

# MODULAR ION EXCHANGE TREATMENT OF MINE WATER AT SOUDAN STATE PARK<sup>1</sup>

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**Abstract:** Soudan State Park contains an underground iron mine which has an average discharge of 60 gallons per minute. Annual average concentrations of copper ranged from 83 to 500  $\mu\text{g/l}$  and 6 to 26  $\mu\text{g/l}$  for cobalt, both in excess of current permit standards of 17  $\mu\text{g/l}$  copper and 4  $\mu\text{g/l}$  cobalt. A sulfate reducing bioreactor and an aerobic polishing pond was initially proposed to treat the discharge water. High levels of mercury in the mine discharge (40 – 60  $\text{ng/l}$ ) caused concerns about the potential for the bioreactor to produce methyl mercury. The Minnesota Pollution Control Agency asked the park to develop an alternate treatment process that would reduce copper and cobalt without increasing methyl mercury. Chemical treatment with a rotating cylinder (RCTS<sup>TM</sup>) was chosen for additional field evaluation, after bench testing showed that treatment with magnesium hydroxide could reduce copper and cobalt concentrations to permit levels. Additional pilot tests were done using lime and increasing pH to about 9.5 was successful in reducing filtered copper and cobalt to below permit levels. Although the RCTS was successful in raising pH and removing filtered metals, solids removal, without a large settling pond, was extremely difficult. The system of settling tanks and bag and cartridge filters generally reduced TSS to around 30  $\text{mg/l}$ , but suspended metals exceeded permit levels. Suspended copper was particularly difficult to remove, and even after 48 hours of settling, suspended copper still exceeded permit levels. Given the problems with suspended metals removal and an approaching enforcement deadline, a decision was made to install mobile modular ion exchange units to treat the entire mine discharge. The system began operating on July 31 2009 and has been successful in treating the discharge water. The system includes filtration to a nominal 1 micron size followed by two 60  $\text{ft}^3$  tanks containing a commercial cation resin. After treatment, cobalt has generally been less than the detection limit of 2  $\mu\text{g/l}$  and dissolved copper has averaged 4.3  $\mu\text{g/l}$ . Unfiltered copper has been difficult to remove. The average unfiltered copper was 16  $\mu\text{g/l}$ . Filtered copper was about 30% of the unfiltered values.

**Additional Key Words:** rotating cylinder treatment system, copper, cobalt

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## **Introduction**

Soudan State Park contains Minnesota's first iron mine and offers tours through parts of the old mine workings. Two high energy physics laboratories have also been constructed at the lowest level of the mine. 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. Additional background and description are provided in previous papers (Eger, 2007, 2009).

## **Background**

Open pit mining at Soudan began in 1884 and continued until 1892, when safety issues dictated that under-ground mining methods were needed to continue to mine the steeply dipping ore body. Over 15.5 million long tons of high-grade iron ore were removed from the mine during its production lifetime. The mine is about 2400 feet deep and contains 18 levels.

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. Pumps are located on three levels to lift the water out of the mine (Maki, 1996).

An evaluation of the mine concluded that about 94% of the total copper load and 44% of the total cobalt load in the discharge came from a single site near the upper levels of the mine (Eger, 2007; Eger et al., 2001). Treatment of that one source was projected to significantly reduce downstream water quality concentrations, although the overall discharge would still be somewhat above the permit limits.

A standard ion exchange system was employed to remove Cu and Co from the source. Shortly after the ion exchange resin was installed, the system became plugged with a precipitate that was primarily  $\text{Al}(\text{OH})_3$ . This problem had not been observed in previous samples or in bench scale testing. As a result, the system did not initially function successfully and the discharge did not meet water quality standards. In 2006, the Department was fined and signed a stipulation agreement. The stipulation agreement required the Department to be in compliance with its existing permit starting August 1, 2009.

A consulting firm was hired to evaluate treatment options and recommended building a wetland treatment system consisting of a sulfate reducing bioreactor and an aerobic polishing pond. The new permit authorizing the construction also included a mercury monitoring requirement. Total Hg of 40 – 60 ng/l, much higher than the 6.9 ng/l standard, was measured in the mine discharge. Mercury concentrations were elevated throughout the upper portion of the mine with some values exceeding 100 ng/l. Limited data from previous studies had shown that although wetland treatment systems could remove total Hg, low levels of methyl mercury could be produced (King et al., 2002; Nelson et al., 2002). Given the high level of Hg in the discharge and the concern over methyl mercury production, construction was postponed.

The Department was asked to develop an interim treatment process that would reduce Cu and Co without increasing methyl mercury and to maintain the same compliance schedule. This schedule compressed the evaluation period and limited the treatment options to systems that could be mobilized fairly quickly. Three systems were evaluated: a modular ion exchange system with a commercial resin, ion exchange using lower cost peat pellets (APTsorb™) and chemical treatment with a rotating cylinder [RCTS™] (Eger et al, 2008; Tsukamoto, 2007). The RCTS™ was initially chosen for additional evaluation.

The RCTS is a mobile chemical treatment system and consists of a lime slurry tank, a dosing tank, a pH controller and the rotating cylinder (Fig. 1). Lime was added to the mine drainage, mixed in the rotating cylinder and discharged into 2 18,000-gallon weir tanks operating in parallel for settling. A combination of bag and cartridge filters was used for final solids removal (Fig. 2). Treatment began on April 15, 2009.

The rotating cylinder treatment system was effective at increasing pH and reducing filtered copper and cobalt to below permit limits. The treatment pH to produce these levels ranged from 9.5 to 9.9 and the total suspended solids generated typically ranged from about 60 - 100 mg/l. The pH typically decreased about 0.5 units as water passed through the cylinder and associated weir tanks, while TSS was reduced by about 50%. Preliminary settling tests suggested that the residence time needed to completely settle the fine particulates might exceed 24 hours. Numerous problems were encountered with the filter equipment and filters. Although discharge TSS was at or near the standard of 30 mg/l, the inability of the filter system to remove fine particulates left suspended metals above permit limits in the discharge (Eger et al., 2009).



Figure 1. Rotating Cylinder Treatment System



Figure 2. Overview of treatment system

Since the RCTS™ and associated settling and filtering equipment did not consistently meet all permit standards, the Department decided to use a modular ion exchange treatment system for the entire discharge. This system could be assembled fairly quickly and could operate outside during the summer to meet the August 1 compliance date.

### **Approach**

#### **System Description**

The current system was designed to treat 150 gpm and includes a holding tank, pre-filtration with bag filters followed by cartridges, and 2 ion exchange tanks (Fig. 3). The ion exchange system was designed by Siemens and uses the same cation exchange resin as the system in the mine that treats the major metal source. Lab and pilot tests were conducted during the winter of 2009 (MNDNR, 2009). During the initial evaluation period, some post-filtration and the use of three ion exchange tanks were evaluated (Fig. 4). A variety of filter types were used in an effort to remove suspended metals from the discharge. Currently pre-filtration is done with a 1 μm AJR nominal filter bag and 1 μm nominal Epic II cartridges. These filters have an estimated efficiency of 60-70%. Currently, these filters are changed once per week, but additional data is being collected to determine an optimum replacement schedule.

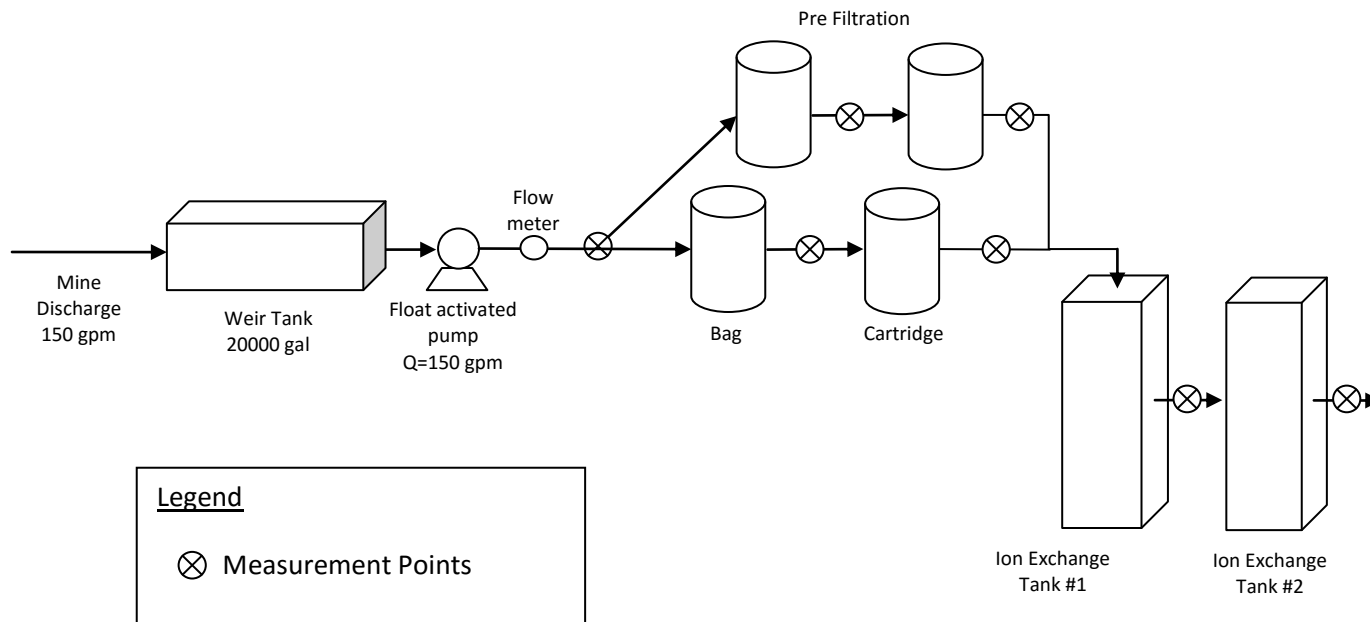


Figure 3. Schematic –Ion exchange treatment, overall mine discharge

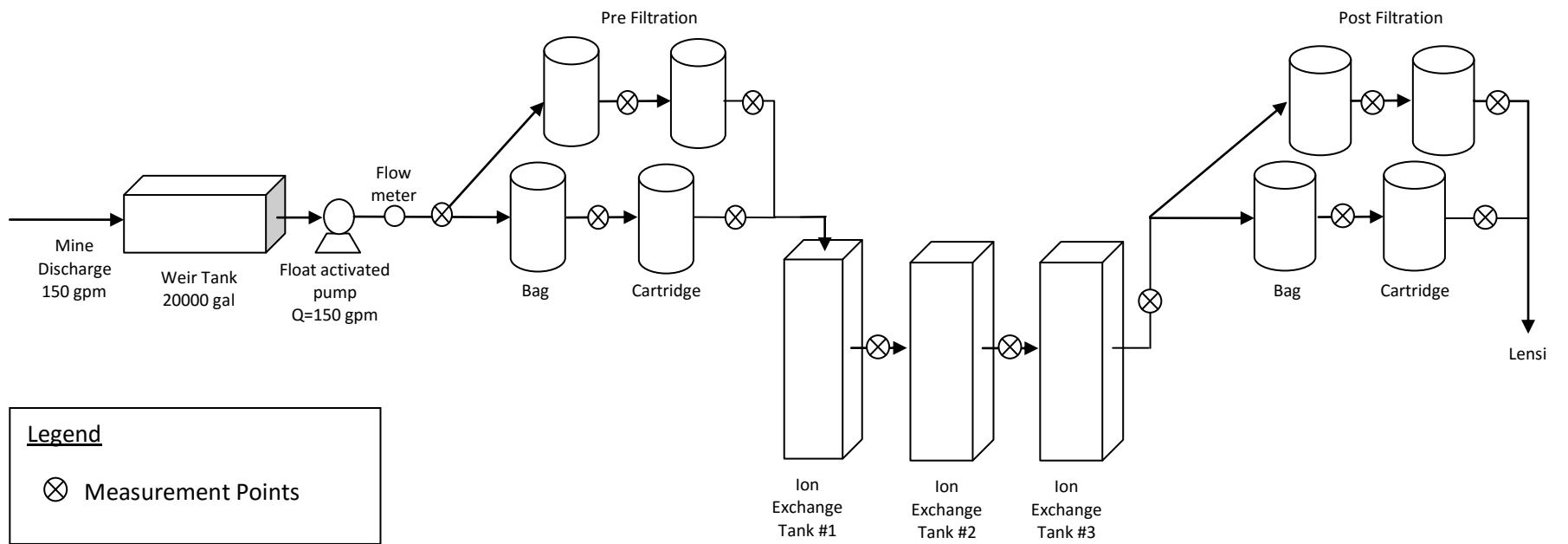


Figure 4. Schematic –Ion exchange treatment with additional ion exchange tank and post filtration, overall mine discharge

## **Methods**

Grab samples were routinely collected from the input, after the filtration unit (combined bag and cartridges), and after each ion exchange tank. Specific conductance and pH were measured on the input, while unfiltered and filtered metal samples (filtered through a 0.45u filter) were collected at all sites for Cu. Since there was almost no difference between unfiltered and filtered Co, only unfiltered cobalt was analyzed. All metals samples were preserved with nitric acid to a pH <2. Frequency varied based on test objectives because different filtration options were being evaluated during the initial period of system operation, but normal sampling was typically once per week.

Samples were analyzed by Northeast Technical Services (NTS) in Virginia, MN or the Department of Agriculture Laboratory (MDA) in St Paul, MN. Both labs are certified by the Minnesota Department of Health and use an ICP-MS for metal analysis. Specific conductance was measured on site with a Myron Specific Conductivity meter, and pH was measured with an Orion Three Star pH meter. The meter was calibrated using pH buffers at 7 and 10 prior to measurement.

## **Results**

### **Copper**

During the time period July 30 to October 27, 2009 unfiltered copper in the mine drainage ranged from 58 to 152 µg/l with a mean of 105 (Table 1). Filtered copper is about 30% of the unfiltered value. The average ratio of unfiltered copper/filtered copper in the input is 3.6. With 1 µm AJR nominal filter bags and Epic II 1 µm nominal cartridges, removal of unfiltered copper has ranged from 0 to about 20%. The average concentration of copper after pre- filtration was 86 µg/l. Additional suspended Cu is removed in the ion exchange tanks. Unfiltered Cu decreases as water moves through the system. The average unfiltered Cu concentration after Tank 1 was 34 µg/l and 16 after Tank 2 (Fig. 5, Table 1).



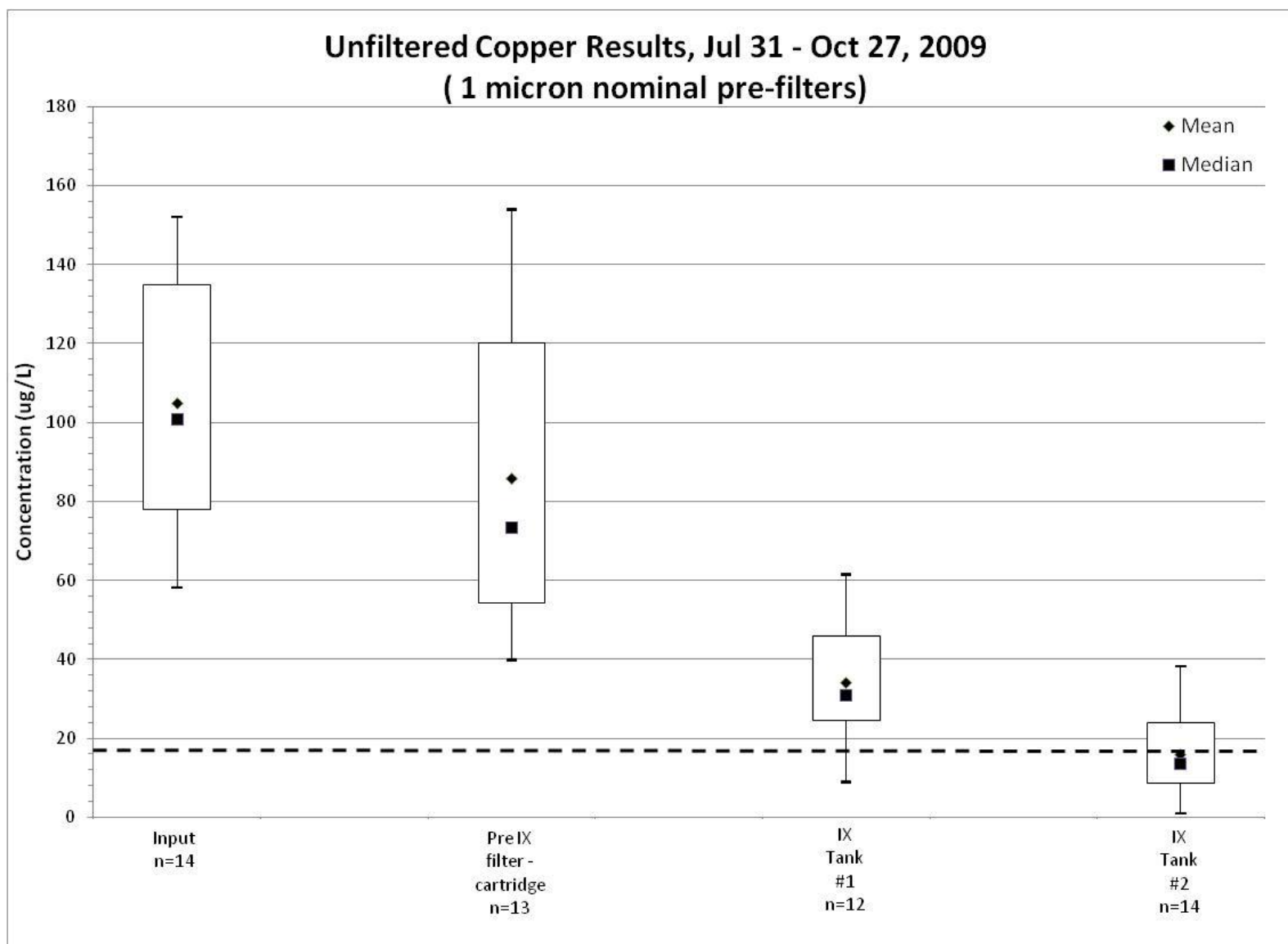


Figure 5. Box plot, unfiltered copper, dotted line = current permit requirement 17  $\mu\text{g/l}$

Table 1. Water Quality Summary Copper (7/30 – 10/27/09)

Site	Samples	Unfiltered (µg/l)			Filtered (µg/l)			
		min	max	mean	Samples	min	max	mean
Input	14	58	152	105	14	15	51	31
After Cartridges	13	40	154	86				
After Tank 1	12	9	62	34	9	2	12	8
After Tank 2	14	<i>1</i>	38	16	15	<i>1</i>	8	4

Notes: Blank = no samples collected. *Italics, values less than the detection limit are set to ½ detection limit for statistical calculations*

The ion exchange tanks are very effective at removing filtered Cu. Copper decreased from an average of 31 µg/l in the input, to 8 µg/l after Tank 1 and 4 µg/l after Tank 2. All filtered copper values were < 17 µg/l after Tank 1 (Table 1).

Cobalt

Cobalt concentrations in the input mine water ranged 6.7 to 10.4 µg/l (Table 2). Essentially all the Co is in the filtered form and over 50% is removed in the first ion exchange tank. After the second tank, Co has been generally less than the detection limit of 2 µg/l since the system began (Fig. 6).

Table 2. Water Quality Summary Cobalt (7/30 – 10/27/09)

Site	Samples	Unfiltered (µg/l)		
		Min	max	mean
Input	13	6.7	10.4	7.6
After Tank 1	7	<i>1</i>	5.6	2
After Tank 2	14	<i>1</i>	1.25	<i>1</i>

Notes: . Blank = no samples collected.

*Italics, values less than the detection limit are set to ½ detection limit for statistical calculations*

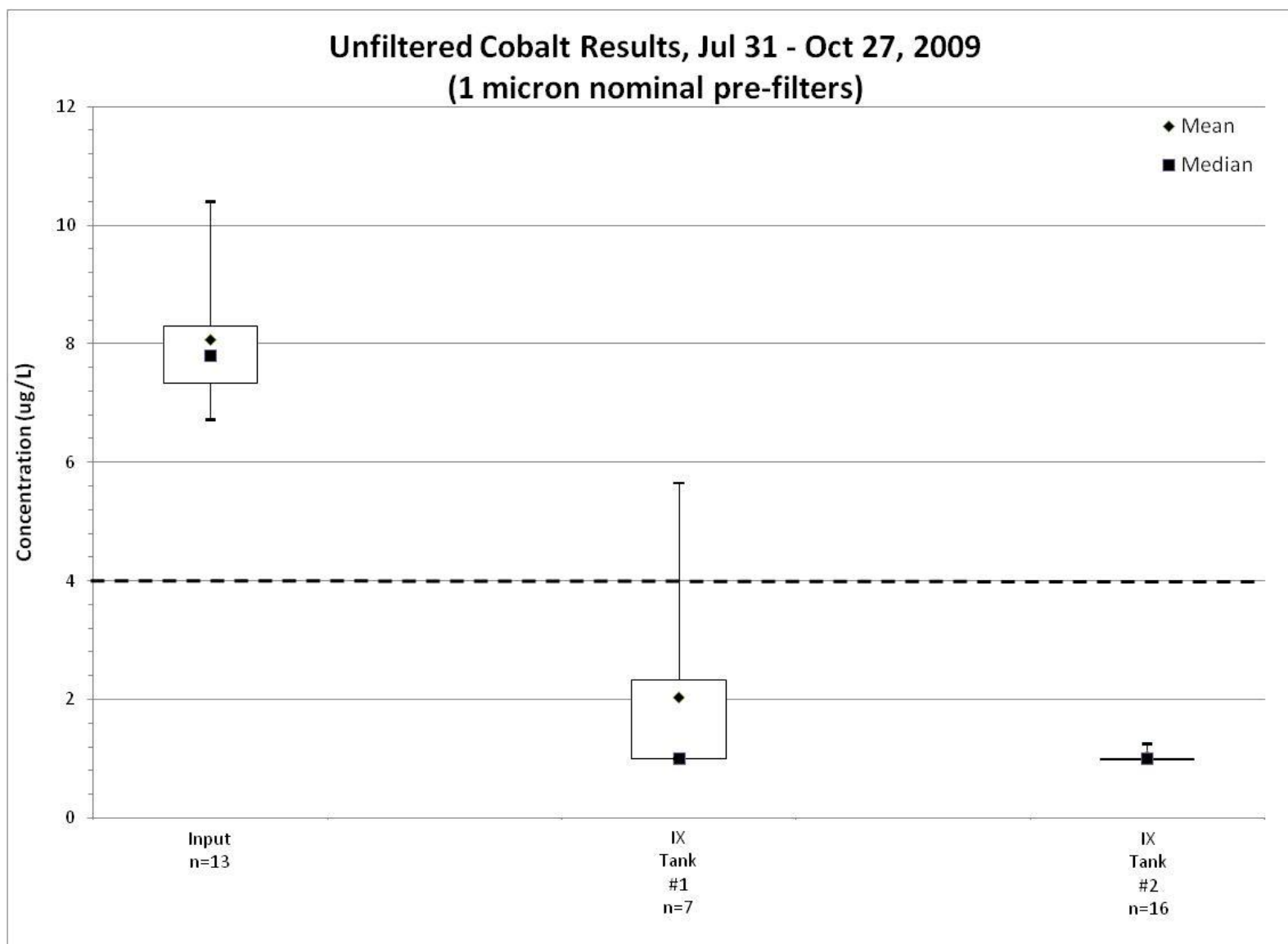


Figure 6. Box plot, unfiltered cobalt, dotted line = current permit requirement 4  $\mu\text{g/l}$

## Discussion

Ion exchange involves the interchange (or exchange) of ions between a solid medium and an aqueous solution. The solid medium can be commercially produced or made from naturally occurring substances (e.g. peat or zeolites). Various resin forms are available to remove either cations or anions. Synthetic organic resins are the predominant type since their characteristics can be tailored to specific applications. The resin used at Soudan is a specific cation resin developed by Siemens and has been used to treat water in the mine since 2004.

The total capacity of the resin is a function of the input water chemistry and metal concentrations. Siemens has estimated that for in mine treatment of Level 10N water, the total capacity should be on the order of 2 lbs of Cu per cubic foot of resin. In contrast, the estimated capacity for treating discharge at the surface, where metal concentrations are 1-2 orders of magnitude lower, is only 0.1 to 0.5 lbs/ft<sup>3</sup>. The ion exchange system is very effective at removing dissolved Cu and Co assumed to be equal to filtered values from the mine and reduced both Cu and Co to levels below the current respective permit levels of 17 and 4 µg/l.

However, the current permit values are for total metals (approximated by unfiltered values). Ion exchange resins are not designed to remove suspended material and Siemens requires that pre-filtration must be included as part of the treatment system to protect the resin. Although the existing 1 µ nominal filtration removes some of the suspended metals, most of the particles in the input water are smaller than 1 µ (Fig. 7). Some of these fine particles are trapped in the resin tanks. After treatment, about 30% of the Cu was in the filtered form and the average ratio of unfiltered to filtered Cu was 3.4 (Table 3).

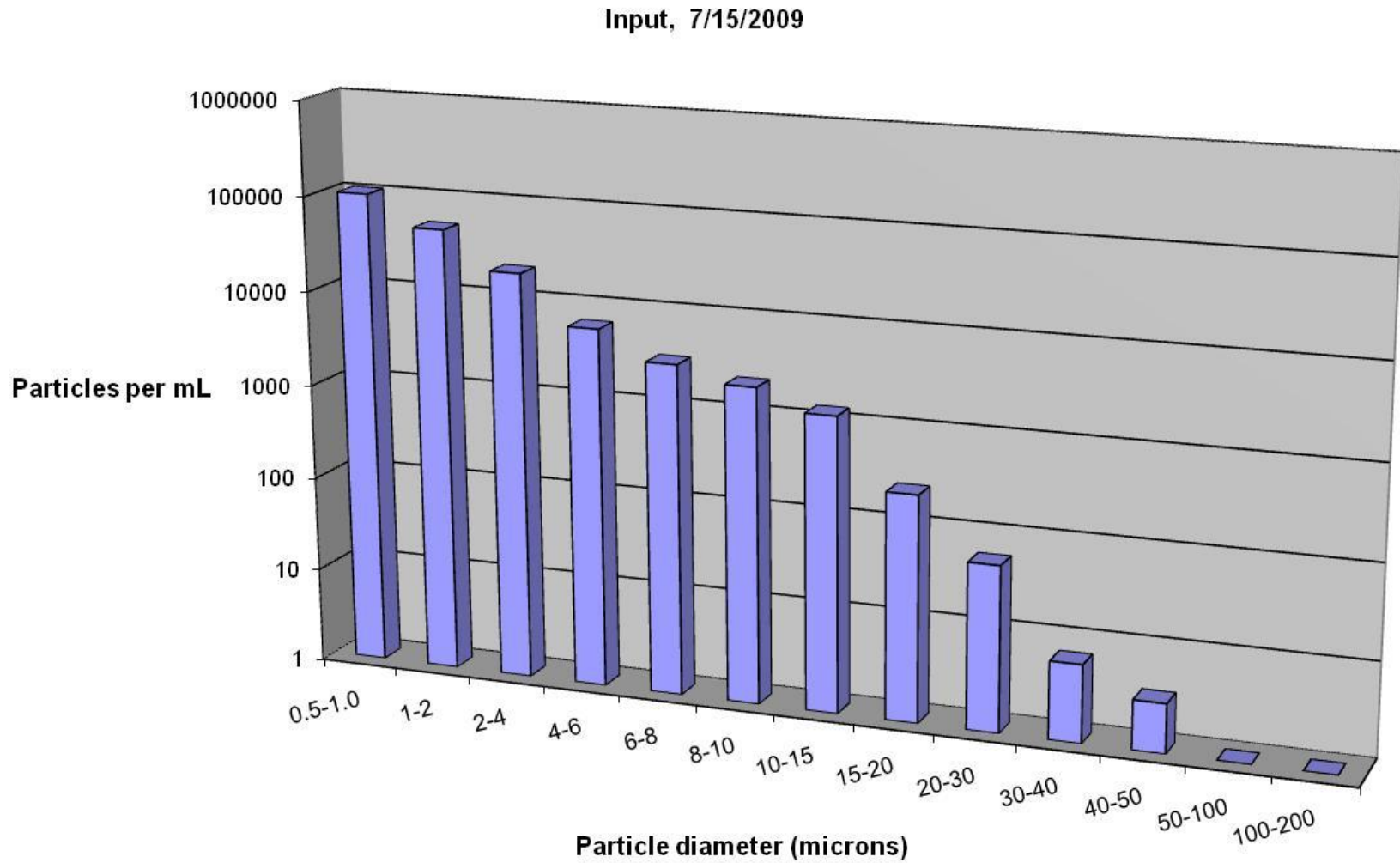


Figure 7. Particle size analysis, mine water discharge, 7-15-09 (Analysis by GE laboratories)

Table 3. Unfiltered and filtered copper ( $\mu\text{g/l}$ ) after treatment (after Tank 2)

Date	Tank 2		Ratio
	UF	F	UF/F
7/31/09	8.7	2.03	4.3
8/1/09	<i>1</i>	<i>1</i>	1.0
8/6/09	26	6.61	3.9
8/11/09	20.8	4.89	4.3
8/18/09	30.5	6.4	4.8
8/24/09	38.2	6.46	5.9
8/24/09	--	--	
8/25/09		7.68	
8/26/09	12.2	3.35	3.6
8/27/09	24.9	5.82	4.3
8/27/09	--	--	
9/4/09	8.97	2.93	3.1
9/11/09	14.80	4.49	3.3
10/13/09	18.40	5.40	3.4
10/13/09	6.00	2.00	3.0
10/14/09	4.10	2.00	2.1
10/27/09	<u>8.70</u>	<u>6.20</u>	1.4
		mean	3.4

Notes: *Italics* = 1/2 detection limit. Underline = data from MDA, all other data from NTS

The removal of suspended material in the tanks increases the resistance to flow and requires additional pressure to force water through the tank. Pressure into Tank 1 increased from around 20 psi when the tank was started (July 30, 2009) to around 80 psi when the tank was replaced on October 13, 2009. During this time about 6.5 million gallons had been treated but flow decreased from 150 to 47 gpm. The initial tank treated about 5.5 million gallons before the flow rate dropped below 100 gpm, which was estimated to be the minimum acceptable flow rate to prevent the weir tank from overflowing.

Based on estimated metal removal capacities of the resin, less than 20% of the ion exchange capacity in the tank had been used (MNDNR, 2010). The tank had to be exchanged due to physical plugging not decreased chemical removal. The median and average filtered copper after tank 1 from July 31 to October 13, 2009 was 8  $\mu\text{g/l}$ . There was no apparent loss of treatment capacity during this time. This shortened life time increases the estimated treatment cost significantly.

Several tests were done with higher efficiency pre-filters in an attempt to remove more of the suspended particles and copper prior to the ion exchange tanks. When the system began on July 30, a 1  $\mu$  cartridge, rated at 99+% efficient at removing particles 1  $\mu$  or larger (“absolute filter”), was used for pre-filtration. Unfiltered Cu in the input during the test was 144  $\mu\text{g/l}$ . The filters removed about 80% of the suspended Cu but plugged after about 2.5 hours having only treated about 15,000 gallons.

Subsequent tests in September and October used a 90% efficient 1 micron filter. Total input copper during these tests had decreased to 70-85  $\mu\text{g/l}$ . Although lower efficiency than the absolute filters, these cartridges removed essentially all of the Cu. The filters treated about 85,000 gallons before plugging, which is equivalent to one day of flow at the annual average flow of 60 gpm. Changing these filters daily would cost about \$600/day not including staff time, and would be logistically and financially impractical. For comparison, the 60-70% efficient filters have treated the equivalent of 1 week’s flow at the annual average flow rate and cost about \$300/week. (The solids removed by the filters are primarily iron oxides and hydroxides and can be safely landfilled so disposal costs are minimal.) However, since the ion exchange tanks cost \$10,000 per exchange, it is important that a balance between filter cost and tank lifetime be found.

Currently different filter combinations and removal with activated carbon are being evaluated for suspended solids removal. Additional tests are planned to examine a sand filter with a fine grained filter media and peat pellets.

The system could not operate outside during the winter so it was moved several hundred feet to the east and an insulated, heated area was constructed accommodate the ion exchange tanks. Since winter flows are much less than summer flows, the surge capacity was reduced to 10,000 gal. Metal removal is still acceptable but the tanks are plugging almost twice as fast as during the summer, which increases the urgency to develop better methods of suspended solid removal.

### **Conclusions**

The modular ion exchange system was successful in meeting permit limits and complying with the terms of the stipulation agreement. The Department has applied for a permit to implement ion exchange as the preferred treatment alternative for the Soudan Mine.

Although the existing system is very effective at removing filtered copper and cobalt, some suspended copper moves through the system. This suspended material plugs the ion exchange tanks before the full chemical removal capacity of the resin can be utilized. As a result, the overall treatment cost is increased significantly. Additional methods to remove solids and reduce Cu concentrations are being investigated.

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