Recovery of a Marketable Iron Product from Coal Mine Drainage

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The purpose of mine drainage treatment systems is the production of an effluent whose quality satisfies either the terms of an NPDES permit or a water quality goal set by a restoration group. An unavoidable consequence of mine drainage treatment is the production of metal-rich sludge. The management and disposal of this waste product is an expensive component of the operation of chemical treatment systems. Passive treatment systems are typically constructed with years of sludge storage capacity -eliminating the need for regular sludge management. Eventually, the sludge contained in passive systems will need to be removed and disposed of. The costs associated with this activity are not known, but are likely to be substantial.

If a marketable value could be found for the sludge produced by mine water systems, the costs of conventional treatment might be decreased and the concerns about long-term maintenance liabilities for passive treatment might be eliminated. The idea that mine drainage sludge might have a useful value is not new. The physical and chemical characteristics of conventional sludge make their value as soil amendments or cementing agents possible (Yeh and Jenkins, 1971; Grady and Akers, 1976). In practice, however, schemes to "harvest" mine drainage sludge have not proven practical or economical.

Hedin Environmental has developed a mine water treatment system that yields clean water and an iron-rich sludge that is marketable to the iron oxide industry. The system uses passive treatment techniques to produce an iron oxide material we refer to as *MDoxide*. This paper describes the current status of the MDoxide project at Hedin Environmental.

The Iron Oxide Industry and Market

Iron oxides are used in a variety of industrial and manufacturing applications. They are valued for their pigmentary, catalytic, and magnetic properties. In 1996 the US produced approximately 125,000 tons of iron oxides with a total estimated value of about $ 100 million. The per ton value of iron oxide products varies from $100/ton to $2,500/ton. The value of an iron oxide product is largely determined by its purity ($FeOOH$, Fe_2O_3 or Fe_3O_4 content), the presence of metal contaminants, and the particle size. Currently, iron oxides are produced in three general manners: through the mining of natural ores, by synthetic produces, and as a byproduct of steel manufacturing.

Natural iron oxides are produced by mining goethite, hematite, and magnetite deposits. Ores are mined in the US and imported from the Mediterranean, South America and Australia.

Natural products vary greatly in composition. The iron oxide content ranges from <50% (for goethite) to as high as 95% (for hematite and magnetite). The value of natural iron oxides is limited by the inability of mechanical grinding processes to decrease particle size to less than 1 mm.

Synthetic iron oxides are produced by a variety of chemical processes. The purest synthetics are produced from the direct precipitation of iron oxide from oxidized and neutralized ferrous sulfate solutions. Major quantities of synthetics are produced from the dissolution and oxidation of scrap iron. Synthetic processes produce products that are very pure and can be ground to particle sizes less than 1 mm. These attributes make synthetic iron oxides the most valuable on the market

Regeneration iron oxides are produced as a byproduct of the recycling of pickling liquors from steel manufacturing. Regeneration processes produce a very pure product, but the particle size limits their value. Most regeneration oxides are being sold to the ferrite industry.

The MDoxide System

Hedin Environmental's MDoxide system precipitates iron from mine water that is buffered with bicarbonate. The system has three general steps. In the first step, the chemistry of the mine water is adjusted to assure appropriate bicarbonate concentrations. In cases where the untreated mine water contains sufficient bicarbonate, no adjustment is necessary. Where bicarbonate concentrations are inadequate, alkalinity is adjusted with limestone. In the second step, iron oxide sludge is precipitated in basins. The basins are designed to both promote the rapid precipitation of a clean iron oxides and to facilitate efficient removal of iron oxide sludge. In the third step, the discharge of the basins is polished so that the final discharge complies with effluent standards or targets. Polishing is achieved with constructed wetlands or chemical treatment.

A patent is pending on the process (# 08/834,236 filed April 15, 1997). The patent makes claims on the general production of an iron oxide product from bicarbonate buffered mine water. Specific design and operational features of the iron oxide production and mine water treatment system are held as trade secrets by Hedin Environmental.

The Quality of the Iron Oxide Product

Samples of iron oxides obtained from existing mine water treatment systems have been analyzed (Fish et al., 1996). The mine drainage samples were all goethite. They were generally comparable to yellow iron oxides (which are also goethite) and more directly comparable to natural siennas. Tables 1 and 2 show summary chemical characteristics for the mine drainage samples, synthetic and natural iron oxide products. Compared to natural goethites, the mine drainage precipitates had substantially higher iron contents and lower trace metal contents. Compared to synthetic goethites, the mine drainage precipitates had lower iron contents and comparable trace metal contents. MDoxides will have chemical characteristics exceeding those shown in Tables I and 2. In particular, we expect to be able to produce a product with a FeOOH content of 85-90% and substantially lower concentrations of aluminum, calcium, magnesium and sodium.

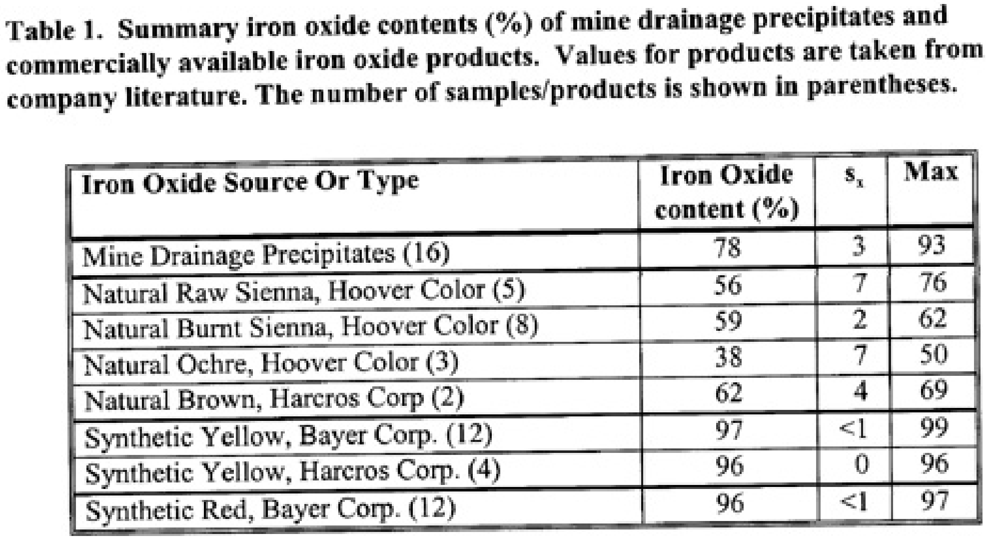

Table 1. Summary iron oxide contents (%) of mine drainage precipitates and commercially available iron oxide products. Values for products are taken from company literature. The number of samples/products is shown in parentheses.

Iron Oxide Source Or Type	Iron Oxide content (%)	s_x	Max
Mine Drainage Precipitates (16)	78	3	93
Natural Raw Sienna, Hoover Color (5)	56	7	76
Natural Burnt Sienna, Hoover Color (8)	59	2	62
Natural Ochre, Hoover Color (3)	38	7	50
Natural Brown, Harcros Corp (2)	62	4	69
Synthetic Yellow, Bayer Corp. (12)	97	<1	99
Synthetic Yellow, Harcros Corp. (4)	96	0	96
Synthetic Red, Bayer Corp. (12)	96	<1	97

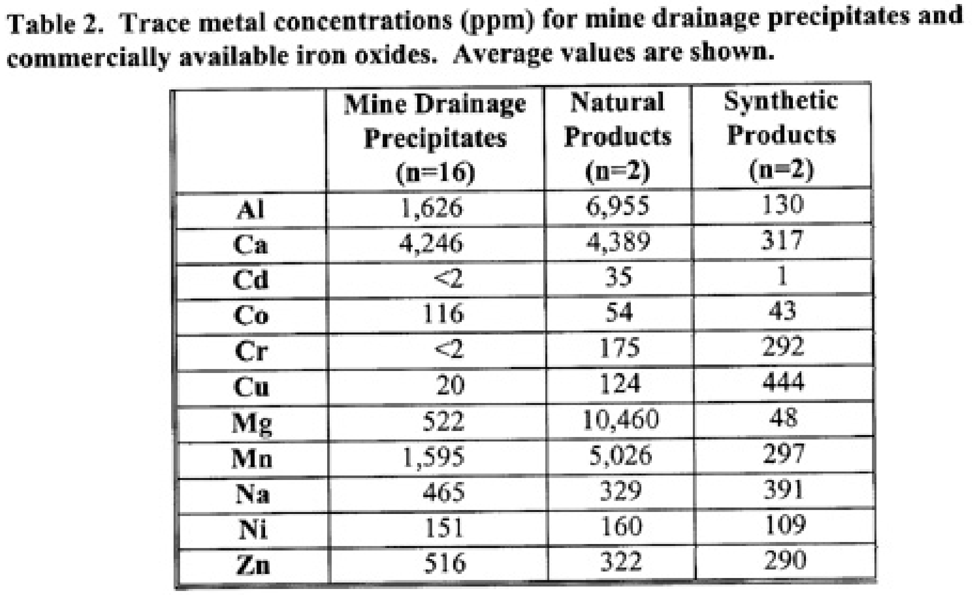

Table 2. Trace metal concentrations (ppm) for mine drainage precipitates and commercially available iron oxides. Average values are shown.

	Mine Drainage Precipitates (n=16)	Natural Products (n=2)	Synthetic Products (n=2)
Al	1,626	6,955	130
Ca	4,246	4,389	317
Cd	<2	35	1
Co	116	54	43
Cr	<2	175	292
Cu	20	124	444
Mg	522	10,460	48
Mn	1,595	5,026	297
Na	465	329	391
Ni	151	160	109
Zn	516	322	290

Particle size is a very important determinant of iron oxide value. Natural products have average particle sizes of 1-10 mm. Synthetic products have average particle sizes of 0.2-1.0 mm. Both natural and synthetic products are processed to decrease particle size as much as is technically and economically feasible. Minimally processed mine drainage precipitates have an average particle size of 1-10 mm. Using conventional grinding technologies, we have decreased the average particle size of MDoxides to 0.4 mm.

The Quality of the System Water Effluent

The passive principles that underlie the MDoxide system are capable of producing an effluent in compliance with standard NPDES permits. Highly successful passive treatment of mine water has been documented at numerous mine sites throughout Appalachia (Brodie 1991; Stark et al. 1994; Hellier et al. 1994; Hedin et al. 1994). Most of the systems included in these studies are surface mines. The feasibility of passive treatment for pump and treat systems is not as well documented. Pump and treat systems offer excellent treatment and MDoxide production opportunities because of the consistent flow and Fe loading. Figure 1 shows the discharge quality of 700 gpm pump and treat system in southern Appalachia. The pumped water is alkaline and contains 45 mg/L Fe. The treatment is a passive system consisting of 11 acres of interconnected ponds and ditches. The discharge of the system has never been out of compliance (Figure 1).

Unpumped artesian flows from abandoned deep mines offer excellent MDoxide production opportunities, but variable flow rates make discharge quality less certain. Table 3 shows the performance of a three acre pond/wetland system that was recently constructed at St. Vincent College (Latrobe, PA) to treat an artesian flow of alkaline Fe-contaminated water. Flows have ranged from 150-350 gpm. The performance has degraded as flow increased. However, the worst performance documented thus far for the system, a 6 mg/L discharge, still represents a 93% decrease in Fe contamination. This high flow effluent quality is acceptable to many stream restoration groups.

How Much Alkaline Fe-Contaminated Mine Water?

The MDoxide process focuses specifically on alkaline, iron-contaminated mine waters. Large sources of appropriate mine water exist in Pennsylvania. In western PA, mining companies pump and treat at least 20,000 gpm of alkaline water that carries approximately 3,500 tons/yr of Fe as FeOOH. Discharges from abandoned mines in western PA account for at least 30,000 gpm of alkaline water containing approximately 5,500 tons/yr of Fe as FeOOH. Discharges from abandoned mines in eastern PA account for at least 100,000 gpm of flow containing approximately 12,000 tons of Fe as FeOOH. These quantities do not include acidic mine waters that could be made net alkaline with limestone. In western PA, we are aware of at least 14,500 gpm of acidic mine water containing approximately 4,500 tons of Fe as FeOOH that could be readily made alkaline with limestone.

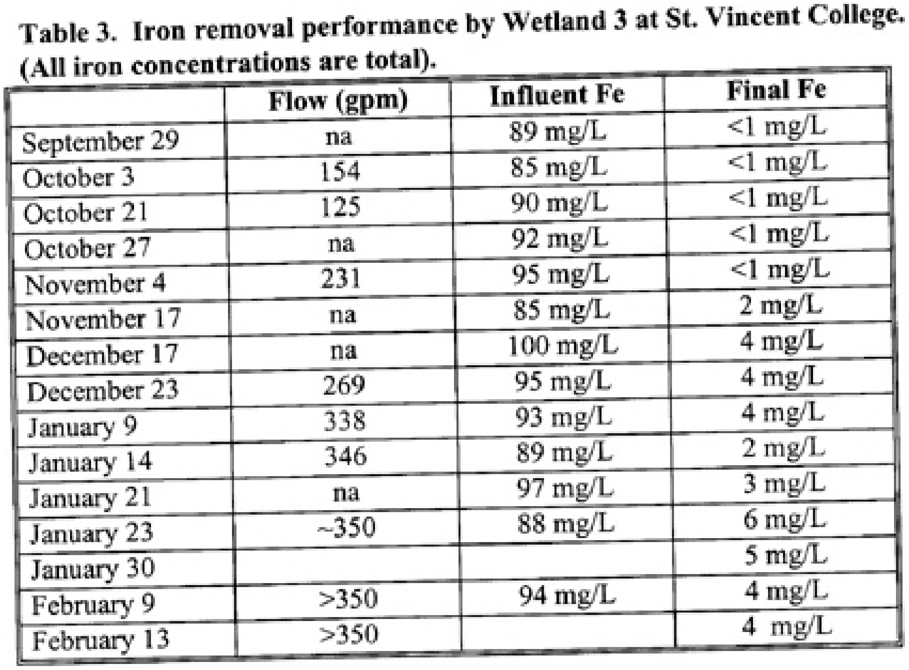

Table 3. Iron removal performance by Wetland 3 at St. Vincent College. (All iron concentrations are total).

	Flow (gpm)	Influent Fe	Final Fe
September 29	na	89 mg/L	<1 mg/L
October 3	154	85 mg/L	<1 mg/L
October 21	125	90 mg/L	<1 mg/L
October 27	na	92 mg/L	<1 mg/L
November 4	231	95 mg/L	<1 mg/L
November 17	na	85 mg/L	2 mg/L
December 17	na	100 mg/L	4 mg/L
December 23	269	95 mg/L	4 mg/L
January 9	338	93 mg/L	4 mg/L
January 14	346	89 mg/L	2 mg/L
January 21	na	97 mg/L	3 mg/L
January 23	~350	88 mg/L	6 mg/L
January 30			5 mg/L
February 9	>350	94 mg/L	4 mg/L
February 13	>350		4 mg/L

To put these quantities into some perspective, the largest iron oxide factory in the US (Bayer's New Martinsville WV facility) produces approximately 50,000 tons/yr. Small-scale iron oxide facilities in the US produce 1,000 - 5,000 tons of iron oxide/yr.

Economics of MDoxide Systems

Conventional lime treatment systems remove Fe from alkaline contaminated mine water at a cost of $400-1200 per ton of Fe treated (as FeOOH). The cost yields a discharge that is in compliance an NPDES pen-nit and accounts for all O&M and sludge management expenses. It does not account for pumping costs.

Passive treatment systems constructed by restoration groups with public funds remove Fe from alkaline contaminated mine water at a cost of approximately $500 per ton of Fe (as FeOOH). This cost accounts for construction of the treatment systems. It does not account for land purchase, O&M costs, sludge disposal, or the expenses accrued by public agencies that promote and facilitate strewn restoration efforts. These systems do not have NPDES permits attached to the discharge.

A cost model developed for the MDoxide system indicates that an effluent in compliance with typical NPDES standards can be produced for many pump & treat discharges as a cost of ~$ 1,000 per ton of FeOOH produced. At sites without an NPDES permit, where an 80-90% decrease in Fe concentrations is adequate, the cost of Fe production is ~$700/ton of FeOOH produced. We presently value the iron oxide product at $100-200 per ton. Thus, the current economic analyses indicate that when the values of the treated mine water *and* the recovered iron oxide product are combined, the MDoxide system provides a cost-effective treatment option for permitted and unpermitted discharges.

Ongoing Research and Development

The MDoxide concept is currently being developed through several lines of investigation. The US Department of Agriculture has provided crucial support through its Small Business Innovation Research (SBIR) Program. SBIR Phase I funding supported the original sampling and analysis of iron oxides from mine water environments. SBIR Phase II funding has supported analyses of the physical characteristics of MDoxides, development of the cost model, and development of an inventory of MDoxide source waters in western Pennsylvania. Current SBIR-supported research is investigating the chemical characteristics of clean iron oxide precipitates, factors that influence the rate of iron oxide production in treatment systems, and developing processing and marketing strategies. The USDA SBIR grant is being conducted through contractual assistance from the University of Pittsburgh (Dr. Rosemary Capo of the Geology Program) and St. Vincent College. A parallel grant from the Ben Franklin Technology Center of Western Pennsylvania is supporting an investigation of the basic chemistry of iron oxide formation in bicarbonate-buffering waters. The research is being conducted by Dr. Brian Dempsey of Pennsylvania State University.

Summary

An innovative mine drainage treatment system that produces both clean water and a marketable iron oxide product is being developed. Current economic analyses indicate that the value of iron oxides is not sufficient to justify the construction the iron oxide production facilities at mine water sites. However, the combination of water treatment values and iron oxide values does result in a system that appears to be cost-effective compared to current technologies. The current application for the technology is iron-contaminated waters that are naturally net alkaline, or acidic waters that can be made alkaline with limestone. Numerous discharges from underground mines in Pennsylvania meet these criteria.

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Figure 1. Effluent pH, Fe and Mn for a 700 gpm pumped discharge. The raw water contains 200 mg/L alkalinity, 45 mg/L Fe, and 33 mg/L Mn.