MINE WATER TREATMENT AT SOUDAN STATE PARK [1]

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Abstract: Soudan State Park contains an underground iron mine which discharges on average around 60 gallons per minute. Annual average concentrations of copper ranged from 0.083 to 0.5 mg/L and 0.006 to 0.026 mg/L for cobalt, both in excess of current permit standards.

The Department of Natural Resources has been working on the site for over 10 years. However, due to budget problems, land ownership issues, internal policies and an unexpected change in water quality, the discharge still exceeds standards. In 2006, the Department was fined and signed a stipulation agreement. A consulting firm was hired to evaluate treatment options and recommended building a wetland treatment system. A sulfate reducing bioreactor and an aerobic polishing pond was proposed. Construction, which was to start in June 2008, was bid at about $600,000.

The new permit authorizing the construction included a mercury monitoring requirement. Northern Minnesota lakes have fish consumption advisories due to elevated mercury levels and low level mercury monitoring is part of all new NPDES permits. Total mercury of 40 – 60 ng/l, much higher than the 6.9 ng/l standard, was measured in the 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 mercury, low levels of methyl mercury could be produced. Given the high level of mercury 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 copper and cobalt without increasing methyl mercury. Three systems were evaluated including; ion exchange process, peat pellets (APTsorb^{TM}) and chemical treatment with a rotating cylinder. The RCTS^{TM} was chosen for additional evaluation. Preliminary results have indicated that treatment with magnesium hydroxide could achieve permit levels for copper and cobalt.

Additional Key Words: wetland treatment, rotating cylinder treatment system, ion exchange, peat pellets, copper, cobalt, mercury

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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 (Fig. 1).

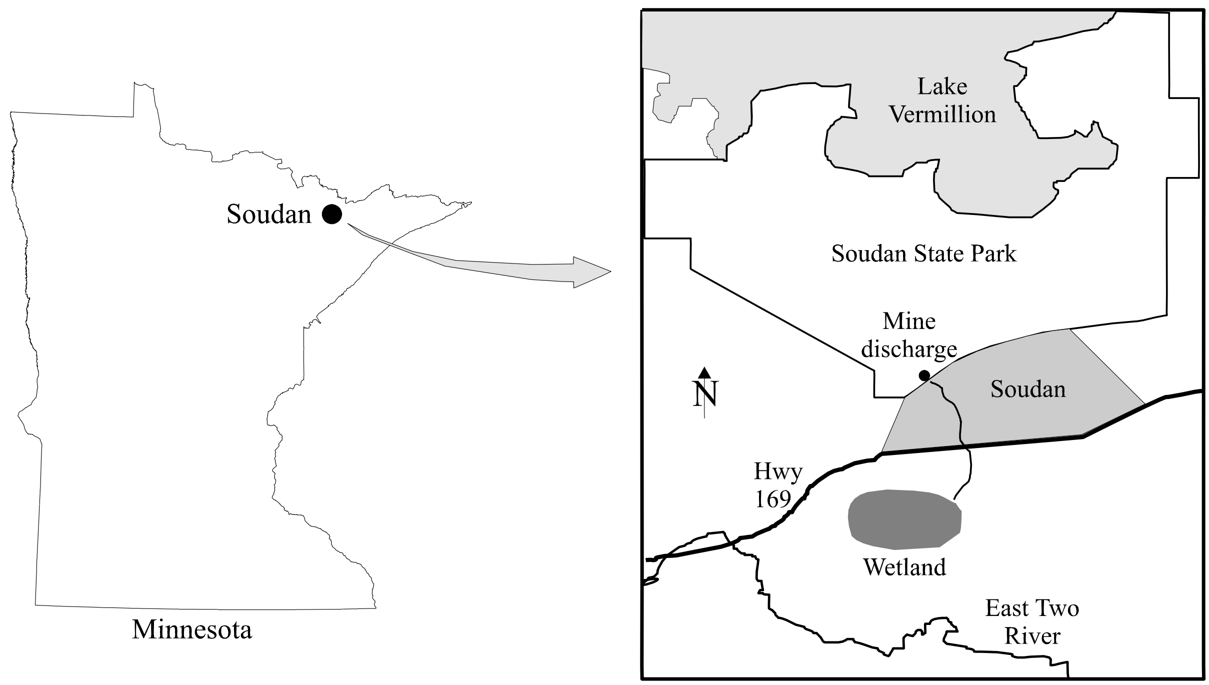


Figure 1. Soudan State Park.

In order to keep the mine dry, an average of 60 gpm is pumped to the surface and discharged. Although this water is circumneutral, it contains Cu and Co that exceed state water quality standards. The pH typically ranges from 6.5-7.5, with annual average concentrations ranging from 0.083 to 0.5 mg/L Cu and 0.006 to 0.026 mg/L Co (Eger, 2007). Current water quality limits are 0.017 mg/L for Cu and 0.004 mg/L for Co. The objective of this paper is discuss new challenges and to provide an update on the attempts to solve the problem.

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 Cu load and 44% of the total Co load came from a single site near the upper levels of the mine (site 10NT, Fig. 2) (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 limits in the permit at that time.

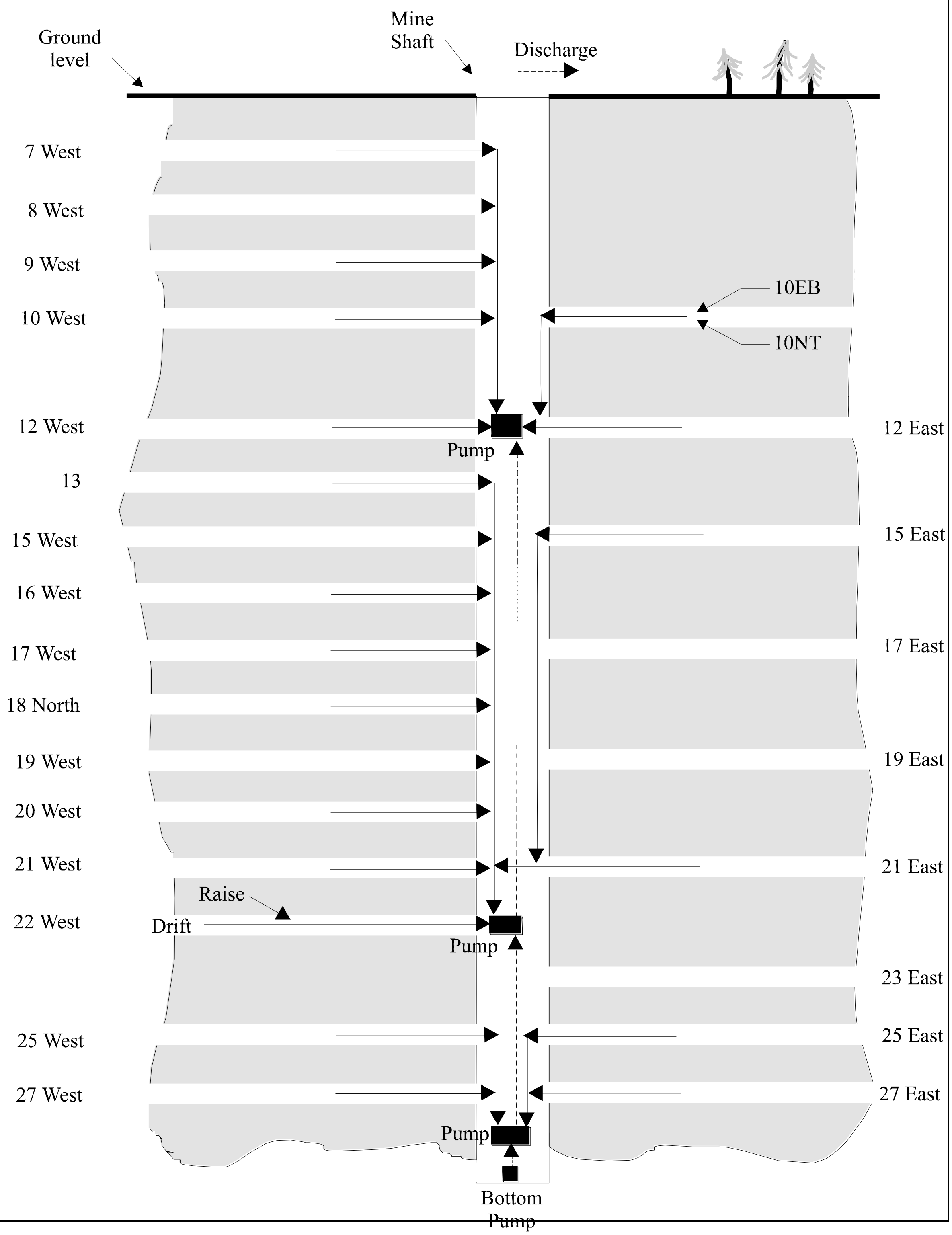
A standard ion exchange system was employed to remove Cu and Co from the source. Shortly after the ion exchange resin was installed, the system became plugged with a precipitate that was primarily Al. This problem had not been observed in previous samples or in bench scale testing. As a result, the system 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. A consulting firm was hired to evaluate a variety of treatment options.

Treatment Options

A number of treatment methods were evaluated for treatment of the discharge:

- Constructed Wetland
- Chemical Precipitation
- Reverse Osmosis
- Ion Exchange
- Passive Organic/Limestone Treatment
- Pipeline to City of Tower Treatment Plant

Figure 2. Flow and sample sites in Soudan Mine.



Total capital costs ranged from $410,000 for a chemical precipitation plant to 5.4 million dollars for a new lagoon cell for the city of Tower wastewater plant. The lowest annual operating costs were for the constructed wetland ($13,600-32,500) and these were about an order of magnitude lower than the other on-site options (Table 1) (Barr Engineering, 2006). Barr recommended that the discharge be treated with a constructed wetland treatment system

Table 1. Cost of treatment options, Barr Engineering, 2006

Treatment Option	Capital Cost, $	Annual operation/ Maintenance, $	Comments
Constructed Wetland	683,000	13,600-32,500	
Chemical Precipitation	410,000	594,000	
Reverse Osmosis	584,000	206,000	Brine disposal not included
Ion Exchange	192,000	277,000	
Passive Organic/Limestone Treatment	532,000	186,000	Includes substrate replacement every 12 years
Pipeline to City of Tower Treatment Plant	5,400,000	75,000	Requires new lagoon to handle additional flow

SEH and Golder Associates were selected for the design contract and proposed a system including an anaerobic sulfate reducing bioreactor and an aerobic polishing pond. Bench testing was conducted to select a treatment media and collect preliminary data on performance. The final design included a settling pond, two sulfate reduction cells and an aerobic polishing cell (Fig. 3). Construction would cost about $700,000 and was scheduled to begin in June 2008.

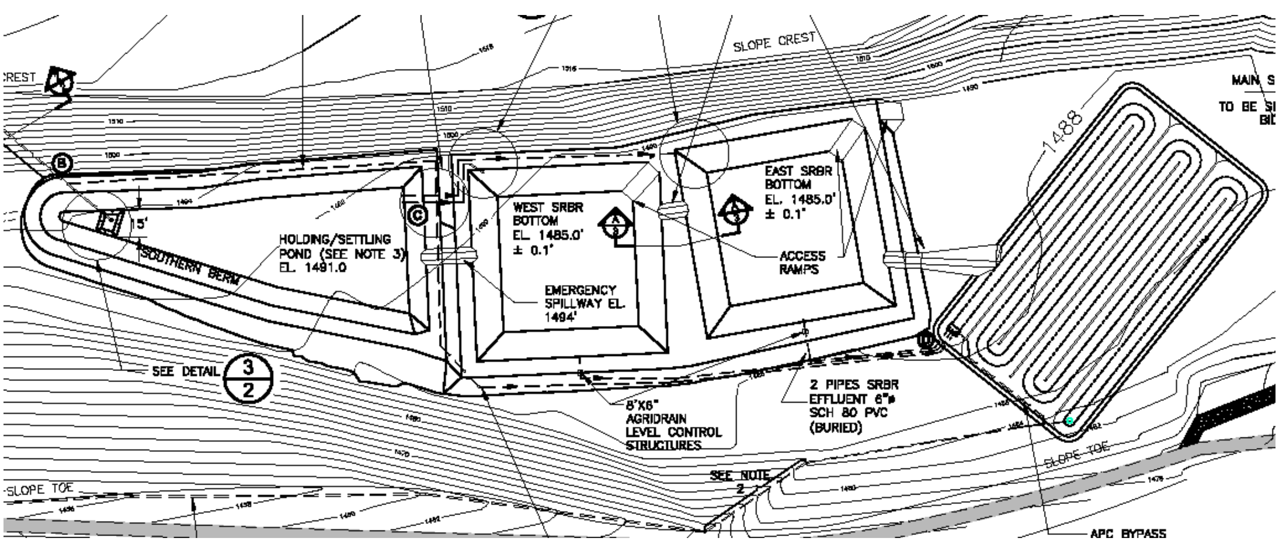


Figure 3. Proposed wetland treatment system

Mercury

The new permit authorizing the construction of the treatment system included a Hg monitoring requirement. Since most lakes in northern Minnesota have fish consumption advisories due to elevated Hg levels, the state is working to control all discharges of Hg and has added low level Hg monitoring to all new NPDES permits. Hg standards range from 1/3 ng/L for waters that drain to Lake Superior to 6.9 ng/L for all other waters.

Mercury samples were collected according to EPA method 1669 and analyzed with cold vapor atomic fluorescence spectrometry (EPA method 1631. Samples of the overall discharge contained total Hg of 40 – 60 ng/l or about an order of magnitude higher than the standard. Filtered values were only about 5-10% of the total values with some concentrations below the standard. Samples were collected at various levels in the mine in an attempt to identify a specific source. Total concentrations were elevated throughout the upper portion of the mine with some values exceeding 100 ng/l. Filtered values were less than total, but still exceeded the standard at a number of sites (Table 2).

Limited data from previous studies had shown that although wetland treatment systems could remove total Hg, low levels of methyl Hg were produced (Eger et al., 2004, King et al., 2002, Nelson et al., 2002). Given the high level of Hg in the discharge and the concern over methyl Hg production, construction was postponed. The Department was asked to develop an interim treatment process that would reduce Cu and Co without increasing methyl mercury.

The systems needed to be installed relatively quickly and handle the entire flow from the mine. Although the overall annual average discharge is 60 gpm, the mine is dewatered with large float activated pumps that typically surge at 150 gpm but during spring flow surge to 300 gpm. Since there is no equalization pond, the system must be designed to handle the entire peak flow. In addition since this site is on the state historic register, any treatment system must be approved by the State Historic Preservation Office and needs to be designed to blend with the historic nature of the park as much as possible.

Three systems were evaluated including expansion of the existing ion exchange process, using peat pellets (APTsorb produced by American Peat Technologies) and chemical treatment with a rotating cylinder (RCTS, Ionic Water Technologies).

Table 2. Summary of Mercury Sampling, Soudan Mine, 2008

Location	Date	Description	Total ng/L	Filtered ng/L	Split sample	
Samples from lowest portion of mine					Total ng/L	Filtered ng/L
27th West	5/28		3.2			
27 East	5/13		7.6			
23 to 25	5/13	collected in drain on level 27	11.9			
Water pumped into level 22	5/28	Includes all water from below level 22, collected as it is pumped into sump on level 22	9.5			
	7/30		8.1			
	8/27				7.9	2.2
Samples from middle portion of mine						
22 and 21	5/13	Water draining from level 22, includes water that drains down from level 21	70.9			
	7/30				124	40.1
13 –20	5/13	Water collected as it drains into sump on level 22	155			
Water pumped into level 12	5/13	Includes all water from below level 12, collected as it is pumped into sump on level 12	103			
Samples from upper portion of mine						
	7/30		102			
	8/27				62.7	3.7
12 East	5/13	Major single flow into mine	29.9			
	7/30		25.3		25.1	9.3
	8/27				23.5	11.2
12 West	5/13		137			
	7/30		157			
10N (via 11)	5/13	Major source of copper	7.2			
	7/30		17.7			
10 East	5/13		37.4			
10 West	5/13		24			
7 to 9	5/13	collected in drain on level 12	40.6			
Overall discharge						
SD001	5/28		59.7	9.8		
SD001	4/24		35.9			
SD001	4/08		40.6			
SD001	7/30		53.6	4.9 (4.8)	66.8	3.5 (2.4)
SD001	8/27				52.9	4.4 (3.7)

At the time of sample it had been piped to level 11 in an attempt to remove Al
Prior to ion exchange treatment
Water currently routed directly to 12, does not currently contact level 11
( ) values, filtered through a 0.2 micron filter

Description of treatment options

Ion Exchange A standard ion exchange system designed by Siemens using a cation resin is currently being used to treat the major metal source in the mine (Fig. 4). Influent Cu ranges from around 3 – 30 mg/l and Co from about 0.2-0.4 mg/l. Ion exchange effectively reduces both Cu and Co to less than 0.005 mg/l. A proposal was developed to use the same technology to treat the entire flow. In order to handle the entire flow from the mine, much larger cylinders would be needed. As a result, the system would need to be installed at the surface and would require a heated building. Estimated installation cost was about $70,000 and the annual operation and maintenance cost was estimated to be on the order of $150,000 (Table 3).

Table 3. Comparison of Treatment Options

System	Installation Cost, $	Annual operating cost Estimates, $	Shut down current ion exchange unit on Level 10	Advantages	Disadvantages
Standard Ion Exchange, Siemen Corporation	70,000	150,000	Yes	Well established treatment technology, minimal maintenance Disposal cost and handling by supplier	Expensive, requires multiple tanks and filters
Ion Exchange, American Peat	150,000 a	90,000 + media replacement and disposal	Possibly	Have tested product	Not tested on large scale, will reduce concentrations but may not meet long term limits, effective on Cu, less effective on Co
Chemical Treatment, Rotating Cylinder, Ionic Water Technologies	120,000 b	Will vary depending on chemical and required dose 20,000-50,000	Yes	Chemical treatment standard technology, will achieve long-term Cu limit, mobile can be set up quickly, can handle peak flow from mine of ~ 300 gpm	Sludge handling, particularly for winter operation, rotating cylinder new application, achieving long-term Co limit

Bids do not include building
a includes tanks and initial media, assumes 5 changes of media per year (17,000 media + 5000 disposal)
b need settling pond or solids removal system

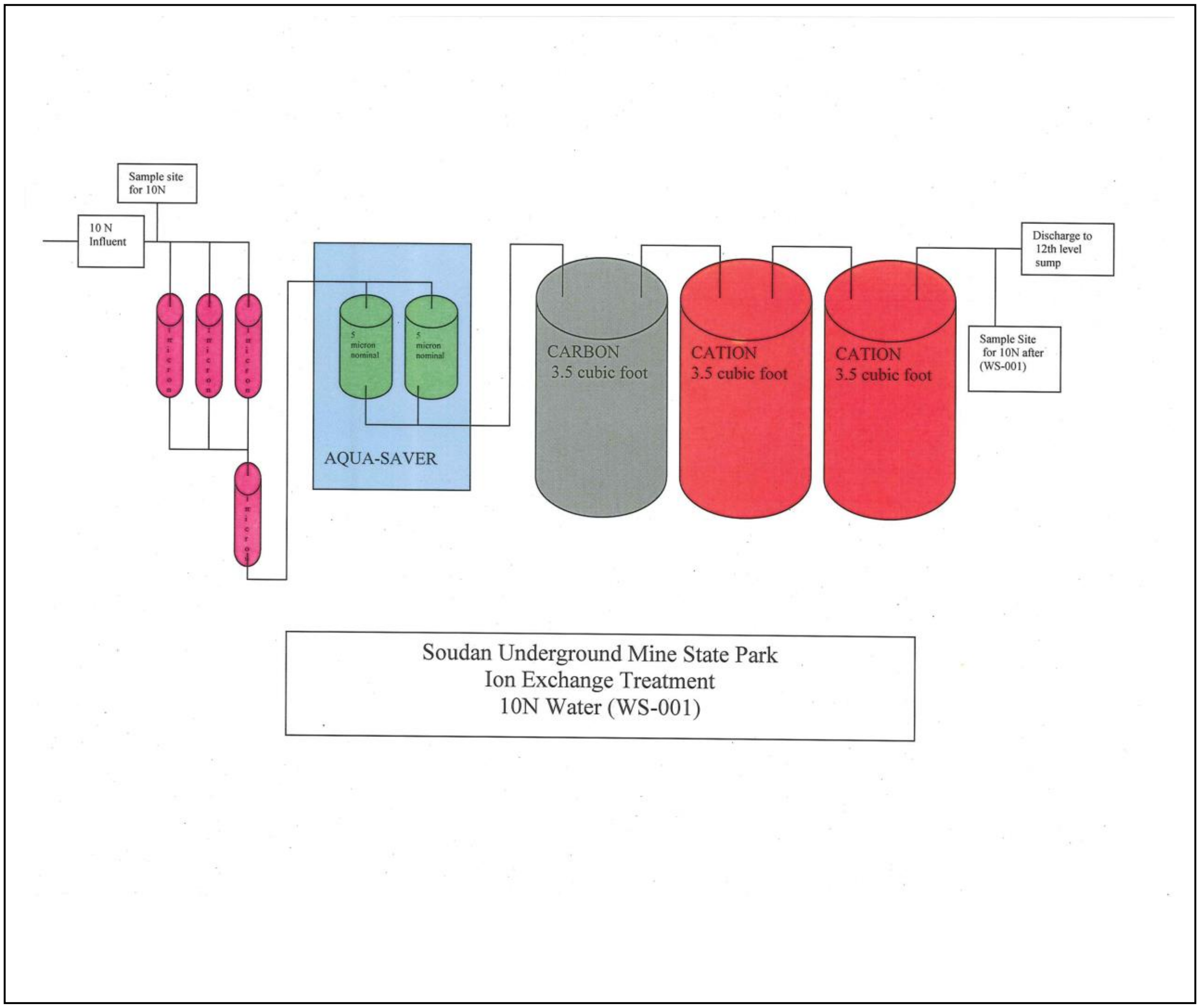


Figure 4. Current ion exchange system

APTsorb (Peat Pellets) 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. American Peat Technologies (APT) has developed a process to convert loose peat into hardened pellets called APTsorb™ (Patent pending) (Fig. 5, 6). 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 good; with estimated conductivities in excess of 1 cm/sec. Pilot tests demonstrated that these pellets could effectively remove Cu and Co from the overall mine drainage. (Eger et al., 2008)

Figure 5. Peat pellets ion exchange media

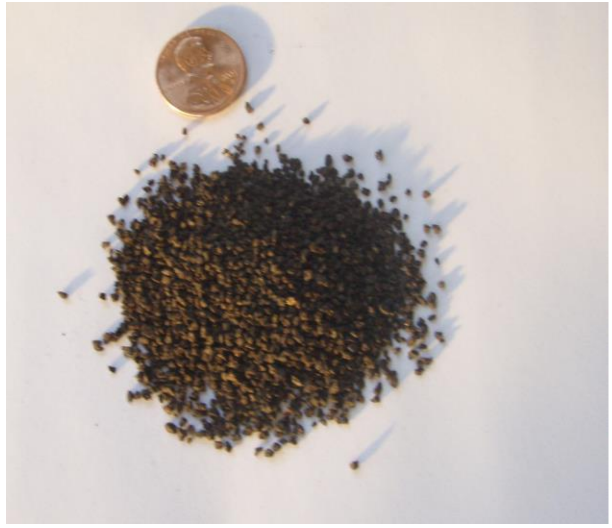


Figure 6. APTsorb

In order to handle the peak flow, a 6000 gallon pressure equalization tank was proposed and 3 large beds constructed from 30 yard roll-offs were proposed. (Fig. 7, 8). American Peat has installed this type of a system at a landfill in northern Minnesota (Green, personal communication). Estimated installation cost was about $150,000 with an annual operating and maintenance cost of around $90,000.

Figure 7. Dumpster for peat pellets

Figure 8. Drainage collection system

Rotating Cylinder Treatment System

The rotating cylinder treatment system designed by Ionic Water Technologies is a mobile unit that can treat up to 300 gpm. (Tsukamoto, 2007)(Fig. 9, 10). This system can apply most neutralizing chemicals commonly used for mine water treatment. The estimated installation cost was about $120,000 with an annual operation and maintenance cost of $20,000-50,000, depending on the chemical selection and dose (Table 3).

Figure 9. Rotating cylinder treatment system

Figure 10. Rotating cylinder

The RCTS was chosen for further evaluation since it was mobile, could be employed quickly and used chemical treatment, and is a widely accepted method for removing trace metals from mine drainage. Typical lime treatment systems increase pH to around 12 and then readjust pH with acid addition prior to discharge. Since one of the goals is to minimize maintenance, a final pH adjustment was not desirable. A bench test was conducted by IWT to determine if Cu and Co could be removed by adjusting the pH to around 9 and precipitating the metals as hydroxides.

Based on previous experience IWT has developed a bench scale test that has provided an indication of the success of RCTS application (Tsukomoto, personal communication). This test involves short term aggressive mixing to simulate RCTS operation. The test evaluated aeration only, lime addition, magnesium hydroxide addition and sodium sulfide addition.

Results

Based on the bench scale test, it appeared that using a fairly high treatment dose of $Mg(OH)_2$ could achieve permit limits with the short contact time in the RCTS. Much smaller doses of lime could potentially be successful, but longer contact times were required (Table 4).

Table 4. Bench test results

	Permit Limits	Untreated		Lowest dose that met standards 526 mg ($Mg(OH)_2$) / L				Best lime treatment 30.8 mg CaO/L			
Contact time				8 ½ min		16 hr		11 min		16 hr	
Parameter		T	F	T	F	T	F	T	F	T	F
pH	6-9	7.75		8.75		8.97		**9.5**		8.54	
Alkalinity mg/L $CaCO_3$		65									
Specific Conductance uS/cm		675									
Copper ug/L	17	405	59		9	8	6		**47**	**79**	16
Cobalt ug/L	4	18	23		5	<1	<1		12	5	4
Iron mg/L		1.860	0.650								
Aluminum mg/l		0.580	0.082								
TSS mg/l	30										

Tests conducted by Ionic Water Technologies 2008
Blanks mean no data were collected, T total, F filtered
Bold values exceed standards

Work in Progress

Bench testing indicated that chemical precipitation can reduce both Cu and Co to permit limits, but removing the precipitated solids offers a short term challenge. Typical RCTS applications use a settling pond for solids removal and a pond is planned for the Soudan site. However, in order to maintain the schedule in the enforcement agreement, full-scale interim treatment must begin by April 1. With temperatures still below freezing in northern Minnesota, the earliest construction could start would be end of May. Interim methods of solid removal including mechanical filtration and the use of coagulants and flocculants are being evaluated.

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