REMOVING SUSPENDED METALS WITH A FINE GRAINED CERAMIC FILTER MEDIA[1]

P. Eger[2]

Abstract: Low concentrations of suspended metals are difficult to remove using standard methods. Sand filters can remove particles down to about 10-20 microns and multimedia filters can remove down to about 5-10 microns. At Soudan State Park, over 90% of the particles are less than about 3 microns and over 75% of the total copper is in the suspended form. An ion exchange treatment system is used to treat the overall discharge of 60 gallons per minute and successfully removes filtered copper and cobalt to < 4 ug/l. The current treatment system uses 1 micron nominal bag and cartridge filters, a carbon prefilter and one to two ion exchange tanks but removal of finely suspended copper has been problematic. Although the average permit limit for total copper of 17 ug/l has generally been met, concentrations sometimes exceed this value as 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 used. At best, only about 20% of the resin capacity was utilized. To provide better filtration a fine grained ceramic media was tested for its ability to remove the finely suspended material. Pilot testing indicated that removal initially was very high with about 90% removal after about 200 bed volumes of flow. Removal decreased to around 40% after about 1000 bed volumes. Pressure also increased with bed volumes treated and backwash is needed between 1000 and 2000 bed volumes. Additional pilot testing is underway with a full scale trial planned for summer 2011.

Additional Key Words: filtration, copper, cobalt

---

[1] Paper was presented at the 2011 National Meeting of the American Society of Mining and Reclamation, Bismarck, ND ***Reclamation: Sciences Leading to Success*** June 11 - 16, 2011. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

[2] Paul Eger, Senior Engineer, Golder Associates, Roseville MN 55117

Proceedings America Society of Mining and Reclamation, 2011 pp 202-213

DOI: 10.21000/JASMR11010202

http://dx.doi.org/10.21000/JASMR11010202

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 1882 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 Trails. Additional background and description are provided in previous papers (Eger, 2007, 2009).

Background

In July 2009 an ion exchange system was installed to treat the entire mine discharge (Eger, 2010). The ion exchange system was designed by Siemens and uses a proprietary specific cation exchange resin. Although filtered metals are removed successfully, the removal of finely suspended Cu has been problematic. Although the average permit limit of 17 µg/l for total Cu has been met, concentrations sometimes exceed this value since finely suspended Cu can move through the system. The suspended Cu also physically plugs the ion exchange resin before the total removal capacity of the resin is exhausted. Tests were conducted with a variety of filters including absolute and nominal filters and a fine grained ceramic filter media in an attempt to find a cost effective method of removing suspended solids.

Approach

System Description

The current system was designed to treat 150 gpm and includes surge tanks, pre-filtration with bag filters followed by cartridges, a carbon tank for additional filtering and 1-2 ion exchange tanks (Fig. 1). 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 µ AJR multilayer filter bag and 1 µ nominal Parker Avasan cartridges. These filters have an estimated efficiency of 60-70%. Currently under low flow conditions (< 60 gpm), bag filters are changed twice per week and cartridges are changed once every one to two weeks, and the carbon tank is manually backwashed about once every two weeks. Better methods of filtration were needed to deal with higher spring flows, improve removal efficiency, possibly eliminate the carbon tank and reduce long term costs. A fine grained ceramic media was tested to determine removal efficiency and the time needed between backwash cycles.

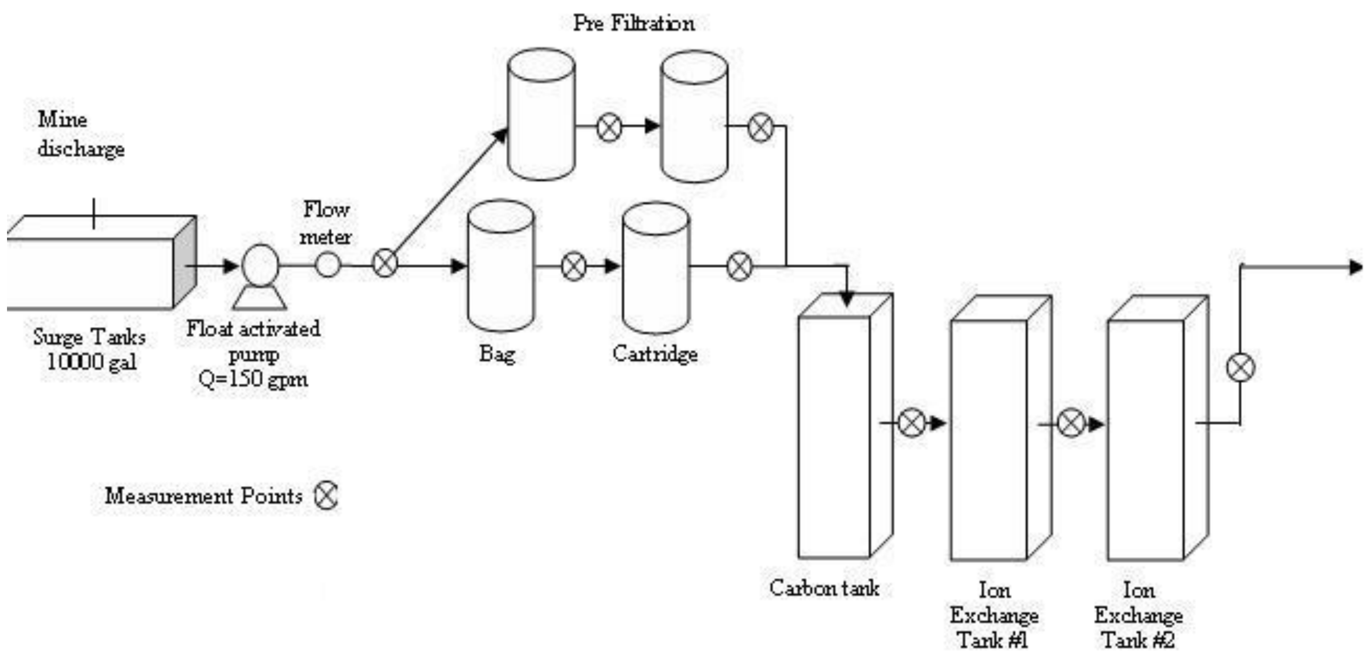

Figure 1. Schematic –Ion exchange treatment, overall mine discharge

Methods

Filter media

The ceramic media is manufactured by Fairmount Minerals and available in a variety of sizes ranging from 600-2000 microns down to 180 to 210 microns (Fig. 2, Table 1). The ceramic media has a larger surface area than comparable sand media (Fig. 3).

Figure 2. Macrolite ceramic media

Table 1. Ceramic media filter size

Mesh size	Microns	Nominal filter rating (microns)
14 X 30	600 X 2000	< 30
20 X 40	400 X 840	< 20
40 X 60	250 X 400	< 5
70 X 80	180 X 210	< 3

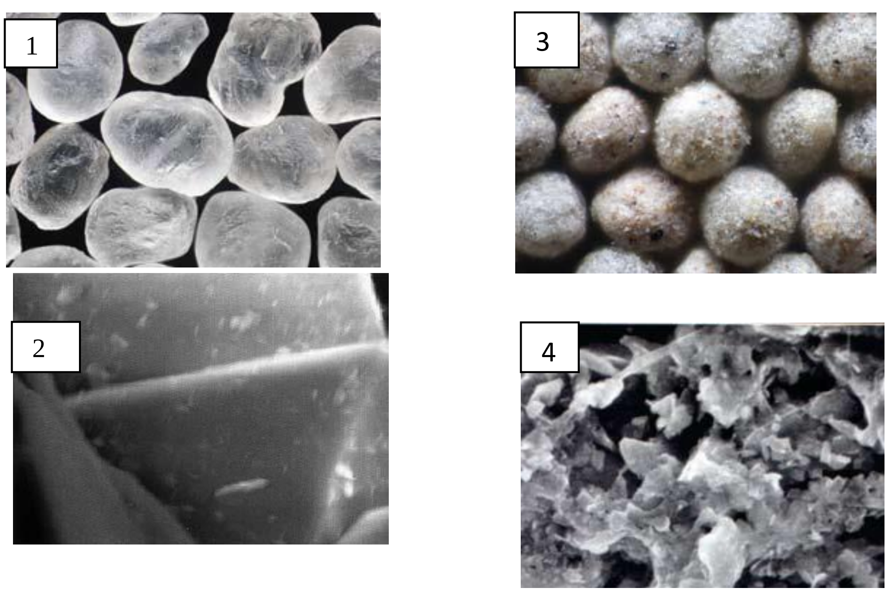

Figure 3. Comparison of sand (1, 2) and Macrolite ceramic media (3, 4) (Images 1 and 3, magnification 100x, images 2 and 4, magnification 2000 x)

Figure 4. 105 liter fiberglass tank with control unit used in pilot test

Laboratory tests

Preliminary laboratory column tests were done by Siemens using the 250-400 micron and the 180-210 micron material. Input and output samples were collected and analyzed for copper and cobalt with an ICP-MS.

A small scale pilot test was conducted in the summer and fall of 2010. A 105 liter fiberglass tank was fitted with a control unit and set up at the park (Fig. 4). Fifteen to thirty liters per minute of the discharge was routed to the unit which provided a hydraulic loading of about 163-326 L/min/m^2 (4-8 gpm/ft^2). Manufacturer's recommended loading rate was 326-407 liters/min/m^2 (8-10 gpm/ft^2). Flow entered through the top of the tank and moved down through the 51 cm of media and the 15 cm of pea gravel at the base of the unit. Water was collected through a screened port and flowed up a standpipe. Input flow was measured with a totalizing Badger Recordall flow meter and flow rate was measured by timing the flow meter. Grab samples were collected of the inlet and outlet and were analyzed for unfiltered and filtered copper and iron as well as for total suspended solids (TSS). All filtered metal samples were filtered through a 0.45 micron filter and all metals samples were preserved with nitric acid to a pH <2. Samples were collected during each operational cycle.

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. Total suspended solids were measured by filtering at least 500 ml through an absolute 0.45 micron filter.

Input flow was initially around 28 liters/minute (7.5 gallons per minute) but was dropped to 15 liters/minute for the latter part of the test. Although the control unit had the capability to automatically trigger backwash, backwash was done manually to insure that media was not lost from the bed and so the backwash could be visually evaluated. Backwash was initiated when the pressure drop increased to 10-15 psi above the initial clean bed pressure. In this pilot, input water was used for the backwash and flowed upward through the bed to fluidize the media and remove the filtered material. In a full scale system, filtered water would be used for the backwash, but the pilot unit did not have this capability. (Since the TSS of the input water was generally < 10 mg/l, the impact on overall performance was estimated to be minor.) After the backwash, a rinse cycle was initiated to insure that any dislodged material was flushed from the bed prior to the next filter cycle. To prevent media from being washed from the bed, the backwash flow had to be kept below 15 liters /minute. Based on manufacturer's recommendations, the backwash time was set to 8 minutes followed by a rinse flow of 4 minutes.

Results

Laboratory

The laboratory test was a short column experiment with only 200 bed volumes treated. The main purpose was to determine if the material could remove the finely suspended Cu in the mine discharge. With the 180 to 210 µ mesh material, total copper was reduced from 58 ug/l in the input to an average of 6.7 ug/l after the media. With the 250 to 400 µ mesh, the average output was 9.6 ug/l but both sizes reduced Cu to below the permit level of 17 ug/l. The smallest media removed over 95% of the suspended Cu, while the larger material only removed 85-90%. Some initial removal of filtered Cu was also observed. (Table 2)

Pilot

Based on the laboratory results, the 180-210 µ material was selected for field testing. Removal of suspended Cu varied as a function of time and bed volume. Initially and immediately following a backwash, suspended Cu removal was on the order of 90% (Fig. 5). The initial pressure going into the bed was around 15 psi. Removal decreased as pressure and bed volumes increased (Fig. 5). Although the backwash water had started to visually clear after the 8 minute cycle, the backwash was not successful in removing all the accumulated solids in the bed and pressure after backwash increased more rapidly. Initially around 850 bed volumes went through the bed prior to backwash. This decreased to around 550 bed volumes. Suspended solids removal generally increased to around 90% after backwash.

Table 2. Laboratory Results

Sample	Copper (ug/l)			Cobalt (ug/l)	
	total	dissolved	suspended	total	dissolved
Input	58	11.5	46.5	8.9	8.8
Media 1: 180 to 210 microns					
100 bed volumes	6.6	6.1	0.5	8.2	8.2
200 bed volumes	6.8	4.3	2.5	8.1	7.9
Media 2: 250 to 400 microns					
100 bed volumes	9.0	4.4	4.6	8.2	7.9
200 bed volumes	10.3	3.8	6.5	7.7	8.0

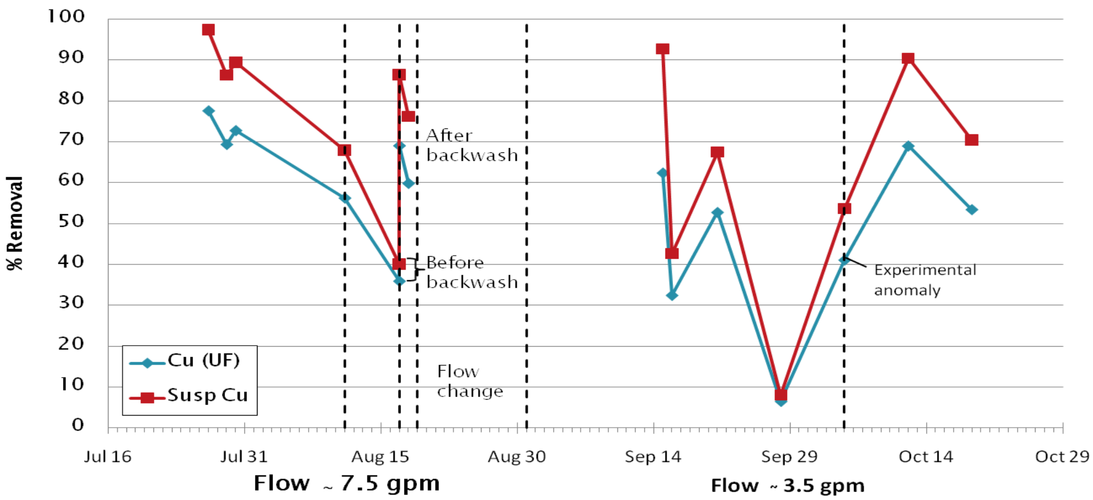

Figure 5. Copper removal vs. time (Dotted lines represent a backwash cycle)

Initial pressure after several backwash cycles increased to 21 psi, suggesting that not all suspended material had been removed from the bed. An air spurge was added in the final phase of the test and appeared to increase solids removal, but there was not enough data to make a quantitative evaluation.

In the second test phase, the input flow was reduced to 15 liters/min to balance the required backwash flow. Samples were collected as a function of bed volume. Suspended Cu removal decreased from around 90% initially to about 10% after 1500 bed volumes (Fig. 6). The last sample collected during the cycle ("experimental anomaly" in Fig. 5) occurred after a surge in pressure presumably pushed solids through the bed. By flushing some solids out of the bed, the removal efficiency increased. (This sample was not plotted in Fig. 6).

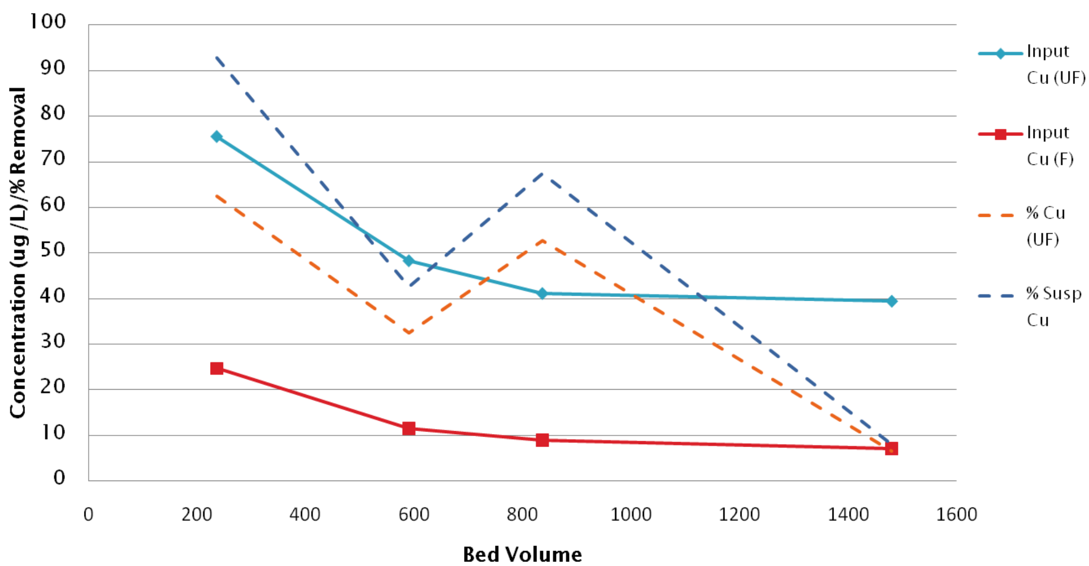

Figure 6. Copper removal vs. bed volume

Discussion

Although the ion exchange treatment effectively removes dissolved Cu and Co, the presence of finely suspended solids in the mine water has caused operational problems and periodically total Cu concentrations exceed the average permit value of 17 ug/l. (Total Cu is still below the maximum allowable concentration of 42 ug/l (Table 3)). The present filtration system of bags and cartridges remove about 20-40% of the fine particles but some of the remaining particles make it through the system. These particles also physically plug the ion exchange tanks causing pressure to increase and flow to decrease. The maximum operating pressure for the tanks is 100 psi. 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 resin should be able to remove 0.002 to 0.010 kg Cu/L resin (0.1 to 0.5 lbs Cu /ft^3). However due to premature plugging, the actual lifetime is less than 20% of the projected life (Eger, 2009).

Table 3. Soudan Underground Mine State Park: Copper and Cobalt, August 2009- August 2010

Date	Total Copper Monthly Average (limit = 17)	Total Copper Daily Maximum (limit = 42)	Total Cobalt Monthly Average (limit = 4)	Total Cobalt Daily Maximum (limit = 9)
July 2009	Ion exchange system installed			
August	14	20	<2	<2
September	8.7	9.1	<2	<2
October	8.5	9.3	<2	<2
November	13	15	<4	<4
December	4.8	5	<2	<2
2010				
January	11	15	<2	<2
February	4.5	4.9	<3	<4
March	8	9	2	2
April	6.5	8.9	<4	<4
May	5.3	8.6	<2	<2
June	12	18	<4	<4
July	9.7	10	2	2
August	7.4	11	<4	<4
September	8.7	14	<2	<2

Data as reported by Northeast Technical Services on the monthly Discharge Monitoring Reports

Since the mine discharge is at a state park, the goal has always been to design a system that would be easy to operate and have as little maintenance as possible. A variety of passive treatment options have been evaluated in the past, but unfortunately timelines and compliance schedules have forced the park to move toward more and more active approaches. Physical filtration initially appeared to provide a cost effective approach. High efficiency or absolute filters (filters that remove over 90% of the particles of a given size) were evaluated and although successful in removing the suspended Cu from the discharge, plugged after only about 1 day of operation. Lower efficiency or nominal filters (filters that remove only about 60% of the particles of a given size) were inexpensive and could be changed once to twice per week with an estimated annual operating cost of about $15-20,000. However, since the ion exchange tanks cost $10,000 for each exchange, the reduction in tank life by about 80% has greatly increased the projected cost for the overall treatment. As a result, the use of the fine grained ceramic media seemed to be a reasonable next step.

Removal with this media has been much higher than the nominal filters but comes with increased cost and maintenance since instead of just changing filters, the media will have to be backwashed and the solids settled and filtered. Projected capitol cost for a 3-tank system with each tank capable of treating 150 gal/min would be at least $100,000. This system would be capable of treating the maximum flow of 300 gpm. Based on the initial pilot test, the media would have to be backwashed about every other day at average flow, and twice a day at peak flow (Table 4). Additional costs would be incurred for settling tanks, a filter press to remove the solids and solids disposal. Some of these costs would also be associated with treating the backwash from the existing carbon tank. Overall, it appears that the ceramic media may be a more cost effective approach (Table 5).

Table 4. Ceramic media Backwash volume

Bed volumes prior to backwash, pilot	850 -1000 bed volumes
Total gallons treated between backwash in full scale (assuming 1 tank with 2 feet media)	162-190,000 gallons
Backwash frequency at average daily flow (86400 gal/day)	~2 days between backwash
Backwash frequency at maximum daily flow (432000 gal/day)	~ ½ day between backwash
Volume of backwash(estimate) Full-scale	1500-2000 gallons
Estimated mass of solids removal per year	600-1200 kg dry

Since the toxic form of trace metals is the dissolved form, Minnesota Rules do allow a permit to contain a total to filtered ratio. After treatment, about 30% of the Cu was in the filtered form and the average ratio of unfiltered to filtered copper was 3.4 (Eger, 2010).

If the average value was applied to the copper limit, the average concentration limit would increase from 17 to 57 µg/l. Additional sources of Cu have been identified in the mine and were collected and routed to the ion exchange treatment system underground.

Table 5. Estimated cost comparison between filtration options

Filtration	Equipment cost	Annual filter cost	Additional pretreatment Before ion exchange	Annual Pretreatment cost[1]	Total annual operating cost
Filter bags Filter cartridges	5,000 10,000	4000 12,500	Yes Carbon tank	30,000 + additional costs for periodic backwash	46,500+ cost for solids handling
Ceramic media	100,000	0[2]	???[3]	Frequent backwash	Cost for solids handling

[1] assumes carbon tank replaced about 4 times per year (~ 8 million gallons per tank)
[2] Media projected to last for at least 10 years
[3] If ceramic media is effective; no carbon tank would be needed

Since that change was made, Cu concentrations in the water pumped out of the mine decreased significantly (Fig. 7). Currently the total Cu is less than the maximum allowable value in the permit (42 µg/l) and the dissolved fraction is less than the average permit value of 17 µg/l.

Although the total/filtered ratio would help bring copper into compliance, essentially all the cobalt is in the filtered form. However, in-mine treatment of a high Co source could reduce the overall Co to around 4 µg/l which could bring the mine into compliance without expensive surface treatment.

Conclusions

Fine grained ceramic filter media offers an approach to remove suspended Cu from the Soudan mine discharge. Unfortunately it increases capitol costs above standard bag and cartridge filtration, but should provide a payback in about 3 to 7years. Additional testing of the pilot unit will occur this winter with a full scale field trial planned for the summer of 2011.

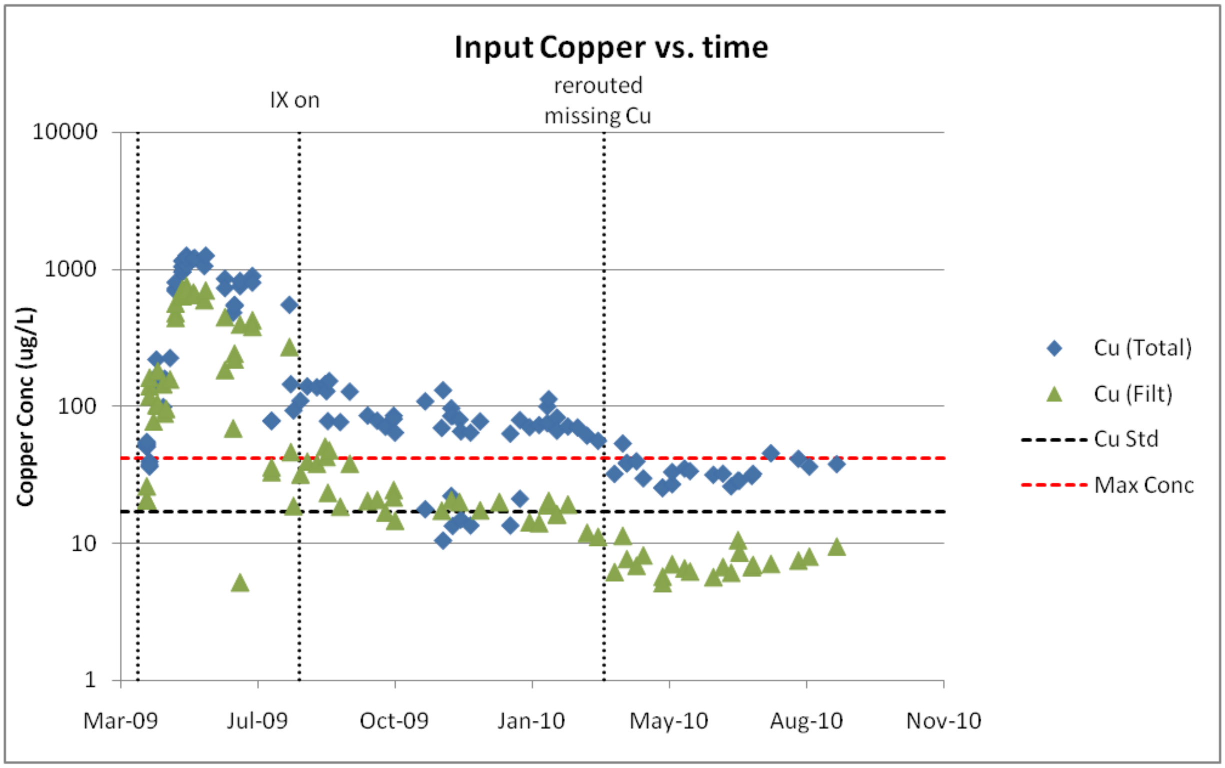

Figure 7. Copper vs. time, Soudan mine discharge

References

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.

Eger, P., 2009. Mine Water Treatment at Soudan State Park. Proceedings America Society of Mining and Reclamation, 2009 pp 400-412. http://dx.doi.org/10.21000/jasmr09010400.

Eger, P., 2010. Modular Ion Exchange Treatment of Mine Water at Soudan State Park, Proceedings America Society of Mining and Reclamation, 2010 pp 248-264. http://dx.doi.org/10.21000/JASMR10010248.