RECOVERY OF MARKETABLE IRON OXIDE FROM MINE DRAINAGE¹

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Abstract. Iron oxide sludge was recovered from a channel at an abandoned coal mine, processed, and used as a raw material in pigment production. The site is a former coal mining and processing facility in southwestern PA. Over the last 60 years, a channel carrying the mine discharge (1500-1800 gpm, pH 6.3, Fe 73 mg/L, alkalinity 313 mg/L as CaCO₃) had filled with iron sludge. As a "proof-ofprinciple" project, approximately 2000 tons of sludge were removed and processed. The sludge was screened and dewatered using frame filter presses. Screening removed vegetative debris, litter, and coal refuse. Dewatering increased the solids content of the product from 25-30% (in place sludge) to 50-52%. A total of 1,000 tons of product were trucked to a pigment manufacturer where it was further dried, calcined, and milled. The company is using the finished product to produce pigments used in a variety of coloring applications. The mine drainage product is replacing natural (mined) sources of iron oxide obtained in the United States and imported from Mediterranean and Asian countries. Work is continuing on developing methods that will decrease the processing costs so that iron oxide can be produced from mine drainage in a profitable manner.

Additional Key Words: AML, AMD, goethite, pigment, dewatering.

Introduction

Many flooded underground coal mines in northern Appalachia discharge large flows of water containing excessive concentrations of iron. Mining companies commonly treat the flows with chemical additions (lime and coagulants) followed by aeration and retention in sedimentation ponds. The resulting sludge is collected and disposed of through burial or injection into the abandoned mine. Some of the deep mine discharges are suitable for passive treatment, although large iron loadings typically require large treatment systems. At sites where passive treatment is technically feasible, state and federal agencies have been reluctant to invest in treatment systems because of concerns about the long-term management of sludge deposits.

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One way to avoid these concerns is to design the systems to produce products whose value will offset long-term operation and maintenance (O&M) costs. This is the idea underlying the "resource recovery" concept that has recently been promoted in Pennsylvania by a variety of groups including the office of Congressman John Murtha 12th Congressional District, Pennsylvania, the United States Department of Agriculture Southern Alleghenies Resource Conservation and Development Area, and the Heinz Endowments (Mikesic et al., 1998).

In 1994, Hedin Environmental (HE) received a Small Business Innovation Research award from the US Department of Agriculture to investigate the feasibility of producing a marketable iron product from coal mine drainage. The study revealed that under bicarbonate-buffered circumneutral conditions, an iron oxide sludge was formed that compared favorably with natural iron oxide ores that are currently mined and marketed for pigmentary characteristics (Fish et al., 1996; Hedin 1998). In 1999, the US Patent Office granted Robert Hedin a patent for the production of pigment-grade iron oxides from polluted mine drainage (Hedin 1999). In 2001, Iron Oxide Recovery, Inc. was formed to pursue the profitable production of iron oxide products from coal mine drainage.

Early in 2000, a potential customer was identified for a goethite product that was at least 45% solids. A "proof of principal" project was initiated to determine whether this semi-finished iron oxide product could be produced from an abandoned mine site using off-the-shelf dewatering and processing technologies. This paper describes progress on the project.

Site Description

The project site is an abandoned deep mine, coal processing, and coking facility located in Lowber PA (Westmoreland County). The mine was closed in the 1930s and a discharge developed in the 1940s. Figures 1 shows the discharge. Water flowed from the entry down a 1,200-foot-long shallow channel to Sewickley Creek, a tributary to the Youghiogheny River. Over the next 60 years, the channel filled with 3-4 feet of sludge and vegetative debris. Figure 2 shows the sludge-filled channel.



Figure 1. The Marchand Mine discharge. Flow is through three pipes that extend through aggregate placed in the entry.

Figure 2. The sludge-filled channel before processing activities.

Chemical and flow characteristics of the discharge were determined in the 1970s by PA's Operation Scarlift program and recently by the University of Pittsburgh and Hedin Environmental. Summary data are shown in Table 1. Flow rates range between 1,300 and 2,000 gpm. Flow rates do not appear to have changed substantially in 30 years. The chemistry of the discharge has moderated. In the 1970s the discharge was net acidic and contained approximately 200 mg/L Fe. Recent measurements indicate that the flow is net alkaline and contains 70-80 mg/L Fe. Despite the moderation, the discharge still produces approximately 600,000 lb/yr of dissolved iron, which degrades two miles of Sewickley Creek.

Table 1. Average Characteristics of the Marchand Mine Discharge

| Period | Flow | рН | Alkalinity | Net Acidity | Fe | Sulfate |
|----------------------|-------|------|---------------------------|---------------------------|--------|---------|
| | (gpm) | (su) | (mg/L CaCO ₃) | (mg/L CaCO ₃) | (mg/L) | (mg/L |
| 1973-75 ¹ | 1,849 | 5.7 | 185 | 108 | 196 | 2,425 |
| 2001 ² | 1,554 | 6.3 | 313 | -180 | 73 | 1,402 |

¹ based on 26 monthly measurements of flow and chemisty;

² based on 31 measurements of flow and 8 measurements of chemistry

Iron sludge from a variety of abandoned deep mine sites has been sampled and analyzed by C. Kairies of the University of Pittsburgh Department of Geology and Planetary Science (Kairies et al., 2001). Summary analyses are shown in Table 2. XRD analyses indicate that the dominant iron mineral in alkaline deposits is goethite (FeOOH). When the iron content is expressed as a solid, the samples are found to be 40-97% as FeOOH. Samples from the Lowber site averaged 85% as FeOOH (personal communication, C. Kairies).

Table 2. Summary of mine drainage sludge composition (Kairies et al., 2001).

| Element | Conc. |
|---------|-----------------|
| Fe | 25 -61 wt% |
| Mn | 0.01 - 3.59 wt% |
| S, Al | <2% |
| As | Up to 3000 ppm |
| Co | Up to 1060 ppm |
| Ni | Up to 700 ppm |
| Pb | 13 - 41 ppm |
| Zn | Up to 760 ppm |
| Cd, Cu | <5 ppm |

Project Execution

In October 2000, an access road and a half acre work area were developed adjacent to the sludge-filled channel. The discharge was diverted into a newly excavated ditch (Figure 3) that combined with the original channel below the work area. The diversion isolated the main area of sludge recovery from flowing water and eliminated the possibility that turbid water would be released to the receiving stream.



Figure 3. The discharge was relocated to a new channel during processing. A weir was installed in the channel.

Sludge removal occurred in the fall of 2000 and spring of 2001. In both cases, sludge was pumped from the channel into a container from which slurry was withdrawn and dewatered using a 100 cubic foot frame filter press. A filter press dewaters by pumping sludge into a multitude of cloth-covered frames (approximately 4 feet by 3 feet by 1 inch) that are pressurized, causing water to be expelled through the cloth pores while the solids are retained within the frames. When extraction of water slows substantially, the press is shut down, opened, and the filter cakes are dropped and conveyed away from press. Once all the cakes are removed, the press is closed and another cycle begins.

During the fall of 2000, sludge was recovered using a power sprayer to manually fluidize the sludge and wash it to the screened intake of a sludge pump. Problems were encountered when the intake screen plugged with vegetation and debris from the bottom of the channel. Debris that passed through the pump screen subsequently plugged a screen on the inlet to the press. Debris that passed into the press occasionally caused the formation of poor quality press cakes. A secondary problem arose from the presence of pebble-sized solids, which filled the slurry tank, interfered with the press intake, and caused poor quality press cakes.

Cake production in the fall of 2000 was slow. Over the 16-day production period, 165 tons of filter cake were produced. Cycle times on the filter press averaged 144 minutes. The long cycle times were attributable to slow sludge recovery and the production of a dilute slurry. In

mid-November, poor production combined with sub-freezing temperatures resulted in termination of activities.

During the spring of 2001, a modified recovery and processing procedure was implemented. Sludge was removed from the channel mechanically using a tractor-driven pump (Figure 4). An excavator positioned in the channel moved sludge to the pump. The resulting slurry was passed through a series of screens that removed most of the vegetative and refuse debris (Figure 5). The screened slurry was pumped into large tanks from which it was pumped to a frame filter press (Figure 6). Two 100 cubic foot frame filter presses were utilized and operated on an alternating basis.



Figure 4. Sludge removal with a tractor pump. Figure 5. Sludge screening.



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Figure 6. The two sludge storage tanks (right), two frame filter presses (left), conveyor, and product.

Operations in the spring of 2001 occurred over a two week period in April. During the 11 days of activity, 845 tons of filtercake were produced. Press cycle times averaged 80 minutes. Cycle times were substantially faster than in the fall of 2000 because the presses were generally provided with an uninterrupted supply of dense slurry.

Results And Discussion

Measurements were made regularly of the moisture/solids content of the press cakes. Percent solids were calculated by dividing a sample's dry weight (2 hours at 110°C) by the wet weight. A sample that looses 40% of its weight upon drying is considered to have a 40% moisture content and 60% solids content.

Sludge samples collected from the original channel contained 25-30% solids. As noted previously, the goal was to produce a clean filtercake with a minimum of 45% solids content. Thirty-four samples from the filter press product were analyzed for moisture/solids. The average solids content was 49.9% (standard deviation 1.7%, standard error of the mean 0.3%). The solids target was achieved.

The quality of the filtercake was affected by the presence of fine debris that passed through the screens. Many of the filtercakes contained visible vegetative material and coal fragments.

The processing of the Lowber product to a finished pigment involved drying, classification, calcination, milling, and blending. Classification removed large debris. During calcination the product was heated to $\sim 900^{\circ}$ C, which dehydrated the goethite to hematite (Fe₂O₃) and volatilized the organic contaminants (vegetation and coal). Milling decreased the product particle size to the 0.5-5 micron range. The final product was blended with other materials to yield finished pigments.

The finished Lowber project was superior in several pigmentary characteristics to finished products produced from natural goethite ores. However, the Lowber material was difficult to handle and dry because its moisture content (50%) was substantially higher than mined iron oxide products (<10% moisture). Few pigment producers are willing to deal with the handling and drying difficulties of a filtercake product. Plans to produce a drier product that would be more readily substituted for existing mining products are being developed.

The presence of organic impurities in the Lowber product prevented its ready use as a finished goethite pigment. Our customer was unwilling to develop low-temperature processing procedures that would remove these contaminants without dehydrating the material to hematite. In order to compete in the goethite market, methods for producing a product free of organic debris must be developed.

The Lowber mine drainage product competes with natural iron oxides that are currently mined at a dozen sites in the US and at hundreds of locations worldwide. Major iron oxide mines exist in Virginia, Georgia, Missouri, Minnesota, and Utah. The major sources for imported natural iron oxides are Cyprus and Spain. At this time, the value of the mine drainage product is limited by the price of competitive mined products – \$100-400 per ton (Potter 2000). These product values are not sufficient to support the construction of mine drainage treatment systems. Systems designed to treat mine water and produce a marketable iron product are currently projected to cost approximately \$500 per ton of iron oxide recovered. The product values do appear to be sufficient to support the management and long-term O&M of treatment systems. If the system is constructed in a manner to facilitate sludge recovery, iron oxides can be produced for \$200-300 per ton (dry weight).

Recently, there has been increasing recognition of the long-term costs associated with AMD treatment systems (active and passive). Private companies that are responsible for mine water Treatment are under pressure to post bonds or fund trusts that guarantee long-term treatment. Public agencies that are funding the construction of treatment systems are recognizing that even passive systems have long-term O&M needs that must be considered. These long-term O&M costs can be lessened or eliminated by considering the potential for iron oxide production before the treatment system is constructed. In Pennsylvania several systems where mine water will be treated through the planned production of iron oxides are being considered.

Conclusions

A saleable iron oxide product was produced from sludge precipitated in a channel at an abandoned deep mine site. Approximately 1,000 tons of product were produced by screening and dewatering techniques. The resulting product was refined by a manufacturer to a finished hematite that was blended with other iron oxides and sold as a finished pigment. The

opportunity exists to construct mine drainage treatment systems where long-term operation and maintenance costs would be minimized by income generated from iron oxide sales.

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