Temperature Independent Removal of Iron in a Passive Mine Water System

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Abstract The Marchand passive system treats a 7.1 m^3/min flow of coal mine drainage containing 72 mg/L Fe to a final effluent with 1 mg/L. Fe removal in this aerobic system is by oxidative mechanisms. The system has not displayed a significant seasonality in effectiveness, despite kinetic considerations that indicate that iron oxidation should differ by an order magnitude between cold and warm periods. Year-round sampling of the treatment ponds revealed a negative correlation between water temperature and pH. Because pH has a positive influence on Fe^{2+} oxidation, this offsets the negative influence of kinetics. The results demonstrate the complexity of iron chemistry in passive treatment systems and caution against their modeling with static chemical assumptions.

Keywords IMWA 2013, passive treatment, iron oxidation, coal mine drainage

Introduction

The treatment of mine water containing elevated ferrous iron (Fe^{2+}) requires oxidation of Fe^{2+} to Fe^{3+} and settling of the ferric oxyhydroxide solids. In passive systems the oxidation is usually considered the rate-limiting step (Dempsey *et al.* 2001). The kinetics of the oxidation are strongly affected by temperature. In climates where air temperatures vary widely, Arrhenius-based calculations indicate that oxidation kinetics will vary tenfold between cold and warm seasons (Stumm and Morgan 1996). This kinetic penalty would make passive treatment impractical in northern latitude temperate climates where stringent effluent limit must be satisfied. In reality, such severe seasonal variation is not commonly observed. Many passive treatment systems have been constructed in the northern latitudes that are effective year-round. One of the best studied systems is the Marchand passive system in Pennsylvania (USA) where a large Fe-contaminated deep mine discharge is consistently treated to < 3 mg/L Fe (Hedin 2008). This paper describes the treatment performance of the Marchand System over the last six years and presents unexpected chemical correlations with temperature that balance the kinetic penalty.

Background

The Marchand Mine passive treatment system is shown in Fig. 1. The system was installed in 2006 to treat a large Fe-contaminated discharge from a flooded underground coal mine and consists of six 1.3 m deep serially-connected ponds followed by a 0.2 – 0.3 m deep constructed wetland. The ponds were constructed in compacted clay (no organic substrate) and have retained an open-water environment. The wetland was constructed with the best available soil (obtained onsite) and planted with a mix of aquatic plant species.

Methods

The system has been sampled approximately monthly since its construction. The final effluent has been sampled 97 times, the influent 67 times, and the effluent of each of the ponds 23 times. Measurements were made in the field of pH, temperature, conductivity, dissolved oxygen, and alkalinity. Raw and acidified sam-
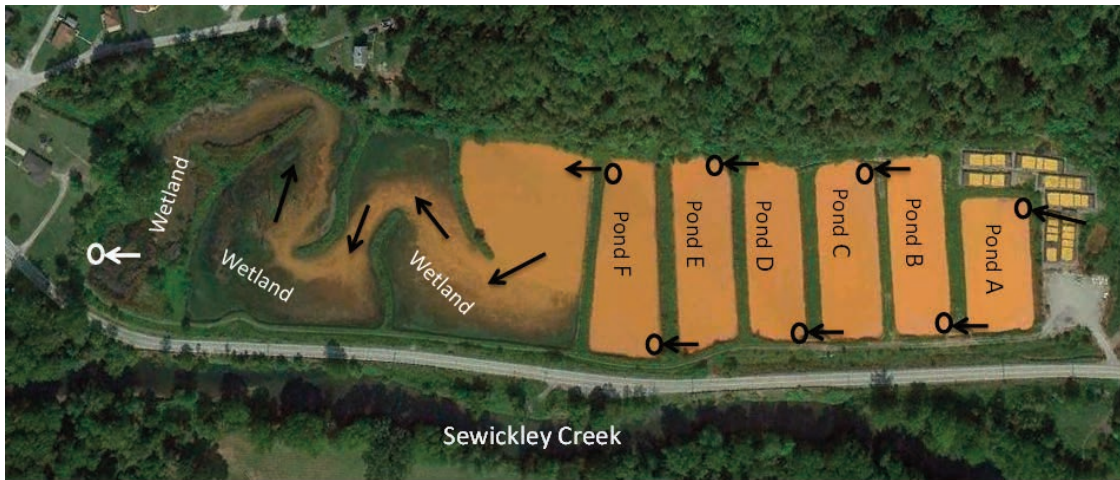
Fig. 1 *Marchand passive treatment system on August 29, 2012. Arrows show flow paths. Circles are sampling points. The system location is 40°14'4.81" N; 79°45'55.63" W.*

ples were collected for laboratory measurements of acidity, Fe, Al, Mn, sulfate and total suspended solids using standard methods (Clesceri *et al.* 2005). On 14 occasions dissolved metals were measured on an extra filtered (0.22 μm) sample. Dissolved Fe was assumed to approximate Fe^{2+} because Fe^{3+} is sparingly soluble at the circumneutral pH found at all stations. CO_2 fugacity was calculated using The Geochemist's Workbench® (Aqueous Solutions LLC). Flow rates were measured with a velocity meter at the piped influent to the first pond.

Results

Table 1 shows the average conditions at the sampling stations since it was constructed. The influent flow rate ranged between 4.8 m³/min and 9.4 m³/min and averaged 7.1 m³/min (Fig. 2a). The influent had a constant water temperature of 14 °C, which is typical of deep mine 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 influent to the last pond (F) ranged between 4 °C and 24 °C. The ponds never froze and retained open water conditions year-round. The temperature of the system's final discharge ranged between 1 °C and 31 °C. Portions of the wetland froze every winter and the wetland surface was largely ice covered during extended cold weather.

	Flow m³/min	Temp C°	DO mg/L	pH s.u.	HCO_3^- mg/L	Fe^{tot} mg/L	Fe^{dis} mg/L	Mn^{tot} mg/L	SO_4^{tot} mg/L	TSS mg/L	CO_2 fugacity
Influent	7.1	13.9	0.8	6.30	407	72.4	66.8	1.2	1,036	25	0.163
A out	na	13.9	4.1	6.46	367	62.7	51.2	1.2	1,109	60	0.106
B out	na	13.8	6.1	6.59	342	54.5	35.7	1.2	1,110	60	0.078
C out	na	13.7	7.0	6.70	316	40.7	20.8	1.2	1,074	50	0.056
D out	na	13.5	7.5	6.82	294	30.0	12.4	1.2	1,083	37	0.042
E out	na	13.3	8.0	6.93	288	19.3	4.9	1.2	1,115	25	0.032
F out	na	13.3	9.3	7.10	281	12.4	1.4	1.1	1,117	16	0.022
Effluent	na	14.5	16.8	7.76	262	1.0	0.1	0.5	1,160	<6	0.0045

Table 1 *Average conditions at the Marchand Mine passive treatment system, Jan 2007 – Dec 2012. TSS is total suspended solids. Al concentrations were <0.1 mg/L for all stations.*
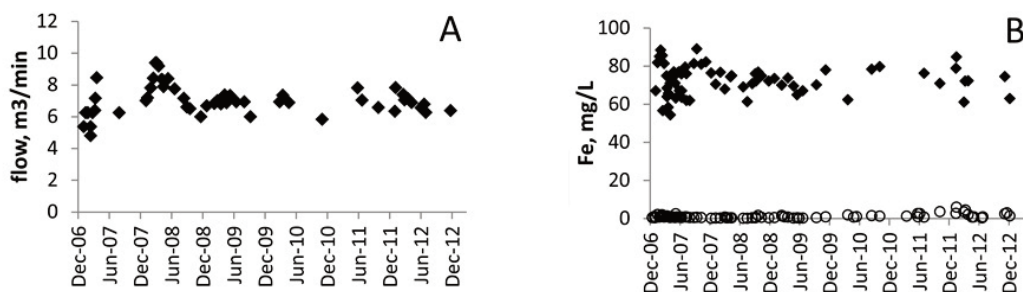
Fig. 2 Treatment performance by the Marchand system. A) Flow rate at system influent; B) Total Fe at the system influent (○) and effluent (●) stations

The mine water was strongly alkaline, anoxic with high CO_2, and contaminated with Fe. The influent Fe concentrations ranged between 54 mg/L and 89 mg/L and averaged 72 mg/L (Fig. 2b). As water flowed through the system, the major effects on water chemistry were decreased Fe, alkalinity and CO_2 and increased pH and dissolved oxygen. The changes in Fe and alkalinity were stoichiometricly consistent with the carbonate neutralization of acidity produced by Fe oxidation and hydrolysis.

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. The treatment system was effective year round. A cold weather decline in the removal of Fe was not evident (Fig. 2b). Table 2 shows correlations between water temperature and chemical parameters. Fe removal 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.

Discussion

Temperature affects the oxidation of Fe^{2+} in the Marchand system through competing impacts on kinetics and concentrations of key chemical parameters. The removal of Fe at circumnueutral pH is generally assumed to be controlled by an abiotic oxidation process where the Fe^{2+} oxidation rate is first order with

	Flow	pH	Alk	Fe(tot)	Fe(dis)	Fe removal Fe(tot)	Fe(dis)	Mn	CO₂ fugacity
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

*Table 2 Temperature correlations for measured and calculated parameters. Correlations significant at the $P = 0.05$ level are labeled with *.*
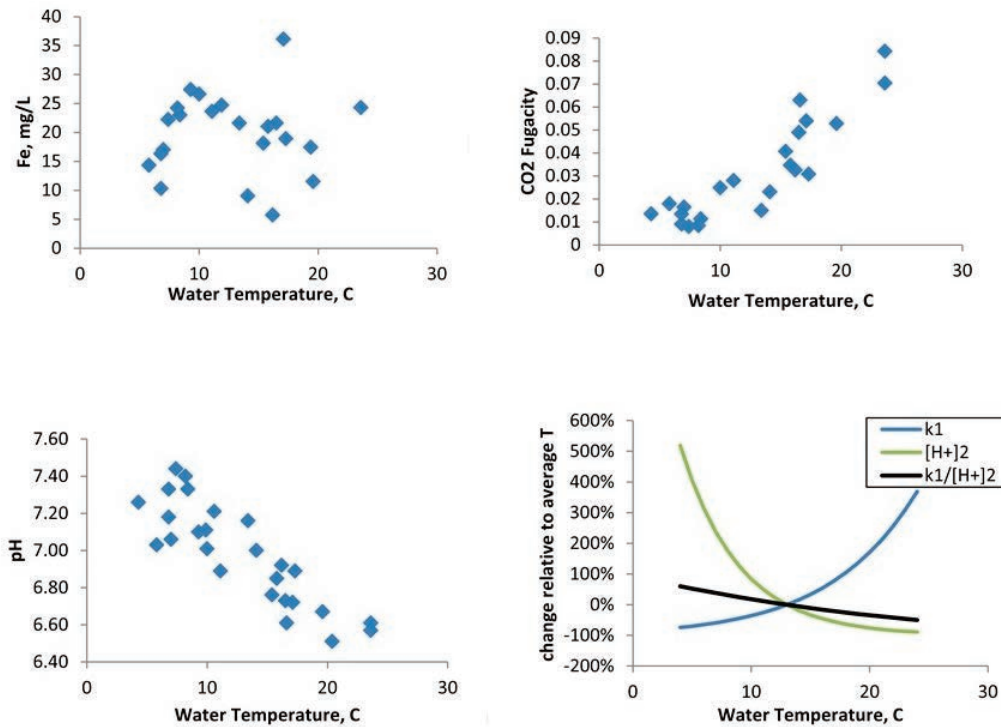
Fig. 3 *Temperature relationships at Pond E Effluent for Fe, CO₂, and pH. The fourth panel shows temperature relationships for k_1 calculated from $e^{(-Ea/RT)}$ where Ea is 23 kcal/mol K, pH calculated from a second order rate relationship where pH values determined from pH-T regression, and $k_1/[H^+]^2$. The plotted values are relative to the average effluent temperature of Pond E.*

respect to Fe^{2+} and O_2 and second order with respect to pH (Stumm and Morgan 1996) as follows:

$$d(Fe^{2+})/d(t) = k_1[Fe^{2+}] [O_2]/[H^+]^2$$

Arrhenius calculations indicate that the kinetic constant (k) changes tenfold over a 15 °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. Fig. 3 shows key temperature relationships at the Pond E effluent. Fig. 3d shows the calculated variation of k_1, $[H]^2$, and the combined factor, $k_1/[H]^2$, with temperature. The graph shows changes relative to the average temperature at the Pond E

effluent. The offsetting effects of k_1 and $[H]^2$ result in little change to $k_1/[H]^2$ over the temperature range observed in Pond E. This result explains the absence a temperature penalty for Fe^{2+} oxidation and hence bulk Fe removal by the treatment system over a wide range in temperature.

The pH in circumneutral mine water systems is largely controlled by carbonate chemistry. CO_2, which is present in excess at Marchand and in most mine waters, degasses to the atmosphere,causing an increase in OH^- and hence pH.

$$HCO_3^- \rightarrow CO_2 (gas) + OH^-$$
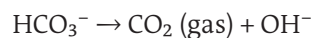
Because of the strong dependence of Fe oxidation on pH and the demonstrated ability of accelerated CO_2 degassing to increase iron oxidation rates (Cravotta 2007; Kirby *et al.*

2009), mechanical aeration is a common practice in conventional treatment systems (Younger *et al.* 2002). Variable CO_2 degassing in passive treatment systems is an unrecognized phenomenon that appears to influence iron dynamics in a similar manner. The degassing of CO_2 in the Marchand ponds was strongly temperature dependent with lower CO_2 fugacities occurring when water temperatures were colder. The direct relationship between CO_2 fugacity and water temperature in the ponds was unexpected because CO_2 solubility increases with decreasing water temperature. The simplest explanation for the inverse relationship between water temperature and CO_2 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 CO_2 which prompts degassing. 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 several 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.

Conclusions

The Marchand system has provided highly effective treatment of a large flow of alkaline Fe-contaminated mine water for six years. Iron removal was not correlated with water temperature, despite Arrhenius-based calculations that predict iron oxidation rates 10 times slower in cold seasons than warm seasons. The kinetic penalty was offset by a strong inverse relationship between pH and temperature which appears to be caused by increased CO_2 degassing at lower temperatures. The findings caution against evaluations of the treatment system performance where temperature effects are predicated based on static chemical conditions and kinetic considerations.

Acknowledgements

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