Treatment of sulphate toxic waters using permeable reactive barriers: batch and flow-through reactor experiments

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Abstract Batch and flow-through reactor experiments have been conducted in order to determine if passive reactive barrier technology could be used to remove sulfate from the pit lake waters at the former Steep Rock iron mine near Atikokan, Ontario, Canada. Batch reactor experiments using horse manure or wood chips + creek sediment (bacterial source) + till + carbonate were successful in inducing bacterial sulfate reduction and reducing sulfate concentrations from 1500 mg/L to <5 mg/L. Flow-through reactor studies were designed to simiulate outflowing pit lake water through a passive reactive barrier. Although these studies are ongoing, initial results show that a barrier containing horse manure, wood chips, till, creek sediment is able to lower sulfate levels by 500 to 700 mg/L.

Key Words pit lake, bacterial sulfate reduction, permeable reactive barrier, flow-through reactor, batch reactor

Introduction

The Steep Rock iron deposit was located beneath Steep Rock Lake requiring a massive engineering project, which included the diversion of the Seine River and the removal of approximately 570 billion litres of water and 225 million m^3 of overburden, in order to open pit and underground mine the ore (Steep Rock Mines, 1943). Mining operations commenced in 1944 and continued until 1979 wherein the pits were left to fill to their present day levels. Currently, the pit lakes of the former Steep Rock iron mine (fig. 1) are characterized by a variety of water quality issues: (i) the recently joined Hogarth-Robert's pit lake is non-stratified, oxygenated and has extremely high concentrations of dissolved sulfate (1200—2000 mg/L), resulting in chronic sulfate toxicity; and (ii) Caland pit lake, which until recently hosted a commercial fish farm, is non-toxic and has an upper oxygenated fresh water lens that overlies an anoxic and moderately saline (200—500 mg/L SO_4^{2-}) water column (McNaughton 2001, Vancook 2005, Goold 2008, Godwin 2010).

One of the foremost water quality concerns is the effects on adjacent water systems at the time water levels in the pits reach the original level of the former Steep Rock Lake (fig. 1). At this

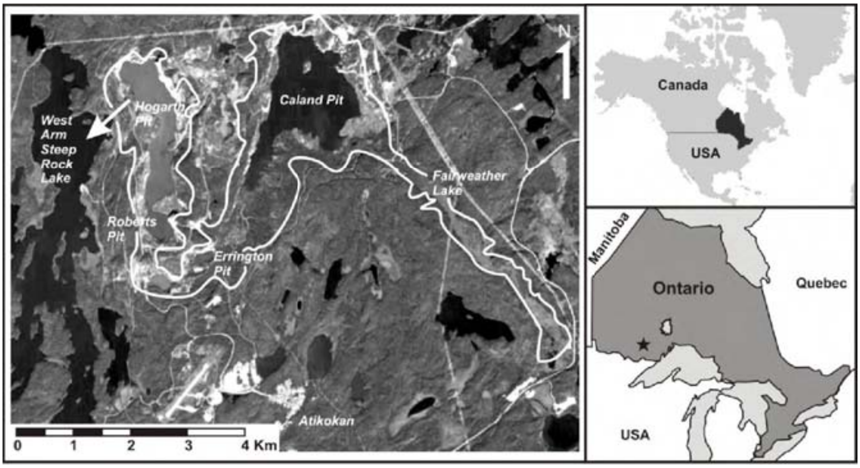

Figure 1 *Map showing location of Hogarth and Caland pit lakes (satellite image from Google Earth). The white outline represents original lake level (prior to draining for mining). The white arrow shows the location where outflow from the pit lakes into the West Arm will occur*

time, waters from the combined pit lakes will flow, along the original watercourse, into the West Arm (fig. 1) wherein these contaminated waters will continue to be transported out of the southern end of the West Arm into the Seine River system and ultimately into international boundary waters between the USA and Canada. Godwin (2010) demonstrated that mixing between Hogarth-Robert's and Caland pit lakes will result in chronically toxic outflow waters characterized by elevated sulfate concentrations (400—900 mg/L). Although in situ treatment may be advantageous in reducing the high sulfate levels of the pit lakes, the volume and depth (≈ 350 m at the time of outflow) of the pit lakes does not allow this to be a viable option. Consequently, sulfate levels have to be reduced from the pit waters prior to outflow to the West Arm. One remediation option is to use a combination of a permeable reactive barrier and a wetland ecosystem. Vancook (2005) demonstrated that Carex sp. was successful in removing the equivalent of 108 Tonnes of sulfur for a 620 ha wetland (surface area of the West Arm), resulting in nearly a 50% reduction of sulfate levels in pore waters. However, sulfate levels of Hogarth-Robert's pit lake (≈ 1500 mg/L) and predicted mixed outflow waters (up to 900 mg/L; Goodwin 2009) are higher than values of Caland water (≈ 300 mg/L) used by Vancook (2005). Consequently, the efficiency of a wetland ecosystem in remediating waters with significantly higher sulfate concentrations is unknown. However, a permeable reactive barrier may be one means of reducing sulfate concentrations in the outflow waters to a more amenable level prior treatment using a wetland ecosystem. The objectives of this study are to use batch and flow-through reactor experiments in order to assess if passive reactive barrier technology could be used to remove sulfate from the pit lake water prior to outflow.

Methods

Batch experiments were conducted to assess the capacity of different treatments to initiate bacterial sulfate reduction in order to lower sulphate and dissolved metals in the outflow water. Batch experiments were conducted using 500 mL, opaque HDPE bottles and filled with one of three treatments: (1) 15% organic matter (either cow manure, horse manure, peat, composted straw or wood chips), 15% creek sediment (sulfate reducing bacteria, SRB, source), 40% till and 30% carbonate rock; (2) 20% organic matter, 45% till and 35 % carbonate rock; and (3) 15% organic matter, 15% molasses (nutrient for the SRB), 40% till and 30% carbonate rock. Each bottle was mixed at a 1:1 ratio by mass. The water used for the experiment was taken at an 18 m depth from Hogarth-Robert's Lake (pH ≈ 7.0 and ≈ 1500 mg/L SO_4^{2-}). Bottles were placed on a "shaker" table to ensure constant mixing of the water and reactive mixtures and bottles were inverted once a week to prevent settling of the reactive mixture.

The results of the batch experiments were used to determine which treatment would be most suitable to use for a single pass, flow-through system, which simulate the properties of a permeable reactive barrier at the bench scale. Reactor columns have an internal volume of 500 cm^3 and were constructed of clear PVC pipe, which was covered with Al foil. Treatments within the reactor columns consisted of a reactive mixture of horse manure and wood chips (1:1 ratio by mass), creek sediment, till and granulated carbonate. Till and carbonate was used to ensure the reactive cell remained permeable, while carbonate was also used to buffer pH. Four different configurations were used and ran in duplicate:

- Columns 1 and 5 – two reactive cells separated by silica sand
- Columns 2 and 6 – two reactive cells bounded and separated by granulated carbonate
- Columns 3 and 7 – two reactive cells bounded by carbonate and separated by silica sand
- Columns 4 and 8 – three reactive cells separated by silica sand

Water sampled from 18 m of Hogarth-Robert's pit lake is passed once through the columns by a peristallic pump at a rate of 0.1 mL/min.

For both batch and flow-through reactor studies major cations and trace metals were determined by ICP-AES and anions by ion chromatography. Alkalinity was measured by titration, where pH, redox and conductivity were measured using a probe/multimeter system. For flow-through experiments, pH, conductivity and redox potential were measured on-line. Hydrogen sulfide was measured using a UV-Vis spectrometer for batch experiments and titration for flow though experiments.

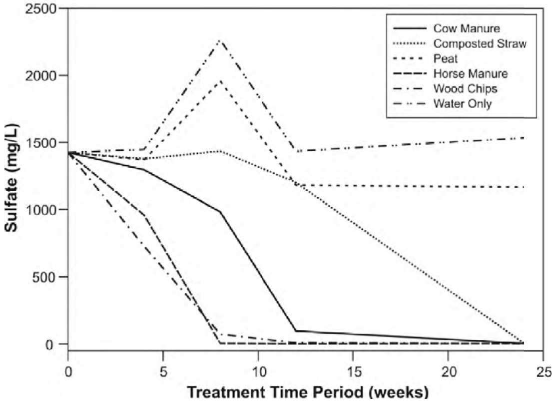

Figure 2 *Variation in sulfate concentration over the duration of batch reactor experiments with organic matter + creek sediment + till + carbonate treatments*

Results and discussion

Batch reactor experiments that contained organic matter + creek sediment + carbonate + till were the most effective at reducing sulfate levels. For these treatments, sulfate concentrations were reduced to <5 mg/L except for the control sample (water only) and where peat is the organic material (fig. 2). Experiments that contained neither the SRB-bearing creek sediment nor molasses were highly variable in terms of sulfate reduction. For these experiments, horse manure and wood chips were effective at lowering sulfate concentrations to 6 and 27 mg/L, respectively, but the other organic substrates only reduced concentrations to between 300 and 1300 mg/L. Treatments with molasses had an increase in sulfate concentration (1900—2300 mg/L SO_4^{2-}). The pH of waters from the molasses-free experiments remained circum-neutral and increased by <0.5 pH units. However, for experiments where molasses was used as a nutrient, the pH of the water decreased by 1 to 2 pH units. Treatments with large reductions in sulfate concentration also underwent a decrease in redox potential (Eh) from an initial value of 100 mV to values between -300 and -100 mV. The concentation of trace metals (Cu, Fe, Zn, Ni, Co, Pb, As, Mn) increased in all treatments, and likely reflect additions from the various organic components. Residency times for the flow-through columns ranged between 70 and 130 hours.Results from the first six-weeks of the flow-through reactor experiments show that sulfate levels were reduced on the order of 500 to 700 mg/L in all reactors (fig. 3). At week 3, large reductions in sulfate concentration were observed in reactor columns 1 and 5; however, since week 4, levels began to rise, possibly reflecting dissolu-

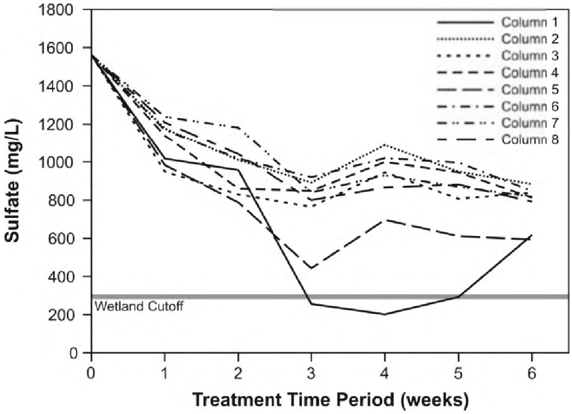

Figure 3 *Preliminary changes in sulfate concentration over time for flow-through reactor experiments. The wetland cut-off values is based on the initial water composition used by Vancook (2005)*

tion of bacterially precipitated sulfides. In addition to the overall decrease in sulfate concentrations, hydrogen sulfide levels have increased from <1 mg/L at the start of the experiment to present levels between 4 and 8 mg/L, while the redox potential rapidly decreased from 279 mV to between -200 and -100 mV in all reactors. Granulated carbonate in the reactors have maintained pH values between 7 and 8. Iron and Mn are the only metals that are consistently above the minimum detection limit, where concentrations have increased from initial values of 0.04 and 0.06 mg/L to values of 40 to 175 mg/L and 11 to 19 mg/L, respectively, in week 1. Iron and Mn have continued to decrease with time to the current values of <7 mg/L and <2 mg/L, respectively.

Mutual decreases in sulfate concentration with redox potential, coupled with increases in hydrogen sulfide concentration indicate that bacterial sulfate reduction was successfully induced in all of the flow-through experiments and for those batch experiments where no nutrient was used. The extent of sulfate reduction was satisfactory in that the resulting outflow waters would likely be amenable for further treatment by a wetland ecosystem. Batch reactor treatments can sufficiently lower sulfate levels where no additional treatment is required; however, the 1:1 water to substrate ratio and required residency time is not considered to be realistic for a field-scale barrier. Although the present concentration of sulfate in flow-through waters is still high, the progressive decrease in sulfate levels indicates that over time a reactive barrier may yield outflow waters with sufficiently lowered concentrations. However, the return to increasing sulfate concentrations in columns 1 and 5 (two reactive cells separated by silica sand) indicates that any field barrier must be carefully engineered in order to prevent the re-dissolution of precipitated metal sulfides. Dissolution of bacterially precipitated sulfides appears to be the result of lower pH waters being produced during sulfate reduction, and can be controlled by adding additional cells of granulated carbonate. Unlike the batch experiments, a flow-through reactive barrier over time does not result in a significant increase in the concentration of dissolved metals, and thus metal toxicity concerns are not an issue.

Conclusions

Both batch reactor and flow-through reactor systems were able to lower the dissolved sulfate content of Hogarth-Robert's pit lake waters by inducing bacterial sulfate reduction. A combination of horse manure and wood chips provided the most appropriate organic substrate for sulfate reducing bacteria, that work in conjunction with a naturally occurring source of sulfate reducing bacteria (creek sediment), till and granular carbonate. Although the degree of sulfate reduction is significant less for flow-through experiments than batch experiments, the increase in dissolved metals is only on the order of a few mg/L, rather than several tens to hundreds of mg/L, thus limiting the likelihood of induced metal toxicity to the outflow waters. Although flow-through experiments are still in progress, the current rate of sulfate reduction suggests that a reactive barrier alone should not be the sole means of remediating the outflow waters from the pit lakes. However, the resulting sulfate concentrations may allow for further treatment by a wetland ecosystem.

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