THE USE OF PEAT PELLETS TO REMOVE COPPER AND COBALT FROM MINE DRAINAGE[1]

Paul Eger[2], Eric Paulson, and Doug Green

Abstract. A low temperature carbonization process has been used to convert peat into a hardened ion exchange material. Peat pellets of about 9.5 mm are produced, which are then crushed to form a low-cost ion exchange media.

Pellets were tested for their ability to remove copper and cobalt from several different mine drainages in northeastern Minnesota. Drainage pH ranged from around 5 to about 7.5, total Cu ranged from about 0.01 to 3 mg/l, and Co from about 0.008 to 0.02 mg/l.

Treatment was most effective for Cu with a removal efficiency of from 80-95%. The total volume treated decreased with increasing concentration, and ranged from 900 bed volumes at a copper input of 3 mg/l to over 7000 bed volumes at low input Cu concentrations. Total Cu removal ranged from 180 to 2900 mg/kg. Cobalt broke through more quickly than copper with total removals ranging from 70 to 95 mg/kg. A modified TCLP test was conducted and showed that Cu and Co were tightly bound to the pellets. The pellets retained over 99.5 % of the Cu and Co.

Projected costs for the pellets are on the order of $2.20/kg or about 5 % of a commercial resin.

[1] Paper was presented at the 2008 National Meeting of the American Society of Mining and Reclamation, Richmond VA, ***New Opportunities to Apply Our Science,*** June 14-19, 2008. R.I. Barnhisel (Ed). Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

[2] Paul Eger is Principal Engineer, Minnesota Department of Natural Resources, St. Paul, Minnesota, 55155. Eric Paulson is Vice President of Engineering and Doug Green is Vice President of Operations for American Peat Technologies, Aitkin, MN, 56431.

Proceedings America Society of Mining and Reclamation, 2008 pp 342-352
DOI: 10.21000/JASMR08010342
http://dx.doi.org/10.21000/JASMR08010342

Introduction

Peat has long been known for its ability to remove metals from water. As a result, metal concentrations in peat have been used as a geochemical prospecting tool and peat has been tested for its ability to treat wastewater (Fraser, 1961, Salmi, 1959, Brown and others, 2000). Up to 10% Cu was measured in peat from the Tantramar Swamp in New Brunswick and Cu concentrations up to 8.9 % have been reported in samples used to treat wastewater (McDonald, 1976; Premi, 1970).

Peat, although relatively inexpensive, tends to be non-uniform and somewhat difficult to handle. Although loose, fibrous peat, can have hydraulic conductivities on the order of 10^{-1} cm/sec, more decomposed and compacted peat can have conductivities of 10^{-3} to 10^{-4} cm/sec. These lower conductivities reduce the overall flow rate and channelization can develop. Recently, American Peat Technologies (APT) has developed a process to convert loose peat into hardened pellets called APTsorb™ (Patent pending) (Fig. 1, 2). These pellets maintain their structure when wet and can be crushed to any size, thereby creating an ion exchange material. Since the product is crushed to a uniform size, flow properties are very good, with estimated conductivities in excess of 1 cm/sec. The purpose of this study was to investigate the ability of the pellets to remove Cu and Co from drainage at Soudan State Park.

Figure 1. Original peat pellets

Figure 2. Peat pellets after crushing

Background

Soudan State Park contains Minnesota's first iron mine and offers tours through parts of the old mine workings. The mine began in 1884 as an open pit but switched to an underground operation in 1892. U.S. Steel operated the mine from the 1920's until 1962, when it closed. In 1965 the mine and surrounding land were donated to the State of Minnesota and is currently operated by the Department of Natural Resources, Division of Parks and Recreation (Fig. 3).

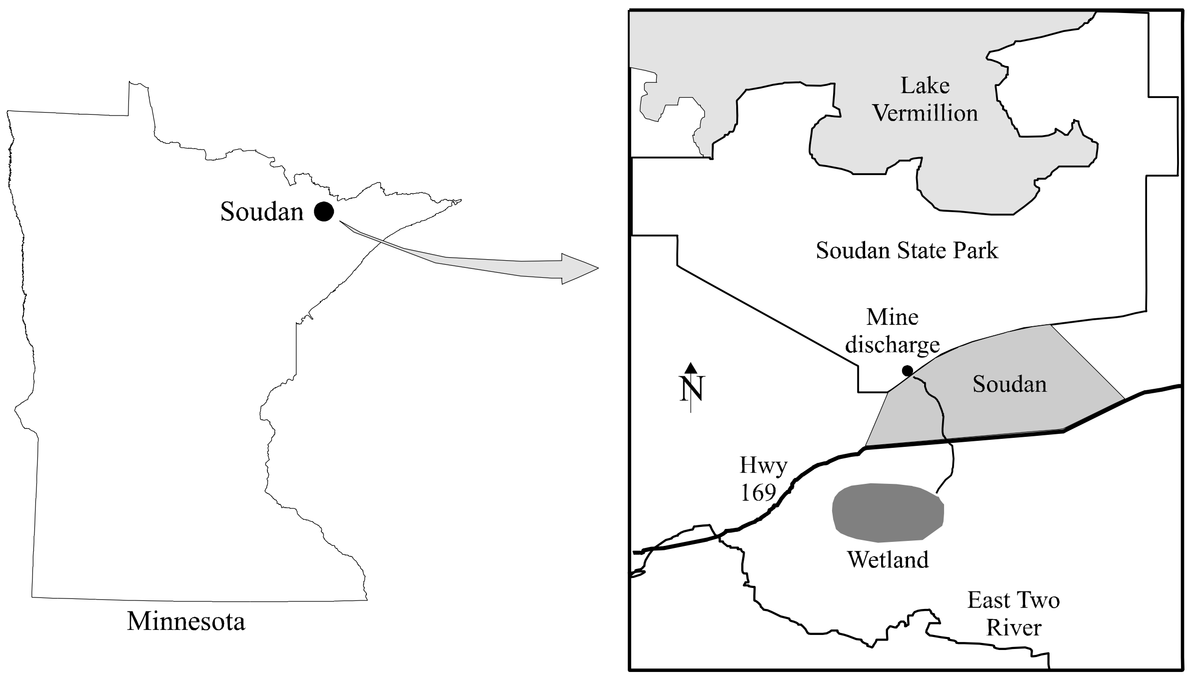

Figure 3. Soudan Mine

Mine water has been discharged ever since the mine began. Water enters the mine through a series of open pits 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. The final discharge is pumped from the mine at an average rate of 60 gpm, with peak flows of around 300 gpm.

The major source of Cu and Co is currently treated with a commercial ion exchange resin. This system effectively reduces both copper and cobalt to less than 0.005 mg/l. Total Cu and Co concentrations in the overall discharge are typically from 0.03-0.08 mg/l and 0.005 – 0.008 mg/l, respectively and exceed the current allowable standards of 0.017 mg/l Cu and 0.004 mg/l Co. Eger (2007) provides a brief history of the mine and a more complete description of the mine drainage issues.

American Peat Technologies had done some preliminary experimental work to evaluate the ability of the APTsorb™ to remove lead in laboratory tests. Their test work had shown that the peat pellets had a high affinity for lead and were expected to be effective in removing other trace metals. American Peat approached the DNR to test the pellets on a field site. Since the current water quality is only slightly above allowable limits, the use of the pellets as a polishing step was investigated.

Methods

A lab study was conducted on 2 different drainages from the mine. Water from the highest metal source within the mine (10 NT) and the total discharge (Level 12) were both tested.

Water Quality

10 NT. This site contributes over 90% of the total Cu mass and about 40% of the total mass of Co to the discharge. The pH typically is less than 5 with historic Cu concentrations ranging from around 3 – 30 mg/l and Co from about 0.2 to 0.4 mg/l. Total and filtered metal values are essentially identical. For this test, two 55-gallon barrels were filled with the discharge from level 10 NT and transported to the APT lab in Aitkin, MN for treatment studies.

These samples were collected after the sump and from the pipe leading to level 12 where the main discharge sump is located. The pH of the sample was 4.7 and contained an average of 1.95 mg/l Cu, and 0.23 mg/l Co.

Mine Discharge (Level 12). This site is a composite of all the individual flows in the mine. The pH is circumneutral, generally ranging from 6.5 – 7.5, total Cu ranges from 0.03-0.08 mg/l, and total Co is generally less than 0.010 mg/l. Filtered Cu is typically about 1/3 of the total value while there is little difference between total and filtered Co.

Water was collected from the main collection sump with a peristaltic pump and filtered on site through a 1 micron filter to remove particulate material that could affect the column. Water was collected over about a two-week period during which the pH was around 7. Water was transported to the APT laboratory for testing. Copper averaged 0.016 mg/l and Co averaged

0.01 mg/l. No additional filtration was done for the influent and effluent samples from the column studies.

Column set up

Columns were constructed from 19 mm clear PVC. Stainless steel screens were placed on the top and bottom of the columns. The peat pellets are somewhat hydrophobic, so they were mixed with distilled water in a small beaker. The mixture was agitated and swirled periodically for about 30 minutes or until there were no pellets floating. Once all the granules had sunk, the entire mixture was poured into the column and the experiment started. Flow was supplied with a peristaltic pump and the columns were operated in an up flow mode. Flow rates and total volume treated were measured on a daily basis and adjusted as necessary. The column was also mixed intermittently to simulate a back flush. The column was inverted periodically during the test to agitate the column and prevent particulate buildup. Flow was not stopped and the entire process took less than a minute. Copper and Co were analyzed on a Perkin Elmer graphite furnace atomic absorption spectrophotometer. Samples were run in triplicate and intermittent samples were also sent to a separate lab for confirmation of the in house results.

Level 10 NT . Due to the higher metal concentrations in this water, 50 grams of media (APTsorb media) were used; the total column volume was 110 ml. The particle size of the peat was 0.6 – 2.0 mm. Feed water was filtered to 1 micron in the lab and fed to the column at 5.5 ml/min to provide an empty bed contact time of 20 minutes. No additional filtration was done for the influent and effluent samples.

Level 12 . Since metal concentrations were much lower than level 10 NT, 25 grams of APTsorb media (0.6 – 2.0 mm) were placed in a column with an empty bed volume of 55 ml. The target flow rate was 5.5 ml/min and provided a empty bed contact time of 10 minutes.

Toxicity Characteristic Leaching Procedure (TCLP) Test

A modified TCLP test was conducted to determine the strength of the bond between the metal and peat. After the column experiment was completed, all the APTsorb in the columns was drained and washed into sample bottles. These samples were then sent to ERA labs in Duluth, MN for the TCLP analysis. A liquid to solid ratio of 2:1 was used for the test, which was a much lower ratio than the standard ratio of 20:1 and should produce a higher, and therefore more conservative, leachate concentration.

<u>**Results**</u>

Level 10 NT

Both Cu and Co were removed initially. Over 99% of the Cu and over 90% of the Co were removed. Initial outflow concentrations were generally about 0.007 mg/l for Cu and around 0.014 mg/l for Co. Cobalt concentrations increased fairly quickly and reached input levels after only about 250 bed volumes had been treated (Fig. 4).

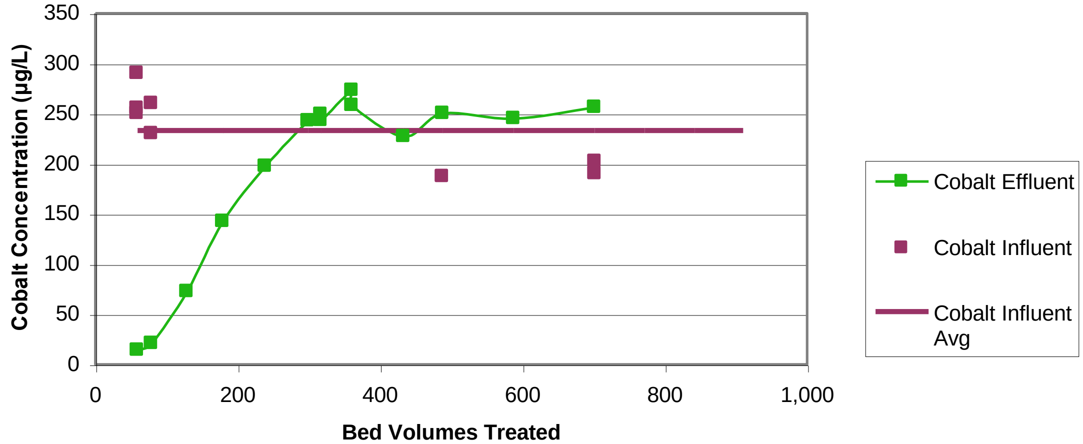

Figure 4. Treatment of Level 10 NT, Co

Copper removal continued with concentrations generally below 0.02 mg/l up to 500 bed volumes. Concentrations began to increase after 500 bed volumes and reached 1.3 mg/l when the test was ended after 900 bed volumes (Fig. 5).

The total mass of Cu and Co removed were 146 and 3.9 mg respectively, which corresponded to a removal of 2900 mg Cu/kg of APTsorb and 80 mg Co/kg APTsorb.

Level 12

Copper and Co were both removed, but with the lower input concentrations the percent removal was lower than for level 10 NT. Initial removals were on the order of about 80% for Cu, and 70% for Co. Copper removal was fairly consistent for the entire test, staying below 0.005 mg/l for the entire duration of the test. The total bed volumes treated were around 7000 (Fig. 6). Cobalt concentrations generally remained below the water quality standard of 0.004 mg/l for about 6000 bed volumes (Fig. 7).

The total mass of Cu and Co removed were 3.9 and 1.6 mg respectively, which corresponded to a removal of 156 mg Cu/kg of APTsorb and 62 mg Co/kg APTsorb.

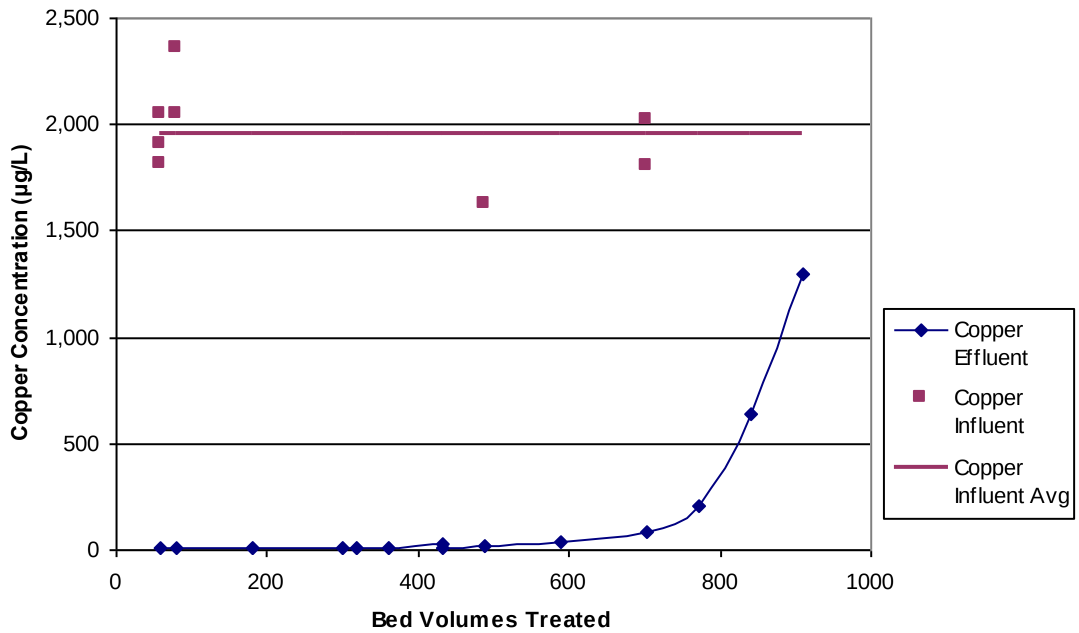

Figure 5. Treatment of Level 10 NT, Copper

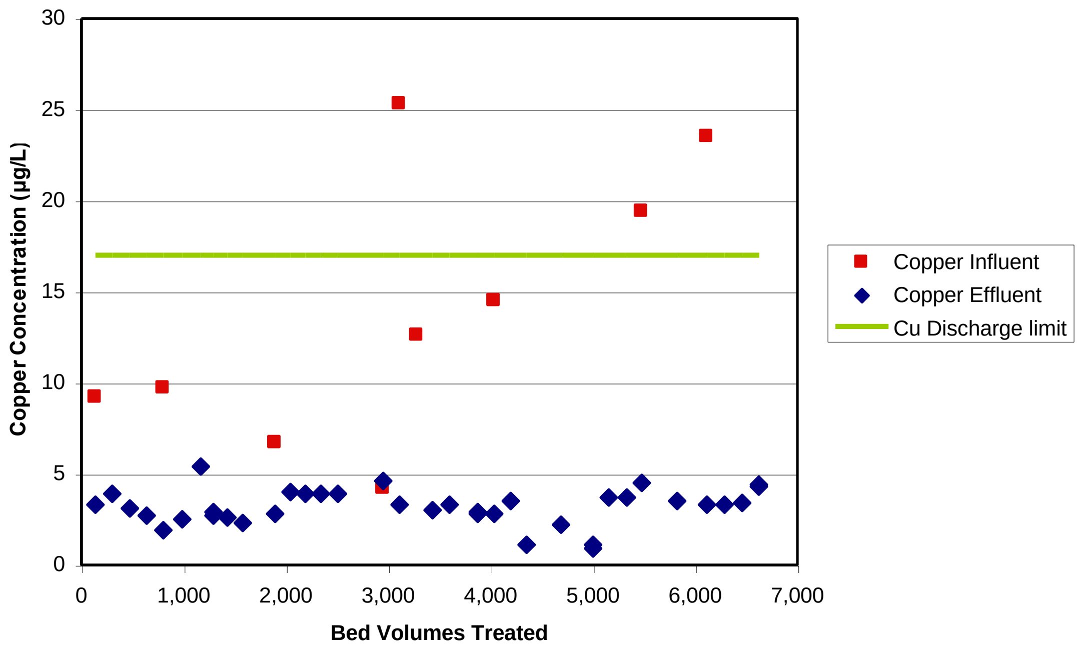

Figure 6. Treatment of Level 12, Copper

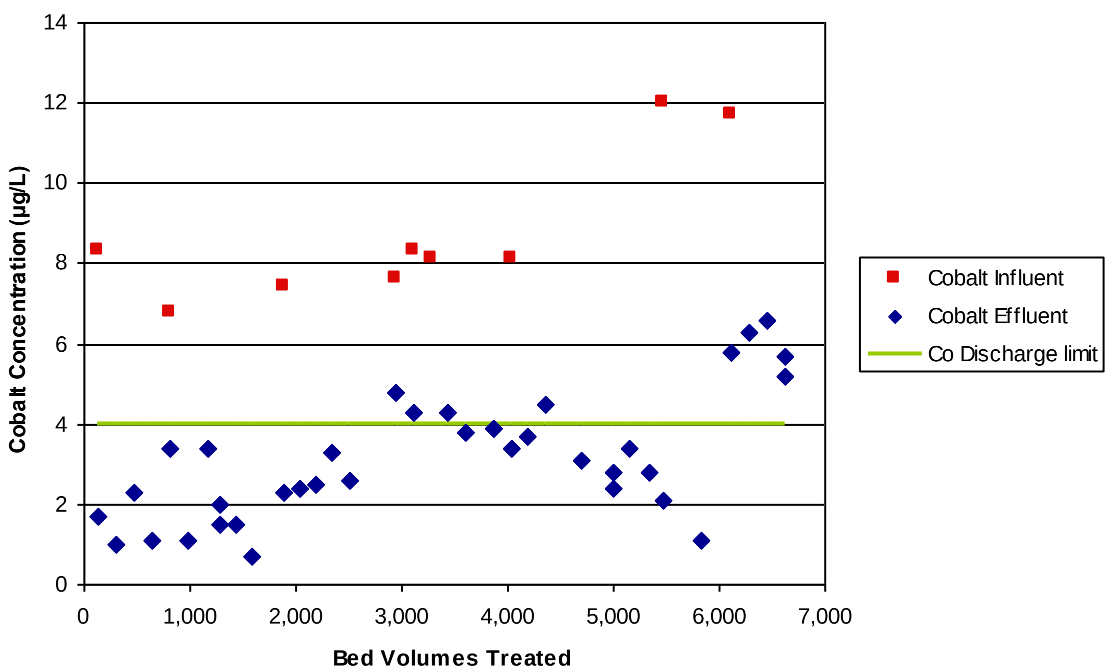

Figure 7. Treatment of Level 12, Cobalt.

TCLP Test

Normal TCLP tests use 100 grams of solid, mixed with 2,000 ml of solution at a fixed pH. The tests performed on these samples were at a much higher concentration of 100 grams of solid to 200 ml of strip solution. Using a higher solid to liquid ratio would tend to maximize the leachate concentration. All Resource Conservation and Recovery Act (RCRA) metals were below detection limits, with the exception of Ba, which was at 0.2 % of the allowable limit for disposal. Small amounts of Cu and Co were released but the pellets retained >99.5 % of the Cu and Co (Table 1).

Table 1. Results from modified TCLP test

	Metal adsorbed during column test (mg)	Metal removed during TCLP (mg)	Metal retained on peat (%)
Level 10 NT			
Copper	146	0.056	>99.5
Cobalt	4.0	0.008	>99.5
Level 12			
Copper	3.9	0.004	>99.5
Cobalt	1.6	0.008	>99.5

Discussion

Ion exchange is a common water treatment technology and a wide variety of commercial resins are available for specific applications. Commercial resins are expensive and are often included as part of a treatment system purchased from a specific producer.

The search for low cost ion exchange materials has led to tests of a wide variety of waste products including peanut hulls, sawdust, algae, pecan shells and corn cobs (Bailey and others 1999; Dastgheib and Rockstraw, 2000; Brown and others, 2000). Peat has been considered and tested as a low cost ion exchange material in a variety of studies (Brown and others 2000; Lapakko and Eger 1988). Data has shown that it can effectively remove metals from solution. However, the non-uniform characteristics of the material have caused handling and flow problems. In some studies, it has been mixed with a granular material to improve flow characteristics (Lapakko and Eger 1988).

The APTsorb material is a hardened pellet with a large surface area (Figs. 8, 9). The pellets are easy to handle and have good hydraulic properties. This allows them to be incorporated into a treatment bed similar to a sand filter. Preliminary pilot studies are underway to investigate the feasibility of using this type of design to treat the Soudan discharge. The pellets can be effectively back flushed so that any particulate matter will be removed and not effect long-term performance. Based on the laboratory results, the complete annual flow from the mine could be treated with about 15,000 lbs of pellets. At the end of the year, the pellets would need to be removed and landfilled and replaced with new pellets. Copper and Co are not listed wastes and concentrations of all RCRA metals easily passed the TCLP limits. The annual cost for pellets and disposal is estimated to be on the order of $20,000. Since the pellets contain about 5% $CaCO_3$ by weight, it would be difficult to acid strip them efficiently. American Peat is investigating a different formulation that would allow acid stripping and reuse of the pellets.

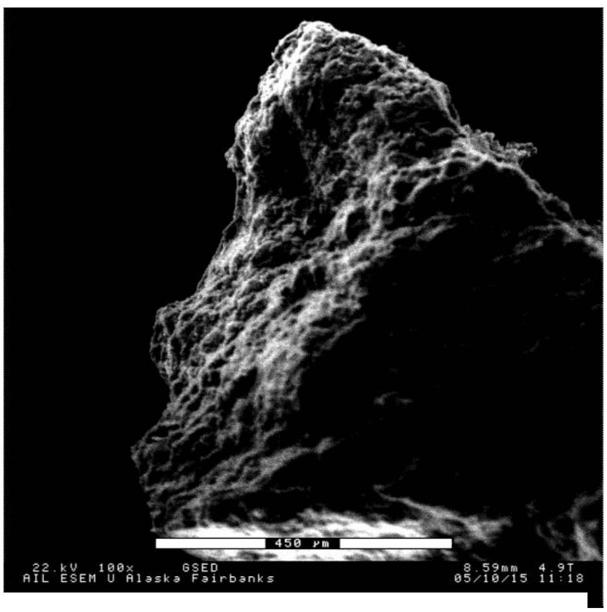

Figure 8. Peat pellet 100x

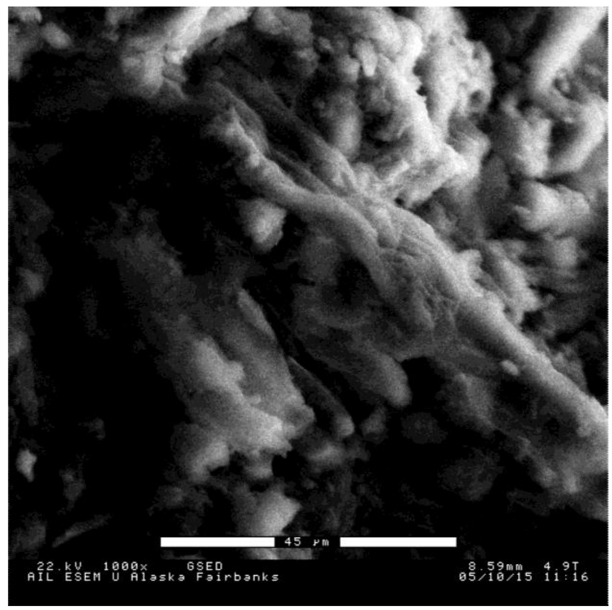

Figure 9. Peat pellet 1000x

Conclusions

Preliminary tests conducted with peat pellets (APTSorb) have indicated that they may offer a low cost solution to removing low levels of metals from Soudan mine drainage. Additional pilot tests using the pellets in a sand filter style bed are underway.

References

Bailey, S. E., Olin, T. J., Bricka, R. M. and Dean, D. 1999. A review of potentially low-cost sorbents for heavy metals. Water Research, Volume 33, Issue 11, Pages 2469-2479 http://dx.doi.org/10.1016/S0043-1354(98)00475-8

Brown, P. A., Gill, S. A. and Allen, S. J. 2000. Metal removal from wastewater using peat Water Research Volume 34, Issue 16, Pages 3907-3916 http://dx.doi.org/10.1016/S0043-1354(00)00152-4

Brown, P., Jefcoat, I. A., Parrish, D., Gill, S., and Graham, E. 2000. Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution. Advances in Environmental Research Volume 4, Issue 1, Pages 19-29 http://dx.doi.org/10.1016/S1093-0191(00)00004-6

Dastgheib S. A. and Rockstraw, D. A. 2001. Pecan shell activated carbon: synthesis, characterization, and application for the removal of copper from aqueous solution. Carbon http://dx.doi.org/10.1016/S0008-6223(00)00315-8

Eger, P., 2007, Solving mine drainage problems at Soudan state park– one step forward, two steps back, Proceedings America Society of Mining and Reclamation, 2007 pp 216-228 http://dx.doi.org/10.21000/JASMR07010216

Gosset, T; Trancart, J-L; Thevenot, D. R. 1986. Batch Metal Removal by Peat - Kinetics and Thermodynamics. Water Research Vol. 20, No. 1, p 21-16, http://dx.doi.org/10.1016/0043-1354(86)90209-5Lapakko, K., Eger, P., 1988 Trace metal removal from stockpile drainage by peat. Proc. Mine Drainage and Surface Mine Reclamation Conference (USM Information Circular 9183), pp. 291-300

MacDonald, R. J., Hage, K. E., Dutrizoc, J. E. 1976. Copper recovery from copper-bearing peat moss. Miner. Res. Program, Miner. Science Lab. Report No. MRP/MSC 76-275

Salmi, M. 1959. On peat chemical prospecting in Finland. International Geological Congress Sym. De Exploration Geoguimica, Tomo 2, pp. 243-254

Vaughan T., Seo C. W. and Marshall, W. E. 2001. Removal of selected metal ions from aqueous solution using modified corncobs. Bioresource Technology Volume 78, Issue 2, Pages 133-139 http://dx.doi.org/10.1016/S0960-8524(01)00007-4