2.85 per lb/day) of Fe treatment capacity. The annual operational costs are \$10,000. If this cost is related to the realized average flow and Fe loading, then the operational costs in 2007 were \$0.011 per 1,000 L of flow or \$0.041 per kg Fe treated (\$0.042 per 1000 gal or \$0.019 per lb Fe). Long-term sludge management costs are expected to be offset by iron recovery. The 25 year total capital and operational costs are \$1,550,000 which, at 4% discount rate, 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 or \$0.253 per kg Fe (\$0.067 per 1000 gal or \$0.115 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 L/min 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 gal). Assuming average cost estimates and a 4% discount rate, over a 25 year period, a lime plant is expected to treat alkaline Fe-contaminated mine water at a cost of about \$0.075 per 1,000 L flow (\$0.30 per 1,000 gal).

Summary

During its first year of operation the Marchand passive treatment system continuously treated a flow of 4,700 – 8,400 L/min 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 U.S. discharge permit criteria. The iron was precipitated in ponds designed to produce a clean iron oxide 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 hours to 68 hours. The discharge degradation during these periods was only 1 mg/L Fe. The kinetic penalties of cold temperatures are 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 is removed after 50 hours of retention and predicted that the final effluent at 68 hours 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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References

- American Public Health Association, 1999. Standard Methods for the Examination of Water and Wastewater (20th Edition), Edited by Lenore S. Clesceri, Arnold E. Greenberg and Andrew D. Eaton. American Public Health Association, American Water Works Association and the Water Environment Federation. Washington. D.C.
- Brodie, G. A., 1990. Treatment of acid mine drainage using constructed wetlands, experiences of the Tennessee Valley Authority, *In* Graves, D. H. Tomljanovich, D. A. (editors), Proceedings of the 1990 Symposium on Mining, OES Publications, University of Kentucky, Lexington, KY, pp 77-83
- Butler, J. N. 1991. Carbon Dioxide Equilibria and Their Applications, Lewis Publishers (Chelsea Michigan). 259 p.
- Dempsey, B. A., Roscoe, H.C., Ames, R., Hedin, R. Jeon, B-H. 2001. Ferrous oxidation chemistry in passive abiotic systems for the treatment of mine drainage. *Geochemistry: Exploration, Environment, Analysis* 1(1):81-89 <http://dx.doi.org/10.1144/geochem.1.1.81>
- Hedin, R. S., Nairn, R. W., Kleinmann, R .L. P.. 1994a. Passive Treatment of Coal Mine Drainage. US Bur Mines Information Circular IC 9389, 35 p.
- Hedin, R. S., Watzlaf, G. R., Nairn, R. W., 1994b. Passive treatment of acid mine drainage with limestone, *J Env Qual.* 23 (6): 1338 – 1345 <http://dx.doi.org/10.2134/jeq1994.00472425002300060030x>
- Hedin, R. S. 1999. Recovery of Iron Oxides from Polluted Coal Mine Drainage. Patent No. 5,954,969. U.S. Patent and Trademark Office, Washington D.C.
- Hedin, R. S. 2003. Recovery of marketable iron oxide from mine drainage. *Land Contamination and Reclamation* 11(2): 93-97 <http://dx.doi.org/10.2462/09670513.802>
- Hellier, W. W., Giovannitt, E. F., Slack, P. T. 1994. Best professional judgment analysis for constructed wetlands as a best available technology for the treatment of post-mining groundwater seeps. *In* Proceedings of the International Land Reclamation and Mine Drainage Conference and

- the Third International Conference on the Abatement of Acidic Drainage. Pittsburgh PA, April 1994. Volume 1 (US Bureau of Mines Special Publication SP 06A-94), pp 60-6.
<https://doi.org/10.21000/JASMR94010060>
- Hustwit, C. C., Ackerman, T. E., Erickson, P. E. 1992. The role of oxygen transfer in acid mine drainage treatment. *Water Environment Research* 64: 817-823. <https://doi.org/10.2175/WER.64.6.10>
- Kirby, C. S., Thomas, H. M., Southam, G., Donald, R. 1999. Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage. *Applied Geochemistry* 14: 511-530.
[http://dx.doi.org/10.1016/S0883-2927\(98\)00071-7](http://dx.doi.org/10.1016/S0883-2927(98)00071-7).
- Lambert, D. C., McDonough, K. M., Dzombak, D. A. 2004. Long-term changes in quality of discharge water from abandoned underground coal mines in Uniontown Syncline, Fayette County, PA, USA. *Water Research* 38(2): 277-288
<http://dx.doi.org/10.1016/j.watres.2003.09.017>
- Nuttall, C. 2002. Testing and performance of the newly constructed full-scale passive treatment system at the Whittel Colliery, Northumberland. *In* Nuttall, C (Ed) *Mine Water Treatment: a Decade of Progress*, University of Newcastle upon Tyne, Newcastle, UK. pp 16-24
- Pullman Swindell, Inc. 1977. Irwin Syncline Basin Mine Drainage Abatement Project, Operation Scarlift. Project No. SL 103-5. Department of Environmental Resources, Commonwealth of Pennsylvania.
- Stark, L. R., William, F. M., Stevens, S. E., Eddy, D. P., 1994. Iron retention and vegetative cover at the Simco constructed wetland: an appraisal through year eight of operations. *In* Proceedings of the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage. Pittsburgh PA, April 1994. Volume 1 (US Bureau of Mines Special Publication SP 06A-94), pp 89-98
<https://doi.org/10.21000/JASMR94010089>
- Wood, S. C., Younger, P. L., Robins, N. S. 1999. Long-term changes in the quality of polluted minewater discharges from abandoned underground coal workings in Scotland. *Quarterly Journal of Engineering Geology and Hydrogeology*, 32 (1): 69-79
<http://dx.doi.org/10.1144/GSL.QJEG.1999.032.P1.05>
- Younger, P. L. 2000. The adoption and adaptation of passive treatment technologies for mine waters in the United Kingdom. *Mine Water Env.* 19(2): 84-97. <http://dx.doi.org/10.1007/BF02687257>.
- Younger, P. L., Banwart, S. A., and R. S. Hedin. 2002. *Mine Water: Hydrology, Pollution, Remediation*. Kluwer Academic Publishers, 442 p. <http://dx.doi.org/10.1007/978-94-010-0610-1>