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Controlling Mine Drainage Problems; New Approaches for Waste Rock Stockpiles

Final Report to the Minerals Coordinating Committee

June 2001

Minnesota Department of Natural Resources Division of Lands and Minerals 500 Lafayette Road, Box 45 St. Paul, MN 55155-4045

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Paul Eger David Antonson



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Executive Summary

An MCC funded literature review identified several promising techniques to control the production of acid drainage from waste rock stockpiles in Minnesota (Leopold et. al., 2001). These included:

- Adding limestone to stockpiles
- Using an organic cover material to reduce oxygen transport into stockpiles
- Covering the reactive sulfides with a non-reactive surface

Funding for covering the reactive sulfides with a non-reactive surface was obtained from the U.S. Environmental Protection Agency, through the Mine Waste Management Program in Montana. The current MCC funding was used to initiate a field experiment to investigate the feasibility of adding fine grained limestone to acid generating stockpile material to prevent acid generation.

Fine grained limestone ("manufactured sand") was added to Archean greenstone rock obtained from Soudan State Park. The rock had an estimated neutralization potential (NP) to acid production potential (APP) ratio of 0.33, and rock with similar sulfur content had produced drainage pH below 6 within 4 to 12 weeks in laboratory tests.

Based on the initial rock characterization data, limestone was added to increase the NP / APP ratio to about 1:1 and to about 3:1. The objective of the experiment was to determine the effectiveness of limestone addition to prevent the formation of acid drainage in a field setting. Only one water sample has been completely analyzed so it was not possible to judge the overall effectiveness of the approach. Sampling will continue for the next several years to examine the success of this mitigation method.

1. Introduction

Future metallic mining in Minnesota will likely occur in igneous rock types and would involve the extraction of sulfide ores. Sulfide minerals are not stable when exposed to oxygen; they react to release acid and metals, producing acid mine drainage. Acid mine drainage is a serious environmental problem and has affected water resources throughout the world. Over 10,000 miles of streams in the United States are currently impacted by acid mine drainage from abandoned or existing mining operations. Before any new mining operation is allowed to develop, mining companies must carefully characterize all their potential waste and determine if it will have the potential to produce acid drainage. Methods to control or treat the drainage must be included in the mining plan before any permits can be issued.

Currently there is no proven way to prevent water quality drainage problems from large waste rock stockpiles. The typical approach has been to cover the stockpile at the end of operation with an impermeable cap. Although this approach can substantially reduce the volume of acid drainage, the covers require long-term maintenance and their lifetime is not know. Acid release from tailings has been reduced by storing the tailings under water. Even with this method some metal release occurs (Aube et al., 1995). The only other widely accepted approach is drainage collection and treatment using an active treatment system. Since mine drainage problems can persist for hundreds of years, collection and treatment is an expensive and usually unacceptable alternative.

2. Objective

The goal of this study is to examine the effectiveness of adding limestone to waste rock to control acid generation, and to compare the effect of different limestone addition rates.

3. Background

There is a high potential for future metal deposits to be developed in the Duluth Complex formation or the greenstone belts of northern Minnesota. Extensive waste characterization and mitigation testing of Duluth Complex material under both laboratory and field conditions have been conducted since the late 1970's (Lapakko et al., 1998), while greenstone material has not been evaluated. Sulfide-bearing greenstone material was identified at Soudan State Park and was removed during 2000 to construct an underground cavern for the expansion of the University of Minnesota's physics laboratory. This material was selected for laboratory and field waste characterization studies and for use as an acid generating material for mitigation tests (Lapakko et al., 2001).

Limestone Addition to Reactive Mine Wastes

General Description of Limestone Addition for Acid Neutralization

Acid release from reactive mine waste may be decreased by the mixing of alkaline solids with the rock. The alkaline solids neutralize acid produced by the oxidation of sulfide minerals. This neutralization has three secondary effects. First, the elevated pH yields an environment which is unsuitable for *Thiobacillus ferrooxidans*, a strain of bacteria which catalyzes sulfide mineral

oxidation. The elimination of these bacteria limits the rate of sulfide oxidation, and therefore, the rate of acid production. Second, the elevated pH enhances the oxidation of ferrous iron and the subsequent precipitation of ferric oxyhydroxides. If the pH is elevated in the immediate neighborhood of iron sulfide mineral surfaces, precipitates will form on the mineral surface. This impedes chemical transport to and from the iron sulfide mineral surface, and consequently, inhibits iron sulfide oxidation and the attendant acid production. Third, as pH increases the equilibrium concentrations of trace metals decrease. The decrease in concentrations is due to increased trace metal precipitation (as hydroxides, oxides, and/or carbonates) and adsorption.

An important factor in the balance between acid production and acid neutralization is the relative masses of the iron sulfide and carbonate minerals. The alkaline dosage requirement can be estimated based on theory or empirical evidence. The theoretical alkalinity requirement can be calculated by assuming that each mole of sulfur produces two moles of acid. Calculation of the acid-producing sulfur content should be based on sulfur associated with iron sulfide minerals. It can also be assumed that each mole of calcium carbonate consumes two moles of acid.

Applications

Numerous studies have been conducted on the application of alkaline materials to neutralize acid released from reactive mine wastes. In general, laboratory results have been promising, whereas field results have been generally less successful. The main problems in the field have been achieving a good mixture of the alkaline material with the waste rock, and preferential flow within large waste rock stockpiles. Most applications at metal mines have either layered acid producing rocks with acid consuming rocks, or tried to blend materials by dumping alternate loads of acid consuming and acid producing material. The problem with the layered approach is that acid is generated within the acid producing layer and, due to preferential flow, is not completely neutralized by the acid consuming layer. Similar problems occur in the approach where the loads are dumped in an alternate manner. The challenge is to develop an approach where the acid consuming material is well distributed throughout the pile and in intimate contact with the acid producing material.

Although visually most stockpiles appear to consist solely of large particles, the interior of these piles contains substantial quantities of fine grained materials. For underground operations, based on the material removed from the AMAX shaft, 38% of the material was less than 1 inch; silt and clay size material comprised about 3% of the mass of the pile (Eger et al., 1980b, Lapakko et al., 1986). Specific surface area increased from $0.6 \text{ m}^2/\text{g}$ for the coarse sand fraction to 2.6 to 4.7 m²/g for the silt and clay fraction. Sulfur content increased from 0.67% for coarse sand to 1.65-1.94% for the silt and clay sized material. As a result, most of the reactive sulfide surface area of the pile was contained within this fine grained material and generated the majority of the acid in the stockpile. Therefore, in order to control acid production reactions within the stockpile, neutralizing material needs to be mixed with the fine- grained material. Adding sand-sized limestone to the stockpile may provide sufficient neutralization to decrease the rate of acid production.

One method to achieve a thorough mixing of the limestone with the acid producing material would be to add the correct amount of limestone to each haul truck as the truck leaves the pit. The truck could drive under a hopper where the limestone would be added directly to the top of the load. This type of system is currently used at the Gold Quarry Mine in Nevada, although the purpose is to add lime to gold bearing sulfide rock to maintain neutral conditions in the leach pad. The limestone would begin to mix with the waste rock as the truck drives to the waste dump and then would be further mixed as the material is dumped.

Fine grained limestone was incorporated into large waste rock stockpiles at the Flambeau Mine in Ladysmith, Wisconsin. A thorough analysis of rock composition and acid generation potential was conducted prior to backfilling the material into the completed open pit. The goal was to prevent acid drainage by incorporating a sufficient amount of limestone to neutralize the existing acidity within the material and any acidity generated prior to the material being submerged by the ground water. To determine the appropriate rate of limestone addition, test pits (each approximately 15 feet deep) were dug into the stockpile and samples were collected and analyzed. Once the acid production potential and the current acid load was calculated, the correct amount of limestone was placed on top of the lift that was to be moved. (The stockpile was moved in 15 foot lifts to correspond with the rock characterization data.) As the rock was picked up and placed in the truck, mixing occurred. Additional mixing occurred as the rock was backfilled into the pit. The pH in the groundwater wells within the backfill has remained neutral since the mine was closed (Lynch, 2001).

4. Methods

Experimental Design

A field test examining the effectiveness of mixing limestone with waste rock to prevent acid generation is presently in progress at the MN DNR Research Site in Hibbing, MN. Three treatments were applied; an untreated control, and 2 limestone treatments. The limestone treatments were designed based on the initial data from the stockpiled rock. The target values were a 1:1 ratio of neutralization potential to acid production and a 3:1 ratio (Appendix 2). Each treatment was constructed in duplicate.

Materials

The limestone mixing tests are being conducted in six polyethylene plastic tanks (d = 48", h = 42"). The tanks are housed in a 20' x 20' lined bin that serves as a double containment system (Figure 1), and are comprised of two control tanks (tanks 1 and 6), two tanks with limestone mixed at an estimated 1:1 ratio (tanks 2 and 5), and two tanks with limestone mixed at an estimated 3:1 ratio (tanks 3 and 4). The tanks were fitted with $\frac{1}{2}$ -inch slotted PVC outlet pipe on the bottom, which drained into a 22 gallon polyethylene plastic sample collection sump (Figure 2). The bottom of the outlet pipe was installed approximately 2 inches above the bottom of the tank. To prevent the waste rock from being permanently saturated, three inches of silica sand was placed in the bottom of each tank. The tanks were then filled to a depth of approximately 31 inches with either rock (control tanks) or rock mixed with limestone, yielding a bed volume of 32.4 cubic feet. Bulk density of the rock was 108.2 lbs/ft³ and was measured by weighing a 5 gallon container of broken rock. Using this density the mass of the bed was calculated as 3506 pounds. The limestone had a bulk density of 86.6 lbs/ft³. The tanks were filled on October 24, 2000 and the only input to the tanks will be from precipitation.

The rock used was Archean greenstone obtained from the Soudan underground mine state park in Soudan, MN. The University of Minnesota initiated a project to enlarge its underground physics laboratory at the park, which resulted in the removal of approximately 22,000 cubic yards of greenstone rock. Before beginning the rock removal a drill hole was bored through the center of the cavern to characterize the rock. The rock was then blasted and removed in four lifts. The explosives used were 75% ANFO, a commercially-prepared combination of ammonium nitrate and fuel oil, and 25% Mine Rite, an ammonium nitrate based water gel. As the rock was removed the walls of the cavern were sealed with "Shot-crete", a mixture of portland cement containing 11% silica fume and $-\frac{1}{2}$ " aggregate.

During the removal of the top lift several drill cuttings samples were collected and, along with the drill core, were analyzed for percent sulfur. Based on these analyses, areas within the bottom three lifts were selected as target zones for obtaining a range of sulfur contents to be used for the field waste characterization tests at the DNR's field research site in Hibbing, MN.

Once an identified area had been blasted, approximately 50 cubic yards of rock was removed from the mine in approximately 1½ cubic yard muck boxes. As each muck box was emptied into a pile a random sample was taken and placed in a one-gallon plastic container for subsequent analyses, to ensure the rock was suitable for the field tests. A total of 25 samples were taken each time an identified area was removed from the shaft. Sulfur analyses were performed at Lerch Bros. in Hibbing, MN. If the results were suitable the rock was loaded into 10 cubic yard dump trucks and hauled to the research site.

One of the 50 cubic yard samples selected and hauled to the research site had a mean sulfur content of 0.67%. This rock was selected for use in the alkaline mixing experiment. The rock was screened to minus $1\frac{1}{2}$ - inch at Casper Construction Inc. in Grand Rapids, MN. A bobcat loader was used to fill the tanks, with the exception of tank 5, which could not be reached with the loader. Instead of shoveling the rock into the tank, the rock was shoveled from the loader into five gallon buckets. These buckets were then dumped into the tank. Three bucket loads were placed in each tank, the loader positioned the bucket just above the tank and the rock was randomly shoveled into the tanks.

For the tanks that had the rock mixed with limestone, the loader scooped a bucket of rock. The limestone (1/3 of the total addition), which had been weighed, was then distributed uniformly over the rock in the bucket (Figure 5). A 1-gallon representative sample of rock was collected randomly from each loader bucket, prior to adding the limestone for the alkaline mixing tanks, for a total of 3 samples per tank. The sample was split, crushed, ground and analyzed. A total of 55 pounds of limestone was added to the 1:1 ratio tanks and 165 pounds to the 3:1 ratio tanks (Appendix 2).

The three rock samples from each tank were composited and a representative split as well as a sample of the limestone were sent for analyses. Samples were analyzed at ACTLABS, Inc. (Tucson, AZ) for total sulfur, sulfate, evolved carbon dioxide as well as whole rock and trace element concentrations (Tables 1 and 2). The limestone used was described by the company as "manufactured sand" and was obtained from CAMAS, Shiely Division, in Eagan, MN. Particle size distribution for the rock samples and limestone was determined by Lerch Bros., in Hibbing, MN (Table 3). Percent moisture of the limestone (5 %) was determined at the MN DNR.

Flow and Water Quality Sampling

The six limestone addition tanks were equipped with a $\frac{1}{2}$ -inch slotted well screen at the base of the tank to collect the drainage. A $\frac{1}{2}$ -inch PVC pipe was plumbed from the outside of the tank to a 22-gallon collection sump. The sump was calibrated in five liter increments and total flow was measured with a ruler. A grab sample for analyses was collected directly from the sump and the sump was then emptied.

The sample schedule has been designed to collect samples on a bi-weekly basis and after selected large rain events. Precipitation is the only water input to the tanks. One inch of precipitation is equivalent to about 30 liters of input water. A 250 mL sample was taken for pH, specific conductance, alkalinity (if pH exceeded 6.30) or acidity, metals, and sulfate analyses. These samples were analyzed for pH and specific conductance directly in the bottle. A 20 mL sample was then taken for analysis of alkalinity or acidity. The remaining sample was filtered for metals and sulfate analysis. Metal samples were acidified with 0.2 mL of Baker Instra-Analyzed nitric acid per 50 mLs. Periodic samples for nutrients (500 mLs) were also taken. Nutrient samples were acidified with 2 mLs of Baker Analyzed sulfuric acid per 500 mLs.

An Orion SA 720 pH meter equipped with a Ross combination pH electrode (model 8165) was used for pH analyses, and a Myron L model EP conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al., 1992). Sulfate was analyzed at the Minnesota Department of Agriculture (MDA) laboratory using the Ion Chromatographic Method (Wastewater Method 4500-SO₄ B) with an Dionex DX300 IC. Ca, Mg, Na, and K samples were analyzed at MDA using a Varian 400 SPECTRAA atomic absorption spectrophotometer in the flame mode.

Trace metals for the initial sample were analyzed at MDA using inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A). Nutrient analysis were conducted at MDA using the Automated Cadmium Reduction Method (Wastewater Method 4500-NO₃ F) on a Technicon AA11 for Nitrate + Nitrite Nitrogen, the Ammonia-Selective Electrode Method (Wastewater Method 4500-NH₃ F) on an Accumet 950 pH/ion meter for Ammonia Nitrogen, the Ascorbic Acid Method (Wastewater Method 4500-P E) on a Perkin Elmer 552 Spectrophotometer for Total Phosphorus, and the Semi-Automated Colorimetric Method (EPA 351.2) with a Bran&Luebbe Traacs 800 for Total Kjeldahl Nitrogen.

5. Results

Materials

Total sulfur for the six samples ranged from 0.40% to 0.56%, with an average of 0.49%. Based on the average sulfur content of the original stockpile (0.67%), the acid production potential was calculated to be 20.9 lbs $CaCO_3$ equivalent / 1000 lbs for the original stockpile and 15.3 lbs $CaCO_3$ equivalent / 1000 lbs for the average composition of the material in the tanks (Table 2). Neutralization potential of the original stockpiled material, calculated using the Sobek procedure, was 6.3 lbs $CaCO_3$ equivalent / 1000 lbs. The estimated neutralization potential (NP) to acid production potential (APP)

was 0.33 (Appendix 2). Additional neutralization potential measurements will be conducted on the samples collected from the alkaline mixing tanks. Trace metal concentrations were low and ranged from less than detection (generally 1- 5 mg/kg) to an average of 142 mg/kg for zinc (Table 2).

Water Quality

After the tanks had been set up, only one sample was collected before the system froze. The sample was collected on November 7, 2000. Additional samples were collected in the spring of 2001 but the analyses could not be completed in time to be included in this report. There was little difference in the pH between the control and the limestone tanks with all values ranging between 7.42 to 7.61. Trace metal concentrations were low in all the samples but nitrate-nitrogen concentrations were extremely high, ranging from 391 to 697 mg/L (Table 4).

6. Discussion

With only one water quality sample analyzed so far, it is obviously too early to judge the effectiveness of the limestone addition. With an estimated NP / APP ratio of around 0.33, the control tanks are expected to generate acid drainage. Laboratory reactors containing greenstone with sulfur content similar to the greenstone in the tanks (0.39 to 0.50% S), produced drainage with pH less than 6 within 4 to 12 weeks. By adding limestone the overall NP / APP ratio was raised to around 1:1 and 3:1. In general, a material with an NP / APP ratio in excess of 3:1 is expected to produce neutral drainage. Samples will continue to be collected to investigate the long term trends.

The elevated levels of nitrate are most likely related to residual concentrations of the blasting agent, which was a mixture of ammonium nitrate and fuel oil. Data collected from field test piles of waste rock from the AMAX test shaft indicated that nitrate concentrations decreased over time to levels consistent with the values in the input precipitation (Eger et al., 1980).

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Parameter	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6	Limestone
S	0.56	0.40	0.50	0.46	0.55	0.48	0.01
S ²⁻²	0.54	0.34	0.48	0.44	0.53	0.46	0
SO4 ²⁻ as S	0.016	0.06	0.02	0.016	0.02	0.02	0.016
CO2	0.40	0.37	. 0.22	0.44	0.44	0.48	<0.05
Al ₂ O ₃	13.86	13.09	12.53	13.12	13.28	13.00	0.47
CaO	0.41	0.37	0.26	0.46	0.32	0.43	27.63
Fe ₂ O ₃	10.65	8.83	8.61	9.38	10.30	9.31	0.87
K ₂ O	1.86	2.03	1.95	1.91	1.85	2.09	0.29
MgO	3.59	2.96	2.91	3.26	3.41	2.89	18.82
MnO	0.068	0.065	0.053	0.089	0.065	0.059	0.081
Na ₂ O	0.36	0.38	0.30	0.39	0.34	0.38	<0.01
P ₂ O ₅	0.15	0.12	0.10	0.12	0.13	0.21	0.03
SiO2	64.70	68.40	69.30	65.96	65.38	67.32	9.68
TiO2	0.587	0.458	0.452	0.522	0.519	0.514	0.026
LOI	4.19	3.73	3.62	3.89	4.02	3.72	41.95
TOTAL ²	100.42	100.44	100.08	99.11	99.60	99.92	99.78

Table 1. Whole rock chemistry (percent) of field limestone addition tanks. Analyses by ACTLABS, Inc.

¹Determined by difference. Values less than the detection limit are assumed to be 0.

²For parameters from Al₂O₃ through LOI.

Parameter	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6	Limestone
Ag	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
As	5	3	6	3	5	4	2
Ац	<5	<5	<5	<5	6	5	<5
Bi	<2	<2	<2	<2	<2	<2	<2
Br	<1	<1	<1	<1	<1	<1	7
Cd	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Co	26	20	21	22	24	22	2
Cr	105	75	65	75	71	76	5
Cs	2.2	2.7	2.0	2.4	2.1	2.5	<0.5
Сц	67	36	44	45	44	45	7
Hf	5.5	6.6	6.3	5.9	6.6	6.5	<0.5
Mo	<5	<5	<5	<5	<5	<5	<5
Ni	97	69	69	82	76	75	3
РЪ	<3	<3	6	<3	5	<3	<3
Rb	68	67	63	57	54	71	<20
Sb	0.3	0.3	0.3	0.3	0.3	0.3	<0.2
Se	<3	<3	<3	<3	<3	<3	<3
ľr	<5	<5	<5	<5	<5	<5	<5
Та	<1	<1	<1	1	1	<1	<1
W	<3	<3	<3	<3	<3	<3	<3
Zn	158	132	132	147	149	135	17

Table 2.Trace metal contents of material in field limestone addition tanks. Analyses by ACTLABS, Inc.; concentrations in mg/kg.
Page 1 of 2.

Parameter	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6	Limestone
Ce	57	76	74	63	72	73	6
La	26.9	34.8	33.2	28.1	32.7	33.3	2.4
Ĺu	0.66	0.85	0.76	0.84	0.82	0.86	<0.05
Nd	27	33	35	31	34	36	<5
Sc	18.1	13.6	13.6	16.2	16.3	15.4	0.5
Ть	0.8	1.1	0.9	0.9	1.0	1.2	<0.5
Th	4.0	5.6	4.9	4.7	4.7	4.9	<0.5
U	1.1	1.3	1.7	0.9	1.1	1.2	0.9
УЪ	4.3	5.5	4.9	5.4	5.2	5.5	0.2
Sm	6.0	7.5	7.3	6.2	7.2	7.4	0.4
Eu	1.2	1.5	1.4	1.2	1.3	1.5	0.1

Table 2.Page 2 of 2. Trace metal contents of material in field limestone addition tanks. Analyses by ACTLABS, Inc.; concentrations in mg/kg.

FRACTION	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6	Limestone
2"	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1 1/2"	97.1	97.3	91.3	90.1	88.9	95.3	100.0
1"	68.2	77.4	80.2	72.6	77.5	82.4	100.0
1/2"	43.3	40.5	53.2	52.4	61.7	54.8	100.0
1/4"	31.5	27.2	37.5	36.2	43.8	42.0	100.0
4M	27.1 ·	22.9	32.4	31.1	37.8	37.8	100.0
10M	16.7	14.2	19.6	18.7	23.1	25.3	87.9
20M	12.6	10.8	14.4	13.6	16.9	19.5	57.1
28M	10.8	9.3	12.0	11.4	14.1	17.0	41.8
35M	9.5	8.2	10.2	9.9	12.1	15.3	30.2
48M	7.8	6.7	6.9	7.9	9.6	13.3	18.5
65M	6.2	5.5	5.1	6.3	7.6	11.6	9.0
100M	5.4	4.6	4.7	5.2	6.3	10.4	4.5
200M	3.4	2.8	2.5	3.1	3.7	8.2	1.4
-200M							

Table 3.Particle size distribution of rock used in field limestone addition tanks and limestone
(percent passing). Analyses by Lerch Brothers, Inc.

Note: All samples were dry screened with the exception of Tank 6, which was wet screened for comparison.

Parameter	Contro	Control Tanks Limestone Tanks Limestone T (1:1 ratio) (3:1 ratio		Limestone Tanks (1:1 ratio)		ne Tanks ratio)
	1	6	2	5	3	4
Volume (L)	35.3	32.7	36.7	34.7	39.0	36.0
Conductance	7500	5600	5000	5800	5700	5750
pН	7.42	7.61	7.46	7.55	7.59	7.61
Alkalinity	50	55	50	60	65	60
Ca	926	689	708	1090	925	785
Mg	104	82.1	84.5	144	112	99.1
Na	257	249	242	396	329	278
K	38	32.8	34.9	54.6	46.3	38.7
Fe	0.393	0.289	0.269	0.491	0.444	0.319
Al	<0.002	< 0.002	< 0.002	< 0.002	0.055	<0.002
Mn	0.0336	0.0477	0.0658	0.0651	0.0694	0.0275
Cu	0.0181	0.0136	0.018	0.0217	0.0183	0.0156
Ni	0.0062	0.0043	0.0055	0.0062	0.0047	0.0042
Со	0.007	0.0053	0.0054	0.0081	0.0071	0.0059
Zn	0.0044	0.003	0.018	0.0075	0.0022	0.004
SO ₄	683	496	733	673	694	374
Si	4.14	3.88	3.08	3.73	4.62	3.97
Total P	0.082	0.082	0.085	0.075	0.093	0.082
NH ₃ -N	1.68	1.49	1.31	1.28	3.69	1.30
NO ₃ -NO ₂	515	391	546	480	697	407
TKN	6.8	4.8	5.3	4.1	8.1	3.5

Table 4. Initial water quality sample for field limestone addition tanks (sample taken on 11/07/00). Specific conductance in μ S, pH in standard units, and all other concentrations in mg/L.

Additional flow occurred between 11/7 and 11/13 but was not sampled. Flow (in liters) was as follows:

Tank 1 = 19.3, Tank 2 = 22.0, Tank 3 = 18.3, Tank 4 = 11.3, Tank 5 = 7.6, Tank 6 = 22.6

Figure 1. Limestone addition tanks set up with double containment.



Figure 2. Details of limestone addition tank setup.



Figure 3. Greenstone rock used for the alkaline mixture experiment.



Figure 4. Limestone used for the alkaline mixture experiment. The limestone product was purchased from Aggregate Resources' Larson Mine on Grey Cloud Island and is called a manufactured sand.



Figure 5. Adding limestone to the loader bucket. Limestone was added to the top and distributed over the rock.



Figure 6. Limestone in loader after addition.



Figure 7. Adding rock and limestone to tanks. The material was scooped from the bucket into the tank.



Figure 8. Rock in tank, 2001.



Figure 9. Alkaline mixture experimental setup, 2001.



Appendix 1

Field notes and observations

10/24/00 - Filled all 6 tanks.

10/27/00 - 1.29" rain on 10/26. No flow out of any tank.

11/2/00 - 0.77" rain. No flow.

11/6/00 - 0.15" rain, tanks are about 1/5 full, by 1130 all flow had slowed to a slow drip.

11/7/00 - 0.96" rain. Measured water volume with rain stick (in). First sample collected from tanks (~750 mL). Pumped water out of sumps. Unable to get all water out so remeasured water for leftover volume. Tanks still flowing at a slow drip (10 to 20 mL/min).

11/8/00 - All tanks still dripping slowly. Measured volumes at 0924.

11/9/00 - All tanks outlet pipes arefrozen (1530). Measured volumes.

11/13/00 - Rain and snow over the weekend. All tanks had frozen outlet pipes, however, must have been slight flow. Measured volumes (1245), pumped out water and sponged tanks dry.

11/14/00 - No flow, all outlet pipes are frozen.

Precipitation Summary:

10/24 - 11/7 = 3.33 inches

11/8 - 11/14 = 0.19 inches

Appendix 2

Calculation of limestone addition rates

This appendix contains information on the bulk material from which the rock for the alkaline addition experiment was obtained and the calculations for the amount of limestone to be added to each tank.

Acid production potential

Based on the average S content of the field test pile (0.67%, Table A2.1), the acid production potential was calculated to be 20.9 lbs $CaCO_3$ equivalent / 1000 lbs . Neutralization potential, calculated using the Sobek procedure, was 6.3 lbs $CaCO_3$ equivalent / 1000 lbs (Table A2.2). Based on the average of six samples from the tanks, the average S was 0.49%, which is equivalent to an acid production potential of 15.3 lbs $CaCO_3$ equivalent / 1000 lbs.

Acid production potential :	0.67% S x 3.125	= 20.9 lbs CaCO ₃ equivalent / 1000 lbs
Neutralization potential:		6.3 lbs CaCO ₃ equivalent / 1000 lbs
Net		14.6 lbs CaCO ₂ equivalent / 1000 lbs

Total rock in the tanks was 3506 lbs. Therefore, for a 1:1 ratio we needed: $3.506 \ge 14.6 = 51$ lbs (actual additon 55 lbs.). Only add enough limestone to provide the missing neutralization potential.

For a 3:1 ratio the total neutralization potential should be 3 times the acid generation rate, so would need:

$3 \ge 3.5 \ge 20.9 =$	219	lbs CaCO ₃ equivalent
inherent NP	22	lbs CaCO3 equivalent
added limestone	55	lbs CaCO3 equivalent

Need an additional 142 lbs limestone, only added 110 lbs, so final NP to APP ratio would be 2.6

if use average S content for tanks, and assume the NP is the same, then

$3 \ge 3.5 \ge 15.3 =$	161	lbs CaCO ₃ equivalent
inherent NP	22	lbs CaCO ₃ equivalent
added limestone	55	lbs CaCO ₃ equivalent

Need an additional 84 lbs. limestone, added 110 lbs, so final NP to APP ratio is 3.5.

Table A2.1. Sulfur analysis for field test pile, source of material for alkaline addition tanks.

25 samples were collected to determine the overall sulfur content of each test pile. The variation of the sulfur content for the field pile which averaged 0.67% is shown in this table.

S content in individual muck box samples
0.29
0.33
0.42
0.45
0.46
0.47
0.48
0.50
0.56
0.58
0.59
0.64
0.66
0.69
0.74
0.75
0.76
0.77
0.79
0.80
0.94
0.94
1.02
1.04
1.09

Table A2.2. Mineralogical content of laboratory samples. Analyses by Louis Mattson, Pengilly, MN.

Mineralogy was determined for each sample in the laboratory characterization experiment. The data in the following table is for greenstone samples that contain sulfur in the range of the material in the alkaline addition experiment.

Mineral	0.39% S	0.50% S	
Pyrite	0.7	0.9	
Melanterite	0.1	0.3	
Siderite	<0.1	4.6	
Quartz	59	59	
Chlorite	21	12	
Sericite	16	21	
Na-Feldspar	1	1	
Ilmenite	1.2	0.4	
Hematite	Trace	0.6	
Magnetite	Trace	Trace	
Apatite	0.3	0.1	
Zircon	<0.1	0,1	
Tourmaline	Trace	Trace	

% Total S	0.67%
%Sulfide S	0.634
SO ₄ as S	0.032
CO ₂	0.462
S_iO_2	65.99
Al ₂ O ₃	12.85
Fe ₂ O ₃	10.48
MnO	0.089
MgO	3.38
CaO	0.226
Na ₂ O	0.203
K ₂ O	1.90
T _i O ₂	0.515
P ₂ O ₅	0.132
LOI	4.02
Total	99.78

Table A2.3.Average whole rock composition of field test pile. Average of data from the 25 muck
box samples.

Sample	pH after H ₂ O ₂	mLs to pH 7.0	pH 7.0 NP	mLs to pH 8.3	pH 8.3 NP	mLs back to pH 8.3	pH 8.3 Final NP
1-1	2.09	16.4	9.0	ns	ns	ns	7.2 est.
1-2	2.04	16.9	7.75	ns	ns	ns	5.95 est.
1-3	2.10	16.9	7.75	ns	ns	ns	5.95 est.
1-4	2.19	16.7	8.25	ns	ns	ns	6,45 est.
1-5	2.06	16.5	8.75	ns	ns	ns	6.95 est.
1-6	ns	16.35	9.125	ns	ns	ns	7.3 est.
1-7	2.02	15.9	10.25	ns	ns	ns	8.45 est.
1-8	2.02	16.8	8.0	ns	ns	ns	6.2 est.
1-9	2.01	16.0	10.0	ns	ns	ns	8.2 est.
1-10	1.93	16.5	8.75	17.3	6.75	17.4	6.5
1-11	1.93	16.6	8.5	17.3	6.75	17.4	6.5
1-12	2.11	17.3	6.75	18.0	5.0	18.1	4.75
1-13	2.01	17.0	7.5	17.5	6.25	17.6	6.0
1-14	1.96	15.7	10.75	16.3	9.25	16.4	9.0
1-15	1.96	17.3	6.75	17.7	5.75	17.8	5.5
1-16	1.98	16.7	8.25	17.2	7.0	17.3	6.75
1-17	1.96	16.9	7.75	17.3	6.75	17.4	6.5
1-18	1.99	18.1	4.75	18.6	3.5	18.7	3.25
1-19	2.00	16.6	8.5	18.2	4.5	18.3	4.25
1-20	1.96	16.8	8.0	17.4	6.5	17.5	6.25
1-21	1.96	17.2	7.0	17.8	5.5	17.9	5.25
1-22	1.97	16.6	8.5	17.2	7.0	17.3	6.75
1-23	1.92	17.2	7.0	17.8	5.5	17.9	5.25
1-24	1.96	16.9	7.75	17.4	6.5	17.5	6.25
1-25	1.95	16.2	9.5	17.3	6.75	17.4	6.5
Blank	1.64	20.1	0	ns	ns	ns	ns

 Table A2.4.
 Neutralization Potentials for 0.67% total sulfur greenstone rock.

Calculated NP = $10.5 \text{ kg CaCO}_3/t$

 $\begin{array}{l} \mbox{Mean NP at pH 7.0} = 8.2 \mbox{ kg CaCO}_3/t \\ \mbox{Mean NP at pH 8.3} = 5.95 \mbox{ kg CaCO}_3/t \\ \mbox{Mean NP at pH 8.3 using est. values} = 6.32 \mbox{ kg CaCO}_3/t \end{array}$

Sample	reactor(s)	%S	Sobek pH 7.0 NP	Peroxide pH 7.0	Sobek pH 8.3 NP	Peroxide pH 8.3 NP	
571	1	0.02	-2.5	2.75	-5.0	1.25	
572	2	0.06	4.5	4.75	2.25	4.0	
573	3	0.09	4.0	5.75	2.5	5.25	
574a	4 & 5	0.12	5	6.75	3.0	6.0	
574b	4 & 5	0.12	6	6.25	3.5	6.25	
575	6	0.12	0.5	3.0	-1.0	2.25	
576	7	0.15	0.75	4.0	0	3.25	
577a	8&9	0.18	2.75	3.75	1.0	3.0	
577b	8&9	0.18	1.5	na	2.25	na	
578	10	0.23		4.0		3.25	
579	11	0.29		3.5		2.75	
580	12	0.39		5.25		4.75	
581	13	0.59		4.0		3.25	
582a	14 & 15	0.65		1.5		0.75	
582b	14 & 15	0.65		8.75		7.75	
583	16	0.78		9.75		8.75	
584a	17 & 18	1.36		5.25		4,5	
584b	17 & 18	1.36		na		na	

 Table A2.5.
 Greenstone reactors NP determinations using Sobek and Modified ABA with peroxide.