

Temperature independent removal of iron in a passive mine water treatment system

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Abstract

The Marchand water treatment system was constructed in Pennsylvania in 2006 to treat a 7 m³/min flow of alkaline coal mine drainage containing 72 mg/L Fe²⁺. The passive system removes Fe through a natural oxidation/hydrolysis/settling process that does not require any energy or chemical inputs. Over the last six years the system has consistently decreased Fe to less than 3 mg/L. Little seasonality in treatment effectiveness is observed despite Arrhenius-based calculations indicating that Fe²⁺ oxidation rates should vary by 5-10 times between warm and cold seasons. The kinetic penalty is offset by an inverse relationship between pH and water temperature that increases Fe oxidation rates in treatment ponds in cold weather. Variation in pH is most likely caused by variable degassing of CO₂. CO₂ fugacity was inversely related to water temperature, which is counter to solubility expectations. The proposed explanation is that water/atmosphere gas exchange is faster during cold weather due to density-driven mixing of the ponds. In addition to year-round effective treatment, the passive system produced a clean iron oxide solid that can be recovered and marketed. The combination of reliable year-round passive treatment and solids recovery makes this treatment technology potentially self-sustaining.

TOC/Abstract Art



Introduction

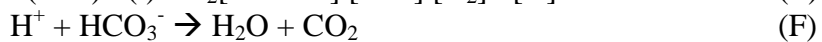
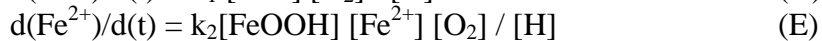
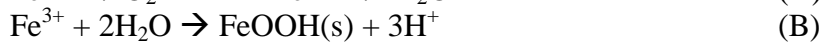
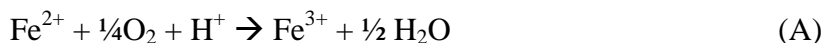
Underground mining of coal commonly results in the release of metal-contaminated waters. These polluted flows persist for decades after mine closure and in the absence of treatment cause major environmental damage. The conventional treatment for mine drainage involves chemical and mechanical technologies that have high energy, reagent, manpower and sludge management costs (1). An alternative approach for Fe-contaminated waters is passive treatment where iron is removed by natural oxidation, settling and biological processes while flow is transferred through the system by gravity (1,2,3). The sludge produced by the passive process is clean iron oxyhydroxide which can be recovered and utilized for pigmentary, ion exchange, and remediation purposes (4,5,6).

The total long-term cost of the passive approach is less than conventional chemical and energy-intensive technologies (7,8). Despite cost savings, the coal mining and reclamation industries have been slow to adopt passive treatment partly because of concerns about its reliability in meeting stringent effluent criteria, particularly in cold climates. Conventional wisdom based on Arrhenius calculations suggests that a 20° C temperature range, as occurs commonly in temperate climates, should cause the kinetics of important chemical reactions to vary by 5-10 times between cold and warm seasons. This variation would make passive treatment unfeasible where year-round effectiveness is required.

This paper presents six years of monitoring data from one of the largest passive treatment systems constructed to date for contaminated coal mine drainage. The system is in temperate Pennsylvania where air temperatures vary widely, yet no seasonal variation in treatment effectiveness exists. Several unexpected correlates with temperature are described that explain the robust capabilities of this treatment technology.

Background

The most common passive method for treating Fe-contaminated mine water is an aerobic approach where ferrous iron is removed through oxidation (A), hydrolysis (B) and settling (C).



At pH values between 3 and 9, Fe³⁺ hydrolysis is rapid and Fe²⁺ oxidation is the limiting chemical step (9,10). Oxidation occurs by homogeneous (D) and heterogenous (E) mechanisms (11,12,13). The rate constant for the homogeneous reaction, k₁, is approximately 5.0 X 10⁻¹⁵ mole/sec at 25°C (E_A of 23 kcal/mol K) and doubles/halves with a 5°C change in temperature (11,12,14). The rate constant for the heterogeneous reaction, k₂, is approximately 3.1 X 10⁻⁸ mole/sec at 25°C (E_A of 18 kcal/mol K) and doubles/halves with a 6°C change in temperature

(12,15). The rates of both abiotic mechanisms are negatively related to H^+ and slow considerably when pH is less than 5 (12,14).

Fe^{3+} hydrolysis is a proton-producing reaction than can result in pH less than 5 in unbuffered waters. For these low-pH waters, iron chemistry is controlled by microbial activity (10,16,17). When there is sufficient buffering, the acidic aspect of iron removal is neutralized (reaction F) and pH is maintained in the circumneutral range where abiotic iron oxidation is favored. Mine waters containing bicarbonate typically have high concentrations of CO_2 , which increases pH through exsolution (reaction G). These discharges are commonly referred to as “net alkaline” because the capacity for acid neutralization exceeds the latent acidity released when reduced metals oxidize and hydrolyze. Net alkaline discharges are particularly suitable for aerobic passive treatment. Many mine drainages from flooded underground coal mines around the world are net alkaline solutions with pH 6-7 and elevated concentrations of Fe (1,2,18,)

Marchand Mine Passive Treatment System

The Marchand passive treatment system was installed in 2006 to treat a large Fe-contaminated discharge from a flooded underground coal mine that had polluted the receiving stream (Sewickley Creek) for 60 years. The system design follows US Bureau of Mine protocols for passive treatment (2) where primary treatment occurs in open-water ponds that collect the bulk of the Fe as iron oxyhydroxide solids and secondary treatment occurs in constructed wetlands where settling, filtration and plant uptake remove residual Fe (3). The treatment system (Figure 1) consists of six serially-connected oxidation ponds that have a total surface area of 21,192 m^2 , a maximum depth of 1.3 m, and an empty volume of 24,673 m^3 . The ponds are lined with geotextile fabric that prevents direct contact with underlying soils and maintains the purity of the iron solids. The liner and water depths limit growth by emergent plants and the ponds retained an open water condition during this study. Water enters and exits each pond in 15 m long troughs that are intended to lessen preferential flow patterns and provide aeration through a 15 cm elevation drop. The ponds are followed by a shallow constructed wetland with a surface area of 23,424 m^2 , water depth of 10 – 50 cm, and an empty volume of 7,059 m^3 . The wetland was constructed with the best available soil (obtained onsite) and planted with a mix of emergent plant species. The planting scheme had mixed success. The vegetation in the wetland has varied between open water, partial cover with emergent plants (*Typha spp.*, *Carex spp.*, *Leersia oryzoides*), and dense growth of the submerged alga *Chara vulgaris*.

Materials and Methods

The system has been sampled approximately monthly since its construction. The sampling has been unbalanced. The final effluent was sampled 96 times, the system influent was sampled 66 times, and the ponds were sampled 23 times. Water samples were collected from the influent trough in each pond and from the final wetland discharge channel (Figure 1). Measurements were made in the field of pH, temperature, conductivity, dissolved oxygen, and alkalinity. Raw and acidified samples were collected for laboratory measurements of pH, alkalinity, acidity, conductivity, Fe, Al, Mn, sulfate and total suspended solids. These parameters are commonly used to evaluate compliance with regulatory and environmental targets in coal mining regions in the US. Routine laboratory analyses were conducted between in 2007 by the Pennsylvania

Department of Environmental Protection Bureau of Laboratories and since 2007 by G&C Coal Analysis Lab Inc. (PA DEP Certification #33-325). Samples were not routinely filtered before acidification, so the results represent total concentrations. On 14 occasions an extra sample was collected at each station and filtered (0.22 μm) before acidification and measurement of metals. In April 2008 samples were collected by Dr. Rosemary Capo and students from the University Of Pittsburgh Department Of Geology of Planetary Science and analyzed for a wider range of parameters so that a complete cation/anion balance could be obtained. All three labs utilize standard APHA and EPA methods (19,20).

CO_2 fugacity and saturation indices were calculated using The Geochemist's Workbench[®] (Aqueous Solutions LLC). Dissolved Fe was assumed to approximate ferrous iron because ferric iron is sparingly soluble at circumneutral pH conditions existing at all sampling stations (14).

Flow was calculated from velocity measurements made at the influent to the first pond. Samples of solids in the treatment system were collected by hand, dried at 105°C to constant weight and analyzed for elemental composition by Activation Laboratories Ltd. (Ontario CA) by lithium metaborate/tetraborate fusion ICP (major elements) and infrared (C and S).

Results

Table 1 shows the detailed chemistry of system influent and final effluent on April 24, 2008. The mine water has an alkaline sodium-sulfate geochemistry which is typical of discharges from flooded underground coal mines in western Pennsylvania. The only metal of environmental concern is Fe. The influent has low dissolved oxygen and very high CO_2 . The influent was in equilibrium with siderite and undersaturated with respect to other carbonate and sulfate minerals. The major effects of the system on water chemistry were decreases in Fe and bicarbonate (HCO_3^-) which were stoichiometrically consistent with the neutralization of acidity produced by Fe oxidation and hydrolysis. The final effluent had elevated nitrate which may be consequence of organic degradation of algal biomass generated the previous summer. Nitrate was not detected in water samples collected from the ponds (not shown).

The influent flow rate ranged between 4.8 m^3/min and 9.4 m^3/min and averaged 7.1 m^3/min (Figure 2a, Table 2). The influent Fe^{tot} concentration ranged between 54 mg/L and 89 mg/L and averaged 72 mg/L (Figure 2b and Table 2). The system decreased Fe concentrations to an average 1 mg/L. Of 96 measurements of Fe in the final effluent, only 4 were higher than 3 mg/L and the highest measurement was 6.0 mg/L. Table 3 shows effluent standards commonly used for permitted coal mine sites in Pennsylvania. The final effluent has consistently satisfied these criteria. Pennsylvania has special effluent standards for passive treatment systems that require 90% removal of Fe and a net alkaline final effluent (26). The Marchand system satisfied these standards as well.

After six years of operation, the system had retained approximately 1,613 tonnes of Fe, of which 1,354 tonnes were contained in the ponds (calculations based on days of operation, flow rate and changes in concentrations of Fe^{tot}). Solids collected in the ponds are predominantly Fe with minor amounts of silica and carbon (Table 4). This composition is typical of iron solids precipitated passively from alkaline Fe-contaminated water where the dried solids are found to

be a mixture of amorphous iron oxyhydroxide and goethite (5,21,22,23). In June 2012 sludge contained in Ponds A, B and C was removed. The recovered sludge is also a pure iron oxyhydroxide solid (Table 4). The iron is stored on site (Figure 1) and is being processed for potential sale as iron oxide pigment.

Figure 3 shows changes in water temperature and Fe chemistry with flow through the system. The influent had a constant water temperature that is typical of groundwater discharges in this region. As water flowed through the system its temperature changed in response to ambient air conditions, which can range between -15 C in winter and +35 C in summer. The temperature of the system's final discharge ranged from 1°C to 31°C (ave. 14.9°C, sd 9.8°C). The ponds never froze while the wetland surface was largely ice covered during extended cold weather. The system decreased concentrations of Fe in a steady manner. The remediation process was rate-limited by ferrous iron oxidation in the ponds and by the settling of iron solids in the wetland. By the time water exited the last pond, dissolved Fe was less than 2 mg/L. The remaining iron was present in a particulate form and removed with flow through the constructed wetland.

The treatment system was effective year round. A cold weather decline in effectiveness was not evident (Figure 2b). Table 5 shows correlations between water temperature and chemical parameters. Fe removal (Fe^{tot} or Fe^{dis}) was not correlated with water temperature. Water temperature was negatively correlated in the ponds with pH and positively correlated with alkalinity. The temperature-pH correlations increased with flow through the ponds and reached a maximum in Ponds E and F (Fig. S1). The temperature correlations disappeared in the wetland.

Figure 4 shows chemical parameters on three days when DO measurements were also made. The days were selected to represent cold (2°C air), moderate (16°C air) and warm (24°C air) weather conditions. As water flowed through the system, its temperature changed consistent with air temperature (Figure 4a). DO was less than 1 mg/L at the influent on all days and increased with flow through the ponds in a manner consistent with the inverse relationship between DO saturation and water temperature (Figure 4b). CO_2 fugacity decreased with flow through the wetland on each day and the lowest fugacity values were on the coldest day (Figure 4c). pH increased with flow through system on each day and the increase in the ponds was greater at colder temperatures (Figure 4d). Fe^{dis} and Fe^{tot} decreased with flow through the system, but there was little difference in removal on the three dates (Figure 4e and 4f). On all dates, Fe^{dis} (Fe^{2+}) was < 1 mg/L at the effluent of the final pond.

Chemical parameters in the wetland did not follow the temperature patterns observed in the ponds. The final DO on the 2°C day was at near saturation, while it was greatly supersaturated on the warmer days when algal blooms were observed. There was a strong inverse correlation between temperature and Mn (table 4) which was likely due to the highly oxidizing conditions created by algal growth during warm weather. The changes in concentration of Mn in the wetland, 0.5 – 1.0 mg/L, were not environmentally significant.

Discussion

Temperature affects the oxidation of ferrous iron in the Marchand system through competing impacts on kinetics and concentrations of key chemical parameters. Arrhenius calculations

indicate that the kinetic constants double/halve for each 5-6° C change in water temperature. It would appear that the treatment system should oxidize iron on cold winter days at 5-10 times slower rates than warm summer days. The kinetic effect is, however, offset by a concentration effect resulting from the inverse relationship between water temperature and pH. Figure 5 shows for each pond the calculated impact on Fe²⁺ oxidation of the individual temperature-related factors and the combined effect of both, $k_1/[H^+]^2$. The combined effect was not strongly related to temperature in any of the ponds. This result explains the absence a temperature penalty for Fe²⁺ oxidation and hence bulk Fe removal by the treatment system.

The pH in buffered mine water systems is largely controlled by carbonate chemistry. Bicarbonate neutralizes protons produced by ferric iron hydrolysis (reaction F), preventing a decrease in pH (as occurs in unbuffered systems). Dissolved CO₂, present at very high partial pressures, exsolves to the atmosphere increasing pH (reaction G). Because of the strong dependence of Fe oxidation on pH and the demonstrated ability of accelerated CO₂ degassing to increase iron oxidation rates (24,25), mechanical aeration is a common practice in conventional treatment systems (1). Variable CO₂ degassing in passive treatment systems is an unrecognized phenomenon that appears to influence iron dynamics in a similar manner. The degassing of CO₂ in the Marchand ponds was strongly temperature dependent with lower CO₂ fugacities occurring when water temperatures were colder (Fig. S2). The direct relationship between CO₂ fugacity and water temperature in the ponds was unexpected because CO₂ solubility increases with decreasing water temperature. The simplest explanation for the inverse relationship between water temperature and CO₂ is that the ponds mix more thoroughly at colder temperatures. When the air temperature is lower than water temperature, the surface waters are continually being cooled and sinking due to density gradients. The mixing continually refreshes the surface with deeper water that is more supersaturated with CO₂ which prompts exsolution. Water temperatures in the ponds never fell below 4°C where mixing stops and ice forms. When air temperatures are warmer than the pond water temperature, the warmer less dense surface water floats and mixing is poor. The surface is not refreshed and gas exchange processes are slowed.

All temperature correlations weakened in the wetland. While the ponds never froze, the wetlands commonly froze in cold weather. The ice cap presumably lessened gas exchange processes. While the ponds are largely devoid of plant growth, the wetlands contained emergent plants and large blooms of the alga *Chara vulgaris* during most spring and summer seasons. The shallow water depths combined with seasonal biological activity create a more dynamic system where temperature relations are more complex and unpredictable than in the simple oxidation ponds.

The year round effective treatment of Fe by the Marchand passive treatment cautions against simplistic evaluations of the natural systems where temperature effects are predicated simply on kinetic considerations. In this case, temperature-related variation in a key chemical parameter, pH, completely offset the kinetic penalty. The underlying cause of the pH variation appears to be the unexpected increase in CO₂ degassing during cold weather. The mechanisms at work in this man-made system may have parallels in other environments where CO₂-supersaturated waters are exposed to variable atmospheric conditions.

The Marchand treatment system has been successful in its six years of operation in three respects. First, it has consistently lowered concentrations of Fe to levels compliant with routine NPDES permits. Second, the treatment has been achieved as a fraction the cost of conventional chemical treatment. The Marchand system was designed, permitted and installed at a cost of \$1.3 million (2006) and its routine operation costs \$5,000/yr (8). A conventional chemical plant would cost approximately \$3 million to install and cost at least \$100,000/yr to operate. Third, the Marchand system produces a pure iron sludge whose value can offset sludge management costs. Conventional treatment produces a chemically heterogenous sludge that has no established value and whose disposal is costly. The combination of effective low-cost passive treatment with the recovery of saleable iron solids makes possible a sustainable treatment approach where the costs of operation are balanced by income from solids recovery and sale.

Acknowledgements

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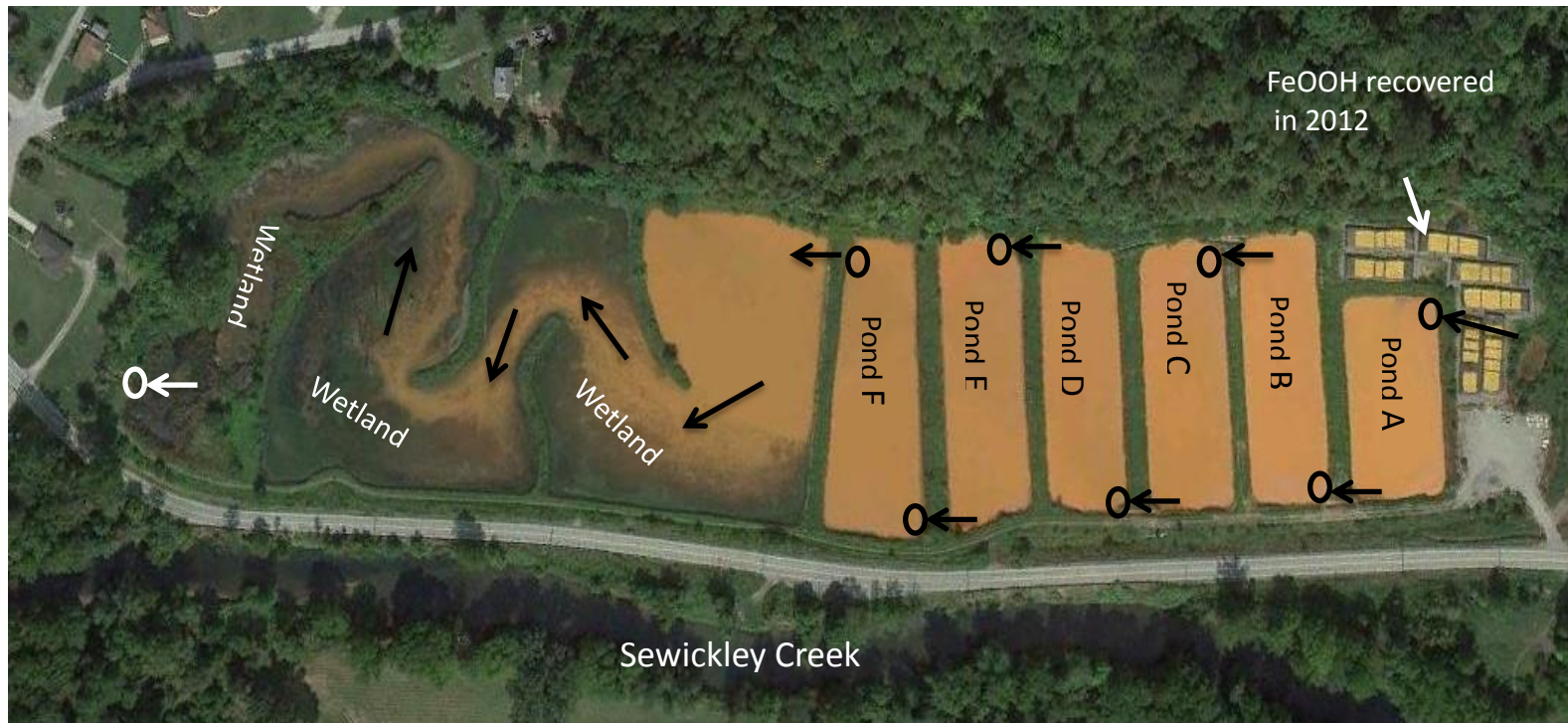


Figure 1. Marchand passive treatment system on August 29, 2012. Arrows show flow paths. Circles are sampling points. The system location is $40^{\circ} 14' 4.81''$ N; $79^{\circ} 45' 55.63''$ W.

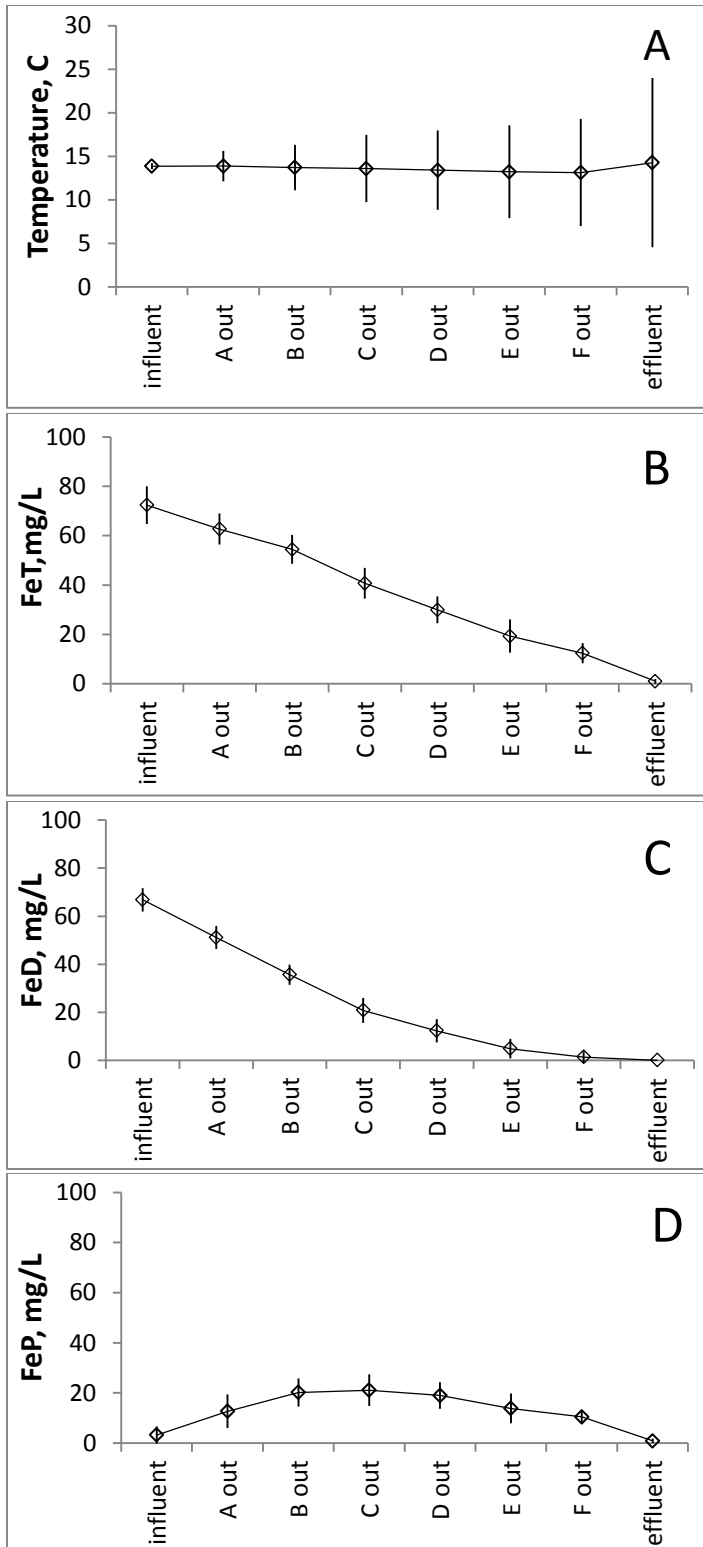
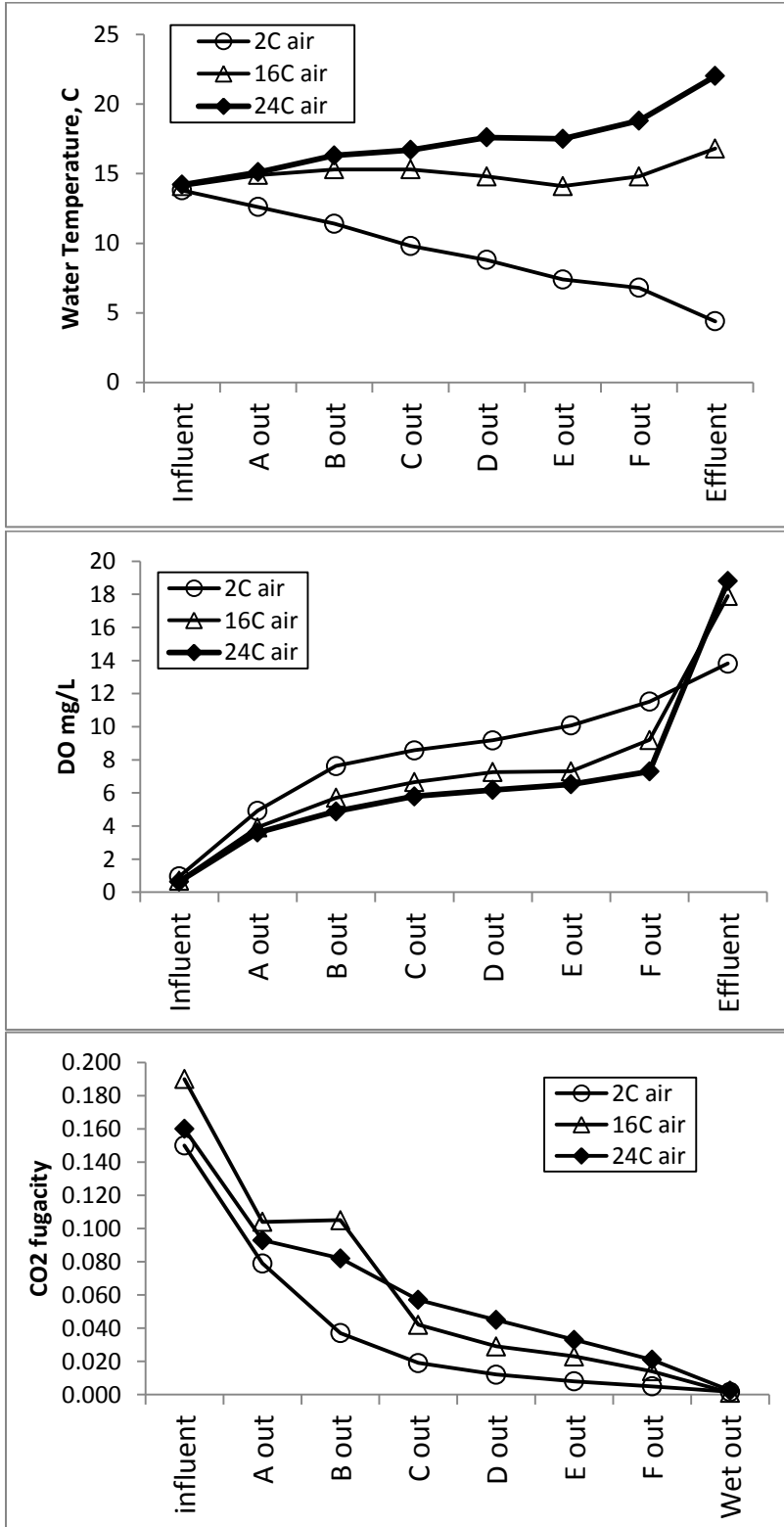


Figure 3. Temperature (A) and concentrations of total Fe (B), dissolved Fe (C), and particulate Fe (D) through the Marchand system. Average values and one standard deviation shown.

Figure 4 (part 1)



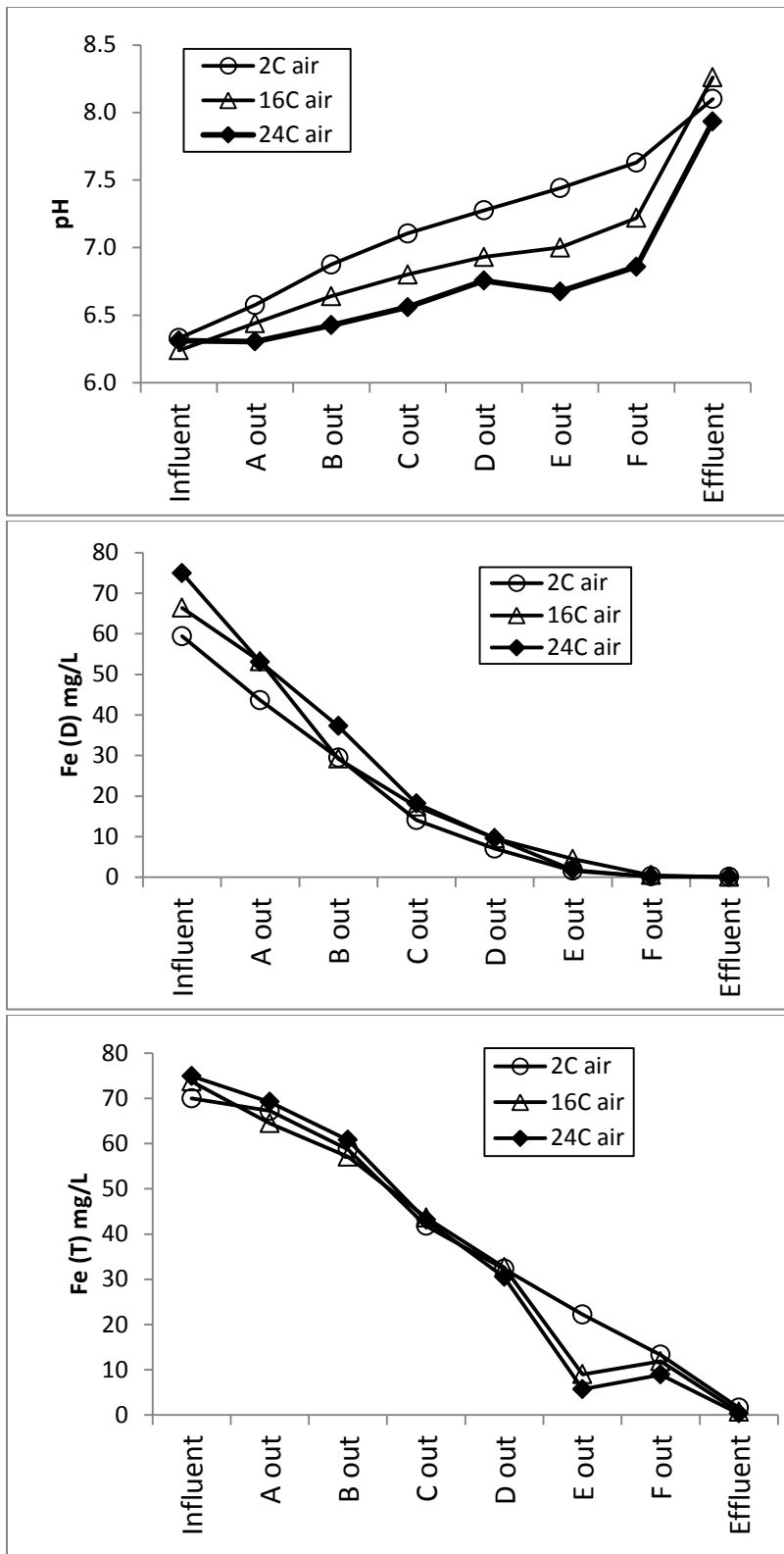
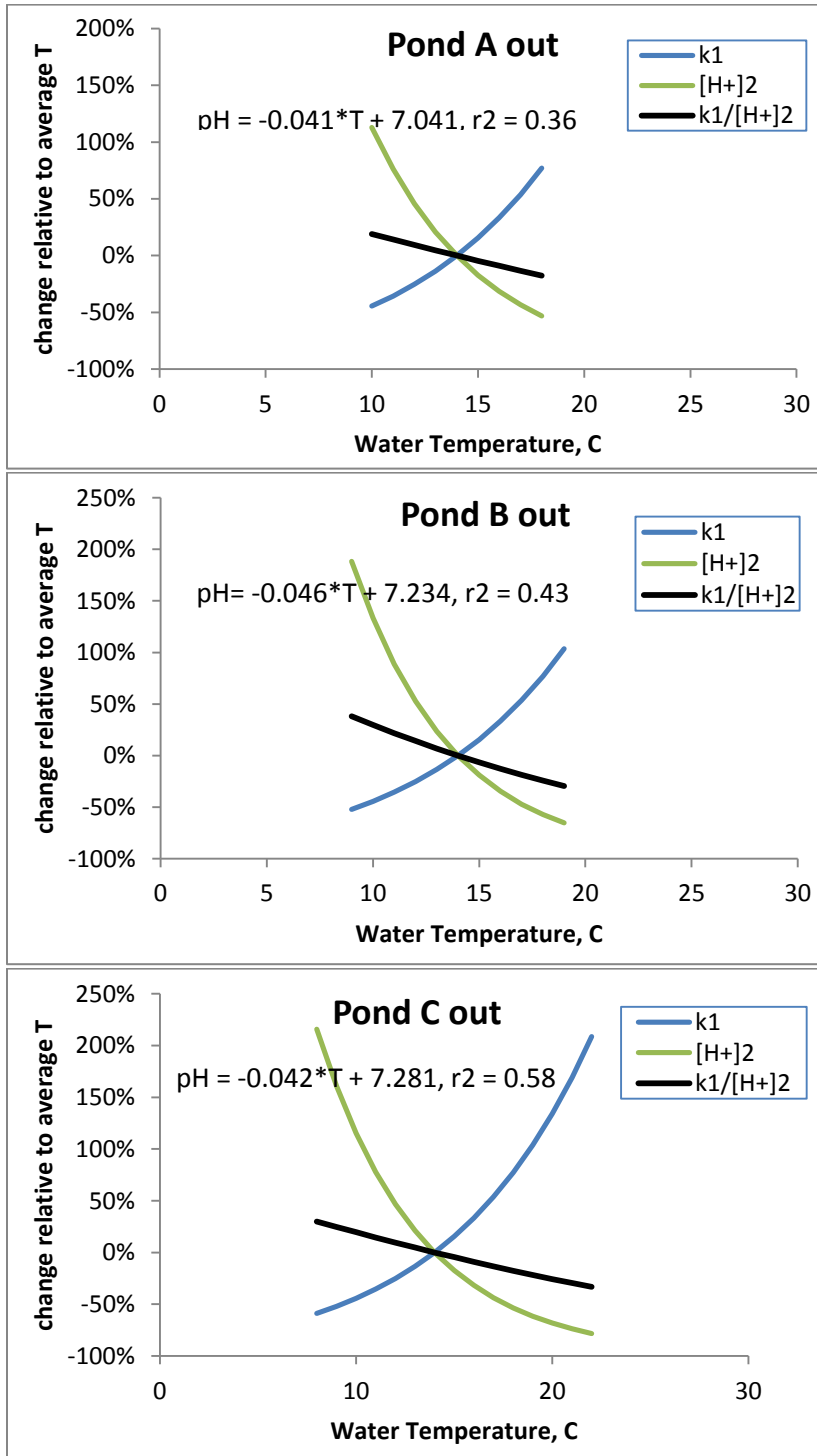


Figure 4. Changes in mine water chemistry with flow through the Marchand system on days with the air temperature was 2°C, 16°C and 24°C.

Figure 5 (part 1)



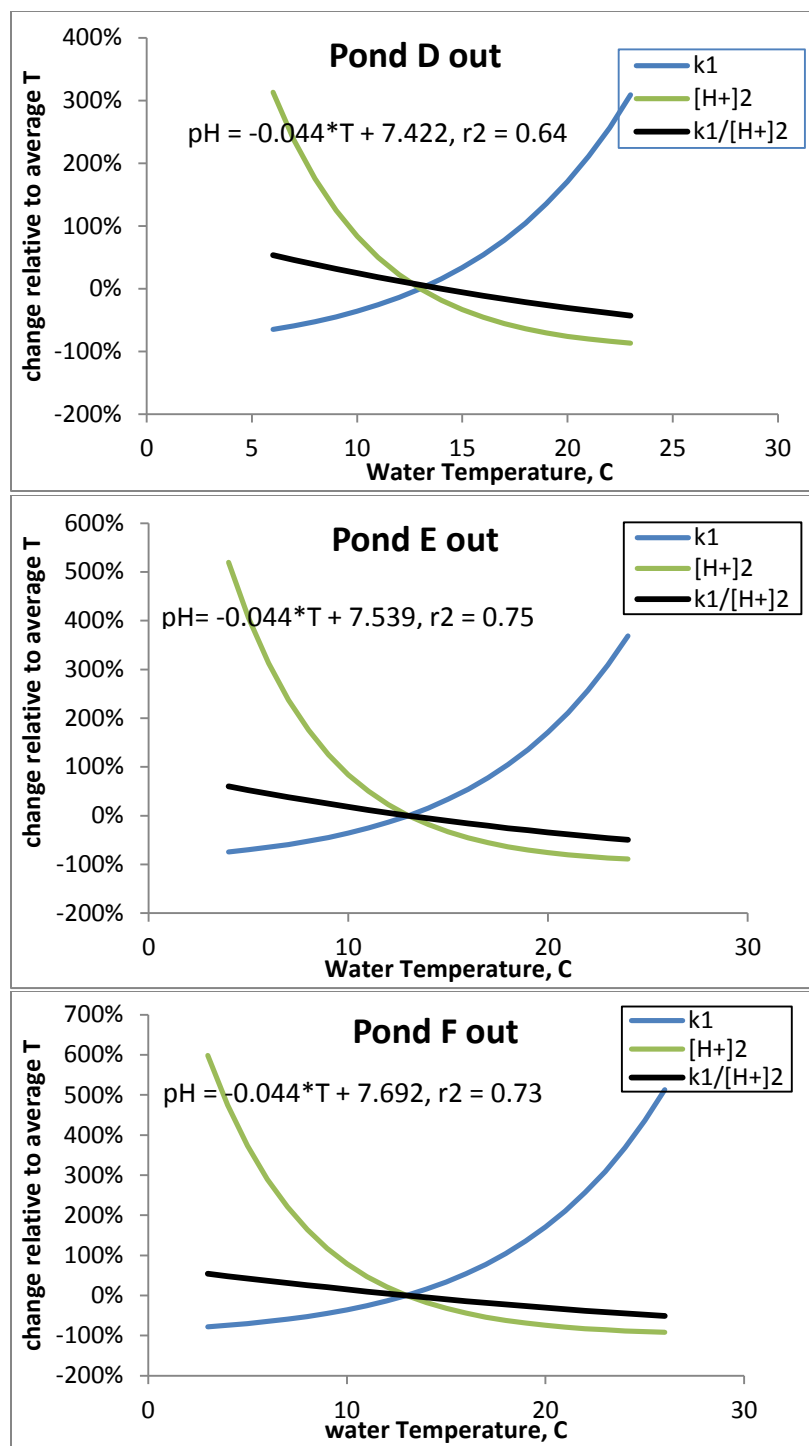


Figure 5. Temperature effects on k_1 , $[\text{H}^+]^2$, and $k_1/[\text{H}^+]^2$ over the temperature range observed in each pond. k_1 at varying temperature calculated from $e^{(-E_a/RT)}$ where E_a is 23 kcal/mol K. pH effect determined from second order rate relationship where pH values determined from pH-T regression equations developed for each pond (shown). The plotted values are relative to the average T in each pond.

Table 1. Chemical characteristics of the Marchand passive treatment system influent and effluent, April 24, 2008. Samples were filtered (0.22 μm) prior to laboratory analyses.

Parameter	Units	Influent	Effluent
Flow	m^3/min	7.9	na
pH	standard unit	6.31	7.93
Temp	$^{\circ}\text{C}$	14.2	22.0
Alkalinity	mg/L CaCO_3	341	228
Dissolved oxygen	ppm	0.65	18.8
Conductivity	μS	2688	2434
CO_2	fugacity	0.1547	0.0027
Na^+	mg/L	479	456
Ca^{2+}	mg/L	154	130
Fe^{2+}	mg/L	58.3	0.04
Mg^{2+}	mg/L	41.2	41.3
Si	mg/L	9.7	5.4
K^+	mg/L	6.1	4.7
Sr^{2+}	mg/L	2.17	1.87
Mn^{2+}	mg/L	0.98	0.11
Ni^{2+}	mg/L	0.028	0.021
Zn^{2+}	mg/L	0.012	<0.003
Al^{3+}	mg/L	<0.05	<0.05
Co^{2+}	mg/L	<0.039	<0.039
SO_4^{2-}	mg/L	1,114	1,057
HCO_3^-	mg/L	416	278
Cl^-	mg/L	125	141
F	mg/L	0.38	0.40
B	mg/L	0.36	0.25
Br^-	mg/L	<0.1	<0.1
NO_2^-	mg/L	<0.1	<0.1
NO_3^-	mg/L	<0.2	7.9
PO_4^{2-}	mg/L	<0.1	<0.1
Cation sum	meq/L	34.2	29.8
Anion sum	meq/L	33.5	30.7
Saturation Index Calculations			
Siderite (FeCO_3)	$\log Q/K$	+0.60	-12.01
Rhodochrosite (MnCO_3)	$\log Q/K$	-1.02	-0.53
Calcite (CaCO_3)	$\log Q/K$	-0.70	+0.77
Magnesite (MgCO_3)	$\log Q/K$	-1.86	-0.21
Dolomite ($\text{CaMg}(\text{CO}_3)_2$)	$\log Q/K$	-0.86	+2.21
Gypsum (CaSO_4)	$\log Q/K$	-0.79	-0.87
Epsomite (MgSO_4)	$\log Q/K$	-11.14	-10.72
Quartz (SiO_2)	$\log Q/K$	+0.42	+0.013
Goethite (FeOOH)	$\log Q/K$	+7.22	+5.44

Table 2. Average conditions at the Marchand Mine passive treatment system, Jan 2007 – Dec 2012. TSS is total suspended solids.

	Flow	Temp	DO	pH	HCO₃⁻	Fe^{tot}	Fe^{dis}	Mn^{tot}	Al^{tot}	SO₄^{tot}	TSS	CO₂
	m³/min	C^o	mg/L	s.u.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	fugacity
Influent	7.1	13.9	0.8	6.30	407	72.4	66.8	1.2	<0.2	1,036	25	0.163
A out	na	13.9	4.1	6.46	367	62.7	51.2	1.2	<0.2	1,109	60	0.106
B out	na	13.8	6.1	6.59	342	54.5	35.7	1.2	<0.2	1,110	60	0.078
C out	na	13.7	7.0	6.70	316	40.7	20.8	1.2	<0.2	1,074	50	0.056
D out	na	13.5	7.5	6.82	294	30.0	12.4	1.2	<0.2	1,083	37	0.042
E out	na	13.3	8.0	6.93	288	19.3	4.9	1.2	<0.2	1,115	25	0.032
F out	na	13.3	9.3	7.10	281	12.4	1.4	1.1	<0.2	1,117	16	0.022
Effluent	na	14.5	16.8	7.76	262	1.0	0.1	0.5	<0.2	1,160	<6	0.0045

Table 3. Effluent standards for permitted coal mine discharges in Pennsylvania (26)

	30-day average	Daily maximum
Fe ^{tot}	3.0 mg/L	6.0 mg/L
Mn ^{tot}	2.0 mg/L	4.0 mg/L
TSS	35 mg/L	70 mg/L
pH	6 – 9	
Alkalinity	Alkalinity > acidity	

Table 4. Composition of solids samples collected from ponds and during sludge removal in June 2012.

	Solids Chemistry (dry weight basis)										
	Al	C	Ca	Fe	K	Mg	Mn	Na	P	S	Si
In place	%	%	%	%	%	%	%	%	%	%	%
Pond A	0.5	1.4	0.2	50.2	0.1	0.1	0.0	0.1	0.1	0.2	3.9
Pond B	0.2	0.9	0.2	52.6	0.0	0.0	0.1	0.2	0.1	0.3	2.5
Pond C	0.4	2.2	0.4	49.8	0.1	0.1	0.1	0.1	0.0	0.3	3.6
Pond D	0.4	2.3	0.3	50.5	0.1	0.1	0.1	0.2	0.0	0.2	4.2
Pond E	0.3	2.7	0.4	49.4	0.1	0.1	0.1	0.2	0.0	0.9	3.5
Recovered											
Ponds A, B, C	0.2	0.7	0.6	52.7	<0.1	0.1	<0.1	0.1	<0.1	0.2	2.0

Table 5. Temperatures correlations for measured and calculated parameters. Correlations significant at the P = 0.05 level are labeled with *.

	Flow	pH	Alk	Fe^(tot)	Fe^(dis)	Fe removal		Mn	CO2 fugacity
						Fe^(tot)	Fe^(dis)		
Influent		-0.25	0.49*	0.33	0.38			0.16	0.31
A out	0.17	-0.59*	0.24	-0.23	-0.19	0.25	0.21	-0.38	0.68*
B out	0.15	-0.65*	0.26	-0.01	-0.31	-0.41	0.02	-0.34	0.74*
C out	0.22	-0.76*	0.43*	0.28	-0.01	-0.27	-0.29	-0.34	0.84*
D out	0.22	-0.80*	0.47*	0.43	0.15	-0.23	-0.35	-0.22	0.85*
E out	0.22	-0.87*	0.45*	0.02	0.11	0.34	0.09	-0.33	0.90*
F out	0.18	-0.85*	0.45*	0.23	0.15	-0.14	0.03	-0.12	0.85*
Effluent	0.22	-0.34	-0.13	-0.15	-0.17	0.14	0.10	-0.73*	0.36

Supplemental Information

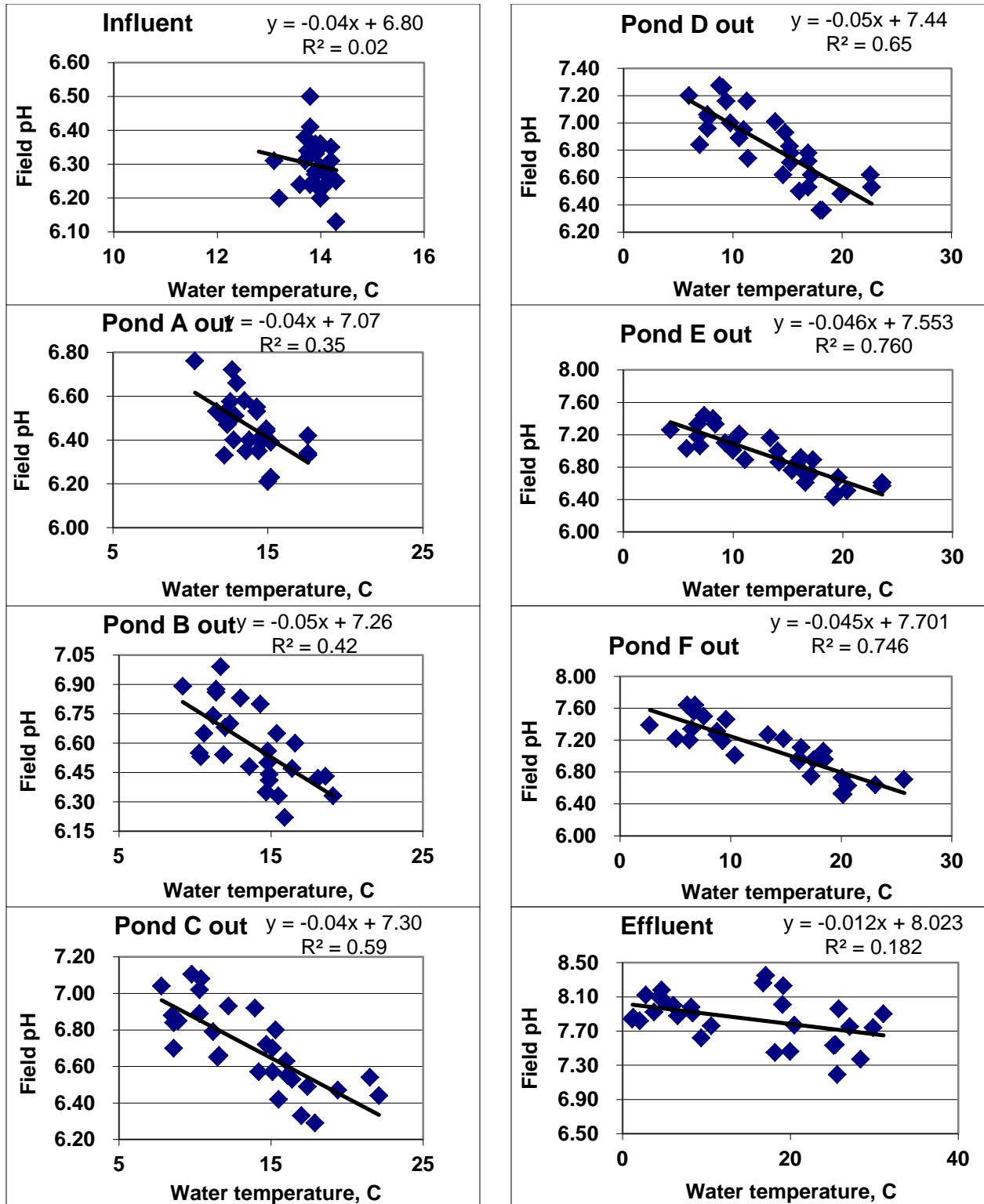


Figure S1. Relationship between water temperature and pH at each sampling point. Note the x-axis scale differs between charts.

Supplemental Information

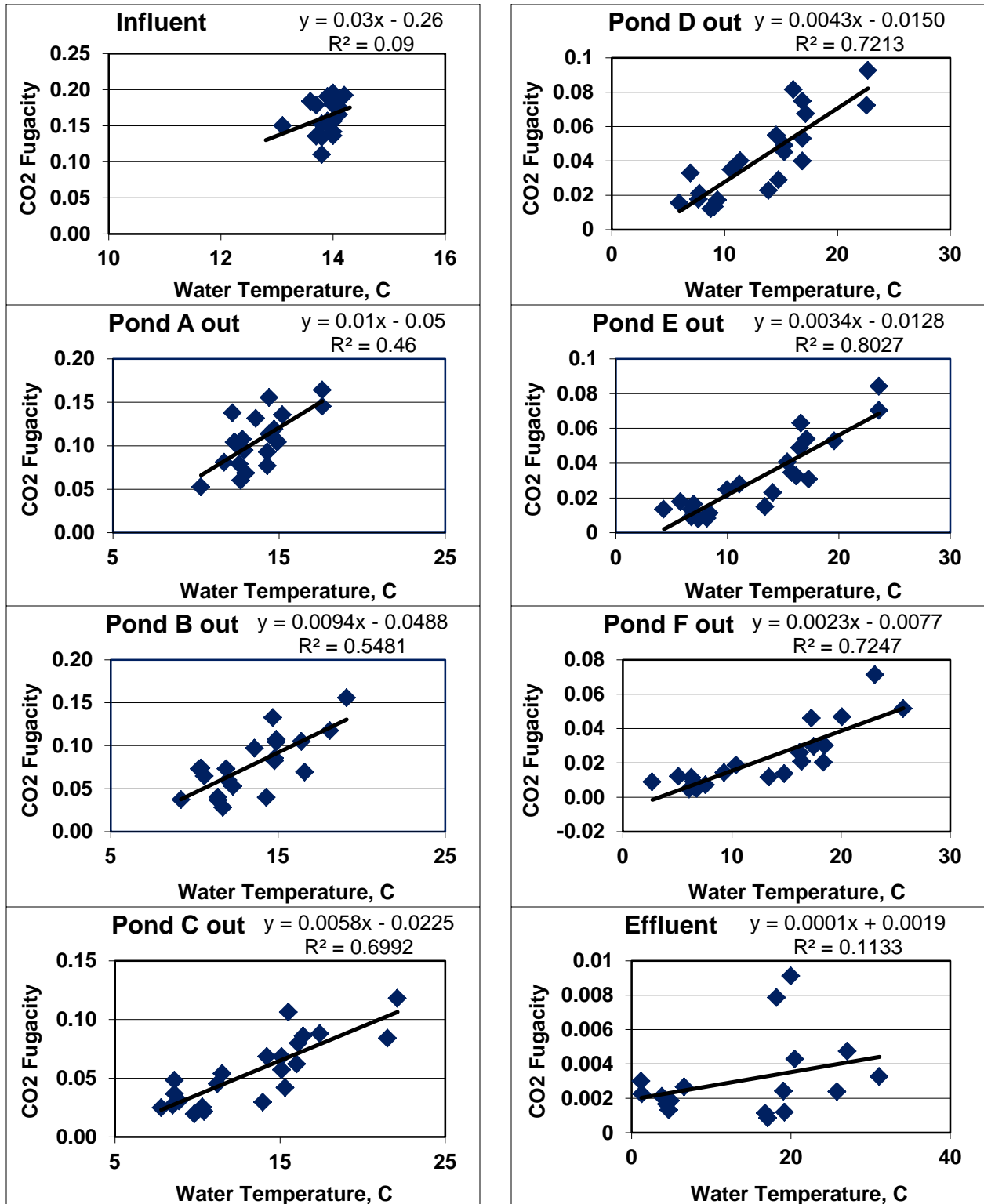


Figure S2. Relationship between water temperature and CO₂ fugacity at each sampling point. Note the x-axis scale differs between charts.

ES&T Rejection of Paper emails

-----Original Message-----

From: onbehalfof+li-office+est.acs.org@manuscriptcentral.com
[<mailto:onbehalfof+li-office+est.acs.org@manuscriptcentral.com>] On Behalf
Of li-office@est.acs.org
Sent: Monday, March 11, 2013 3:28 PM
To: bhedin@hedinenv.com
Cc: li-office@est.acs.org; est@uiowa.edu
Subject: Final decision on ES&T manuscript es-2013-00074b

11-Mar-2013

Journal: Environmental Science & Technology Manuscript ID: es-2013-00074b
Title: "Temperature independent removal of iron in a passive mine water treatment system"
Author(s): Hedin, Robert

Dear Dr. Hedin:

Thank you for considering Environmental Science & Technology for your manuscript submission. It has been forwarded to reviewers for their consideration, and the reviews are enclosed. After careful consideration, I regret to inform you that the manuscript cannot be accepted for publication in ES&T.

I hope that the reviewers' comments are of help to you if you choose to revise the manuscript for submission to another journal.

I wish you much success in your future research. Please accept my thanks for the opportunity to consider your contribution for Environmental Science & Technology.

Sincerely,

Prof. Xiang-dong Li
Associate Editor
Environmental Science & Technology
Phone: 919-918-3912
Fax: 202-513-8660
Email: li-office@est.acs.org

Reviewer(s)' Comments to Author:
Reviewer: 1

Comments:
Review attached.

Reviewer: 2

Comments:
AMD passive treatment was evaluated at a multi-pond site. It was reported that Fe removal was just as effective during the winter as during the summer. This seemed counter-intuitive based on chemical kinetic issues. This result is very interesting and deserves to be published in some format. However, the final explanation for the effect was pretty simple (increased wind in the winter leading to faster removal of CO₂ and higher pH). It could even be that the result is not generalizable. Consequently the authors should consider shortening substantially, retaining the stunning aerial photo and just one or possibly two plots, and publishing as a technical note (whether in this journal or elsewhere) rather than as a research article, or publish with the current length in another journal.

Some specific comments:

(1) I found the use of fugacity for CO₂ and mg/L for DO to be troublesome. Why not be consistent and use similar terminology to express the concentration or relative partial pressure of O₂ and CO₂ in the same way? Also, fugacity has dimensions of pressure, while fugacity coefficient is dimensionless.

(2) Page 4/14, line 19: The only flow data was based on velocity into the first pond. Stratification or other physical characteristics of the system were not evaluated or reported. Flow and mixing within the basins apparently was crucial to understanding the result (no decrease in Fe-oxidation with lower pond temperatures). This suggests that there could be more short-circuiting during the summer and more wind-induced and thermal-induced mixing during the winter. In order to add to the knowledge base about how these systems work, it seems crucial to be able to describe the flow regimes as a function of season.

(3) The discussion section seems weak and speculative. The important observation was that the pH was higher than expected in the winter, and the proposed explanation was increased gas transfer due to better mixing in the winter, but without any documentation other than the original observation that the pH was higher.

(4) The cost comparison in the final paragraph of the paper was not documented. It might be better to provide comparative costs based on designs that can be documented, or provide more data for these design costs, or provide comparative costs for active versus passive systems with similar flow and AMD strength.

(5) Several items in Table 1:

The extremely high DO (18.8 mg/L) must reflect an algal bloom and the sample must have been taken at the peak productivity hour - that is perhaps not representative of average conditions, including the pH.

As noted above, fugacity units are pressure, but anyway it seems better to report all dissolved gases using similar units.

That's a huge alkalinity at the effluent side, which typically means the ALD is over-designed, and consequently perhaps this site has a higher pH and is not as representative of most AMD passive systems as it should be.

Where did all that nitrate come from, especially does it mean that there's storm runoff that enters the ponds and that could possibly affect the results and conclusions?

From: Bob Hedin [bhedin@hedinenv.com]
Sent: Friday, March 29, 2013 5:40 PM
To: Xiang-dong Li
Subject: RE: Final decision on ES&T manuscript es-2013-00074b

Prof. Xiang-dong Li

Thank you for considering the paper. I have been in contact with one of the reviewers who was disappointed to hear that the paper was not going to be published. Reviewer 2 has some reasonable comments about the paper, but made one that has bothered me. The reviewer states that the results were not generalizable because the water chemistry of the system is unusual due to its pretreatment with limestone.

"That's a huge alkalinity at the effluent side, which typically means the ALD is over-designed, and consequently perhaps this site has a higher pH and is not as representative of most AMD passive systems as it should be."

The "ALD" that reviewer 2 refers to is a limestone pre-treatment system that is used in some treatment systems to add alkalinity to acid mine water. The treatment system presented in the paper does not contain an ALD or any pre-treatment with limestone. The paper never discusses an "ALD" or even limestone treatment. As noted in the background section, the "huge alkalinity" is natural and is typical of hundreds (thousands?) of discharges flowing from flooded mines around the world. It concerns me that the reviewer imposed a treatment assumption into his review of the paper that was artificial, unwarranted and incorrect. I believe that this error biased his review and his opinion that the results were not generalizable and therefore not appropriate for the broad ES&T audience.

The review makes other comments about the interpretation of the findings that have merit and could be handled in a rewrite.

Sincerely,

Robert Hedin

Dear Dr. Hedin,

I have read through the two reviewers' comments again. The point you referred to is not the only drawback of the present study and I am unwilling to change the decision. Thank you again for your interest in ES&T, and I look forward to your new contribution in the future.

Best wishes,

Dr. Xiang-dong Li
Associate Editor
Environmental Science & Technology
Email: li-office@est.acs.org
Phone: 919-918-3912
