

**CHEMICAL CHARACTERIZATION OF IRON OXIDE PRECIPITATES FROM
WETLANDS CONSTRUCTED TO TREAT POLLUTED MINE DRAINAGE¹**

by

Caryl L. Fish², Robert S. Hedin³, Jonna M. Partezana²

Abstract. The passive treatment of abandoned mine drainage using wetlands will produce a significant amount of iron rich sludge which will require costly removal and disposal. An alternative to disposal may be the use of this iron oxide material as pigments which could defray some of these costs. In this research, iron deposits from five alkaline mine drainage wetlands were collected and a series of standard tests were run. The tests included loss on ignition, moisture, pH, acid soluble metals, oil absorption, and water soluble matter. The results of these tests were compared to those achieved using commercially available natural and synthetic iron oxides. The results indicate that iron oxides from constructed wetlands have chemical properties that are intermediate to those of natural and synthetic iron oxide products.

Additional Key Words: Acid mine drainage, constructed wetlands, iron oxides

Introduction

Passive methods of treatment for iron contaminated mine waters have been developed in recent years (Hedin et al. 1994). The principle technique used to treat this mine drainage is to pass the water through a constructed wetland, where the iron precipitates as iron oxide. Because passive methods are cost effective when compared to chemical alternatives (Brodie 1990), many private companies, public reclamation agencies, and non-profit conservation organizations are adopting this technology. Interest in passive techniques has been tempered, however, by concerns about the long-term costs of managing the iron oxide sludge that collects in the wetlands. It is anticipated that

mine operators and reclamation groups will need to remove the metal-rich precipitates from passive systems every 5 to 20 years (the period depends on the design of the individual systems). Since the sludges are not classified as hazardous, they can be legally disposed of in an active mine backfill or in a public landfill. The costs associated with collecting and legally disposing of the iron oxide wastes, however, may be substantial.

The possible recovery and utilization of iron oxides from passive treatment systems has not been previously considered in detail. A significant iron oxide industry exists in the United States. In 1990, 123,000 mtons of iron oxides were

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²Chemistry Department, Saint Vincent College, 300 Fraser Purchase Rd., Latrobe, PA 15650.

³Hedin Environmental, Suite 216, 634 Washington Rd. Pittsburgh, PA 15228.

produced for use as pigments in construction materials and coatings, as industrial catalysts, in foundry sands and in animal feeds. These iron oxides were produced from natural sources, by synthetic processes, and as a by-product of steel manufacturing. Natural iron oxides are produced by mining hematite, goethite, or magnetite deposits. Synthetics are produced through the oxidation and neutralization of solutions containing ferrous or elemental iron, or as a by-product of aniline production. Because synthetics are of higher purity than the natural iron oxides, they demand a higher price (Mauney 1994, Templeton 1990).

The purpose of this study was to evaluate precipitates from alkaline mine drainage wetlands as a potential

source for iron oxide. The study focused on alkaline mine water (pH > 6.0) due to its faster precipitation rates, existing treatment sites, and potential for future wetlands construction. In Western Pennsylvania, constructed wetlands are currently being designed for several discharges that will precipitate more than 250,000 pounds of iron oxide per year. These wetlands will provide a large source of passively precipitated iron oxides.

Experimental

Sample Collection

Samples were collected during July 1995 from five alkaline mine drainage wetlands (Table 1) which were either natural or constructed wetlands used for the treatment of abandoned mine

Table 1: Descriptions of Sampling Sites

Site	Year	Builder	Design	Flow gal/min	Iron Conc. (mg/L)		Substrate	Water Source	Coal Seam
					Influ.	Efflu.			
Bubbler	1970	Unknown	Bore Hole	300	80	80	Wood	Deep Mine	Pgh.
Saint Vincent	1982	Boy Scout Troop	Natural	30	80	5	Soil	Deep Mine	Pgh.
Cedar Grove	1989	Natural Resource Conservation Service	Settling Pond 2-3 Wetlands LS Cell	41.2	92	41	Clay	Deep Mine	Pgh.
Howe Bridge	1991	Mill Creek Coalition	ALD Ditches 2 Ponds	34	265	185	Clay LS SMC	Abandoned Well	Clarion
Morrison	1990	Glacial Mining Company	ALD Ditch Settling Pond 2 Cells	1.7	151	56	Clay Manure	Surface Mine	Clarion
Tennessee	1992	Confidential Company	Pump Discharge Ditch	750	45	<1	Clay	Surface Mine	Sewanee

Pgh. - Pittsburgh
LS - Limestone

SMC - Spent Mushroom Compost
ALD - Anoxic Limestone Drain

drainage. Four of these sites (Saint Vincent, Cedar Grove, Howe Bridge, and Morrison) are located in western Pennsylvania. The Tennessee wetland is located near Chattanooga, TN. A sixth site (locally known as the Bubbler) was a wooden weir receiving mine drainage from a bore hole. It was chosen to determine the effect of precipitation in a non-vegetative area.

In each wetland site, three sampling areas were chosen: one close to the influent point of the wetland, one in the center of the wetland, and one near the effluent point of the wetland. A flow of water was present at each sampling point. Grab samples of the solid iron oxide precipitates were collected and placed into two gallon polyethylene bags. Two bags were collected at each sampling area. Each bag was filled with precipitate and water from one third to one half of its capacity. The Bubbler sample was taken directly from the first and second sections of the weir.

Commercial Iron Oxides

Samples of commercial iron oxides were obtained from the Bayer

Corporation, (Pittsburgh, PA) and Hoover Color Corporation (Hiwasee, VA). The Bayer samples, Bayferrox 130M and Bayferrox 940, were synthetics produced by the aniline process. The Hoover samples, 202RS Raw Sienna and 308BS Burnt Sienna, were natural iron oxides.

Sample Preparation

All samples were air dried in a greenhouse (maximum daytime temperatures 38° - 47° C) for 5-7 days. Once dried, the samples were crushed to a powdery consistency using a pestle. Most of the plant debris was removed by passing the samples through a 0.850 mm sieve. The sieved material was then further ground to pass through a 0.425 sieve. The fine material resulting from this sieving was placed in polyethylene bags and sealed for future use.

Analytical Methods

American Standard Test Methods (ASTM) procedures for pigments were done in duplicate to test the precipitates (Table 2) and the commercial iron oxide.

Table 2: ASTM Pigment Methods

Designation	Title	Procedure
D 1280-84	Standard Test Methods for Common Properties of Certain Pigments	4. Loss on Ignition and Ash 5. Matter Soluble in Water 6. Hydrogen Ion Concentration*
D 280-81	Standard Test Method for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments	Method A-For Pigments that do not Decompose at 110°C
D 1483-84	Standard Test Method for Oil Absorption of Pigments by Gardner-Coleman Method	
D 185-84	Standard Test Method for Coarse Particles in Pigments, Pastes, and Paints	Insoluble Dry Pigments, Except Metallic Aluminum and Bronze Powders

* Revisions in this method are noted in text.

Revisions were made to method D 1280-84 (Procedure 6 - Hydrogen Ion Concentration) upon consultation with an iron oxide manufacturer. The electrode used was an Orion Ag/AgCl Sure-Flow Electrode, Model number 9172BN. First, the cool sample solution was stirred with a glass stir rod sixty times. It was then allowed to settle for two minutes. After that time, the electrode was placed into the sample, stirred slightly and allowed to sit for an additional two minutes. The pH reading was taken after the two minute wait.

Metal Analysis

Sample Digestion. Each solid sample was digested by adding 100 ml of concentrated nitric acid (69.0-70.0% Baker Analyzed Nitric Acid) to a weighed portion of the precipitate in a 400 ml beaker and heated on a hot plate to induce boiling. The solution was reduced to 25 ml or less and filtered through Whatman 40 ashless filter paper to remove the acid insoluble material from the solution. The residue was then air dried and weighed to determine the percentage of acid insoluble found within the iron oxide sample. During filtering, the solution was transferred into a volumetric flask and diluted to 100 ml. After dilution, the flasks were sealed, labeled, and placed into a 3-5 °C refrigerator for storage.

Analysis. The sample digestates were analyzed for iron and twelve trace metals - cobalt, nickel, lead, aluminum, calcium, manganese, chromium, magnesium, sodium, zinc, copper and cadmium. The analysis was done using the inductively coupled plasma atomic emission spectrophotometer (ICP-AES) (Varian Liberty 200). All of the samples were analyzed in duplicate on the ICP. A standard curve for each element was determined at the beginning of each run using two multi-element standards. (Table 3) Since the ICP is linear over several orders of magnitude only two standards were necessary. The standard concentrations were determined from trial runs with representative precipitated iron oxide. Wavelengths for each element were chosen to minimize interference from the high concentrations of iron.

Table 3:Elemental Wavelengths and concentrations of Standards

Element	Wavelength (nm)	Standards (ppm)
Co	345.350	1,10
Ni	352.454	1,10
Pb	368.348	1,10
Al	396.152	1,10
Ca	317.933	50,100
Mn	257.610	5,10
Fe	260.709	100,500
Cr	267.716	1,10
Mg	279.553	5,100
Na	588.995	5,10
Zn	213.856	1,10
Cu	324.754	1,10
Cd	228.802	1,10

A control check was also run for each set of samples. To analyze for iron, the samples were diluted 1 to 100.

Results and Discussion

Pigment Tests

The dried and sieved (0.425 mm sieve) precipitates were subjected to a variety of pigment tests similar to those used in the pigment industry to test the commercial iron oxide. The results from these tests on the wetland precipitate are shown in Table 4. The results from commercial iron oxide are given in Table 5. Loss on ignition for the wetland precipitates is in the same range as the yellow iron oxide (Bayferrox 940) and much higher than the red iron oxide (Bayferrox 130M). Since this test is in part an indication of the purity of the iron oxide, it is encouraging. The oil absorption test is also encouraging since this is an indication of the suitability of the precipitates pigments in paint applications. For the most part the wetland precipitates are very similar to the commercial iron oxides in terms of oil absorption.

Table 4: Pigment Tests for Wetland Precipitates

	Bubbler	Saint Vincent	Cedar Grove	Howe Bridge	Morrison	Tennessee
0.850 Sieve (% retained)		3.16 ^{0.23}	11.56 ^{5.76}	20.08 ^{13.99}	17.14 ^{12.19}	41.68 nd
Ignition Loss (% lost)	13.74 ^{0.04*}	16.82 ^{2.13}	16.83 ^{0.35}	16.68 ^{0.31}	16.98 ^{0.17}	14.79 ^{0.95}
Soluble Matter (%)	0.80 ^{0.09}	1.00 ^{0.05}	0.95 ^{0.05}	1.00 ^{0.09}	0.36 ^{0.10}	0.65 ^{0.11}
pH	6.38 ^{0.04}	6.82 ^{0.06}	6.94 ^{0.07}	5.26 ^{0.13}	6.06 ^{0.42}	7.20 ^{0.11}
Oil Absorp. (%)	118.8 ^{2.88} 0	83.90 ^{7.91}	88.60 ^{2.14}	81.40 ^{10.47}	81.19 ^{3.63}	65.50 ^{10.24}
Moisture (%)	9.08 ^{1.76}	5.17 ^{0.54}	8.25 ^{1.65}	8.74 ^{4.12}	2.90 ^{0.40}	6.24 ^{3.72}
0.045 mm sieve (% retained)	21.00 nd	17.33 ^{6.87}	10.40 ^{10.07}	18.60 ^{16.68}	10.85 ^{11.04}	9.12 ^{5.31}

Superscripts are 95% confidence limits

Table 5: Pigment Tests for Commercial Iron Oxide

	Bayferrox 130M	Bayferrox 940	Hoover 308BS	Hoover 202RS
Ignition Loss (% lost)*	0.6	13		
Soluble Matter (%)*	0.2	0.25		
pH	6.47 ^{0.09+}	4.1 ^{0.02}	7.07 ^{0.12}	6.97 ^{0.02}
Oil Absorption (%)	37.84 ^{0.84}	89.4 ^{0.72}	64.1 ^{3.43}	45.9 ^{6.09}
Moisture (%)*	0.4	0.25		
0.045 mm sieve*	0.002	0.04	0.1	0.05

*Taken from product literature

+Superscripts are 95% Confidence limits

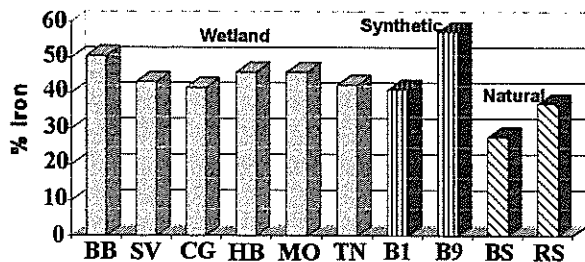
The meaning of the two sieve tests should be clarified. The 0.850 mm test is not a pigment test but a measurement of the miscellaneous material that is found in the wetland precipitates and is removed with a large size sieve. This material included leaves, grass and other biotic material. The 0.045 mm test is a critical test for the pigment industry since the particle size must be consistent to provide consistent blending by the customers. However, it should be noted that this is a test for final product iron oxide that is sold to the customer and the wetland precipitates were not processed except in a rudimentary fashion. Further processing (i.e. grinding) would certainly decrease the values for this test.

The final two tests (moisture and water soluble matter) also have much higher values for the wetland precipitates than the commercial iron oxide. Once again the results from these tests would change considerably with some simple processing such as rinsing the precipitates and then more thoroughly drying them.

Metals Analysis

The results of the metal analysis for the precipitates are shown in Table 6 and the commercial iron oxides in Table 7. The most important metal analysis is, of

Figure 1: Concentration of Iron in Precipitates. BB = Bubbler, SV = Saint Vincent, CG = Cedar Grove, HB = Howe Bridge, MO = Morrison, TN = Tennessee, Bl = Bayferrox 130M, B9 = Bayferrox 940, BS = Hoover 308BS, and RS = Hoover 202RS .



course, the percent iron in the precipitates. As can be seen in Figure 1, the percent iron is similar in the precipitates to the synthetic iron oxide and somewhat higher than the natural iron oxide.

Results from four of the other metals analyzed are shown in Figure 2. For aluminium and manganese the concentrations are somewhat higher than the synthetic iron oxide but lower than the natural. The analysis for copper shows all the wetland precipitates to be lower than both the synthetic and natural iron oxides. The zinc results indicate some diversity in the wetlands with zinc concentrations from the Bubbler, Saint Vincent, Cedar Grove and Tennessee sites being lower than the concentrations in the commercial iron oxide. The values from the Howe Bridge site are close to the concentrations of the high zinc commercial products. The Morrison site is substantially higher in zinc concentration than any of the other samples. This illustrates that there is some diversity in the wetland precipitates and that critical commercial applications may require careful screening of the precipitates used.

Metals in the mine drainage are most likely the source of the trace metals in the precipitates. Therefore, mine drainage with high concentrations of metals would produce precipitates with high metal concentrations. The water soluble matter is probably associated with ions such as Na^+ , SO_4^{2-} , and Cl^- present as water soluble salts. The concentration of sodium in the Bubbler, Saint Vincent, and Cedar Grove sites is much higher than at the other sites. The water soluble matter is also much higher at these sites. The Howe Bridge site does not fit into this pattern, however, with relatively low sodium concentrations and high water soluble matter.

Conclusion

In general the wetland precipitates have many similar characteristics to commercial iron

Table 6: Concentration of Metals in Wetland Precipitates

Metals	Bubblers	Saint Vincent	Cedar Grove
Co (ppm)	23.66 +/- 40.32	45.77 +/- 12.60	51.66 +/- 7.86
Ni (ppm)	20.71 +/- 2.70	16.86 +/- 1.94	22.70 +/- 25.05
Pb (ppm)	27.24 +/- 1.94	72.88 +/- 36.92	68.28 +/- 34.71
Al (ppm)	259.9 +/- 8.6	3322 +/- 1639	820.1 +/- 57.12
Ca (ppm)	3825 +/- 113	5310 +/- 664.1	5004 +/- 287.4
Mn (ppm)	328.4 +/- 11.4	735.2 +/- 386.7	144.1 +/- 37.43
Cr (ppm)	2.97 +/- 0.07	74.04 +/- 136.3	0.18 +/- 0.35
Mg (ppm)	347.6 +/- 11.1	728.6 +/- 216.1	359.2 +/- 25.6
Na (ppm)	422.1 +/- 4.6	1141 +/- 1182	1284 +/- 137
Zn (ppm)	125.0 +/- 5.1	93.44 +/- 9.06	69.71 +/- 5.05
Cu (ppm)	18.87 +/- 1.56	22.24 +/- 1.71	15.34 +/- 0.75
Cd (ppm)	< 0.10	<0.10	3.01 +/- 1.96
%Fe	50.45 +/- 0.08	43.11 +/- 6.44	41.41 +/- 2.28

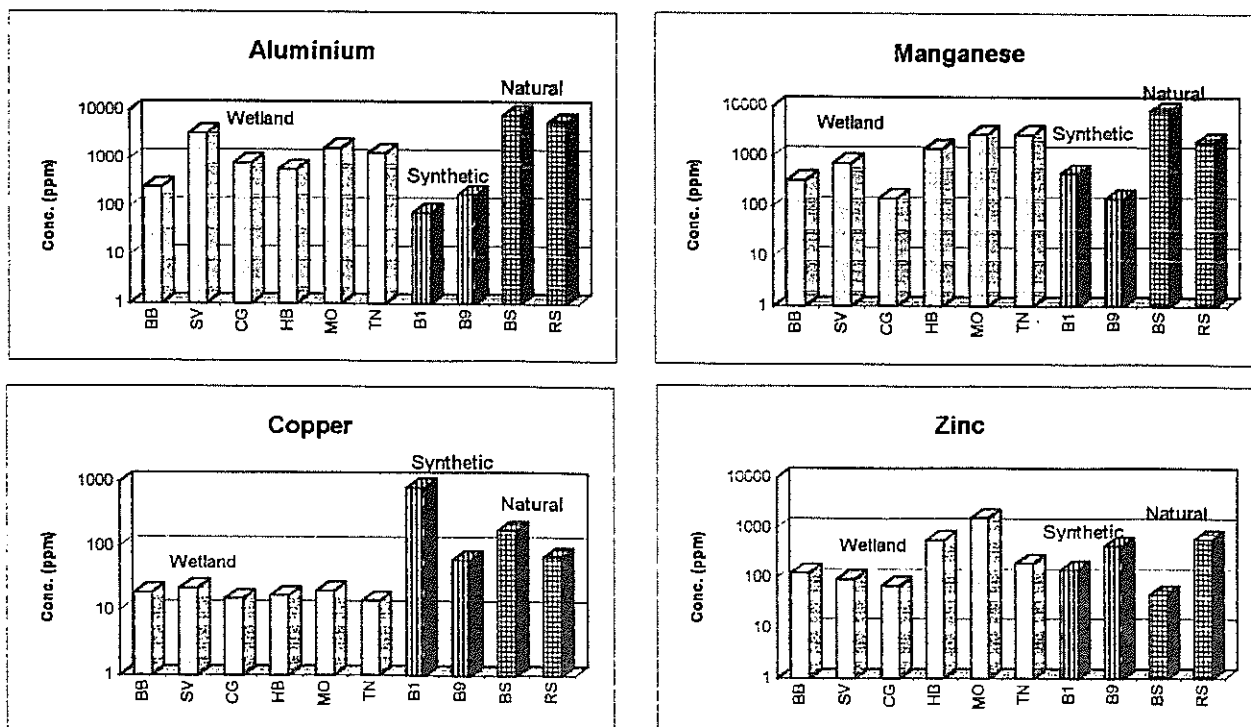
Metals	Howe Bridge	Morrison	Tennessee
Co (ppm)	72.13 +/- 20	276.4 +/- 28.0	108.3 +/- 9.5
Ni (ppm)	156.16 +/- 63.53	325.3 +/- 73.8	200.6 +/- 24.5
Pb (ppm)	86.97 +/- 35.85	84.76 +/- 34.86	17.93 +/- 20.71
Al (ppm)	600.0 +/- 180.6	1660 +/- 511	1321 +/- 894
Ca (ppm)	1060 +/- 31.20	1401 +/- 203	6038 +/- 1392
Mn (ppm)	1383 +/- 193	2716 +/- 278	2694 +/- 715
Cr (ppm)	<0.10	0.15 +/- 0.30	1.35 +/- 1.74
Mg (ppm)	343.8 +/- 50.20	355.9 +/- 42.4	586.8 +/- 164.5
Na (ppm)	73.88 +/- 17.24	88.17 +/- 9.80	40.95 +/- 5.50
Zn (ppm)	569.4 +/- 108.2	1570 +/- 184	195.6 +/- 45.9
Cu (ppm)	17.10 +/- 1.68	20.21 +/- 1.80	14.21 +/- 0.62
Cd (ppm)	0.05 +/- 0.097	<0.10	<0.10
%Fe	45.88 +/- 4.68	45.74 +/- 10.58	42.30 +/- 8.67

Table 7: Concentration of metals in commercial iron oxide

Metals	Bayferrox 130M	Bayferrox 940	Hoover 308BS	Hoover 202RS
Co (ppm)	43.62 +/- 15.25	42.29 +/- 6.06	62.21 +/- 2.01	45.48 +/- 6.74
Ni (ppm)	182.6 +/- 38.7	34.93 +/- 7.38	146.2 +/- 21.2	173.13 +/- 4.20
Pb (ppm)	34.50 +/- 1.89	45.61 +/- 1.64	73.39 +/- 15.8	69.17 +/- 22.43
Al (ppm)	77.21 +/- 18.46	183.7 +/- 16.9	8153 +/- 268	5757.8 +/- 94.7
Ca (ppm)	152.5 +/- 45.7	259.5 +/- 23.8	7512 +/- 210	1264.9 +/- 108.4
Mn (ppm)	450.6 +/- 89.0	143.1 +/- 10.7	8094 +/- 69	1958.4 +/- 57.6
Cr (ppm)	479.6 +/- 86.5	105.1 +/- 13.0	159.6 +/- 1.3	190.7 +/- 3.2
Mg (ppm)	20.07 +/- 4.47	76.08 +/- 5.74	10343 +/- 156	10577 +/- 303
Na (ppm)	160.4 +/- 15.4	622.1 +/- 23.7	393.5 +/- 1.5	264.4 +/- 1.0
Zn (ppm)	145.7 +/- 17.6	434.9 +/- 29.9	46.99 +/- 2.94	597.7 +/- 308.5
Cu (ppm)	826.6 +/- 73.6	61.69 +/- 3.60	177.9 +/- 2.1	69.09 +/- 0.10
Cd (ppm)	<0.10	0.50 +/- 0.35	68.52 +/- 0.36	1.58 +/- 2.79
%Fe	40.99 +/- 0.97	57.11 +/- 0.83	27.63 +/- 0.47	37.06 +/- 0.44

Figure 2: Selected Metals Concentrations in Wetland Precipitates and Commercial Iron Oxide.

Wetland: BB = Bubbler, SV = Saint Vincent, CG = Cedar Grove, HB = Howe Bridge, MC = Morrison, TN = Tennessee
 Synthetic: B1 - Bayferrox 130M, B9 - Bayferrox 940
 Natural: BS = Hoover 308BS, RS = Hoover 202RS



oxide. The iron concentrations, oil absorption, and ignition loss are all reasonably close to the commercial iron oxide. Several of the other parameters such as moisture, 0.045 mm sieve, and water soluble matter are significantly different. However, this difference may be due to a lack of processing such as grinding, washing, or vigorous drying. The inclusion of some of these processing steps may bring these values closer to the commercial products.

The results of the metal analysis are interesting in that they show the precipitates to be between the synthetic and the natural iron oxides in concentration for several metals. They are also significantly lower in copper and chromium concentration than both the natural and the synthetic material.

These results are encouraging and would indicate that the wetland precipitates do have some potential as a raw material for commercial iron oxide. There is some additional processing that will be necessary to make a consistent product, but additional evaluations are justified.

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