Advances in the Production of Marketable Products from Mine Water Treatment Systems

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Abstract
The solids produced from the treatment of mine drainage have attributes whose values can off-set sludge management costs. We have produced 30% moisture, <1 cm products from coal mine drainage since 2000. The solids have marketable pigmentary and chemical characteristics. Pigmentary applications are in the earth tone color range. The best pigment is produced through aerobic passive treatment of Fe-contaminated waters at pH 6-8. Mine drainage solids have chemical reactivity that is associated with the Fe, Al, and Ca content. The solids have been used in the treatment of phosphate, arsenate, selenite, and lead. For these applications, the ideal chemical composition of the solid may vary with the target contaminant. Recent testing on the P content of animal manures fount that a mixed metal solid produce by a lime plant unexpectedly lessened soluble P better than a pure iron oxide. The finding that solids recovered from mine drainage systems can be processed to a marketable condition is affecting how the treatment systems are designed.

Keywords: iron oxide, acid mine drainage, adsorption, passive treatment

Introduction
The treatment of mine drainage produces large quantities of waste sludge whose disposal is often very costly. These costs can be partially or fully offset if the sludge is processed into saleable products. This has been a goal of researchers and treatment plant operators for decades. The economic feasibility of the concept requires that the costs to create the products are less than the combined value of product sales and the avoided sludge disposal costs. The sustainability of the concept requires that the process can produce products with consistent quality and in quantities large enough to support long-term customer needs. Without these assurances, customers are unlikely to make long-term purchase commitments that are necessary to justify investments in sludge processing technologies.

For the last decade, Iron Oxide Recovery, Inc (IOR) has been producing an iron product from the solids precipitated from coal mine drainage. The concept grew from our mine water consulting business and the recognition that sludge produced in passive treatment systems was chemically and physically different than sludge produced in chemical treatment systems. The characteristics of passively produced iron sludges were investigated (Fish et al., 1996), several potential markets identified, and a plan to produce an iron product for the iron oxide industries were advanced (Hedin 1998, 1999). Since 2000, IOR has sold 3,300 tons of dry products to pigment, coal mining, water treatment, and soil remediation companies. The advances have involved research into the characteristics of mine water solids produced from a variety of environments in the eastern US. This paper describes that research effort.

Methods
Samples of sludge were collected from mine drainage discharge locations and treatment systems. Generally, 100 – 1,000 cc samples were collected by hand into a sealed plastic container. Sub-samples were drained and dried at 105^{o}C in a Fisher Scientific Isotemp oven. Moisture content was determined by comparing the wet and dry weights. Sub-samples of the dried material were submitted to Activation Laboratories (Ontario, CA) for elemental analysis. All samples were analyzed for major elements by ICP following a lithium borate fusion (Code 4B). Selected samples were analyzed for total C and S by infrared (Code 4F-C) and additional trace elements by ICP (Code 4B-INAA and Code 4B1 Total Digestion ICP).

Surface area measurements were made by the BET method on dried samples provided to the University Of Pittsburgh Swanson School Of Engineering and the PennsylvaniaStateUniversityCenter for Innovative Sintered Products.

Background

The chemical and physical characteristics of mine drainage solid products depend on three parameters:

1. mine water chemistry
2. treatment methodology
3. solids processing methodology

Mine Water Chemistry

In the eastern US coal fields, the routine mine water contaminants are acidity, iron (Fe), aluminum (Al) and manganese (Mn). The specific concentrations for these contaminants vary depending on the overburden geochemistry and the site hydrology. Many coal sections contain both acid acid-producing pyrite and alkalinity-producing carbonate minerals. The mine drainage chemistry is dependent on the relative presence of these minerals and the mine hydrology. Flooded mines that contain carbonate strata generally produce alkaline water containing ferrous iron and low concentrations of Al and Mn. The same lithology in an un-flooded free draining hydrologic setting produces low pH acidic water containing Al, ferric iron, ferrous iron and Mn. In portions of Appalachia, the primary carbonate is siderite and the mine water produced is acidic and contains ferrous iron and Mn, but little Al or ferric iron. Numerous mine discharges are acidic and contain a variable mix of Fe, Al, and Mn.

Treatment Methodology

Treatment technologies used in the eastern coal fields can be divided into passive, mechanical, and chemical strategies. The passive technology most applicable for large scale sludge production is the treatment of alkaline Fe-contaminated flows with aerobic ponds and wetlands (Hedin 2008). The alkaline flow can be natural or generated with limestone. Recently, oxic limestone beds have been used to treat acidic water containing Fe, Al, and Mn. Methods for cleaning the sludge that accumulates in the aggregate beds are being developed that could make substantial sludge recovery possible (Wolfe et al. 2010).

Mechanical techniques that produce large quantities of sludge include the aeration of alkaline Fe-contaminated discharges. Mechanical aeration techniques increase gas transfer which accelerates iron oxidation processes. The settling ponds that follow the aerators collect iron sludge. Many types of aerators are utilized in the coal fields.

Chemical treatment involves the addition of chemicals that accelerate the formation of solids and inherently produce large quantities of sludge. The two types of chemicals used in the eastern coalfields are oxidizers and caustic neutralizers. Hydrogen peroxide is used to treat alkaline Fe-contaminated discharges. It oxidizes ferrous iron without the need for aerators or neutralization. Sludge is collected in settling ponds. Caustic chemicals are used to neutralize acidity and raise pH above 9 which accelerates the removal of Fe, Al, and Mn. The removal ferric iron and Al occurs with neutralization while ferrous iron and Mn removal generally require aeration. Two types of caustic chemicals are used: lime and sodium hydroxide. Liquid sodium hydroxide is very simple to utilize, does not require electricity, and provides effective removal of all metals. Its high cost limits its use to low flow and remote sites. Lime, CaO and $Ca(OH)_2$, is the cheapest caustic reagent. However, when it is purchased dry, its efficient use requires slakers, mixers, aerators, and clarifiers which add considerably to the capital cost. The use of liquid lime decreases capital requirements but increases the cost of the reagent. Lime plants are most common chemical treatment technique for large flows of contaminated mine drainage in the eastern US. Lime plants produce large quantities of sludge.

Solids Processing Technology

To date, all sludge products have required processing in order to meet technical specifications of costs concerns. All sludge requires dewatering because the transport of wet sludge with 10 – 25% solids is prohibitively costly. Dewatering techniques used to date include filter presses, belt presses, geotubes, and passive drying in sludge basins. Sludge that has dewatered to at least 45% solids can be transported in trucks without the loss of water. The dewatered sludge is either sold as a raw unprocessed product or relocated to a facility for further processing. The processing depends on the quality requirements and specifications provided by the customer. All applications identified so far require further drying to at least 60% solids and screening to a uniform product solids content and particle size. The standard product sold to customers to date is 60-70% solids and screened to less than 1 cm.

Subsequent processing needs depend on the product use and currently are done by the customer. Pigmentary applications require drying to at least 95% solids, size reduction and calcination. Ion exchange applications can benefit from further size reduction. Reactive iron media applications may require chemical reduction (to magnetite or zero valent iron) and size reduction.

Results

Table 1 shows the major chemical composition of solids collected from a variety of environments. Several generalizations are possible.

Purity

The purest solids are iron oxides produced without the addition of caustic chemicals. Semi-pure iron oxides are most commonly produced from alkaline waters with high concentrations of Fe. Under these alkaline conditions pH is maintained between 6 and 7 which promotes abiotic iron oxidation and the formation of goethite and ferrihydrate. The principle secondary element of these solids is silica which is present at 1.5 – 2.5%. The source of silica could be quartz or clay that is washed or blown into the treatment systems or the co-precipitate of silica with ferrous iron at circumneutralpH.

The passive precipitation of Fe from low pH waters is slow (even with microbial catalysts) but large deposits sometimes accumulate around abandoned discharges over decades of time. In Pennsylvania dozens of such deposits exist at AMD discharge sites. These are the purest iron solids collected to date because at low pH less Si precipitates and calcite formation cannot occur. Limited data indicates that acidic iron oxides have higher S than alkaline solids, likely due to the formation of the ferric oxyhydroxysulfate mineral schwertmannite.

Calcium can be a secondary component of semi-pure iron oxide solids. Calcium is present at 1-3% in sludge produced in mechanical systems where the water is aerated. Aeration degasses CO_2 which typically raises the pH to ~8. If the water is strongly alkaline, $CaCO_3$ forms. This is also apparent in passively precipitated sludges where the pH is above 7.

Hydrogen peroxide treatment of alkaline Fe-contaminated water produces a semi-pure iron oxide that contains secondary concentrations of Si and Ca. The reason that H_2O_2sludges contain high Ca is unknown because the chemical does not cause a rapid increase in pH.

Table 1. Chemical composition of solids produced from a varying AMD chemistries using varying treatment technologies. (na- data not available)

	Mine Water Chemistry				Solids Chemistry										
	pH	Fe	Al	Mn	Al	C	Ca	Fe	K	Mg	Mn	Na	P	S	Si
		mg/L	mg/L	mg/L	%	%	%	%	%	%	%	%	%	%	%
Reference Minerals															
Goethite, FeO(OH)								62.9							
Ferrihydrite, $xFe_2O_3.yH_2O$								58-66							
Calcite, $CaCO_3$						12.8	40.0								
Gypsum, $CaSO_4$ 2H2O							23.3							18.6	
Chemical, lime															
Donaldson	7	40	<1	1	0.2	na	34.6	2.6	0.0	0.4	0.1	0.0	0.0	0.4	0.6
Elizabeth, lime	6	800	1	na	0.1	na	9.0	31.0	0.0	5.2	0.4	0.0	0.0	2.0	0.7
Brandy	3	70	3		1.6	6.5	21.0	10.0	0.0	4.8	1.1	0.1	0.0	1.7	1.3
Antrim	3	10	15	10	5.1	na	22.3	5.6	0.0	2.1	2.4	0.1	0.0	1.0	2.9
Toby 2010	4	24	9	13	6.0	2.8	18.4	7.4	0.0	4.8	1.6	0.0	0.0	4.1	2.7
Chemical, NaOH															
Monview	6	60	<1	1	1.8	na	2.6	45.3	0.0	0.3	0.3	1.1	0.0	na	1.8
Halfway	3	40	20	20	6.6	na	2.6	4.1	0.1	14.7	8.9	0.2	0.0	na	3.4
KJ Pond 4	3	1	10	15	3.5	na	4.9	0.2	0.1	18.9	9.9	0.1	0.0	na	2.6
Chemical H_2O_2															
Wildwood	7	15	<1	<1	0.1	na	1.3	51.3	0.0	0.0	0.1	0.1	0.2	0.1	1.5
Harmar	6	40	<1	na	0.2	na	2.6	49.5	0.1	0.1	0.1	0.3	0.0	na	1.4
Mechanical															
Hoyman	7	40	<1	8	0.0	na	0.9	56.6	0.1	0.1	0.1	0.1	0.0	na	1.4
Lion	7	80	<1	na	0.2	na	3.1	47.6	0.1	1.7	0.1	0.1	0.0	na	1.6
Saxman IBS	6	70	1	na	0.4	na	0.8	52.2	0.1	0.1	0.1	0.0	0.0	na	4.3
Passive															
Marchand A	6	75	<1	1	0.2	1.4	0.3	54.3	0.0	0.0	0.0	0.1	0.1	0.2	2.3
Marchand E	7	25	<1	1	0.1	2.7	1.2	54.6	0.0	0.1	0.1	0.2	0.0	0.3	2.5
Elizabeth, pipes	6	800	1	na	0.1	na	0.3	48.4	0.0	0.0	0.0	0.0	0.0	1.0	2.1
Hughes	3	40	3	1	0.1	na	0.0	54.0	0.0	0.0	0.0	0.0	0.0	1.8	0.7
Brubaker	3	90	12	na	0.1	na	0.0	53.6	0.0	0.0	0.0	0.0	0.0	na	0.4
Keen	3	60	<1	na	0.0	na	0.0	57.3	0.0	0.0	0.0	0.0	0.0	na	0.3

The most widely used caustic chemical is lime, CaO and $Ca(OH)_2$. Lime sludge is typically very impure because of the formation of calcium compounds. Gypsum forms when the sulfate concentration of the mine water is greater than 2,000 mg/L. Also most mine waters have high CO_2 contents and treatment with lime forms calcite, $CaCO_3$. For most of the lime sludge samples, the dominant element is calcium. An exception is lime sludge collected at metal mine site that uses a rotating cylinder treatment system (Tsukamoto and Moulton 2006). This lime sludge is the only one collected that is dominated by the targeted contaminant metal.

Particle Size

Several measures of particle size have been made on selected solids. One characteristic that is apparent with drying is that pure iron oxide solids are more easily reduced to a small particle size than impure iron oxide solids or lime solids. Figure 1 shows the particle size distribution of products that were air dried to 60-70% solids and screened in the field through a 1 cm screen. The two passive solids, which have a high Fe content, have similar particle size distribution. The lime solids do not reduce to as small a particle size with simple screening action. Because the lime solids are harder, obtaining a smaller particle size will require mechanical size reduction processing.

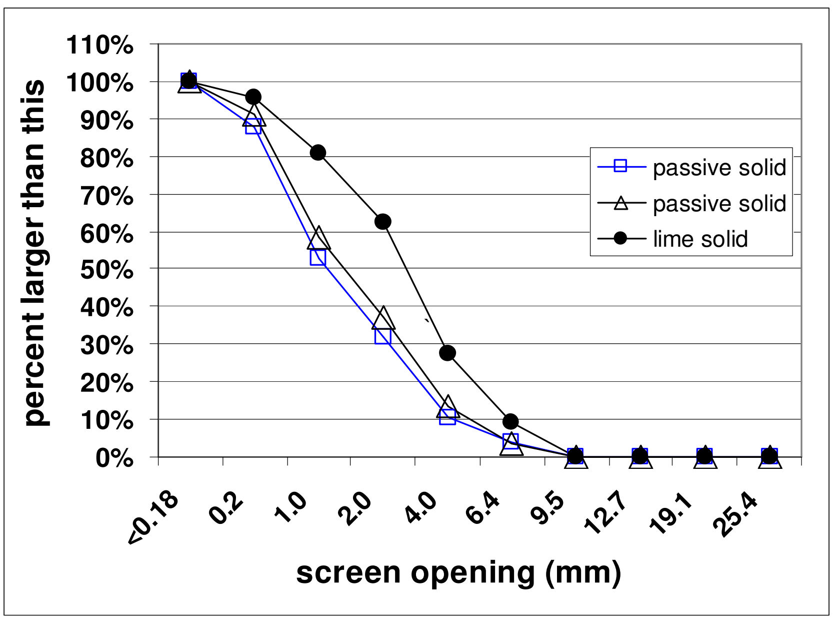

Figure 1. Particle size measurements for mine drainage treatment solids collected from passive and lime systems.

Surface Area

The use of mine drainage solids in remediation depends largely on chemical composition and surface area. Table 2 shows surface area measurements for samples that were dried (<1 % moisture) and hand screened through a 0.075 mm screen prior to measurement of surface area by the BET method. Passively precipitated iron oxides had higher surface area than lime produced solids.

Table 2. Surface area measurements for mine drainage solids

	Lab	Treatment	Composition	m^2/g
Site M	Pitt	Passive	95% FeOOH	175
Site H	Pitt	Passive	95% FeOOH	215
Site F	Pitt	Passive	90% FeOOH	119
Site M	PSU	Passive	95% FeOOH	125
Site F	PSU	Passive	90% FeOOH	128
Site H	Pitt	Lime	90% $CaCO_3$	23
Site B	PSU	Lime	85% $CaCO_3$	68
Site 2A	Pitt	Lime	Unknown	80
Site 3A	Pitt	Lime	Unknown	144

Discussion

Two general uses for mine drainage solids have been identified to date. Iron oxide solids that have strong pigmentary characteristics have value as crude pigments that are then processed to finished pigments. The processing, which IOR does not do at this time, involves drying, calcination, particle size reduction, and blending. The end product is a dry powder pigment that is used in paints, stains, concrete, and plastics.

Pigment-grade iron oxides can be obtained from a variety of sources. Pigment-grade iron oxides are commonly mined. Iron oxide is produced synthetically as by-product of aniline production and from the reprocessing of pickling liquors. Iron oxides can be produced through the controlled oxidization of elemental iron or from the neutralization of ferric chloride solutions. Because of the multiple sources the market for iron oxide is highly competitive.

In general, the pigmentary quality and value of mined iron oxides is much less than iron oxide produced synthetically. Iron oxide produced from mine drainage currently fills a niche between these two sources. Mine drainage products are more pure and have smaller particle size than mined products. However, the purity of mine drainage iron oxides cannot match that of synthetic production processes. Mine drainage iron oxides cannot claim the "nanno-scale particle size" that synthetic iron oxides do, however, size reduction of the mine drainage solids has not been explored yet.

Solid Reactivity

Iron-rich solids have chemical characteristics that are valued in remediation applications. Iron oxides are well known for their high sorption capacity. They are particularly good sorbents for oxyanions such as arsenate, selenite, and phosphate. Synthetic iron oxide is commonly used in the treatment of arsenic contaminated drinking water. Bayer Corporation produces an iron oxide powder specifically for As water treatment under the trade name Bayoxide E33.

Iron oxide sorbs selenite which is an intermediate in the oxidation of selenium to water soluble selenate. Iron oxide produced passively from mine drainage has been found to a particularly good sorbent of selenite and can significantly decrease the release of selenate from mine wastes (Ziemkiewicz 2011). Mine drainage iron oxide is currently being used in several experiments to test its ability to decrease Se concentrations in field settings.

Iron Oxide is a strong sorbent of phosphate, which is a common water pollutant in agricultural areas. A recently completed project demonstrated that mine drainage solids have the ability to substantially decrease the soluble phosphate fraction of dairy and swine manure. Figure 2 shows the effect of two mine drainage solids (MDR) on water extractable phosphorus (WEP) in dairy manure. The "Farm" material is a high-Fe passively produced solid. The Brandy material is lime sludge solid with a high

$CaCO_3$ content. The chemical composition of both is presented in Table 1. Both materials decreased WEP with increasing dose, but the lime solid was more effective. This result was verified in bench scale sorption tests and is attributed to the reactivity of the calcite with dissolved phosphate. This is the only result to date where lime sludge outperformed clean passive sludge in any test. Because the strong need for P-control in manure management operations, this finding is potentially beneficial for lime treatment plants.

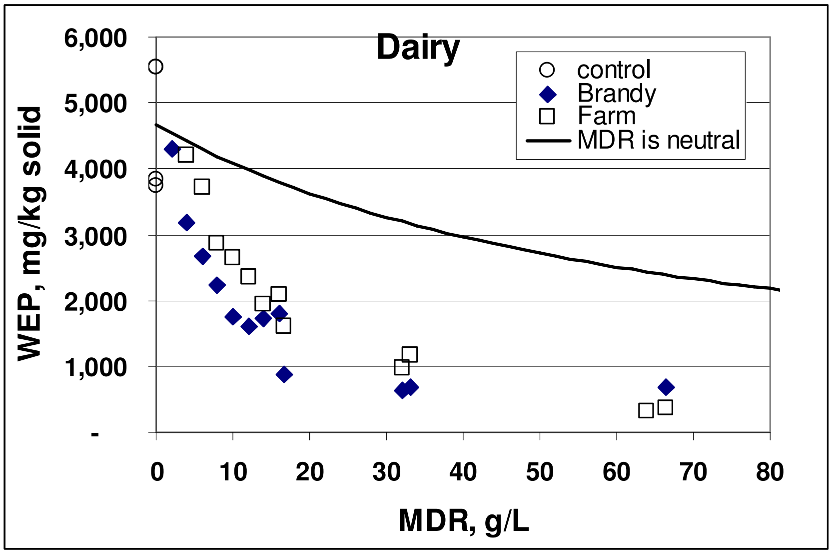

Figure 2. Effect of Mine Drainage Treatment Residuals (MDR) additions on the water extractable phosphorus concentration in a Pennsylvania dairy manure.

Iron oxide is also a good sorbent of lead, cadmium, copper, and zinc. When added to contaminated soils, sorption onto the solid can decrease extractable metals to safe concentrations and mitigate the need for expensive soil removal and disposal. Slater UK makes a propriety soil remediation mixture called TRAPPS that contains iron oxide produced from mine drainage. TRAPPS has been used in the remediation of Pb-contaminated shooting ranges in the eastern US.

Summary

Mine drainage treatment solids have chemical and physical characteristics that can be developed into useful products. The feasibility of this concept depends on the ability to make a product with consistent chemical and physical properties that markets value. The products that IOR has produced from mine drainage fall between the existing product niches established by mined iron oxide products and ones made synthetically by chemical companies. The company has sold 3,300 tons of mine drainage solids to customers, mostly for use as earth tone pigments, and developing new products that find value in the chemical reactivity of the treatment solids.

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Acronyms

AMD
IOR