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# Environment Canada

Water Science and  
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# Environnement Canada

In Situ Treatment of Mine Drainage Water Using Porous  
Reactive Walls

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## Management Perspective

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Oxidation of sulfide minerals in mine tailings leads to the release of high concentrations of sulfate, ferrous iron and other metals to the moving pore water. As this pore water is displaced downward into underlying permeable geologic materials, plumes of contaminated groundwater develop. This tailings-derived groundwater can migrate for long distances from impoundments and, in some cases, can eventually discharge to nearby surface waters. A potential technique for the remediation of tailings-derived groundwater is porous, permeable reactive walls. These walls are installed in aquifers downgradient from the tailings impoundment by excavating aquifer material and replacing it with a permeable reactive mixture. This paper evaluates reactive mixtures selected to promote bacterial-sulfate reduction and metal-sulfide precipitation reactions. The mixtures contain a blend of solid-phase organic carbon sources, including wood chips, saw dust, composted sewage sludge, composted sheep manure and leaf mulch, to promote bacterial sulfate reduction; agricultural limestone to provide an initial pH suitable for bacterial growth; and bottom sediments from a local creek as a bacteria source. In laboratory batch tests, all the mixtures evaluated resulted in rapid reduction of sulfate and metal sulfide precipitation after an initial acclimation period. Column tests indicate the rate of sulfate reduction is sufficiently rapid for potential treatment at groundwater velocities typical of field settings. A small-scale field test was initiated in October, 1993 at the Nickel Rim mine tailings impoundment near Sudbury, Ontario. Preliminary results indicate sulfate and metal removal is occurring within the cell. Proceeding along the flow path in the cell, the extent of removal increases, with a decrease in sulfate concentrations from 3500 mg/L to 7 mg/L and a decrease of iron from 1000 to < 5 mg/L. These decreases coincide with increases in alkalinity, pH and dissolved hydrogen sulfide. The results of the studies suggest the use of porous reactive walls is a potential alternative for the prevention and remediation of acid mine drainage.

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**In Situ Treatment of Mine Drainage Water Using Porous Reactive Walls.** D.W. Blowes\*, Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, N2L 3G1, C.J. Ptacek, National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, L7R 4A6, and K.R. Waybrant, J.G. Bain, W.D. Robertson, Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, N2L 3G1.

Porous reactive walls installed in the path of plumes of tailings-derived groundwater have the potential to prevent and remediate acid mine drainage and dissolved metal release. Various forms of organic carbon were added to a reactive wall located in an aquifer downgradient from a mine-tailings impoundment at the Nickel Rim mine site, Sudbury, Ontario. Bacterially catalyzed sulphate reduction and metal sulphide precipitation reactions decreased  $\text{SO}_4$  concentrations from 3500 to 7 mg/L and Fe concentrations from 1000 to <5 mg/L, and increased pH and alkalinity. These results indicate that sulphate-reducing reactive walls represent an effective and economically viable alternative solution to many acid mine drainage problems. Laboratory tests indicate treatment of other metals, Pb, Zn, Cu, Cd, and Ni is possible using this technology.

## INTRODUCTION

Oxidation of sulphide bearing minerals within the unsaturated zone of mine tailings impoundments, results in low quality drainage waters characterized by low pH and high concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{2+}$  and other dissolved metals. At many locations water affected by sulphide oxidation is displaced downward to the groundwater system and ultimately discharges into surface water bodies potentially damaging aquatic and terrestrial ecosystems.

Current abatement techniques for controlling or treating mine drainage are often costly and at some mine sites, impractical. Current research at the University of Waterloo offers an alternative passive approach through the use of porous, permeable, geochemically-reactive walls which incorporate bacterially mediated sulphate reduction (Blowes et al., 1994, Waybrant et al., 1994). These geochemically engineered walls are installed in the pathway of flowing contaminated groundwater resulting in in-situ treatment (Figure 1).

Sulphate reducing bacteria catalyze the oxidation of organic carbon coupled with the reduction of sulphate to sulphide through the reaction:

$$\text{SO}_4^{2-} + 2 \text{CH}_2\text{O} \longrightarrow \text{H}_2\text{S} + 2 \text{HCO}_3^-$$

where "CH<sub>2</sub>O" represents a simple organic carbon (Tuttle et al., 1968; Wakao et al., 1979). The sulphide produced subsequently reacts with dissolved metals, resulting in the precipitation of metal sulphides:

$$\text{Me}^{2+} + \text{H}_2\text{S} \longrightarrow \text{MeS} + 2 \text{H}^+$$

where Me<sup>2+</sup> denotes a metal such as Cd, Fe, Ni, Cu, Co and Zn.

The focus of our present research is laboratory batch and

column experiments, and a small-scale field trial to assess the long-term effectiveness of a range of different organic sources for promoting sulphate reduction and precipitation of metal sulphides. The optimum materials as determined from the batch studies are currently being tested under dynamic flow conditions. Finally, a small-scale field trial has been initiated at the Nickel Rim mine tailings impoundment located near Sudbury, Ontario. This paper presents a summary of the experiments under way and a brief summary of the preliminary results.

## **LABORATORY AND FIELD EXPERIMENTS**

### **Batch Experiments**

Laboratory batch experiments were used to assess the potential for a single organic source or mixture of different sources to promote sulphate reduction. Several experiments have been conducted which included five different sources of organic matter: leaf compost, sawdust, wood chips, sheep manure and sewage sludge. The bacteria source used for these batch studies was collected from the anaerobic zone of a local creek. Agricultural limestone was also added to ensure optimum pH conditions for the bacteria. The reactive organic carbon mixture, plus creek sediment and limestone were placed in a well-sealed, glass reaction flask. Anaerobic conditions were maintained throughout the experiments, as indicated by the low Eh values and production of a sulphate-reduction product,  $H_2S$  gas.

### **Sampling**

The reaction flask contained two ports from which substances could be removed or added by piercing the teflon lined septum on the port with a syringe. Samples were obtained by withdrawing an aliquot of sample from one of the ports, while at the same time injecting  $N_2$  gas in the other port in order to ensure that conditions remained anoxic. The batch experiments were sampled as a function of time and under a closed system environment.

Measurements of pH, Eh and alkalinity were determined immediately after sampling. The pH and Eh were measured unfiltered, under a closed, oxygen-free system and a filtered sample was used for determining the alkalinity. Samples were filtered through a 0.45  $\mu m$  cellulose acetate filter paper and both acidified and unacidified samples were collected and stored at 5°C until analyses of  $SO_4$ , Fe, Mn, Zn, Ni, Ca, K, Na, Mg, and DOC were completed. Analyses were conducted by Fenwick Laboratories within 30 days of sampling.

### **Column Experiments**

Flow-through column experiments were conducted to assess removal of  $SO_4$  and dissolved metal under dynamic flow conditions. Three 40 cm x 5 cm columns were packed with reactive materials including wood chips, sawdust, composted municipal sewage sludge, leaf compost from a municipal recycling program, and composted sheep manure. Reactive mixtures were selected on the basis of the batch experiments. The column experiments were conducted in a glove box under anaerobic conditions.

### **Sampling**

Samples were collected to determine pH, Eh, alkalinity and

concentrations of  $\text{SO}_4$ , Fe, and other metals. Measurements of pH and Eh are made in sealed vials. Samples were filtered and preserved in the same manner as for the batch tests.

#### **Small-Scale Field Trial**

A small-scale field test of the reactive-wall system was initiated in October 1993. A test cell was excavated into the path of the Fe (II)- and  $\text{SO}_4$ -rich plume emanating from the Nickel Rim tailings impoundment near Sudbury, Ontario. The reactive mixture for the cell was based upon early results of the batch experiments. The test cell (1.2m x 1m x 1.2m; l,w,d) was hand dug 75 meters from the base of the tailings dam, near the front of the plume (as in Figure 1). Water influent to the test cell has high  $\text{Fe}^{2+}$  (500-900 mg/L) and  $\text{SO}_4$  (2300-3600 mg/L) concentrations, pH near 5, Eh near 450 mV, and a mean annual temperature of  $\approx 10^\circ\text{C}$ . Alkalinity of the water, attributed to carbonate, is less than 30 mg/L. The odour of  $\text{H}_2\text{S}$  is detected randomly throughout the aquifer, suggesting that indigenous sulphate reducing bacteria are active. In September, 1994 two additional test cells were installed 125 m down gradient of the tailings dam. Samples were collected at the field site using the methods of Blowes (1990).

### **RESULTS AND DISCUSSION**

#### **Batch Experiments**

The batch experiment results show that sulphate reducing conditions developed rapidly after an initial acclimation period and the removal of metals from solution was rapid and sustained as long as sulphate is not limiting (Figure 2). Subsequent additions of sulphate, iron and other metals resulted again in rapid and sustained removal.

#### **Column Experiments**

A preliminary column experiment was initiated in August, 1993. Additional column experiments were initiated in March, 1994. The columns were packed with mixtures of organic carbon sources selected from those examined during the batch tests. The columns were saturated with  $\text{SO}_4$ -rich water containing approximately 500-1000 mg/L  $\text{SO}_4$ . Within 30-40 days a population of sulphate-reducing bacteria became acclimated and reducing conditions were established. Monitoring of effluent  $\text{SO}_4$  concentrations indicated that  $\text{SO}_4$  reducing conditions were continued at experimental flow-rates of 3-10 m/yr, a dimensionless velocity of 8-24 pore volumes/yr. The sulphate reduction reaction resulted in removal of  $\text{SO}_4$  from an input concentration of 500-1000 mg/L to  $<20$  mg/L.

In August, 1994 the source water was changed to a solution containing approximately 3000 mg/L  $\text{SO}_4$  and 800 mg/L Fe. This solution also contained low concentrations of Mn, Ni, Pb and Zn. Concentrations of these metals were based on observations made previously at mine tailings impoundments. Preliminary results indicate partial removal of  $\text{SO}_4$  and complete removal of Fe. The removal of  $\text{SO}_4$  is anticipated to increase as the bacterial population acclimates to the increased  $\text{SO}_4$  concentrations.

#### **Small-Scale Field Trial**

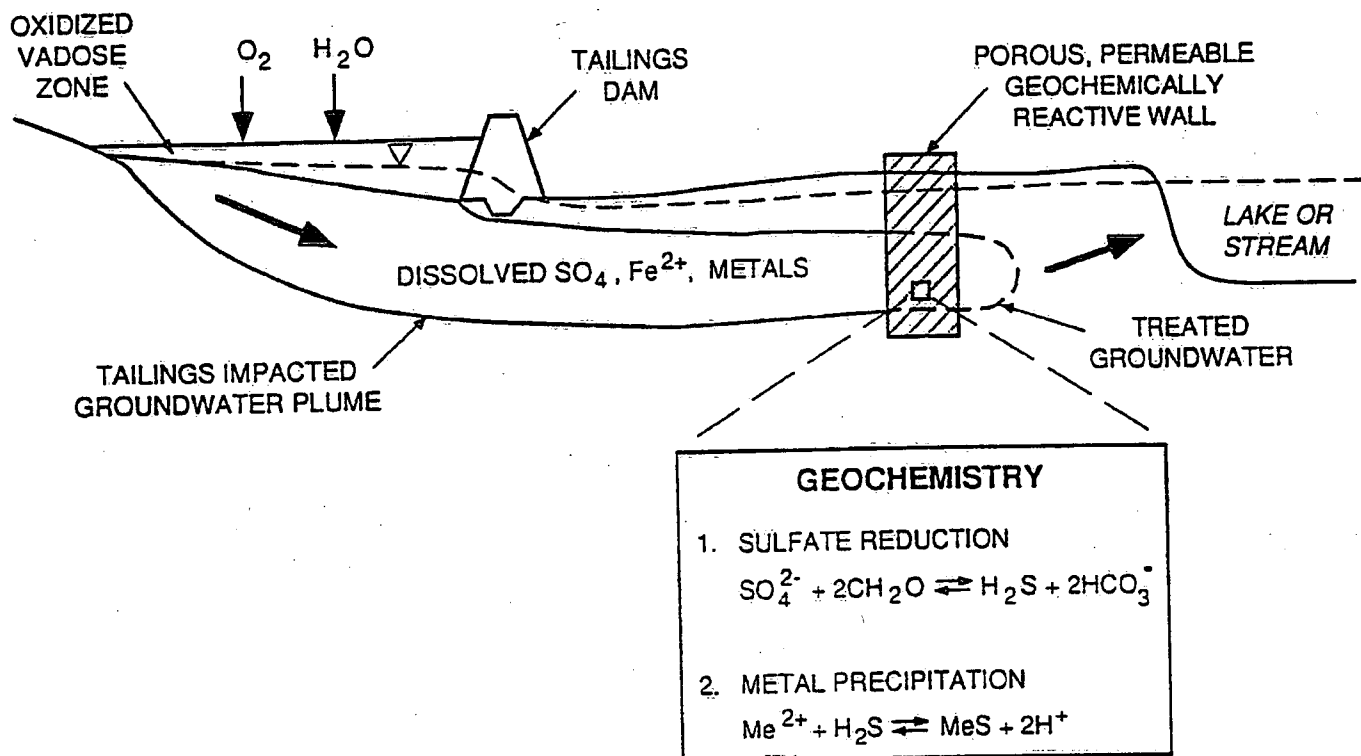
Water in the test cell was sampled 7 months after the cell was installed. Analyses indicate that heavy metal attenuation is occurring in the cell. Proceeding along the flowpath in the cell, the extent of metal attenuation increases. Sulphate reduction and dissolution of limestone added to the cell have acted to increase pH to near neutral (6.3 to 7.1) and alkalinity to >1000 mg/L CaCO<sub>3</sub>. Iron (II) concentrations decrease from 1000 mg/L to <50 mg/L after travelling <0.5 m through the cell. Lowest iron concentrations are <10 mg/L. Sulphate concentrations also decrease with travel distance in the cell, dropping from 3500 mg/L to <1000 mg/L over 0.5 m. Lowest SO<sub>4</sub> concentrations in the cell are ≈5 mg/L. Dissolved metals such as Al, Ni and Zn decrease to below drinking water quality guidelines in the cell. H<sub>2</sub>S is present at 0 to >5 mg/L; this, in addition to low Eh in the cell suggests that sulphate reduction is the dominant process leading to the removal of dissolved metals as sulphides.

#### CONCLUSIONS

The preliminary results of the laboratory experiments and the initial small-scale field trial suggest that sulphate-reducing conditions can be established and sustained in aquifers downgradient of inactive tailings areas. The net acid generating capacity of the tailings discharge water was removed and a net acid consuming water produced. These results suggest that the use of porous reactive walls is a potential alternative for the prevention and remediation of acid mine drainage.

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**Figure 1.** Schematic of a porous reactive wall at a mine tailings site.

# Sawdust, Leaf and Sheep Compost Mixture (Batch Study #4)

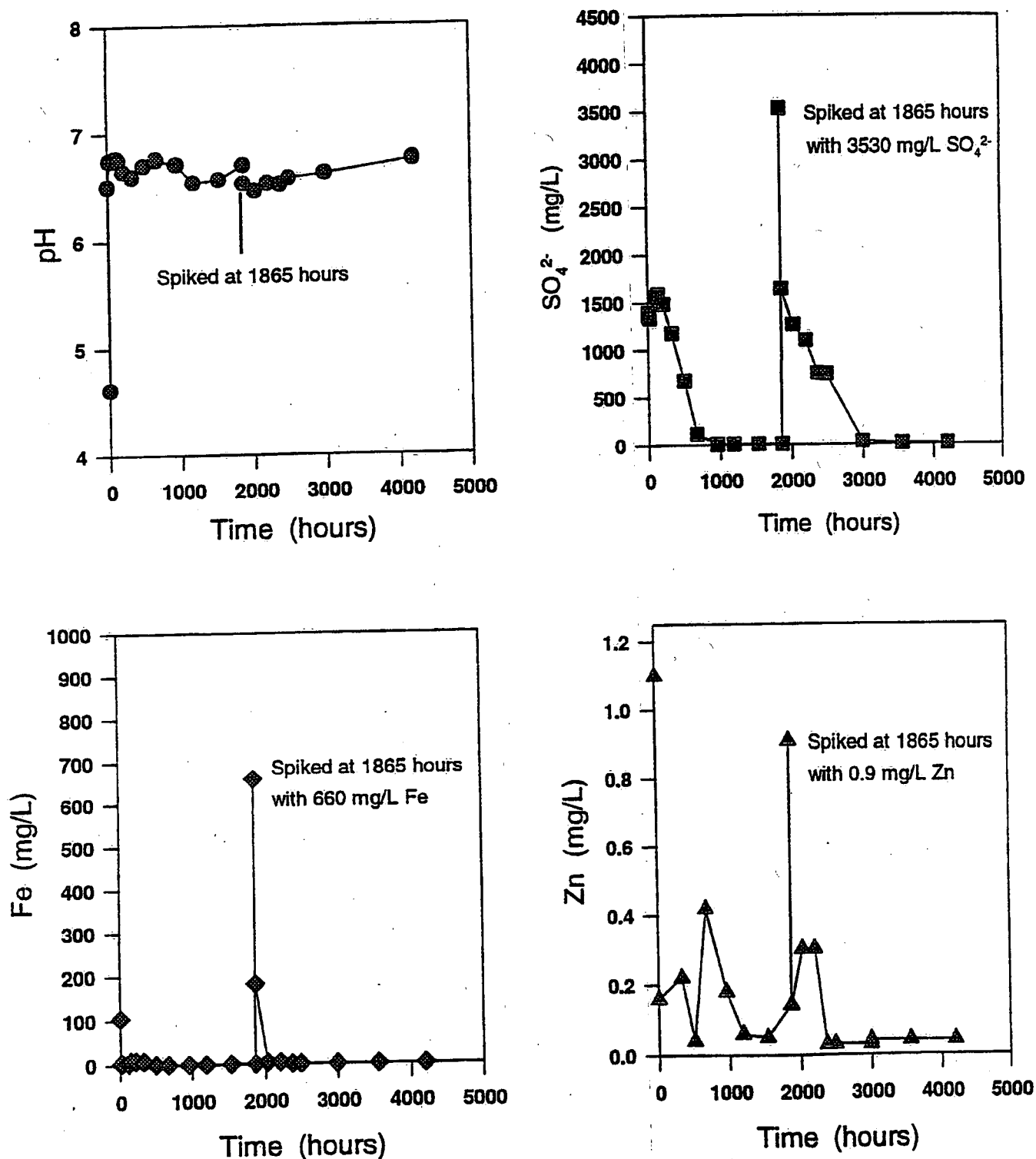


Figure 2. Geochemical results of laboratory batch experiments.



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