SUSTAINABLE MINE DRAINAGE TREATMENT THROUGH THE PASSIVE PRODUCTION OF SALEABLE IRON OXIDE SOLIDS[1]

Robert S. Hedin[2]

Abstract. Iron is the most common metal contaminant of coal mine drainage. Its treatment creates a metal-rich sludge whose management accounts for a substantial portion of the total treatment costs. For decades, researchers have searched unsuccessfully for cost-mitigating uses for mine drainage sludge. This paper describes our progress in the development of a passive treatment process that yields iron oxide sludge that has valuable pigmentary characteristics. Samples of iron solids were collected from a variety of environments. All samples from chemical treatment systems were impure because of the coprecipitation of multiple chemical parameters. Only passive treatment systems yielded sludge pure enough to be considered for pigmentary applications. At several sites, the purity of the samples from passive systems was substantially decreased by the presence of alumino-silicate minerals introduced by inflows of surface water containing sediment. Mechanical and moderate chemical treatment, that was intended to accelerate iron oxidation without the precipitation of non-target elements, caused the precipitation of calcium-containing minerals that lessened the pigment strength. Solids collected from passive systems where the pH ranged below 6 were pure, but were weak pigments. Saleable pigment-quality iron solids were produced from passive systems where sediment inflows were minimal and the pH was maintained between 6 and 7. A treatment system that produces saleable iron solids through passive treatment techniques has the potential to provide self-sustaining mine drainage treatment.

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[2] Robert S. Hedin, President, Iron Oxide Recovery, Inc., 195 Castle Shannon Blvd, Pittsburgh PA 15228

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Introduction

The successful treatment of polluted mine drainage requires that chemical conditions are created to promote the neutralization or precipitation of contaminant constituents and that sufficient retention is provided to accommodate the kinetics of the chemical and physical processes. The establishment of favorable chemical conditions is usually accomplished through the addition of chemicals that act directly on the contaminants or indirectly through pH adjustment. Typically the removal of contaminants involves two steps: 1) the formation of a solid phase of the contaminant, and 2) the retention of the solid within the treatment system. The separation of the solid contaminant from the water is often the rate-limiting part of the process. Liquid/solid separation is usually accomplished through settling processes in basins.

An effective treatment system must provide enough retention time to allow the contaminant removal processes to proceed to completion. Clarifiers and some settling basins maintain retention time through the continuous removal of solids. Many settling basins are periodically cleaned out to restore retention. Solids removed from the basins are typically disposed of through burial or injection into abandoned mine voids. The cost of solids management is a major component of the total cost of mine drainage treatment.

A sustainable mine drainage treatment system maintains the chemical and physical conditions necessary to achieve discharge targets without large inputs of materials, energy or manpower. Passive treatment systems can maintain the chemical conditions necessary to meet target discharge criteria with limited annual inputs. Some mine discharges are naturally buffered and do not require the addition of alkaline reagents. Some acidic discharges can be neutralized through the slow dissolution of limestone. It has proven practical to install enough limestone to provide decades of neutralization with minimal annual effort. Some discharges are being treated passively through bacterial processes that are supported by organic substrate. It has proven practical to install enough organic substrate to support a decade of bacterial activity, also with minimal annual effort.

Passive systems are especially sensitive to retention time because the chemical and biological remedial processes are typically slow. Like all treatment systems, passive systems retain solids that consume system volume, decrease retention, and eventually degrade treatment performance. One solution for this problem has been to build passive systems with large solids storage capacity, so that solids management is avoided for decades. The "avoidance" strategy has proved acceptable for small discharges with modest passive treatment systems. The approach has been generally unacceptable for large discharges where the initial capital costs are substantial and the financial consequences of unmanaged solids accumulation are more apparent.

A sustainable way to manage solids is to treat them as a resource whose value offsets the cost of their management. This approach shifts treatment of the solids from a waste perspective to a product perspective. Feasibility requires a value-adding use of the solids. If the value is sufficient to offset the costs of solids recovery and processing, then the critical retention time in the treatment system can be sustained at no net cost to the operator.

At this time, self-sustaining mine drainage treatment systems are most appropriate for coal mine discharges contaminated primarily with Fe. A reliable passive treatment approach has been developed for these waters that involves alkalinity adjustment with buried limestone (if needed) and aerobic precipitation of Fe in ponds and wetlands (Hedin et al., 1994a; Hedin et al., 1994b;

Younger et al., 2002). In 1995, Hedin Environmental, Inc. initiated research into the production of saleable products from Fe-contaminated mine water. The research was prompted by the observation that many Fe-precipitating systems have negligible effect on other water constituents (Hedin et al. 1994a), suggesting that the Fe solids retained were relatively pure. The research determined that the Fe oxides that precipitate in passive systems can be pure enough to have market value, particularly as raw unfinished pigment (Fish et al., 1996). A method for producing saleable Fe oxide from mine drainage was developed and patented (Hedin 1999). A pilot-scale Fe recovery project was conducted where methods of recovering and processing Fe solids from mine drainage systems were developed (Hedin and Weaver, 2002). Between 2001 and 2005, 1,600 short-tons of Fe solids (dry weight) were recovered from mine drainage sites, processed, and sold as unfinished pigments.

As part of our research program, samples of Fe sludge have been collected from mine drainage systems and analyzed for chemical characterizations. The goal of the program is to determine the purity of Fe samples collected from a variety of precipitation environments so that conditions that produce saleable Fe solids can be identified. This paper describes the results of our sampling efforts and discusses progress on the development of a self-sustaining mine drainage treatment technology.

Methods

Solid samples were collected from ponds, wetlands, and treatment systems. The samples were collected by scooping sludge from the sampling area and then transferring a small composite portion into a sealed plastic bag. The samples were dried at 105°C to constant weight. The weight loss was used to calculate moisture content.

$$\text{Moisture (\%)} = 100 \text{ X } (W^{fresh} - W^{dry\ 105}) / W^{fresh} \qquad \textbf{(1)}$$

Solids content was calculated from the moisture.

$$\text{Solids (\%)} = 100 - \text{Moisture (\%)} \qquad \textbf{(2)}$$

A portion of the dry sample was provided to ActLabs, Inc. (Tucson, AZ, www.actlabs.com) for analysis of major elemental constituents by fusion ICP. Samples were mixed with lithium metaborate and lithium tetraborate flux and fused in an induction furnace. The molten mix was dissolved in nitric acid, which was analyzed for Al, Si, Fe, Mn, Mg, Ca, P, Na, and K using inductively coupled plasma optical emission spectrometry (Analytical code 4B, http://www.actlabs.com/methsub_code4b.htm). Weight losses during the fusion step were reported as Loss On Ignition (LOI). The major elements were reported as the presumed oxide solid and as a percentage of the original sample weight. The mineral percentages were added to the LOI percentage to provide a total weight. A total value of "100" indicates that the analytical parameters accounted for 100% of the sample's original weight.

As will be discussed, the LOI for samples consisting predominantly of Fe oxide is due primarily to dehydration of the Fe oxyhydroxide compounds. In order to estimate the Fe oxide content of the original dried sample, a "Fe-LOI" value was calculated by adjusting the reported Fe_2O_3 percentage by the LOI percentage. The calculation is shown below.

$$\text{Fe-LOI} = Fe_2O_3 / (100 - \text{LOI}) \qquad \textbf{(3)}$$

Results and Discussion

Tables 1, 2, 3, and 4 present analytical results for the samples. As noted, the mineral phases reported represent those presumed present in the ashed samples and do not represent the mineral forms in the original samples. The "Total" values reported for each analysis shows the percent of the original weight accounted for by the analytical results. In almost every case, the totals were 99-100%, an indication that the analytical parameters accounted for the major non-volatile elemental components of the samples.

LOI arises from components of the samples volatilized during high-temperature ashing. Contributors to LOI include:

- CO_2 evolved when organic compounds that are oxidized and carbonate compounds are calcined;
- SO_2 evolved when sulfur-containing compounds are calcined; and
- H_2O evolved during heat-induced changes in Fe oxyhydroxide compounds.

X-ray diffraction has indicated that the primary crystalline form of Fe in the raw samples is goethite (FeOOH) (Fish et al., 1996). The amorphous phase is likely Fe hydroxide ($Fe(OH)_3$). During ashing, the compounds loose water and weight as shown below.

$$2FeOOH + heat \rightarrow Fe_2O_3 + H_2O \qquad \textbf{(4)}$$

$$2Fe(OH)_3 + heat \rightarrow Fe_2O_3 + 3H_2O \qquad \textbf{(5)}$$

The dehydration of FeOOH results in 10% weight loss. The dehydration of $Fe(OH)_3$ results in 25% weight loss. Synthetic Fe oxide products that have a reported purity of 99% and are characterized mineralogically as FeOOH have a weight loss of 13% (www.hoovercolor.com). Thus, even "pure" FeOOH contains more water than is indicated by the stoichiometry and likely contains $Fe(OH)_3$.

All samples were visibly inspected after drying. Some samples contained copious amounts of roots and organic matter. These samples were not included in subsequent chemical analyses because one of the primary goals of the study was to identify clean deposits of Fe solids. We believe that the organic components of the samples presented in this paper were negligible. Calcite and dolomite contribute to LOI through their evolution of CO_2 during ashing. Most of the samples contained < 1% of Ca and Mg, so this source of LOI is also negligible.

Sulfur-containing compounds contribute to LOI through their evolution of SO_2. Iron oxyhdyroxylsulfate compounds such as schwertmannite, $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$ are known to form in some acidic mine water environments (Bigham et al., 1990). These compounds only form when the pH is less than 3.5. If schwertmannite was present, its ashing would result in a 17% weight loss. This LOI is within the range anticipated from FeOOH and $Fe(OH)_3$. XRD has not identified schwertmannite in any samples; however, it is possible that an amorphous form may be present in samples collected from low-pH environments. For samples collected from acidic environments, the contribution of SO_2 to the LOI cannot be discounted. For these samples, it may be inaccurate to characterize the LOI-adjusted Fe values as FeOOH and $Fe(OH)_3$.

Chemical Characteristics of Passively Precipitated Iron Sludge

Table 1 shows the characteristics of Fe sludge samples collected from environments where precipitation occurs by passive processes. The sampled sites include passive treatment systems intended to precipitate Fe solids and locations where no treatment system exists but Fe sludge accumulated naturally. The results are organized according to the pH of the environment in which the precipitation occurs. One set of samples was collected from an alkaline environment where the pH was maintained between 6 and 7. A second set of samples was collected from a transitional environment where the discharges have pH 5.5- 6.5, but are insufficiently buffered with alkalinity and develop lower pH conditions as Fe hydrolysis occurs. The third set of samples was collected from acidic environments where the pH is always less than 4.

Samples collected from the alkaline environment were predominantly Fe oxide with small amounts of Si and Al compounds. The Si and Al were partly due to the presence of alumino-silicate clays. Most of the sites did not exclude surface waters and inflows of sediment-laden water occurred during runoff events. However, not all of the Al and Si is attributable to the inflow of sediment. The Sax, Wil, and Hon samples were collected from locations that were protected from inflows of surface water. These samples still contained 5-6% Si. It appears that Si co-precipitates with Fe in alkaline environments with pH 6-7. This process currently limits the purity of Fe oxides produced in the alkaline environment, with total exclusion of surface waters, to 92-93%.

Samples collected from the transitional environmental had similar Fe contents to the alkaline samples, but were more pure because of lower concentrations of Si and Al. These samples had higher LOIs (average 21.1%) than the alkaline samples (average 16.8%). As the samples were clean, the difference in LOI must be associated with a higher water content and/or the presence of sulfate. Because the samples had such low non-Fe elements, the Fe-LOI adjusted values were very high. High-temperature treatment of the transitional pH Fe solids would produce a 98-99% pure Fe oxide material.

Table 2 shows the results of samples collected from sites where active treatment was occurring. The treatment processes include NaOH and $Ca(OH)_2$ addition. The sludges collected from the sites were heterogeneous and the precipitation of non-target minerals was evident. The NaOH treatment systems precipitated Mg, presumably as $Mg(OH)_2$. The lime treatment systems precipitated Ca, probably as both un-reacted $Ca(OH)_2$ and as $Ca(SO_4)$. The impurity of these sludges makes the identification of valuable uses unlikely.

Table 3 shows the results for samples collected from systems where the pH was maintained at less than 8, but mechanical, physical, and chemical means were used to stimulate Fe oxidation. The mechanical and physical systems stimulate oxidation through aeration, which strips dissolved CO_2 and generally causes the pH to rise to 7-8. The chemical additions include hydrogen peroxide (H_2O_2), which directly effects oxidation, and modest NaOH addition that is intended to only raise the pH to 7-8.

Table 1. Chemical characteristics of Fe sludge samples collected from passive environments. All values are percent. "Fe-LOI" is an approximation of the percent of Fe oxide present in the original sample and was calculated from equation 3. "pH" indicates the water pH in the sampling area.

Site	**pH**	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	**MnO**	**MgO**	**CaO**	**LOI**	**TOT**	**Fe-LOI**
Wil	6-7	76.4	6.7	0.5	0.01	0.04	0.21	16	100	91
Hon	6-7	79.8	4.9	0.1	0.13	0.06	0.30	13	98	92
Sax	6-7	74.4	5.0	0.7	0.05	0.05	0.64	18	99	91
How	6-7	72.2	9.0	1.8	0.08	0.09	0.06	16	100	86
Key	6-7	73.7	7.6	0.8	0.06	0.06	0.31	17	100	89
War	6-7	77.1	1.9	2.5	0.03	0.04	0.16	17	99	93
Scrb	6-7	76.3	6.6	0.9	0.01	0.08	0.26	15	100	90
Phil	6-7	63.9	9.9	1.7	0.09	0.13	1.72	22	100	82
Low	6-7	75.3	5.4	1.7	0.04	0.06	0.11	17	100	91
Clear	3-6	64.9	0.6	0.3	0.01	0.02	0.05	34	100	98
Dit	3-6	77.6	0.7	0.0	0.03	0.01	0.01	22	100	99
Shet	3-6	75.8	0.3	0.0	0.00	0.02	0.03	24	100	99
Neid	3-6	77.1	2.7	0.3	0.07	0.04	0.09	19	100	96
Keen	3-6	78.8	1.3	0.1	0.02	0.04	0.04	20	100	98
TyB	3-6	81.9	0.7	0.1	0.01	<0.01	<0.01	17	100	98
TyA	3-6	81.7	0.2	<0.1	0.01	0.01	<0.01	18	100	100
Horn	3-6	79.4	1.6	0.3	0.02	0.01	0.04	17	99	96
Tob	3-6	77.6	1.3	0.2	0.00	0.03	0.03	20	99	97
Hall	3-6	78.3	0.6	0.2	0.01	<0.01	0.02	20	99	98
Mor	2-3	59.0	0.6	0.5	0.02	0.08	0.95	37	99	94
Bru	2-3	76.5	0.8	0.2	0.01	0.03	0.02	23	100	99
Hunt	2-3	34.1	50.0	2.5	0.02	0.08	0.03	13	100	39

Table 2. Composition of sludge collected from chemical treatment systems. All values are percent.

Reagent (contaminants)	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	**MnO**	**MgO**	**CaO**	**LOI**	**TOT**
NaOH (Fe, Al, Mn)	5.8	7.4	12.5	12.0	24.1	3.6	30	95
NaOH (Mn, Al)	0.3	5.5	6.6	12.8	31.6	6.9	28	92
$Ca(OH)_2$ (Fe)	4.5	0.8	<0.1	0.2	0.5	48.9	41	97
$Ca(OH)_2$ (Fe, Al, Mn)	27	4.8	4.0	2.8	2.9	24.3	30	96

Table 3. Composition of sludge at sites where oxidation is promoted, but pH is maintained < 8. All values are percent. "Fe-LOI" is an approximation of the percent of Fe oxide present in the original sample and was calculated from equation 3.

Oxidation promoter	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	**MnO**	**MgO**	**CaO**	**LOI**	**TOT**	**Fe-LOI**
Spray	76.3	4.6	0.9	1.2	0.3	1.6	14	99	89
Vigorous aeration	74.1	5.8	3.1	0.0	0.2	1.3	15	100	87
Mixing	74.6	9.3	0.7	0.2	0.2	1.2	14	100	87
Aerator	80.8	2.9	<0.1	0.2	0.1	1.3	14	99	94
H_2O_2	70.7	3.1	0.4	0.2	0.2	3.6	21	100	90
H_2O_2	75.7	2.5	0.4	0.1	0.2	5.0	14	99	88
NaOH	64.8	3.9	3.5	0.4	0.5	3.7	21	99	82

All of the samples from systems where oxidation was promoted contained Fe contents that were similar to the passively precipitated samples. However, the samples also contained elevated Ca concentrations. The most likely source of the Ca is calcite, which can precipitate from alkaline mine waters when the pH increases. The mechanism by which H_2O_2 causes Ca precipitation is unknown.

Factors Affecting the Purity of Passively Precipitated Iron Solids

The primary contaminants of passively precipitated Fe solids are Si and Al. The purity of the material is dependent on the minimization of these constituents. An important controllable source of Al and Si is the inflow of sediment-laden water into treatment ponds. Most of the sediment is clays and silts that are various forms of alumino-silicate minerals.

Figure 1 is a drawing of a pond that receives a continuous flow of Fe-contaminated mine water (1,100-4,500 L/min, pH 6.5, Fe 30 mg/L) and, as a result, is brightly colored with Fe oxide. The drainage flows down a channel and enters the eastern side of the pond. The pond also received flow from a culvert that drains storm-related runoff from crop fields and discharges into the northwestern corner of the pond. The final discharge from the pond is in the southwestern corner. The sludge in the pond was sampled in order to determine its purity and potential for recovery. Sampling points are shown in Fig. 1 and the analytical results are shown in Table 1.

Solid samples collected from the discharge channel contained 77% Fe_2O_3 and 7% silica compounds. These samples are indicative of the chemical quality of the sludge if the pond could be isolated from sediment-laden storm inflows. Samples collected from the western and central portions of the pond, where the storm flows enter, contained more than 15% Si and Al compounds and had Fe concentrations as low as 22%. These sediment-contaminated Fe solids have no value. The eastern portion of the pond contained Fe sludge slightly contaminated with mud. Solids in the channel and the eastern portion of the pond have chemical and physical characteristics similar to Fe solids that have been recovered, processed, and sold for their pigmentary values.

Plans are underway to clean out the pond and redesign it so that sediment-laden storm flows are diverted around. As a result, the pond should accumulate clean Fe solids, characteristic of the solids collected from the channel.

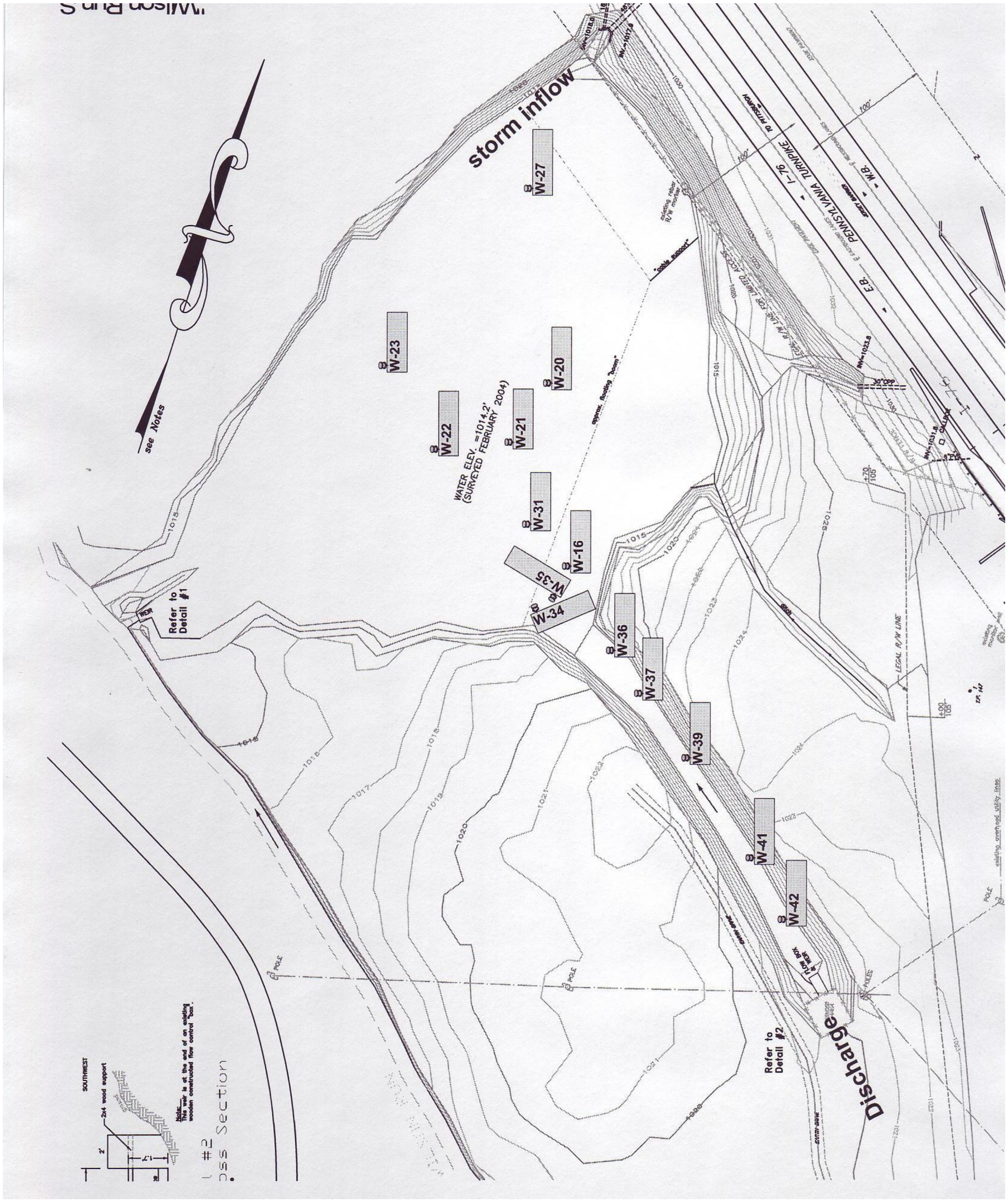

Figure 1. Sludge sampling locations at the Wilson Site.

Table 4. Composition of solids samples collected from the Wilson site. All values are percent. "Fe-LOI" is an approximation of the percent of Fe oxide present in the original sample and was calculated from equation 3.

Sampling location	Fe_2O_3	SiO_2	Al_2O_3	MnO	MgO	CaO	LOI	Tot	Fe-LOI
Channel, W-42	76.4	6.7	0.5	0.01	0.04	0.21	16	100	91
Channel, W-41	75.5	6.2	0.5	0.02	0.06	0.23	17	100	91
Channel, W-39	76.5	6.1	0.2	0.03	0.03	0.26	16	100	92
Channel, W-37	77.6	6.6	0.4	0.02	0.05	0.17	15	100	91
Channel, W-36	74.7	5.6	0.5	0.05	0.05	0.72	18	100	91
Pond East, W-16	70.9	9.0	1.4	0.03	0.13	0.38	18	100	86
Pond East, W-34	71.3	8.5	1.2	0.05	0.13	0.77	18	100	86
Pond East, W-35	72.4	7.9	1.1	0.04	0.09	0.74	17	100	87
Pond Central, W-21	62.2	14.0	2.3	0.03	0.23	0.70	18	99	76
Pond Central, W-31	22.0	44.7	11.2	0.10	0.77	2.03	15	99	26
Pond Central, W-20	59.5	15.3	3.0	0.04	0.35	1.24	19	100	74
Pond West, W-22	66.8	10.4	1.6	0.04	0.19	0.82	19	100	83
Pond West, W-23	53.0	21.7	4.1	0.04	0.35	0.85	18	99	64
Pond West, W-27	31.0	29.4	9.4	0.27	0.73	3.39	22	99	40

Production of Saleable Iron Oxide

The pigmentary characteristics of the Fe oxide samples have been evaluated by potential pigment customers. Samples that contain less than 50% Fe oxides have weak pigment properties and are of no value. Many clean samples have also been rejected because of poor pigmentary characteristics. To date, all Fe solids that had saleable pigmentary characteristics were recovered from an alkaline environment with pH 6-7 where Fe precipitation occurred by passive means. Iron oxides collected from environments where pH ranged below 6 had substantially weaker pigment than the ones collected from a circumneutral pH. Samples collected from environments where oxidation was accelerated by mechanical or chemical means (Table 3) were noticeably browner and were not saleable as pigment at this time.

The pigmentary characteristics of the Fe solids can be improved through pretreatment with limestone. At the How site, the untreated mine water is net acidic and Fe solids originally precipitated at pH 3-5. These solids had weak pigmentary characteristics. The discharge was directed into a passive treatment system that included pretreatment with limestone (anoxic limestone drain) followed by aerobic treatment where the pH was 6-7. The Fe solids recovered from the treatment system had strong pigment characteristics and were saleable.

Sustainable Mine Drainage Treatment

The results to date indicate that sustainable mine drainage treatment is possible in situations where the dominant contaminant is Fe, where the pH of the precipitation environment can be maintained between 6 and 7, and where the precipitation process is passive. These conditions exclude acid mine drainage that contains Al or is so acidic that the pH cannot be reliably maintained in the circumneutral range. These conditions also exclude AMD that is chemically appropriate, but site constraints make necessary the use of kinetic stimulants such as chemicals or mechanical devices. Despite these limitations, there are many areas in Appalachia where these conditions can be satisfied. Flows from flooded deep mines in northern Appalachia are commonly alkaline and contaminated with Fe. When there is sufficient land area available, passive treatment is often feasible. The significant cost savings that accrue from passive treatment can make modest pumping schemes, where the water is relocated to a suitable site, cost-effective. This approach is also appropriate for acidic mine drainage that can be reliably made alkaline with an anoxic limestone drain. Hundreds of small and moderate flows in northern and central Appalachia meet the ALD criteria.

Conclusions

The realization of self-sustaining minewater treatment requires that the high cost of solids management be mitigated. The recent sale of Fe solids removed from four AMD sites as raw pigment provides an innovative solution for the solids management problem. The potential for solids sale as pigment is, however, limited. Solids collected in active chemical systems are not pure enough to be utilized for pigment applications or any application that values purity. Solids collected from systems where Fe oxidation is stimulated through mechanical or chemical additions can be pure, however the samples collected in this study were not strong pigments. Solids collected from environments where the pH ranged below 5 were pure, but were not strong pigments. The best pigments were recovered from waters with pH 6-7 where Fe precipitated by completely passive processes. These conditions are amenable to hundreds of discharges from coal mines in Appalachia. At these sites, the installation of a passive system that treats minewater with a minimum of inputs and is self-cleaning through the production of saleable Fe solids is feasible.

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