

Experimental Constraints for the Source of Sulfate Toxicity and Predictive Water Quality for the Hogarth and Caland Pit Lakes, Steep Rock Iron Mine, Northwestern Ontario, Canada

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Abstract

Two adjacent pit lakes, Caland and Hogarth, were formed after the closure and subsequent flooding of the Steep Rock iron mines, Ontario Canada. The two pit lakes are markedly different in their water composition and quality. Results from the water-rock reaction experiments indicate that the high sulfate concentration and toxicity of Hogarth pit lakes could only be produced from oxidation of pyrite within the buried ore zone by ground water, whereas the near neutral pH of both lakes reflects subsequent interaction with carbonate wall rock. The differences in water chemistry between Hogarth and Caland pit lakes are attributed to differences in the pyrite content of the buried ore zone. Initial toxicity tests using *Lemna minor* (duckweed) indicate that the mixed discharge water will have chronic toxic effects. Further qualitative analysis of toxicity tests will allow for more accurate prediction of these detrimental effects.

Key words: sulfate, aquatic toxicity, *Lemna minor*, pit lakes, water-rock interaction, pyrite oxidation

Introduction

Decommissioning of the Steep Rock iron mines, located in northwestern Ontario, in 1979 has led to the development of Hogarth and Caland pit lakes (see Fig. 1 Conly et al., this volume). Although the geology of the two pits is largely similar (Kusty and Hudleston, 1999; see Fig. 2 Conly et al., this volume), there are distinct differences in water composition and quality: i) Hogarth pit lake is chronically toxic due to highly elevated levels of dissolved sulfate (1200-2000 mg/L); and, ii) Caland is non-toxic and is characterized by moderate levels of dissolved sulfate (200-500 mg/L sulfate). With continued filling, the two pits will merge between 2030 and 260, and discharge into the adjacent Seine river system. The objectives of the study are two use water-rock reaction experiments and toxicity identification evaluation in order to: i) determine the source and control(s) on sulfate levels between the two lakes; and, ii) determine the water quality upon mixing of the pit lakes prior to outflow.

Methods

Water-rock reaction experiments

Three different types of water-rock reaction experiments were conducted:

- 1) PVC reaction columns (e.g., Gilbert et al., 2003) were constructed to simulate ground water-bedrock and rainwater-tailings/waste rock interactions. Crushed rock (1-2 mm particle size) was added to the columns, in addition to a 5 cm layer of carbonate wall rock was added to some of the columns. Approximately 30 mL of water was extracted from each column at three hours, one day, five days, seven days and then each successive week for 14 weeks. At each sampling interval, ground water and rain water stock solutions were added (if required) to ensure that the water level remained at the level of the upper surface of the crushed waste rock.
- 2) Batch experiments (c.f. Newbrough and Gammons, 2002) were conducted to study the interaction between ground water and the different pit wall rock lithologies at varying water to rock ratios. Crushed homogenized 1 to 2 mm rock was combined with water in opaque HDPE bottles at water to rock ratios (by mass) of 100:1, 1:1 and 1:3. The sealed bottles were placed on a shaking bench and left for a period of three months, after which time water was sampled and analyzed.
- 3) Reaction columns were also used to empirically model changes in water chemistry following mixing of the pit lakes and subsequent reaction with wall rocks. The columns were filled with mixtures, at varying ratios, of Hogarth and Caland water and crushed rock, contained in a nylon bag (pore size 100 μ m) that was suspended within the column. The mass of crushed rock used resulted in a water to rock ratio of ~10:1. The mass of the individual lithologies is proportional to the surface area of wall rock in contact with the pit waters at the time of outflow from the two pit lakes.

The chemical composition of the reagent waters (pit lake water, ground water and rain water) and experimental waters was determined accordingly: 1) one aliquot of water was treated with 5% v/v of trace metal grade HNO₃ for cation and trace metal determinations using a Varian Vista Pro ICP-AES; and, 2) a second aliquot of water (untreated) was used for the determination of Cl⁻ and SO₄²⁻ using a DIONEX DX-120 dual channel chromatograph. All analyses were conducted at Lakehead University. Temperature and pH were determined, prior to acidification for ICP-AES analysis, using an Accumet AB15 pH meter.

Toxicity Testing

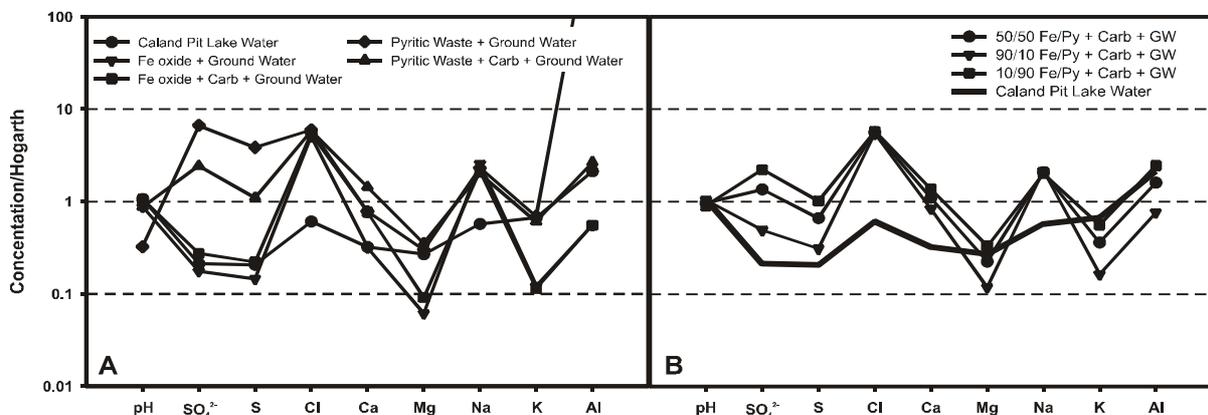
Initial toxicity testing was conducted using a mixing series of varying ratios of water from Hogarth and Caland in order to simulate the water chemistry at the time of merging and discharge of the pits. The toxicity evaluation procedure used is based on Environment Canada's biological test method for measuring the inhibition of growth of *Lemna minor* (Environment Canada, 1999). After 1 week of incubation, all fronds were counted regardless of color, size, or viability and the data analyzed using ToxCalc v5.0. An additional series of water quality tests are currently being conducted, in which the mixed waters are being reacted (over a 3 month period) with crushed pit wall rock in reaction columns (see above) in order to evaluate the effects of water-rock reaction on water chemistry and toxicity.

Results and Discussion

Water-rock reaction experiments

Results from the column leaching experiments indicate that the high SO₄²⁻(aq) concentration of the pit lakes could only be produced from ground water oxidation of pyritic portions of the iron ore zone (Fig. 1a).

Figure 1 Normalized plots, to the average composition of Hogarth pit lake, showing the (A) relative concentration of pH, anions and cations from goethite-hematite and pyrite waste rock reaction column experiments, and (B) results of mixing between leachates derived from goethite-hematite and pyrite waste rock.



To generate the near neutral pH of either pit lake requires subsequent interaction with Mosher Carbonate (Fig. 1a). Figure 1b shows the results of mixing the leachates derived from goethite-hematite and pyrite waste rocks. Consequently, the pit waters are likely produced from the mixing of ground waters derived from both iron oxide and pyritic portions of the ore zone that were subsequently buffered by carbonate wall rock. Ground water interaction with the submerged ore zone is favored because pit water – wall rock interactions (~100:1 water:rock ratios) cannot generate the high sulfate levels (Fig. 2). However, discrepancies between experimental waters and measured Hogarth pit lake water (e.g., Mg) likely reflect: i) interaction of pit lake water with other wall rock units; ii) other ground water contributions (Fig. 2); and, iii) precipitation of saturated mineral phases (goethite + hematite ± gypsum).

Figure 2 Batch reaction results for 100:1 and selected 1:1 water-rock reaction experiments normalized to the average composition of Hogarth water.

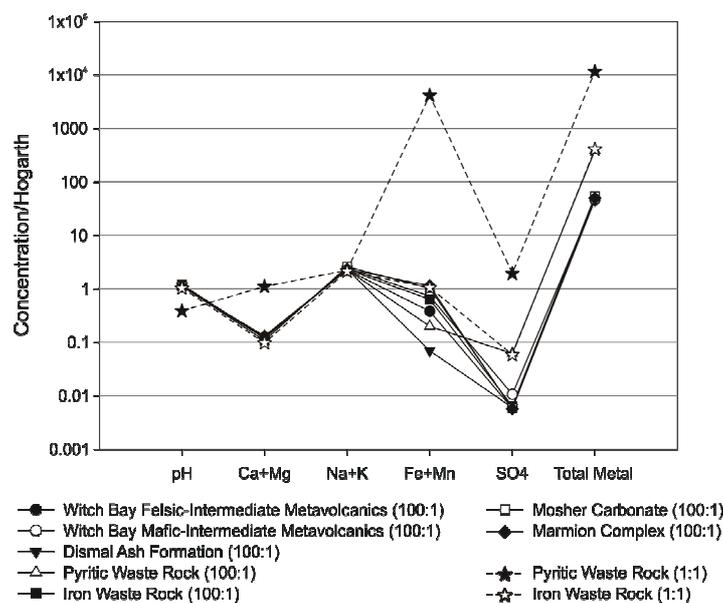
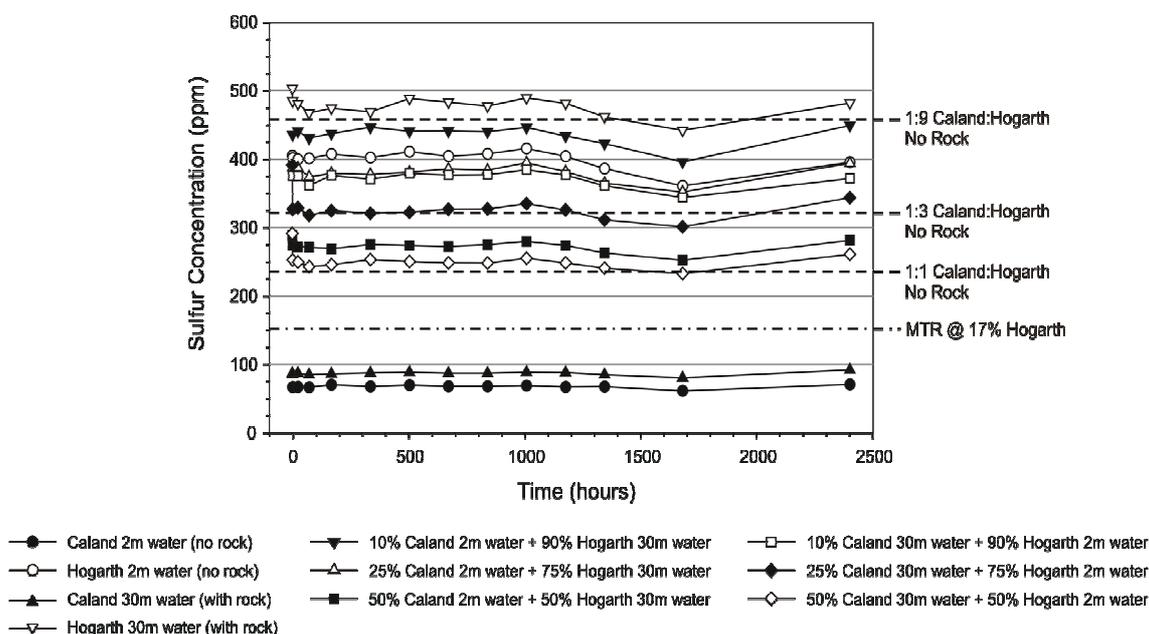


Figure 3 Sulfur concentrations of reaction column experiments for water quality prediction upon outflow in 2030-2060. MTR is the minimum toxic response based on non-rock buffered mixing experiments (see Table 1).



Toxicity testing

Because the toxicity testing procedure was modified in order to use a mixture of the two lakes, our initial analyses reported abnormal results. Normally the test is performed using a dilution series of a toxicant (effluent) and analysis software (ToxCalc v5.0), which compares the number of fronds that grow in relation to the concentration of toxicant. These are all relative to the number of fronds that grow in a sample of pure nutrient media (i.e., toxicant concentration of 0 ml/L). In this experiment the solution that was considered to have 0 ml/L of our toxicant (Hogarth water) was a sample of 100% Caland water. Since it was discovered that the water from Caland had an effect on the growth of the plants our quantitative results (Table 1) did not coincide with qualitative observations.

Table 1 EC-25 values using *Lemna minor* for Hogarth and Caland water mixtures.

Water and Depth	Season and Date	EC-25 value (%)
Hogarth 2m x Caland 30m	Winter 2007	99.9
Hogarth 2m x Caland 2m	Winter 2007	57.8
Hogarth 2m x Caland 2m	Summer 2007	84.6
Hogarth 2m x Caland 30m	Summer 2007	30.6
Hogarth 30m x Caland 2m	Summer 2007	17.7
Hogarth 30m x Caland 30m	Summer 2007	0
Hogarth 2m x Caland 30m	Fall 2007	40.1
Hogarth 30m x Caland 2m	Fall 2007	38

EC-25 value: the effective concentration which inhibits growth by 25%

Summer 2007 Hogarth 30m and Caland 30m mixed water illustrates the limitation of the analysis method, which indicates that the mixed water is not chronically toxic. In fact, it indicates that at full strength, water from Hogarth has no more of a detrimental effect on the growth of the plants than the control water, which in this case was water from Caland. The qualitative observations of this mixture show that this mixture did cause a reduction in growth since there were many fronds that experienced chlorosis and necrosis as well as a reduction in size, all of which indicated chronic toxicity. Therefore, in addition to the quantitative statistical analysis, it is necessary to incorporate qualitative observations to make a more accurate assessment of toxicity. This procedure was repeated and these results were again analyzed using ToxCalc v5.0; however, fronds that were experiencing chlorosis and single fronds (indicating colony destruction) were counted as “dead” fronds. This modification to the method allowed a better understanding of the quantitative results. However, to quantify the qualitative data a computer imaging software program will be used to analyze overall color and coverage area of the fronds in future tests. Toxicity results from rock-buffered mixed water experiments are pending; however, sulfur levels are higher in rock buffered experiments than non-buffered experiments (Fig. 3), suggesting that mixed outflow waters will be chronically toxic.

Conclusions

1. Column and batch experiments indicate that the high sulfate concentration can only be produced from ground water oxidation of pyrite lenses within the buried ore zone, whereas the near neutral pH reflects subsequent interaction with carbonate wall rock.
2. The difference in sulfate concentration between Hogarth and Caland pit lakes is attributed to differences in the pyrite content of the buried ore zone.
3. Assessment of toxicity solely on a statistical basis was found to be misleading. Rather qualitative observations of these mixtures show that many of the fronds display evidence of chlorosis and necrosis as well as a reduction in size, all of which indicate chronic toxicity.
4. At this point many of the initial mixes predict chronic toxicity effects upon outflow. A qualitative analysis is needed and will be carried out to better predict and understand the effects of the mixed discharge water.

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