Toxicity Treatment Evaluation of Mine Final Effluent- Using Chemical And Physical Treatment Methods

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Abstract

An initial toxicity identification evaluation (TIE) protocol determined that ammonia, nitrate/nitrite, cyanide, cyanate, dissolved organic carbon, copper and zinc were possible toxicants in a gold mine effluent.

Therefore, a bench-scale toxicity treatment evaluation (TTE) of a gold mine effluent was investigated. The objective was to produce a treated effluent that is non-acutely lethal (non-toxic) to rainbow trout and *Daphnia magna*. Six treatment options were evaluated to remove or reduce toxicity caused by the suspected contaminants. The six treatments investigated included: (1) Granular activated carbon (GAC) + zeolite; (2) air stripping + GAC; (3) zeolite + GAC; (4) multi-stage GAC; (5) alkaline chlorination + dechlorination; and (6) bentonite clay based polymers.

This paper presents the test results obtained. Based on the bench-scale evaluation, results were compared and one option was selected as a preferred treatment to proceed to the capital and operational cost estimate. The paper also presents the results of the capital and operational cost estimate.

Background

SGS Lakefield Research Limited conducted a toxicity treatment evaluation (TTE) and process development for Agnico-Eagle Mines Limited Division Laronde mine and mill final effluent waters (Laronde effluent). The treatment process objective was to produce final effluent that is non-acutely lethal (non-toxic) to rainbow trout and *Daphnia magna*.

The base case TTE evaluation was conducted on a representative sample of final effluent that was a mixture of treated tailings water, treated acid rock drainage, and treated water pumped from the underground mine that was collected at Laronde in May 2001. The TTE evaluation tests were completed in May, June and July and the findings are presented in this paper.

Verification Analyses

The sample of effluent water collected at Laronde in May 2001 was shipped to SGS Lakefield Research for verification of chemical composition and toxicity prior to bench-scale testing. The data included as Table 1 presents the chemical composition of the final effluent sample collected in May 2001 compared to historical effluent and sedimentation ponds' chemistry and toxicity data. The chemical composition of the May sample was verified by Laronde staff, and the sample was deemed representative for use in water treatment tests to reduce toxicity.

Procedures and Results of Water Treatments Tested To Reduce Toxicity

Six treatment processes were tested to remove or reduce toxicity caused by the contaminants identified as potential toxicants, namely ammonia, nitrate/nitrite, cyanate / thiocyanate, dissolved organic carbon (DOC), copper and zinc. The six processes tested were:

- Multi-stage granular activated carbon (GAC);
- Air stripping + GAC;
- GAC + Zeolite;
- Zeolite + GAC;
- Alkaline chlorination + dechlorination; and
- Bentonite clay based polymers.

The flowsheets illustrating the testing procedures for each process are included as Figures 1 through 6.

The summary of the results of chemical and bioassays obtained for the six processes tested are presented in Table 2. The results will be discussed in the following section.

Discussion of the Results

The results for the six chemical and physical water treatments tested will be discussed in detail in this section, beginning with Multi-stage Granular Activated Carbon (GAC).

Multi-stage GAC

The multi-stage GAC flowsheet is presented as Figure 1. The GAC was packed into four columns (in series) and the final effluent was passed through the column at a rate of 4 bed volumes per hour (maximum theoretical). Successive bed discharge volumes were collected for chemical analysis and toxicity testing.

Bed volumes were selected for analysis of total ammonia, nitrate, nitrite, DOC, cyanate, thiocyanate, dissolved metals. Table 2 shows that compared to the baseline chemical analyses, the multistage GAC process reduced the hardness slightly from 1820 mg/L (as $CaCO_3$) in the untreated sample, to 1440 mg/L (as $CaCO_3$), indicating that calcium fouling of the carbon may be occurring. Concentrations of cyanide, nitrate, nitrite, DOC and copper were reduced to below the analytical method detection limits (MDL).

The multi-stage GAC treated sample was non-lethal to *Daphnia magna*, but was acutely lethal to rainbow trout (LC50 = 48.8%). As expected, the GAC treated sample was toxic to rainbow trout as a result of elevated ammonia concentrations. The predicted Toxicity Units (TU=9.15) exceeded the measured TU (2.05) for rainbow trout. Based on the treated sample chemical composition, ammonia (TU = 9.15) accounted for all of the rainbow trout mortality observed. In the case of *Daphnia magna*, the predicted TU (1.35) was only slightly higher than the measured TU (<1).

Air Stripping plus GAC

The flowsheet used for this test is presented as Figure 2. The final effluent was adjusted to pH 11 with hydrated lime. The temperature was maintained at ambient (where reaction rates may be slightly faster than at colder temperatures). The pH-adjusted water was air stripped for a total of 10 hours and sub-samples were collected at 1, 5 and 10 hours. To minimize carbon fouling with calcium carbonate, the air stripped water was adjusted to a pH of approximately 8.0 using carbon dioxide prior to being pumped into the GAC column. Bed volumes were collected and a sub-sample of the solution was analyzed for: total ammonia, nitrate, nitrite, DOC, cyanate, thiocyanate, dissolved copper and zinc. The "Air Stripping + GAC" treated sample was non-lethal to *Daphnia magna*, but was lethal to rainbow trout. Air stripping treatment was not effective to reduce toxicity to trout because the concentration of total ammonia was only slightly reduced from the baseline of 32.6 mg/L to 23.8 mg/L as shown in Table 2. The predicted TU (5.81) exceeded the measured TU (1.41) for rainbow trout. Based on the treated sample chemical composition, ammonia appeared to account for most of the rainbow trout mortality observed. In the case of *Daphnia magna*, the predicted TU (1.32) was only slightly higher than the measured TU (<1).

Zeolite plus GAC

The flowsheet used for this test is presented in Figure 3. The zeolite and GAC are ion-exchange materials that can treat effluent at natural pH. The zeolite + GAC media will adsorb contaminants until loaded. The main function of zeolite is the removal of ammonia. This zeolite + GAC treatment reduced the concentration of total ammonia from 32.6 mg/L in the untreated sample, to 1.3 mg/L (Table 2). Final treated effluent concentrations of cyanate, thiocyanate, nitrate, DOC and copper were reduced to less than the analytical MDL. Hardness substantially decreased from 1820 mg/L (as $CaCO_3$) in the untreated sample, to 180 mg/L (as $CaCO_3$). The high removal of hardness (as $CaCO_3$) indicates that rapid fouling of the zeolite may be an operational concern. To better utilize the zeolite or to prevent zeolite fouling by Ca, the sample should first be adjusted to pH 6.5 with CO_2 and then decanted to feed zeolite column.

When either GAC or zeolite were used alone, the toxicity remained. However, when they were used in combination in series with each other, they produced a non-toxic effluent to both *Daphnia magna* and rainbow trout. The predicted and measured TUs were less than one for both species.

GAC plus Zeolite

The GAC plus zeolite flowsheet is presented in Figure 4. The treatment reduced the concentration of total ammonia from 32.6 mg/L in the untreated sample, to 0.3 mg/L (Table 2). Hardness was substantially reduced from 1820 mg/L (as $CaCO_3$) in the untreated sample, to 131 mg/L (as $CaCO_3$). The high removal of calcium by the GAC plus zeolite indicates that calcium fouling on the ion exchange materials will likely be an operational concern. The GAC + Zeolite treated effluent sample was non-lethal to rainbow trout and *Daphnia magna.* The predicted and measured TUs were less than one for both species.

Alkaline Chlorination and Dechlorination

The flowsheet for the Chlorination-Dechlorination test is presented as Figure 6. Treatment reduced the concentration of total ammonia from 32.6 mg/L in the untreated sample, to 0.1 mg/L (Table 2). Concentrations of cyanide, nitrate, nitrite and copper were reduced to less than the analytical MDL. DOC decreased from 12.4 mg/L in the untreated effluent to 3.9 mg/L. Sulphate increased slightly from 2200 mg/L to 2500 mg/L.

Alkaline chlorination + dechlorination produced an effluent that was non-toxic to rainbow trout but toxic to *Daphnia magna*. The toxicity to *Daphnia magna* may have been caused by an increased level of total dissolved solids (TDS) from reagent use (lime, sodium hypochlorite, sodium metasulphite) and sulphate, or slight residual chlorine concentrations. Sulphate increased slightly from 2200 mg/L to 2500 mg/L, and since these concentrations were above the LC50 of 2360 mg/L sulphate, it may explain some of the toxicity to *Daphnia magna*.

Clay Based Polymer Treatment

The flowsheet for the clay based polymer test is presented in Figure 6. The treatment increased the concentration of total ammonia from 32.6 mg/L in the untreated sample, to 41.2 mg/L (Table 2). Cyanate, thiocyanate, nitrate, nitrite, DOC and copper concentrations in the untreated sample were 21, 57, 2.78, 22, 12.4 and 0.011 mg/L, respectively. In the treated sample, cyanate, thiocyanate, nitrate, nitrite, DOC and copper concentrations were reduced to 16, 16, 2.6, 18.1, 9.9 and <0.005 mg/L, respectively. Sulphate increased slightly from 2200 mg/L to 2500 mg/L.

In the case of *Daphnia magna*, the predicted TU (2.35) was slightly higher than the measured TU (<1). The Clay Based Polymer treated sample resulted in partial *Daphnia magna* immobilization.

The predicted TU (14.98) was similar to the measured TU (>16) for rainbow trout. However, the measured TU could only be estimated, since the lowest concentration tested resulted in complete (100%) rainbow trout mortality. Based on the chemical composition of the sample, ammonia (TU = 1.75) and nitrite were responsible for the toxicity to trout.

Conclusion: Preferred Treatment

Based on the six bench scale evaluations conducted, the preferred treatment to reduce the toxicity to *Daphnia magna* and rainbow is the GAC plus zeolite option.

Economic Evaluation and Capital Cost Estimate of GAC plus Zeolite

Based on the bench-scale evaluation, the GAC + zeolite option was selected as a preferred treatment to proceed to the capital and operational cost estimate. To treat an effluent at flowrate of 350 m^3/h containing about 60 mg/L of thiocyanate and about 32 mg/L of ammonia using GAC + zeolite, the capital cost was estimated to be US $10.6 (C$15.9) millions. In terms of capital cost per kg of annual contamination removal capacity, the capital cost for the GAC treatment constitutes an investment of US$81 (C$121) per kg in annual CNS removal capacity and the capital cost for the zeolite treatment constitutes an investment of US$103 (C$154) per kg in annual ammonia removal capacity. The operating cost was estimated to be close to one million US dollars annually (C$1.5 M) or US $0.67 (C$1.00) per m^3 of water treated. The operating costs in term of kg of contaminants removed are US$8.48 (C$12.72) per kg of CNS removed for the GAC portion and US$4.95 (C$ 7.42) per kg of ammonia removed for the zeolite portion.

It appears that the GAC + zeolite option is a very expensive treatment. This treatment was rejected due to its high capital and operating costs and because the process was not degrading the contaminants but removing them transferring the concern into solid waste management. It was recommended that alternative lower cost options be investigated and evaluated.

Recommendations For Future Investigation-Alternative Lower Cost Treatments

Additional testing (biological, UV peroxide, etc.) has been recommended to develop other lower cost alternative treatments. The industrial scale biological plant at Homestake mine has demonstrated that biological systems are alternative lower cost options that warrant further investigation

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Table No. 1 Verification Analyses and Toxicity Data

Parameter (mg/L)	SGS Lakefield Research Verification Analyses of Final Effluent (May 6, 2001)	Agnico-Eagle Minesite Historical Final Effluent Analyses (Mar 4/99 – Feb. 20/01)	Beak Nalmet Study Final Effluent Analyses (Dec 16/99 – Feb 20/01)
pH (unit)	8.05	7.8 - 9.2	7.44/9.08
TDS	3320	-	3060/-
CN total	0.05	0.005 - 0.36	0.021/-
CNO	21	3.9 - 231	/50.4
CNS	57	73 -293	-/-
(NH_3+NH_4)-N	32.6	20 - 88	43.8/15.8
NO_2 as N	2.78	-	5.82/34.8
NO_3 as N	22	-	59.4/70.9
SO_4	2200	1350 - 2370	2290/1660
DOC	12.4	35 - 96.6	29.9/89.5
Ca	713	470 - 670	562/540
Cu	0.016	0.02 - 0.14	0.076/0.085
Na	177	-	296/346
Zn	0.02	<0.01 - 0.26	0.358/0.00894
Daphnia magna (48h LC50)	59.7%, 1.7 TU	1 - 50.5 TU	27%, 3.7 TU/15%, 6.7 TU
Rainbow trout (96h LC50)	70.7%, 1.4 TU	1.6 - 27.3 TU	-/-

Table 2 Summary of Test Results after Water Treatment

Parameter	Baseline	GAC+ Zeolite	Air Stripping + GAC	Zeolite + GAC	Multi-stage GAC	Chlorination + Dechlorination	Clay Based Polymer
pH, unit	8.05	8.20	8.25	8.74	8.20	8.02	7.40
(NH_3+NH_4)-N mg/L	32.6	0.3	23.8	1.3	35.5	0.1	41.2
CNO mg/L	21	< 1	1	< 1	< 1	< 1	16
CNS mg/L	57	< 0.2	< 0.2	< 0.2	< 2	< 2	16
NO_2 as N mg/L	2.78	< 0.3	0.17	0.2	< 0.6	< 0.06	2.6
NO_3 as N mg/L	22	< 0.05	< 0.05	< 0.05	< 0.5	< 0.05	18.1
DOC mg/L	12.4	< 1	< 1	< 1	< 1	3.9	9.9
Dissolved Cu mg/L	0.011	< 0.005	< 0.005	< 0.005	< 0.005	< 0.08	< 0.005
Dissolved Zn mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.01
Total Cu mg/L	0.016	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Total Zn mg/L	0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
SO_4 mg/L	2200	2100	2200	2200	2000	2500	2500
Conductivity µmhos/cm	2710	3940	3220	4100	3000	5440	3630
Hardness as $CaCO_3$ mg/L	1820	131	1520	180	1440	1770	1890
DO mg/L	9.4	8.4	8.0	8.6	9.0	8.7	7.6
Mortalities or Immobile							
Daphnia magna, 48h LC50 TU	12 of 12	0	0	0	0	12 of 12	2 of 12
Rainbow trout, 96h LC50 TU	7 of 7	0	7 of 7	0	8 of 8	0	9 of 9
Toxicity Units	TU	TU	TU	TU	TU	TU	TU
Daphnia magna, 48h LC50 TU	1.68	< 1	< 1	< 1	< 1	40*	< 1
Rainbow trout, 96h LC50 TU	1.41	< 1	1.68	< 1	2.05	< 1	40*

**interpolated by convention is >16*

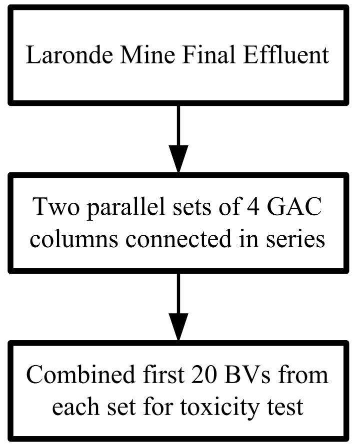

Figure 1 Flowsheet of Bench-scale Multi-stage GAC Treatment Evaluation

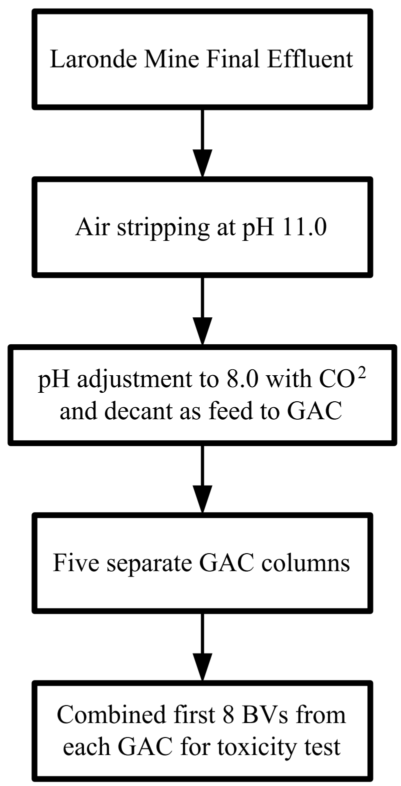

Figure 2 Flowsheet of Bench-scale Air-stripping + GAC Treatment Evaluation

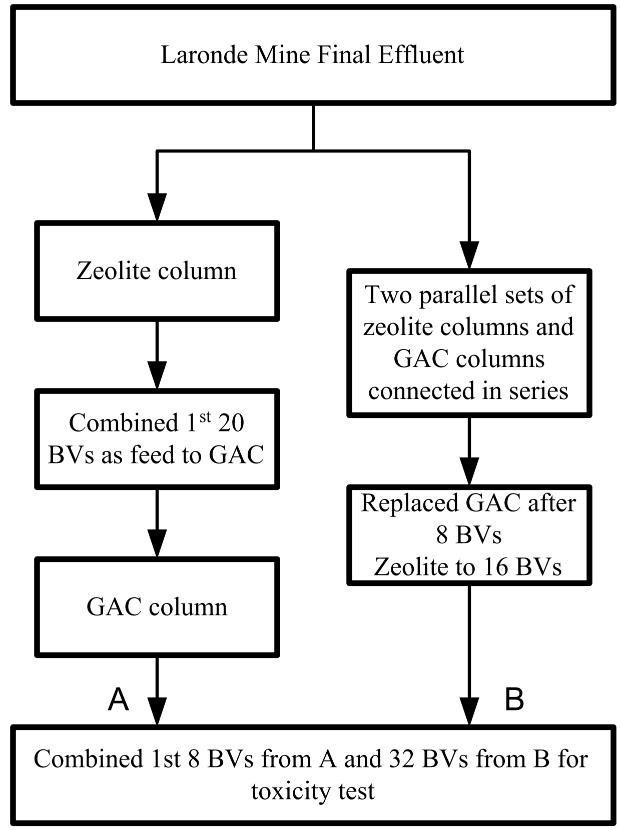

Figure 3 Flowsheet of Bench-Scale Zeolite + GAC Treatment Evaluation

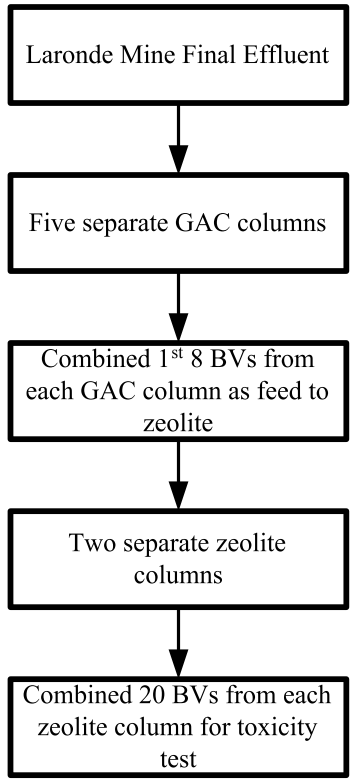

Figure 4 Flowsheet of Bench-scale GAC + Zeolite Treatment Evaluation

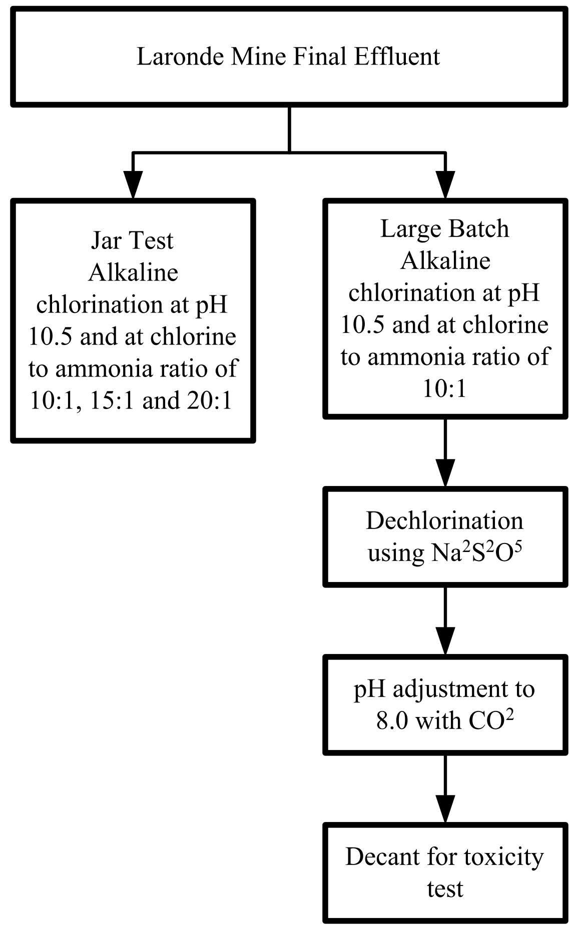

Figure 5 Flowsheet of Bench-scale Chlorination and Dechlorination Treatment Evaluation

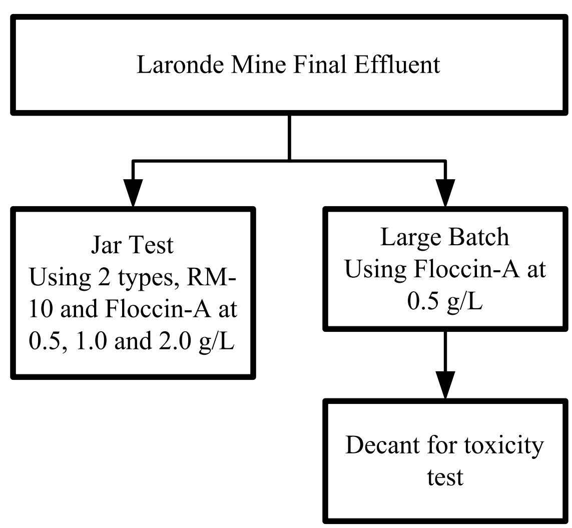

Figure 6 Flowsheet of Bench-scale Bentonite Clay Based Polymer Treatment