

The Use of Peat Pellets to Remove Trace metals from Mine Drainage

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Abstract

A patented low temperature carbonization process has been used to convert peat into a hardened ion exchange material. Peat pellets of about 3/8 inches 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 copper ranged from about 0.01 to 3 mg/l, and cobalt from about 0.008 to 0.02 mg/l.

Treatment was most effective for copper 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 around 7000 bed volumes at low input copper concentrations. Total copper removal ranged from 180 to 2900 mg/kg of APTsorb. Cobalt broke through more quickly than copper with total removals ranging from 70 to 95 mg/kg of APTsorb. A modified TCLP test was conducted and showed that copper and cobalt were tightly bound to the pellets. The pellets retained over 99.5 % of the copper and cobalt.

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 % copper was measured in peat from the Tantramar Swamp in New Brunswick and copper 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 APTsorbTM (Patent pending) (Figures 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 copper and cobalt 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 (Figure 3).

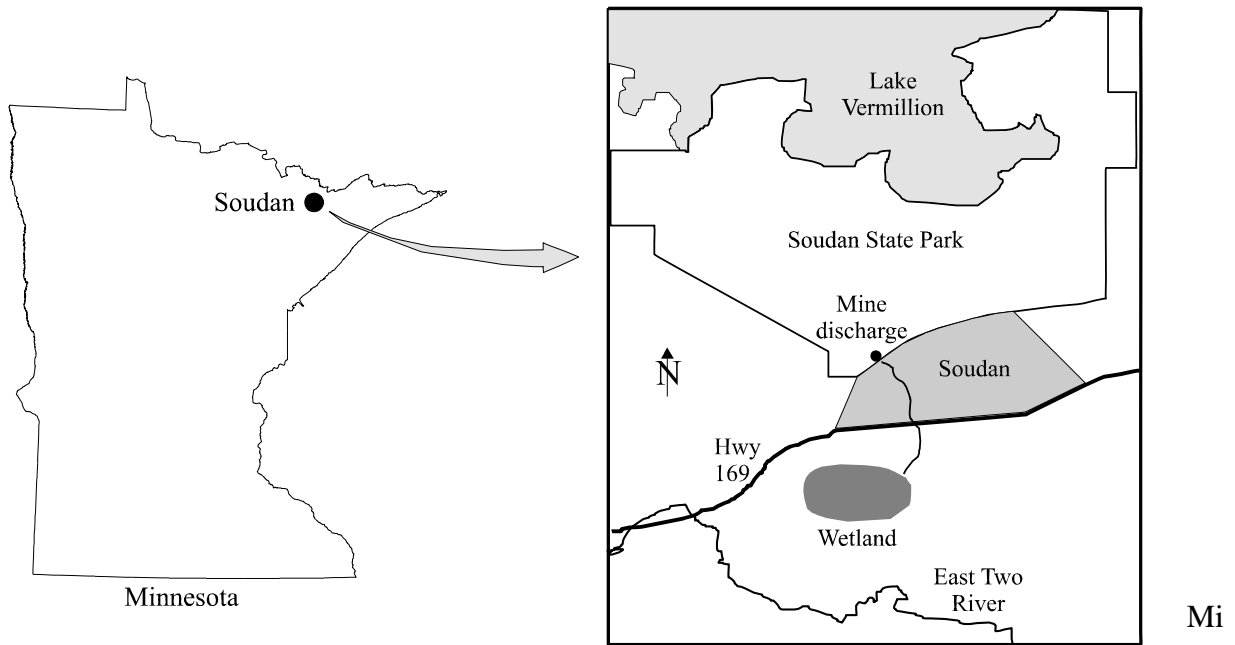


Figure 3. Soudan Mine

ne 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 copper and cobalt 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 copper and cobalt concentrations in the 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 copper and 0.004 mg/l cobalt. The history of the mine and a more complete description of the mine drainage issues are described in Eger, 2007.

American Peat Technologies had done some preliminary experimental work to evaluate the ability of the APTsorbTM 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 (10NT) and the total discharge (Level 12) were both tested.

Water Quality

10 NT

This site contributes about 40% of the total mass of cobalt and over 90% of the total copper to the discharge. The pH typically is less than 5 with historic copper concentrations ranging from around 3 – 30 mg/l and cobalt from about 0.2 to 0.4 mg/l. Total and dissolved metal values are essentially identical. For this test two 55-gallon barrels were filled with the discharge from level 10 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 0.23 mg/l cobalt, and 1.95 mg/l copper.

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 copper ranges from 0.03-0.08 mg/l and total cobalt is generally less than 0.010 mg/l. Dissolved copper is about 1/3 of the total value while there is little difference between total and dissolved cobalt.

Water was collected from the main collection sump with a peristaltic pump and filtered on site through a 1 micron filter. Water was collected over about a 2 week period during which the pH was around 7. Water was transported to the APT laboratory for testing. Dissolved copper averaged 0.016 mg/l and dissolved cobalt averaged 0.01 mg/l.

Column set up

Columns were constructed from $\frac{3}{4}$ " 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 was begun. 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. Flow was not stopped and the entire process took less than a minute. Copper and cobalt were analyzed on a Perkin Elmer graphite furnace AA. Samples were run in triplicate and intermittent samples were also sent to a separate lab for confirmation of the in house results.

Level 10

Due to the higher metal concentrations in this water 50 grams of media (APTsorb media) were used and the total column volume was 110 ml. The particle size of the peat was 10 to 30 mesh. Feed water was filtered to 1 micron in the lab and fed to the column to provide an empty bed contact time of 20 minutes.

Level 12

Since metal concentrations were much lower than level 10, 25-grams of APTsorb media (10 to 30 mesh) 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.

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.

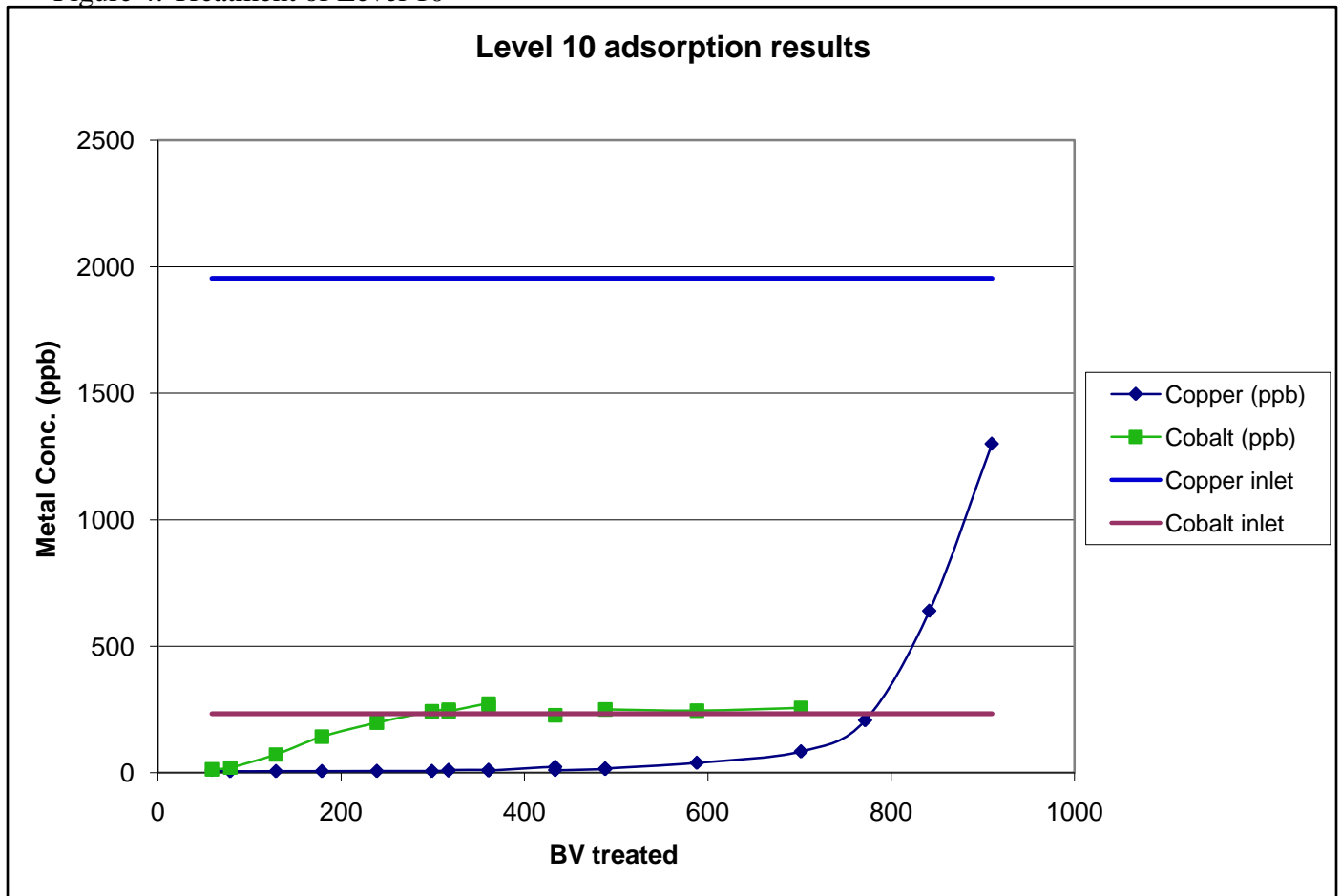
Results

Level 10

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

The total mass of copper and cobalt 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.

Figure 4. Treatment of Level 10

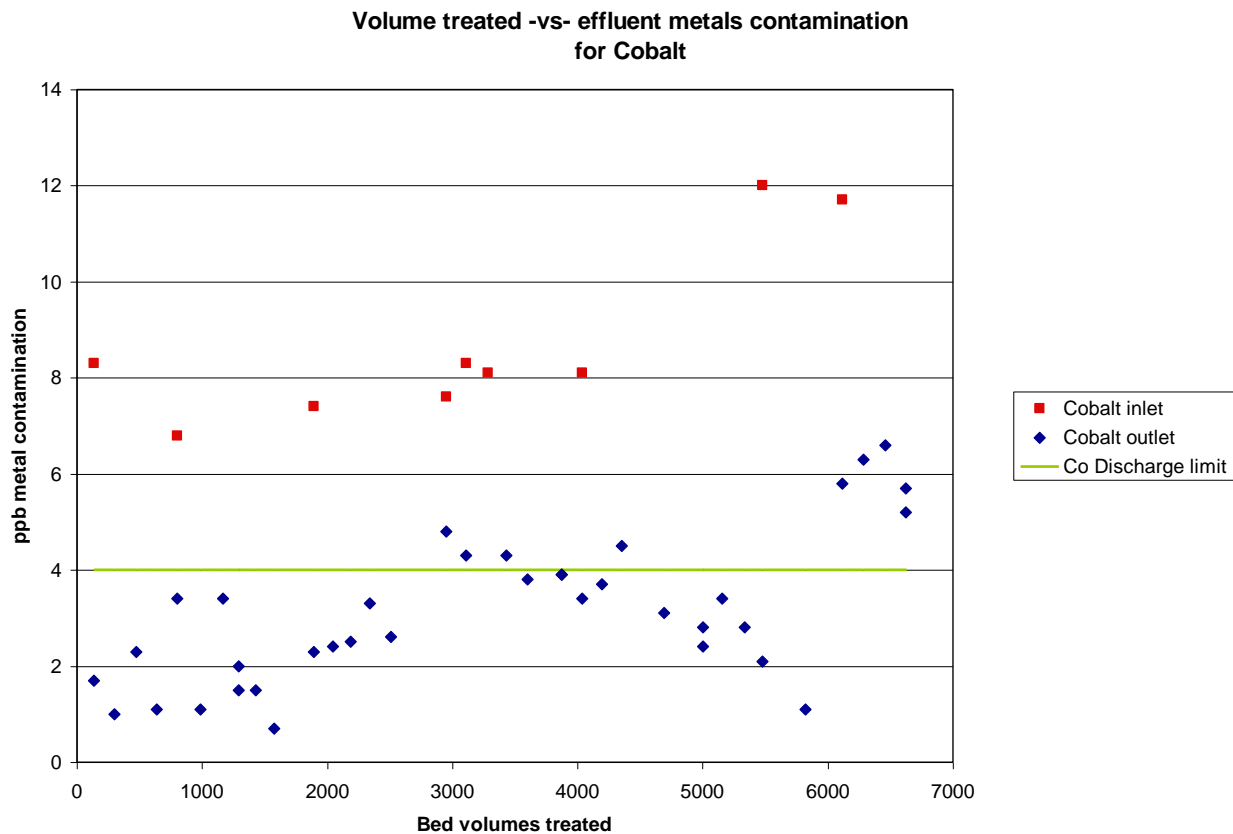


Level 12

Copper and cobalt were both removed but with the lower input concentrations, the percent removal was lower than for level 10. Initial removals were on the order of about 80% for copper, and 70% for cobalt. Cobalt concentrations generally remained below the water quality standard of 0.004 mg/l for about 6000 bed volumes (Figure 5). 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 (Figure 6).

The total mass of copper and cobalt 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 12, Cobalt



TCLP test

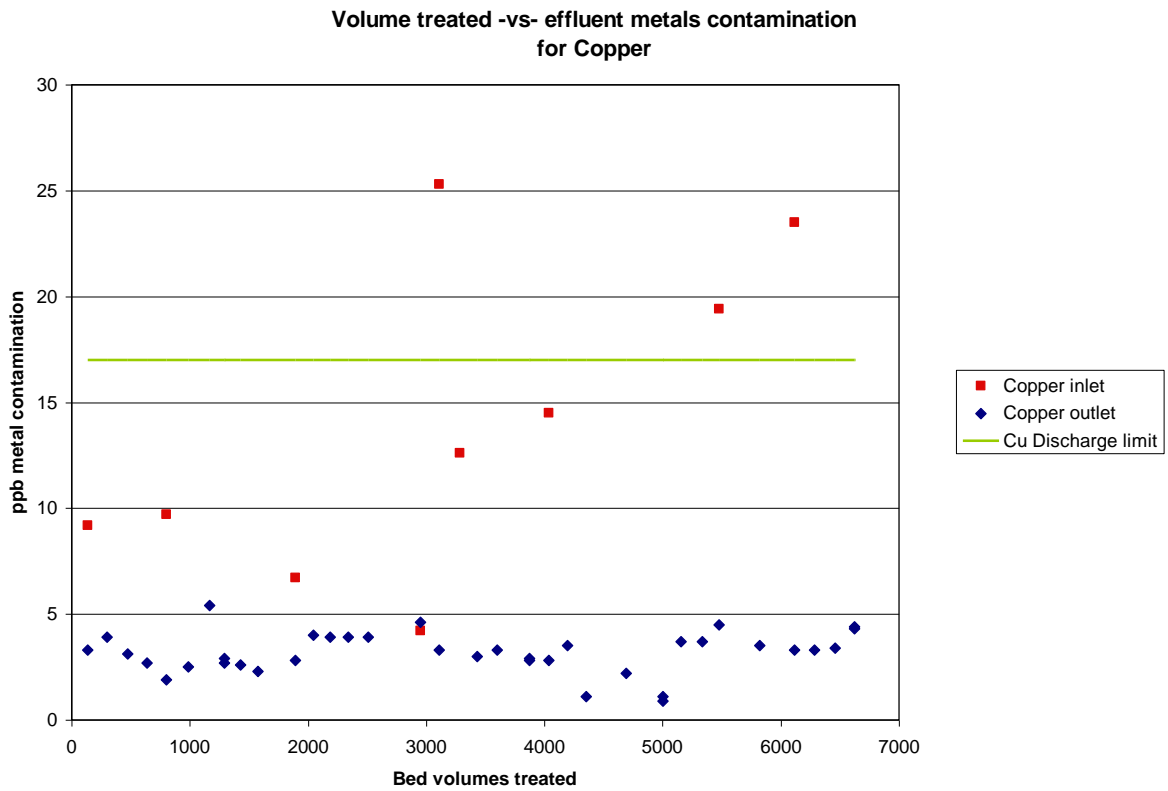
Normal TCLP tests use 100 grams of solid, mixed with 2000 ml of solution at a fixed pH. The tests performed on these samples were at a much higher concentration of 100 grams of solid to 200 ml of strip solution. Using a higher solid to liquid ratio would tend to maximize the leachate

concentration. All RCRA metals were below detection limits, with the exception of barium, which was at 0.2 % of the allowable limit for disposal. Small amounts of copper and cobalt were released but the pellets retained >99.5 % of the copper and cobalt (Table 1).

Table 1. Results from modified TCLP test

	mg adsorbed during column test	mg removed during TCLP	% retained on peat
Level 10			
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

Figure 6. Treatment of Level 12, Copper



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 made handling and flow properties concerns. 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 (Figures 7, 8). 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 cobalt 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.

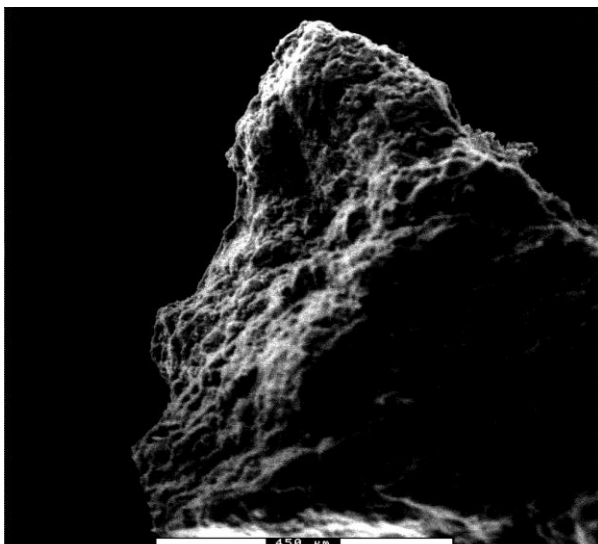


Figure 7. Peat pellet 100x

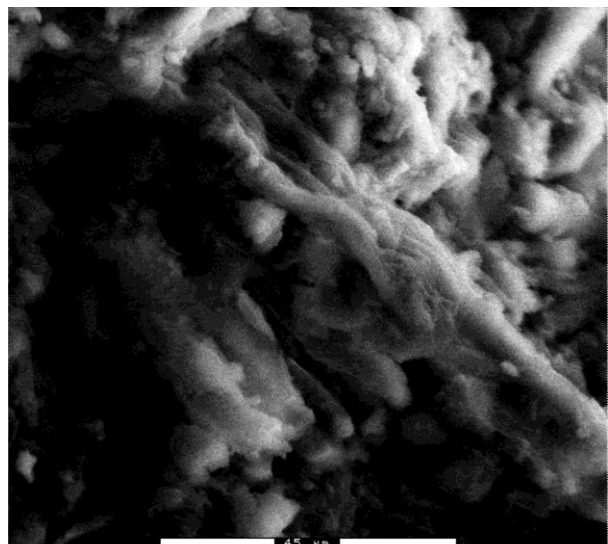


Figure 8. Peat pellet 1000x

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.

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