

Solving mine drainage water issues with peat-based sorption media

by P. Eger, P. Jones and D. Green

Abstract ■ The Soudan Mine was Minnesota's first iron mine, operating from 1882 to 1962. The mine was donated to the State of Minnesota in 1963 and became a state park in 1965. The mine discharge contains elevated copper and cobalt concentrations and has been treated with an ion-exchange-resin-based system since 2009. The system includes flow equalization tanks, bag and cartridge filters, a carbon tank and two commercial ion exchange tanks. Although effective, the system's high cost, inefficient removal of suspended material and substantial maintenance have been ongoing and troublesome issues.

In November 2012, we initiated a pilot test using a peat-based sorption media. This media is produced from raw reed-sedge peat through a patented, low-temperature carbonization process that produces a hardened granular sorption material. The granules are uniform, have high hydraulic conductivity and maintain the high metal affinity of natural peat.

Mine water was pumped through the peat-based sorption media without any pretreatment. Copper input concentrations typically ranged from 30 to 60 µg/L but increased to a high of 364 µg/L in the summer of 2013. Since startup, more than 60 million L (16 million gal or 32,000 bed volumes) have been treated, with average removal rates of 75 percent for particulate copper and 60 percent for dissolved copper. Backwash is required at about 4,000 bed volumes, but with a combination of air sparging and high-flow backwash, the suspended material is removed from the media.

One tank of the peat-based sorption media was found to remove copper similarly to the first four components of the existing system. By reducing size and complexity, reductions in operation and maintenance costs are possible. A comparison of the estimated costs indicate that replacing the four initial components with the single media tank has the potential to reduce annual operating costs by more than half from around \$163,000 to \$70,000.

Mining Engineering, 2016, Vol. 68, No. 2, pp. 38-43.

Official publication of the Society for Mining, Metallurgy & Exploration Inc.

<http://dx.doi.org/10.19150/me.6468>

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Introduction

Soudan Underground Mine State Park contains Minnesota's first iron mine and offers tours through parts of the old mine workings. In addition, two high-energy-physics laboratories had been constructed on the mine's lowest level. Openpit mining at Soudan began in 1882 and continued until 1892, when safety issues dictated that underground mining methods were needed to continue to mine the steeply dipping ore body.

U.S. Steel operated the mine from the 1920s until 1962, when it closed. The mine and surrounding land were donated to the State of Minnesota in 1963 and are currently operated by the Minne-

sota Department of Natural Resources, Division of Parks and Recreation.

To keep the mine dry, an average of 230 L/min (60 gpm) of water is pumped to the surface and discharged. Although this water is circumneutral, it contains copper and cobalt in concentrations that exceed state water quality standards. The pH typically ranges from 6.5 to 7.5, and prior to treatment the annual average concentrations ranged from 83 to 500 µg/L for copper and 6 to 26 µg/L for cobalt (Eger, 2007). Current water quality limits are 17 µg/L for copper and 4 µg/L for cobalt. The objective of this paper is to discuss the existing water treatment and examine a new treatment approach.

Background

During the operation of the mine, more than 15.5 million t (17 million st) of high grade iron ore were removed. The mine is about 730 m (2,400 ft) deep and has 18 levels (Eger, Johnson and Wagner, 2001).

Water enters the mine through a series of openpits and fractures, with some flow occurring on all levels of the mine. Water flows along small ditches on the side of the mine drifts and is collected in a sump on each level. Pumps are located on three levels to lift the water out of the mine (Maki, 1996).

A detailed evaluation of the flow and water quality inside the mine found that about 94 percent of the total copper and 44 percent of the total cobalt came from a single site near the upper levels of the mine (Eger, 2007; Eger, Johnson and Wagner, 2001). Treatment of that one source was projected to significantly reduce downstream metal concentrations, and in 2005 a commercial ion exchange system consisting of a carbon tank and two ion exchange tanks was installed in the mine to treat this source.

Shortly after the system was installed, it plugged with a precipitate that appeared to be primarily aluminum hydroxide. Prior to system startup, there had been no precipitate observed in any of the samples or in bench-scale testing. Eventually, the problem was controlled through the installation of a series of filter cartridges to remove the majority of the precipitate prior to the water entering the ion exchange system. However, since it took some time to develop a solution, the system was not effective initially, and the discharge did not meet water quality standards. In 2006, the Department was fined and signed a stipulation agreement with the Minnesota Pollution Control Agency.

As a result of that agreement, a second commercial ion exchange system was installed on the surface in July 2009 to treat the entire mine discharge. The in-mine system continued to treat the major source (Eger, 2010). The surface treatment is a larger version of the in-mine system and uses a proprietary, specific cation exchange resin manufactured by Siemens. Although dissolved metals are removed successfully, the removal of finely suspended copper has been problematic. The average permit limit of 17 µg/L for total copper is being met, but concentrations sometimes exceed this value because finely suspended copper can move through the system. The suspended copper also physically plugs the ion exchange resin before the total removal capacity of the resin is exhausted. At best, only 20 percent of the chemical capacity of the resin is utilized before the resin physically plugs. Maintenance and treatment costs could be reduced if a more cost-effective method to remove the suspended material could be implemented.

Approach

The existing surface system treats around 300 L/min (80 gpm) of water and includes a surge tank, prefiltration section with bag filters followed by cartridge filters, a break tank, a carbon tank for additional pretreatment, and two ion exchange tanks (Fig. 1). A variety of filters were tested in an effort to combine effective removal with acceptable lifetime. Currently, prefiltration is done with a 1-µm AJR multilayer filter bag and 1-µm nominal Parker Avasan cartridges. These filters have estimated efficiencies of 60 to 70 percent. Under low flow conditions of < 230 L/min (60 gpm), the bag

filters are changed about once per week and the cartridges are changed once every one to two weeks. The carbon tank is manually backwashed about once every two weeks. Despite this level of pretreatment and maintenance, plugging continues. We therefore initiated a pilot study using a peat-based sorption media to determine if this could remove both suspended and dissolved copper and cobalt, improve performance and reduce maintenance and costs (Fig. 1). The study was conducted in two phases: phase I compared the performance of the peat media with the existing system; and phase II addressed long-term performance and media lifetime.

Methods

Peat-based sorption media. American Peat Technology (APT) had developed a patented process to convert raw reed-sedge peat into hardened granular media called APT-sorb™ (Fig. 2). These granules maintain their structures when wet and can be sized to any specification, making them easily adaptable to existing treatment system technologies. The standard media have granules ranging in size from 0.6 to 2 mm (equivalent to -10, + 30 mesh), with estimated hydraulic conductivity of 1 cm/sec. Metal removal capacities measured in laboratory equilibrium tests were from 1 to 15 percent dry weight metal. The media has porous surfaces with large surface areas, which are expected to facilitate the capture of suspended material (Fig. 2). Previous small-scale pilot tests showed that the media could remove both suspended and dissolved copper from mine drainage (Eger, Paulson and Green, 2008). In the present study, a full-scale pilot test was initiated in November 2012 to evaluate the ability of peat-based sorption media to treat the entire mine discharge.

Pilot system. A 3,800-L (1,000-gal) pressurized tank containing 1,900 L (500 gal) of the peat-based sorption media was designed so that the media could be easily backwashed to remove particulates. Water enters through the upper manifold, flows down through the media into the gravel collection layer and out the bottom manifold. Backwashing is done by simply reversing the flow.

Flow rates were varied from 38 to 380 L/min (10 to 100 gpm) over the course of the study to determine the effect of residence time on removal. Water quality samples were collected from the input and output of the peat media tank and periodically from the individual components of the existing system. Samples were filtered and acidified on site and analyzed for copper by APT using a Perkin Elmer PinAAcle 900 graphite furnace. Periodic quality control samples were run by Pace Laboratories in Virginia, MN. All cobalt values were analyzed by Pace. Samples analyzed by APT were analyzed directly without total digestion, while Pace did a total digestion on all samples.

The peat media tank was backwashed every 4-6 weeks using water that had been filtered with the existing bag and cartridge filters. The media was air sparged for about 10 minutes to lift and mix the media and break up the particulate that had accumulated on the surface. After the air sparge, backwash flow was increased gradually to about 1,330 L/min (350 gpm), which was sufficient to fully fluidize and expand the bed but did not flush media from the tank. The complete backwash, including a preliminary air sparge, backwash and final rinse, took about 30 min to complete and required about 19,000 L

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(5,000 gal) of water. In a full-scale system, the backwash water would be sent to a conical settling tank, and the solids would be filtered with a small filter press.

Results

Phase I: Comparison of treatment systems.

Copper. The initial objective of the pilot test was to compare metal removal between the two systems at comparable flow rates. Flow rates generally ranged from 115 to 190 L/min (30 to 50 gpm). Samples were collected from before and after the peat media tank as well as after each component in the existing system. A total of 17 million L (4.5 million gal) was treated by the peat media system during this test.

The total copper concentrations in the mine discharge generally varied from 20 to 40 $\mu\text{g/L}$, and the dissolved copper concentrations ranged from 5 to 10 $\mu\text{g/L}$. The current permit limit for the mine is 17 $\mu\text{g/L}$. In the existing surface system, total copper concentrations decreased after each component, and was less than 5 $\mu\text{g/L}$ after the last ion exchange tank. After the peat sorption media tank, total copper concentrations ranged from 4 to 13 $\mu\text{g/L}$ and were always less than the permit limit of 17 $\mu\text{g/L}$ (Fig. 3).

Cobalt. The cobalt in the mine water was essentially all dissolved, and concentrations ranged from 7 to 12 $\mu\text{g/L}$. In the existing surface system, cobalt concentrations were below the permit limit of 4 $\mu\text{g/L}$ after the first ion exchange tank and essentially below the detection limit of 0.94 $\mu\text{g/L}$ after the second ion exchange tank. With the peat-based sorption media, cobalt was removed initially but increased to above the permit limit after only about 2.3 million L (630,000 gal) had been treated (Table 1).

Figure 1

Treatment system layout.

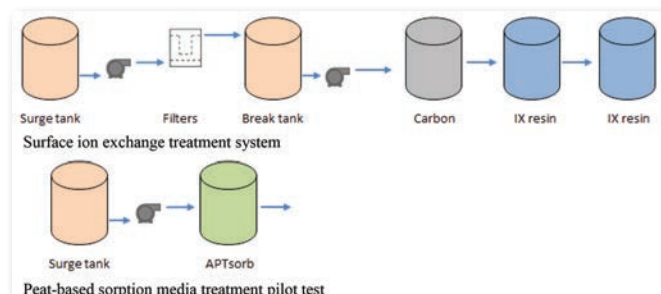
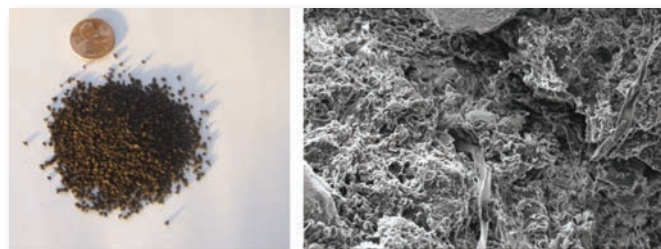


Figure 2

APTSorb granules (left), and APTSorb surface at 1500x magnification (right).



Phase II: Long-term performance, treatment lifetime.

During this phase, flow through the peat-based media tank varied from 190 to 380 L/min (50 to 100 gpm), with 190 L/min (50 gpm) being the typical flow. This corresponded to a loading rate of 104-208 L/min/m² (2.5-5 gpm/sq ft) and empty bed contact times of 5-10 min. Starting in May 2013, there were problems with the in-mine ion exchange treatment system and total copper concentrations in the mine discharge began to increase. They reached a high of 364 $\mu\text{g/L}$ in July. The problems with the in-mine system were corrected, and by October, concentrations began to decrease and returned to the typical range of 30-50 $\mu\text{g/L}$ (Fig. 4). Treatment continued until November 2013 when the system had to be shut down and moved to a new treatment location.

When concentrations in the mine water increased, the peat media tank continued to remove both total and dissolved copper, but concentrations exceeded the permit limit of 17 $\mu\text{g/L}$ (Figs. 4 and 5). When the influent copper concentrations decreased in the fall, the effluent concentrations also decreased and the discharge met the permit limit. Dissolved copper was removed continuously throughout the study despite an order of magnitude variation in input concentration. There was no evidence of any copper release from the media when the input concentrations decreased and returned to the values comparable to the original input.

Discussion

Copper. Although the existing ion exchange treatment effectively removes suspended and dissolved copper, the presence of finely suspended solids in the mine water has caused operational problems, and periodically total copper concentrations have exceeded the average permit value of 17 $\mu\text{g/L}$. The present pretreatment system of filter bags, filter cartridges and carbon tank, on average, removed 58 percent of the total copper. However, the remaining solids enter the ion exchange tanks and physically plug the resin, causing the pressure to increase and flow to decrease. The total capacity of the resin is a function of the input water chemistry and metal concentrations. Siemens has estimated that for the surface discharge the

Figure 3

Comparison of existing surface system and peat media pilot test system, November 2012 to April 2013.

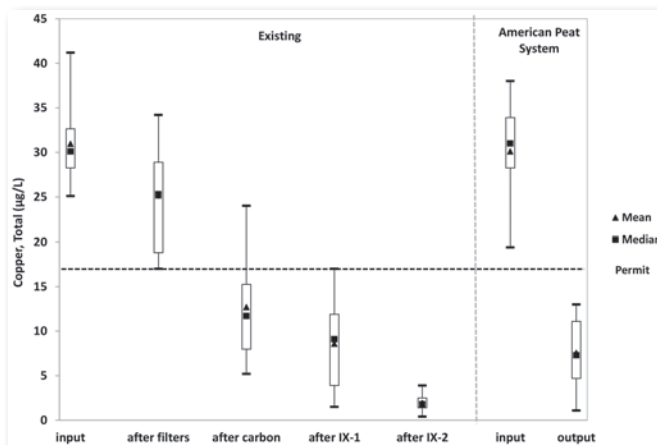


Table 1

Copper and cobalt concentrations before and after lag-tank addition.

Bed volumes	Cobalt concentration (ug/L)*			Copper concentration (ug/L)*		
	Influent	After APTsorb	After Siemens	Influent	After APTsorb	After Siemens
577	6.9	0.47		41.4	0.5	
1,003	9.1	1.4		31.6	3.8	
1,227	7.2	2.3		36.4	5.3	
1,566	7.2	5.8		35.2	10.8	
2,529	9.3	9.2		34.3	12.0	
3,751	11.4	10.7		32.0	10.2	
3,996	12.3	10.3		31.0	7.9	
A lag tank containing Siemens media was added at about 27,810 bed volumes						
27,817	9.1**		0.47	119.4	12.5	1.7
27,871	9.1**		0.1	135.2	28.8	7.4
28,971	9.1**		0.1	103.7	49.9	1.4

*Permit limits are 4 µg/L for cobalt and 17 µg/L for copper. Green values are in compliance, while red values exceed these limits. Blank cells = not analyzed. **No input samples were collected after the Siemens tank was added. Value is average input over pilot study.

resin should be able to remove 0.002 to 0.010 kg of copper per liter of resin (0.1 to 0.5 lb of copper/cu ft of resin). However due to premature plugging, the actual lifetime is less than 20 percent of the projected life (Eger, 2009).

Standard ion exchange tanks are not designed for backwashing, and the resin manufacturers do not want the ion exchange media to be backwashed for two primary reasons: (1) The media is very light and expensive and could easily be lost during a backwash. (2) The treatment is optimized if a concentration profile is developed. In standard ion exchange applications, the concentration of metal on the media decreases with depth of the media, and backwashing would disrupt that profile (Korsenecki, 2012).

In contrast, the peat media tank was designed to be easily backwashed. Over the year of operation, less than 5 percent of the media was lost during all the backwashes. The loss per backwash decreased as the procedure was optimized. In addition, the development of a concentration profile is not critical for performance and is easily outweighed by the advantages of being able to use the media for both physical and chemical removal. The peat media has a large internal surface area, and it is believed that this contributes to its ability to effectively remove the finely suspended material. Backwashing the media effectively removed nearly all of the trapped suspended material, and the pressure drop over the media returned to near zero after each backwash.

The peat media effectively removed the dissolved copper throughout the entire pilot test, even when input concentrations increased to over 100 µg/L. Peat has long been known for its affinity for dissolved trace metals, with the removal mechanisms generally thought to be a combination of physical adsorption, chemisorption, ion exchange, complexation, and adsorption-complexation (Brown, Gill and Allen, 2000).

Metals are tightly bound to the substrate with less than 0.5 percent of the sorbed copper being released in either

Figure 4

Unfiltered copper results, November 2012-2013.

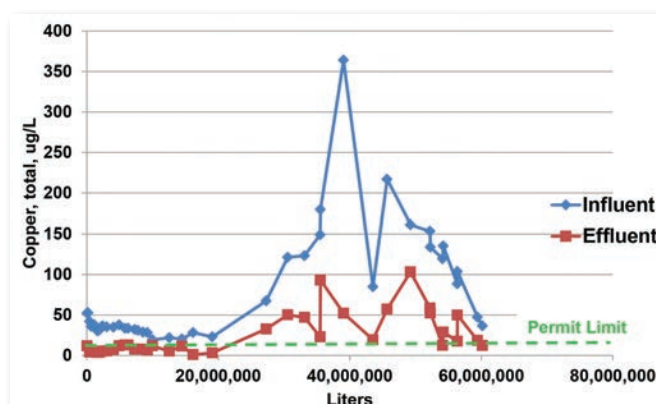
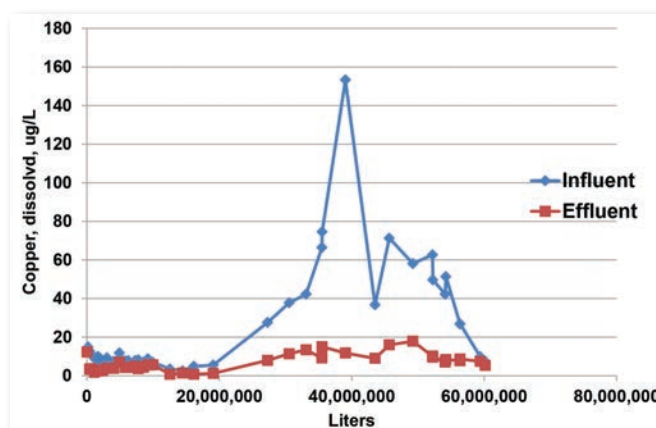


Figure 5

Dissolved copper results, November 2012-2013.



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synthetic precipitation leaching procedure (SPLP) or toxicity characteristic leaching procedure (TCLP) extractions, which suggests that the metals are covalently bonded to the media (Eger, Paulson and Green, 2008; Eger, 2007).

Cobalt. Although the peat media has substantial capacity for copper, the capacity for cobalt at the low input concentrations present in the Soudan discharge is low. This is consistent with the general affinity of humic acid and peat for trace metals, in that cobalt is one of the least readily sorbed metals (Kerndorff and Schnitzer, 1980). In order to achieve compliance, an additional treatment step using a commercial ion exchange resin is included in the proposed treatment system.

Proposed treatment system. The study results indicate that one tank of peat-based sorption media can provide copper treatment equivalent to or better than that of the first four components of the existing system, consisting of bag and cartridge filters, a break (holding) tank, a carbon tank and an ion exchange resin tank, and eliminates a pumping step. However, the media cannot effectively remove cobalt at the low input levels. Therefore, a system is proposed consisting of a lead tank of peat media and a lag tank of ion exchange resin provides a polishing step for copper and removes the cobalt from the discharge. This was tested near the end of phase II, with both copper and cobalt concentrations reduced to below permit limits (Table 1).

Reducing the complexity of the system by replacing the first part of the existing system with a tank of peat media has the potential to reduce the overall cost of treatment. Table 2 shows a comparison of the estimated annual operating cost for the existing system, totaling to \$163,000, and that for the proposed system, with a lead tank of peat media and a lag tank of Siemens ion exchange resin, totaling to \$70,000. In addition, by eliminating the bag and cartridge filters, maintenance and potential workers' compensation issues could be reduced, bearing in mind that there had been several reports of back pain following maintenance activities on the filter units (Essig, personal communication, 2014).

Conclusions

Peat-based sorption material was effective at removing both suspended and dissolved copper from the Soudan Underground Mine discharge. One tank of media can replace the existing system components of bag and cartridge filters, a holding tank, a carbon tank and a standard commercial ion exchange resin tank, and provide equivalent or better treatment. Reducing the size and complexity of the system has the potential to reduce cost and maintenance. Annual operating expenses are projected to decrease by more than 50 percent from around \$163,000 to \$70,000. ■

Disclosure statement

American Peat Technology sells APTsorb as a commercial sorption material.

Table 2
Estimated costs in detail.

APTsorb system				Existing system			
Component	Cost/rental ^a	Months/exchanges	Yearly total	Component	Cost/rental ^a	Months/exchanges	Yearly total
APTsorb tank	\$650 per month	12	7,800	Housing, filter bags and cartridges	\$2,900	12	\$34,800
Replacing/disposal of APTsorb media	\$14,700	2 ^b	29,400	Carbon tank	\$550 per month	12	\$6,600
One Siemens ion exchange tank	\$900 per month	12	10,800	Carbon replacement	\$8,500	4 ^c	\$34,000
Ion exchange resin regeneration	\$11,000	2	22,000	Two Siemens ion exchange tanks	\$1,800 per month	12	\$21,600
				Ion exchange resin regeneration	\$11,000	6 ^d	\$66,000
Total estimated annual operating costs			\$70,000				\$163,000

^aSiemens rental and regeneration (exchange) fees are based on 2013 costs.

^bBased on pilot test; the peat media treated 16 million gal.

^cBased on 8 million gal.

^dAt a minimum, the lead ion exchange tank has to be replaced four times per year and the lag ion exchange tank twice per year, for a total of six exchanges per year. Most of the field data suggest that the lead tank would need more frequent replacement.

Additional notes: (1) Labor costs are not included but are higher for the existing system. For the existing system, the filters need to be changed every one to two weeks, and the carbon tank is backwashed every two weeks. The carbon and ion exchange tanks are removed and installed by park staff. The APTsorb system requires backwashing every four to six weeks, with each backwash taking 30 min. All APTsorb media handling (installation, removal and disposal) are performed by APT staff and are included in the costs in the table. (2) Costs to handle the backwashed solids (collection, settling, filtration and disposal) are not included in the costs. Since both systems have a backwash, the costs were believed to be comparable for both systems.

Acknowledgments

We would like to thank Jim Essig and the staff of the Soudan Underground Mine State Park for all of their help with this project.

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