Long-term minimization of mine water treatment costs through passive treatment and production of a saleable iron oxide sludge

Robert S Hedin

Hedin Environmental, 195 Castle Shannon Blvd, Pittsburgh, PA, USA, bhedin@hedinenv.com

Abstract

Passive technologies are generally the preferred post-closure treatment technology because of the potential for lower long-term costs than conventional chemical technologies. Passive systems produce solids and their management is often the primary long-term treatment liability. If the solids have valuable characteristics, their recovery and sale can produce income that offsets costs and decreases the long-term treatment liability. The Marchand passive system was constructed in 2006 to treat a high flow of alkaline Fe-contaminated mine water. The system has effectively decreased Fe from 70 mg/L to 1 mg/L, on average. The system accumulates approximately 420 ton/yr iron solids which accounts for about 7% of the system's volume. In 2012, 725 mton-solid of Fe sludge was removed and recovered in an on-site dewatering system. The cost to recovery the iron solids was \$158/mton-solid. The dewatered sludge is being relocated and processed to a screened 60% solids product at an additional cost of \$164/mton-solid. The processed solids are being sold as crude pigment. Other uses that value the purity and adsorption capacity of the iron oxides are being investigated. The presentation will describe these research projects.

Key words: passive treatment, iron oxide, sludge management

Introduction

Mine water treatment responsibilities often extend beyond mine closure and can represent a major economic liability. Passive technologies are generally the preferred post-closure treatment technology because of the potential for lower installation and long-term costs than conventional chemical technologies. Like all treatment technologies, passive systems produce solids and their management can be a significant long-term treatment liability. If the solids have valuable characteristics, their recovery and sale can produce income that offsets costs and decreases the long-term treatment liability.

The Marchand treatment system in Pennsylvania (USA) is a good example of the opportunity provided by passive treatment and solids recovery. For decades Sewickley Creek and the Youghiogheny River were polluted by Fe-contaminated flow from the abandoned Marchand Mine. In 2005 the Sewickley Creek Watershed Association (SCWA) obtained funding from the Pennsylvania Department of Environmental Protection to install passive treatment at the site. An aerobic system was installed that precipitates iron oxide sludge in settling ponds and polishes the water with a constructed wetland (Hedin 2008). The system has effectively retained Fe and contributed to the restoration of Sewickley Creek and the Youghiogheny River. The need to manage iron solids produced by the system was recognized during the design and features were included to facilitate sludge recovery and to assure that purity of the iron solids. In 2012 sludge was removed from three of the ponds. The solids were captured and are currently being processed for sale as iron oxide. This paper will describe the system's performance, sludge recovery efforts, realized and potential markets for the iron oxide product.

Methods

Water samples were collected from the influent/effluent of ponds and wetland and analyzed in the field for pH, alkalinity and temperature, and by a laboratory for Fe, Mn, Al, sulfate, acidity, and total suspended solids. All metal concentrations are total values, except on some occasions when a filtered (0.22 um) sample was collected for determination of dissolved Fe.

Solid samples were collected by hand from ponds or dewatering sludge. Moisture content was determined from the difference in weight of the fresh sample and one dried at 105°C for at least 4 hours. The resulting solid sample was stored in a sealed plastic bag to prevent rehydration. Samples of the solids were analyzed by Activation Laboratories LTD (Ancaster, Ontario, CAN) by the "4E-Exploration" package. Concentrations of 72 elements were determined by either instrumental neutron activation or ICP analysis of an acid extract of the solids (www.actlab.com).

Marchand Treatment System

The Marchand treatment system was installed in 2006 to treat a large discharge from an abandoned flooded underground coal mine. The system consists of six ponds arranged in series and a large constructed wetland (Hedin 2008). The ponds were constructed in native compacted soils that were covered with a geotextile fabric and 15 cm of aggregate to protect the purity of the iron sludge produced during recovery operations. Each pond was constructed with a ramp and sump in one corner to facilitate the placement and operation of a tractor-powered sludge pump. The wetland was constructed with native soils and planted with native wetland vegetation. The wetland does contain any features to protect the quality of the iron solids or to facilitate their removal.

Table 1 shows the average flow rate and chemistry for the system between 2006 and 2016. The influent mine water has an average flow rate of 7,088 L/min and contains 70 mg/L Fe. As water flows through the system Fe is oxidized and precipitated as iron oxide. The system lowers Fe concentrations to an average 1 mg/L (Figure 1). The final effluent has ranged as high as 6 mg/L (Figure 2) with higher concentrations typically observed in winter months when the wetland vegetation is reduced. The frequency of higher Fe discharge has increased in the last three years. This is attributed to the accumulation of Fe sludge (and decrease in retention time) and preferential flow paths that have developed in the wetland due to plant growth and animal activity.

Table 1. *Average characteristics of the Marchand treatment system, Nov 2006 – Apr 2016.*

	Flow	**pH**	**Alk**	**Fe^{tot}**	**Fe^{dis}**	**Mn**	**Al**	**SO_4**
	L/min	s.u.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Influent	7,088	6.30	334	71.6	63.3	1.2	< 0.5	1,141
P6 Eff*	na	7.10	231	12.5	1.3	1.1	< 0.5	1,122
Effluent	na	7.75	217	1.1	0.1	0.5	< 0.5	1,163

* effluent from last (sixth) pond.

The system treats flow from an abandoned mine and the final discharge is not subject to regulated effluent criteria. If the system had a discharge permit, the final effluent would need to be have pH 6-9 with a maximum of 7 mg/L Fe and a monthly average less than 3 mg/L Fe. The system would satisfy these limits.

Table 2 shows the elemental composition of solids collected from the treatment ponds. The solids are approximately 95% iron oxide and are a mixture of amorphous ferric oxyhydroxides ($Fe(OH)_3$ and geothite ($FeOOH$). The major secondary elements are Si, Ca and C which likely represent the precipitation of quartz (SiO_2) and calcite ($CaCO_3$) and algal growth.

Table 2. *Content of major elements in Marchand iron solids. Values are dry weight basis.*

Al	**C**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**P**	**S**	**Si**
%	%	%	%	%	%	%	%	%	%	%
0.2	0.7	0.6	52.6	< 0.1	0.1	< 0.1	0.1	< 0.1	0.2	0.9

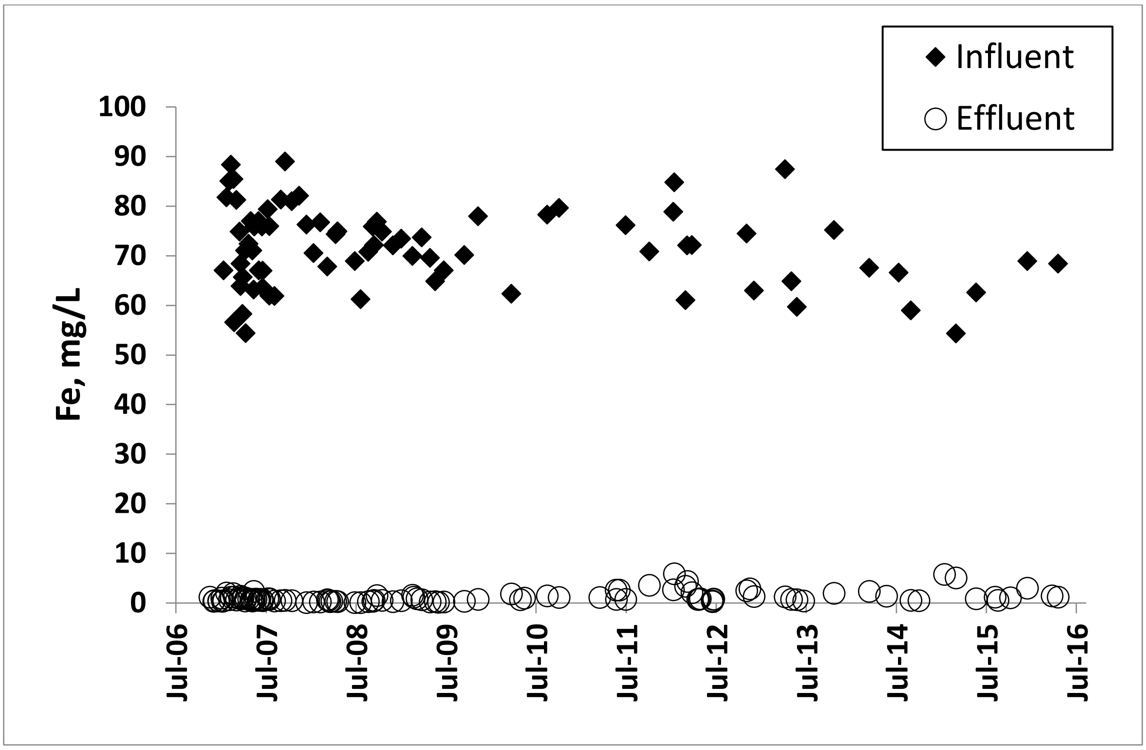

***Figure 1** Influent and effluent concentrations of Fe for the Marchand passive treatment system;*

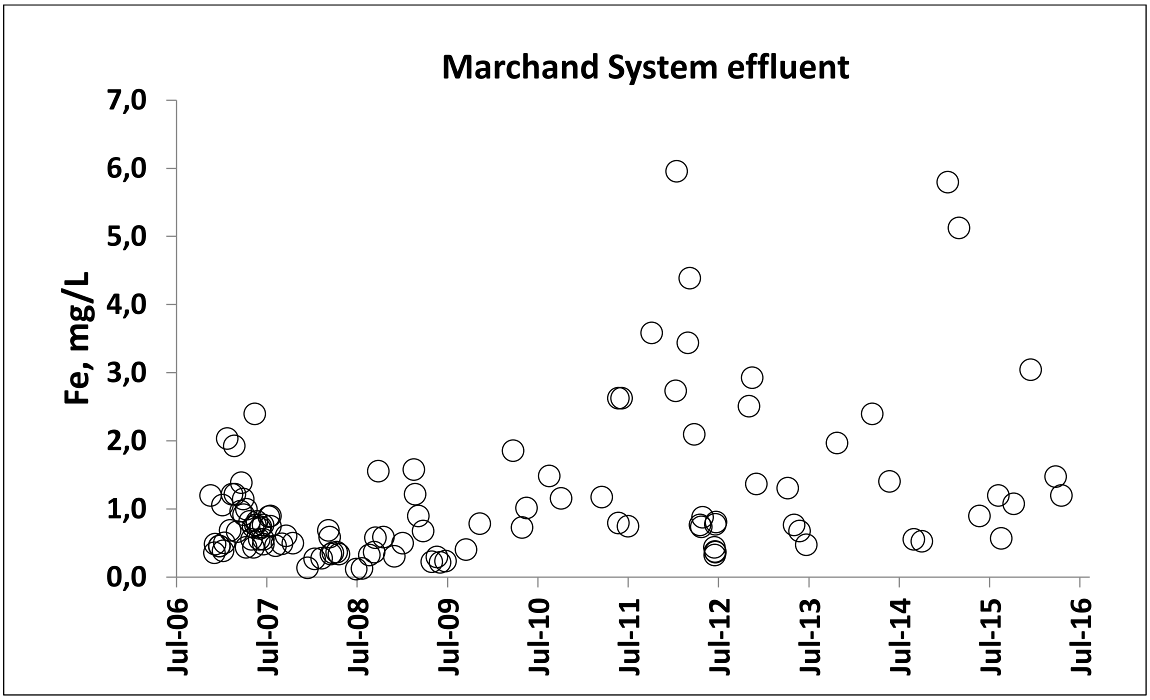

***Figure 2** Effluent concentrations of the Marchand passive treatment system.*

A common concern about the solids recovered from mine water treatment systems is the content of hazardous metals. Table 3 shows concentrations of hazardous metals identified in US EPA regulations. The significance of these metal concentrations will vary depending on the use of the iron oxide. In the case of iron oxides included in agricultural practices, the US EPA Part 503 Biosolids Rule provides metal limits (Table 3). The Marchand solids do not exceed any of the Part 503 limits.

Table 3. *Content of hazardous metals in Marchand iron solids. Restriction limits for US EPA Part 503 Biosolids Rule are also shown. Values are dry weight basis.*

	As	**Cd**	**Co**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Se**	**Zn**	**Hg**
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb
Marchand	23	2.0	4	14	10	< 2	9	11	< 3	23	< 1
Part 503 limits	41	39	na	1,500	1,500	57	420	420	36	2,800	57

The ponds account for 59 mg/L (82%) of the system's total Fe removal. At 7,088 L/min, the ponds are removing 220 mtons of Fe/year and precipitating 419 mton/yr of iron oxide solids. Samples of the in-place sludge indicate a solids content of approximately 20% and a wet density of 1.2 kg/L. Averaged over all the ponds, iron sludge accumulates at a rate of approximately 8 cm/yr (depth). The ponds, which are 1.2 m deep, are losing approximately 7% of their volume each year due to iron sludge accumulation.

Recovery of Iron Oxide Sludge

In 2012 iron sludge was removed from the first three ponds of the Marchand system. For each pond's cleanout the process involved: 1) bypassing mine water around the pond; 2) removal of clear water overlying the settled sludge; and 3) slurrying and pumping of sludge out of the pond. At the Marchand site sludge was pumped into Tencate geotubes (http://www.tencate.com) which dewatered the sludge to 25-30% solids. The geotubes were cut open and the solids were stacked. Over time the sludge dewatered further to 40-45% solids. At other sites where sludge has been recovered from treatment systems it was pumped into specially constructed sludge basins which, because they are reusable, are less expensive than the geotube approach.

Table 4 shows the costs of installation and operation of the Marchand system. The costs are adjusted to current (2016) dollars using the US Bureau of Reclamation Cost Index for earthen dam construction. The system cost $1,212,770 to install in 2005/06. (This cost includes engineering, permitting, and project management by the owner.) Since 2006 system operation has required: 1) routine inspections and sampling, 2) repairs/upgrades, and 3) sludge removal. Routine monthly inspections are $5,000/yr. Upgrades had involved repairs to berms, cleanout of pipes clogged with iron sludge and debris, and the replacement of pipes with open troughs. As of 2016 all the pipes which were prone to plugging have been replaced with large open troughs that are easy to maintain.

Sludge removal costs are divided into pumping and capture/dewatering. All costs are expressed as dollars per mton of solid. The 2012 sludge pumping effort recovered approximately 725 mtons solid. The unit cost for sludge pumping was $59/mton and the unit cost for sludge capture and dewatering was $99/mton (both 2016 dollars). Based on experiences at other sites, the dewatering costs could be significantly lowered with the use of reusable sludge basin.

Sludge that has been dewatered to at least 45% solids is suitable for trucking to a customer or processing plant. Few customers are currently willing to accept a 45% solids unscreened product. IOR operates a processing facility where iron oxide is dried to 60-70% solids and screened to < 1 cm. This product is usable by customers. The cost to truck the sludge to the plant is $54/mton and the cost to process the material is $110/mton. The total cost to produce a 60-70% dry screened product from the Marchand iron sludge is $322/mton.

Table 4. *Costs for the installation and operation of the Marchand passive treatment system.*

	Realized Cost	**Cost in 2016**
Installation	$1,212,770 (2004)	$1,702,042
Capital Improvements		
Berm repairs	$15,000 (2010)	$16,515
New trough installation	$33,759 (2012)	$33,863
New trough installation	$22,000 (2016)	$22,000
Total Capital Costs		$1,774,420
Periodic Major Maintenance		
Sludge removal	$42,702 (2012)	$42,833
Sludge capture/dewatering	$72,073 (2012)	$72,294
Total Sludge Management	$114,445 (2012)	$115,127
Routine Operation and Maintenance	$5,000/yr	$5,000

Sales and Markets

Since 2000 Iron Oxide Recovery has sold 4,120 mtons of iron oxide. 92% of the sales has been as crude pigment. The remaining 8% has been for non-pigmentary applications. Approximately 600 mtons of the production was iron oxide recovered from ponds at the Marchand site prior to the construction of the treatment system. The remaining production was from five passive treatment systems and three sites where iron oxide had precipitated naturally from coal mine drainage.

Realized and potential markets for iron oxide recovered from mine drainage systems are discussed below

Pigment Iron oxides have pigmentary characteristics that that have been recognized and utilized for thousands of years. Two pigments are available from mine drainage solids. The raw iron oxide (goethite) is considered a yellow pigment while a calcined product (hematite) is considered a red pigment. These two pigments are used to produce the earth tone color palette. Iron oxide pigments are produced by mining natural deposits and synthetically by chemical processes. The market for iron oxide pigments is large (Tanner 2016). In 2014 the US consumed approximately 220,000 mtons of finished iron oxide pigments at an average value of $1,270/mton. Natural iron oxides are produced domestically and imported. Approximately 2,000 mtons of natural iron oxides were imported in 2104 at an average value of $520/mton. The Marchand iron oxide is generally considered a natural iron oxide. However, its purity and pigmentary strength are comparable to synthetics.

Hoover Color Corporation (Hiwassee, Virginia, USA) is a primary customer of IOR. HCC processes the IOR product to a 95% solids, calcined, milled red pigment that is used for blending and marketed specifically as EnvironOxide™ (http://www.hoovercolor.com/products/pigments/type/environoxide/). The pigment's characteristics are particularly suited for wood stains and most of the dark wood stains produced in the USA contain iron oxide from mine drainage.

The pigment market is very competitive. Asian synthetic iron oxides are available in the USA for about $800/mton. Finished synthetic iron oxide pigments cost $1,500-2,000/mton.

Control of Soluble Phosphorus The release of phosphorus (P) from land-applied manure is a common water quality problem. Iron oxide decreases the mobility of P through sorption and the formation of ferric phosphate. IOR has recently cooperated in research into the use of mine drainage solids to lessen the solubility of P in land-applied manures (Sibrell et al 2015). Amendments of 6-10 g/L of iron oxide (solid) to dairy and swine manure decreases soluble P by at least 50% in both laboratory and field trials. This use of mine drainage solids may be restricted by environmental policies that define mine drainage solids as industrial wastes and prohibit their use in agricultural activities. Analysis of the mine drainage solids for hazardous metal content is necessary before this use can be considered (e.g., Table 3).

Control of Hydrogen Sulfide Iron oxide is useful for the control of hydrogen sulfide (H_2S) through its ability to inhibit activity by sulfate reducing bacteria and through its reaction with H_2S. H_2S production in manure storage facilities can create hazardous air quality conditions. Recent research at Pennsylvania State University found that Marchand iron oxide completely suppressed H_2S production in gypsum-amended dairy manure. Iron oxide is used to remove H_2S from natural gas. Sulfurtrap[R] is an iron oxide based H_2S scavenger used in a fixed bed technology (http://www.chemicalproductsokc.com/h2s-scavenger).

In H_2S applications the Fe^{3+} content of the iron oxide is of primary importance. Iron oxides produced from mine water have a very high Fe content (Table 2) and application into this market will probably be driven by price competition with synthetic iron oxides.

Control of Selenium Release by Mine Spoils Selenite and selenate both sorb to iron oxides. As a result, Se is only a problem in the eastern USA coal fields where there an absence of Fe in the drainage. A recent experiment by Donavan and Ziemkiewicz (2014) showed that amending Se-rich coal refuse with iron oxide obtained from mine drainage significantly decreased the release of Se in drainage.

Treatment and Stabilization of Hazardous Metals Iron oxides readily adsorb hazardous metals and lessen their solubility in water and environmental mobility in soil environments. Iron oxides are especially good sorbants of arsenate (Daus et al.2004). Lanxess Corporation sells an iron oxide media for the treatment of As-contaminated waters (http://bayferrox.com/en/products-applications-bfx/industries/water-treatment/).

Iron oxides can stabilize hazardous metals in soils. Liu et al (2014) amended metal-contaminated soils with mine drainage iron oxide solids and found significant decreases in the availability of Cd, Cu, and Zn. Iron oxide is component in TRAPPS amendment system which is used to decrease the mobility of Pb in contaminated soils (http://www.slateruklimited.co.uk/trapps_firing_range.html). Iron oxides recovered from mine drainage perform as well as commercial grade iron oxides and provide a significant cost advantage because it is feasible to use a 60% solids screened product.

Stimulation of Plankton Growth Fertilization of Fe-deficient oceans with iron oxide has been proposed as a method for stimulating plankton growth and sequestering carbon in deep ocean sediments. Fertilization efforts to date have mainly utilized ferrous sulfate which is rapidly oxidized to iron oxide after addition to the marine waters. The direct use of iron oxide should be feasible (Hedin and Hedin 2014). This application values Fe content. Ferrous sulfate is available for $100/mton which, at 20% Fe, is equivalent to $500/mton-Fe. The processed Marchand IO, at $322/mton, is equivalent to $610/mton-Fe.

Conclusions

Passive systems can effectively treat Fe-contaminated coal mine drainage. The long-term effectiveness of the systems depends on management of the iron sludge that is produced. The Marchand passive system has operated for 10 years and has gone through one sludge recovery effort. Costs were carefully monitored. The cost to recover and dewater iron sludge on site was $$158/mton-solid. This cost can be decreased with more efficient dewatering processes. The cost to process the dewatered sludge to a screened 60% solids product was $164/mton-solid. The total cost to produce a marketable product was $322/mton-solid. The iron oxide product is currently being sold to a pigment company who processes it into finished earth-tone pigments. Other applications of iron product that have been researched or tested on a limited scale are: control of soluble P in animal manures; control of H_2S production in manures storage facilities; removal of H_2S from natural gas; and treatment/stabilization of metal contaminated waters and soils.

References

Adler PR, Sibrell PL (2003) Sequestration of phosphorus by acid mine drainage floc. J Env Qual 32:1129-1129

Daus B, Wennrich R, Weiss H (2004) Sorption materials for arsenic removal from wastes: a comparative study. Water Research 38:2948-2954

Donovan JJ, Ziemkiewicz PF (2014) Selenium adsorption onto iron oxides layers beneath coal-mine overburden spoil. J Environ Qual 42:1402-1411

Hedin RS (2008) Iron removal by a passive system treating alkaline coal mine drainage. Mine Water Environ 27:200-209

Hedin RS, Hedin BC (2014) Increasing oceanic carbon fixation through Fe fertilization: opportunity for mine water? Mine Water Environ 34:105-111

Liu R, Altschul EB, Hedin RS, Nakles DV, Dzombak DA (2014) Sequestration enhancement of metals in soils by addition of iron oxides recovered from coal mine drainage sites. Soil and Sedimennt Contamination 23:374-388

Sibrell PL, Penn CJ, Hedin RS (2015) Reducing soluble phosphorus in dairy effluents through application of mine drainage residuals. Comm Soil Sci and Plant Anal 46:545-563

Tanner AO (2016) 2014 Minerals Yearbook, Iron Oxide Pigments. USGS. Washington D.C.