TREATMENT OF MINE DRAINAGE WATER USING *IN SITU* PERMEABLE REACTIVE WALLS[1]

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Abstract: Porous, permeable reactive walls placed in the path of plumes of tailings-derived groundwater have the potential to prevent and remediate acid mine drainage and dissolved metal release. A test cell, simulating a reactive wall, was placed in an aquifer downgradient from the Nickel Rim mine tailings impoundment, near Sudbury, Ontario, to remove metals and sulfate from the flowing groundwater. Various forms of organic carbon were added to the test cell to promote bacterial sulfate reduction and metal-sulfide precipitation. Within a distance of 1 m along the groundwater flow path, concentrations of SO_4 decreased from 3500 to 7 mg/L, Fe concentrations decreased from 1000 to < 5 mg/L, and the pore-water pH and alkalinity increased as a result of sulfate-reduction reactions. These results indicate that sulfate-reducing reactive walls represent a potentially effective and economically viable alternative solution to many acid mine drainage problems.

Key Words: Acid mine drainage, remediation, sulfate reduction, metal-sulfide precipitation, permeable reactive walls

Introduction

The oxidation of sulfide minerals in inactive mine-tailings impoundments and waste-rock piles results in the generation of low-pH conditions and the release of high concentrations of dissolved sulfate, ferrous iron and other metals to the flowing pore water. At many locations in Canada, tailings impoundments are underlain by permeable, unconsolidated geological materials. Downward displacement of mill process-water, discharged into the impoundment with the tailings, and precipitation recharge-water which has been affected by sulfide-oxidation reactions has resulted in the development of plumes of tailings-derived groundwater. The nature and chemical composition of these plumes depend on the nature of the tailings, and the hydrogeologic setting. At many locations, these plumes contain high concentrations of sulfate and dissolved metals (1 - 3). At a number of locations, discharge of tailings-derived groundwater from aquifers to surface-water systems results in the degradation of surface-water quality. The development of remedial techniques applicable to tailings impoundments underlain by permeable geological materials is an important aspect of addressing the environmental problems associated with sulfide-bearing mine wastes.

The oxidation of sulfide minerals proceeds rapidly as the tailings drain after decommissioning, because the travel distance for O_2 gas is short in the initial stages of oxidation. As sulfide minerals are depleted from the near surface tailings, the length of the gas-diffusion path increases, and the rate of sulfide oxidation declines (4). As a result of this sequence of processes, the maximum concentrations of sulfide-oxidation products are derived during the early stages of tailings oxidation. Numerical modelling indicates that the rate of generation of sulfide oxidation products is most rapid in the 10 to 25 years

immediately following tailings decommissioning (5). At many sites in northern Canada, the period of peak oxidation has passed. Remedial programs focused on preventing sulfide oxidation by isolating the sulfide minerals from atmospheric oxygen with soil or water covers are not well suited to these older tailings impoundments. These covers can be used, however, to augment other approaches for remediation, such as pump-and-treat systems or permeable reactive walls.

Accepted practice for treatment of contaminated groundwater from industrial and hazardous waste sites is to pump the water to ground surface and remove the contaminants with a conventional water treatment plant. Because of the long duration of sulfide-oxidation reactions in mine wastes, this approach to groundwater remediation is not well suited to mining-related environmental problems. Development of alternative technologies, therefore, is desirable.

Porous, permeable reactive walls, designed to stimulate sulfate-reduction and metal-sulfide precipitation reactions, are an alternative technique for treating tailings-derived groundwater (Fig. 1). These reactive walls are installed in aquifers downgradient of contaminant source areas. Aquifer materials are excavated and replaced with a reactive mixture. Contaminated groundwater is allowed to passively flow through the reactive materials, where treatment through transformation, precipitation or adsorption reactions occurs (6 - 11). Reactive walls are advantageous over conventional pump-and-treat technology, because the need for well installation, pumping, above-ground treatment facilities, and facilities for disposal of treatment waste sludges is eliminated.

This paper describes preliminary field experiments conducted to assess the suitability of permeable, reactive walls for treatment and prevention of acid mine drainage. A small-scale field experiment was initiated at the Nickel Rim mine tailings impoundment, near Sudbury, Ontario (Fig. 2). An experimental test cell, containing solid-phase organic carbon to promote sulfate-reduction reactions, agricultural limestone to maintain near-neutral pH conditions, and aquifer sand to maintain the permeability of the test cell, was installed into the path of a plume of tailings-derived water at the Nickel Rim site. Monitoring of the test cell was conducted over the year following the installation.

The test-scale reactive wall installed at the Nickel Rim site was intended to induce sulfate-reducing conditions within the aquifer downgradient of the tailings impoundment. Sulfate-reduction reactions can be generalized through the equation:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$$ (1)

where CH_2O represents organic carbon. This reaction consumes organic carbon and sulfate and produces hydrogen sulfide and bicarbonate. In several environments sulfate-reducing conditions have been noted to be accompanied by increases in pore-water pH and alkalinity and by decreases in the concentrations of dissolved metals (12 - 15), due to the precipitation of metal sulfides through reactions of the form:

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+$$ (2)
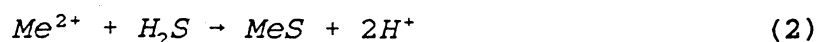
where Me^{2+} represents a dissolved divalent metal.

Sulfate-reducing reactions have been observed to lessen the severity of the environmental effects of mine drainage in a number of settings. For example, Machemer and Wildeman (12) attributed the neutralization of acidic drainage, and decreased dissolved metal concentrations, to sulfate-reduction reactions occurring in a constructed wetland. Dvorak et al. (13) have exploited sulfate-reduction reactions in surface reactors used for treating acidic drainage derived from coal-mine wastes. Béchard et al. (14) have used decomposing organic matter to promote sulfate-reduction reactions in a trench receiving acidic drainage derived from the oxidation of pyritic shales at the Halifax International Airport. In addition, the Boojum ARUM system uses a sulfate-reduction step to remove metals from surface water affected by sulfide-oxidation reactions (15).
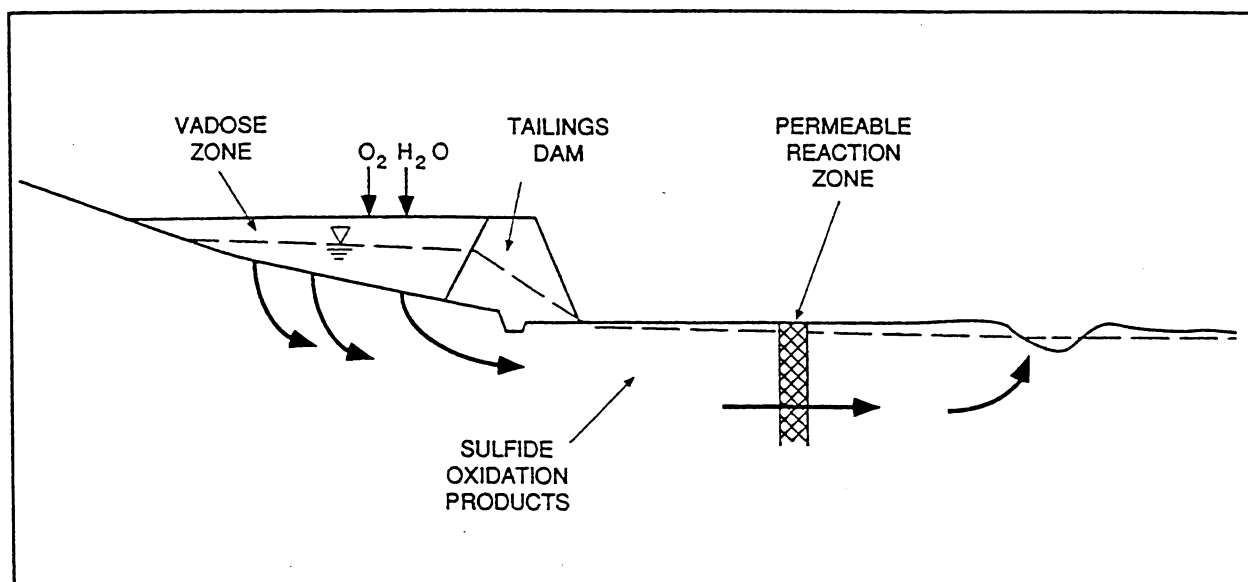
Figure 1. Treatment of mine-tailings derived groundwater using a permeable reactive wall.

These systems are designed to treat surface water that has been affected by sulfide-oxidation reactions. As a result of exposure to atmospheric O_2, these waters are generally acidic and highly oxidized. Within aquifers, tailings derived waters are isolated from atmospheric O_2, preventing the oxidation of Fe(II). Plume water at many locations is near-neutral in pH and reduced in Eh. These conditions are well suited for the initiation of sulfate-reducing conditions. The overlying water column assures isolation from atmospheric O_2, as required for the development of sustained sulfate-reducing conditions. In addition, groundwater flow rates range from a few tens of centimeters to a few tens of meters per year, much slower than surface-water flow rates. These groundwater velocities are suitable for *in situ* water treatment by sulfate-reduction reactions.

The selection of reactive materials for use in the permeable reactive wall is critical to the successful treatment of dissolved constituents. The optimal mixture will be reactive enough to remove the target contaminants from the flowing groundwater at natural groundwater velocities, and sufficiently stable to remain active for an economically viable period of time. Waybrant et al. (16) have conducted laboratory batch and column experiments designed to compare the attributes of different organic carbon sources, and to assess optimal mixtures for use in a reactive wall. Materials used in the field study were selected upon the basis of these laboratory studies.

Methods

In October, 1993, a small-scale test cell was installed in the sand aquifer, approximately 75 m downgradient of the western edge of the Nickel Rim mine tailings impoundment (Figs. 3, 4). To install the cell, aquifer material was excavated and replaced with a reactive mixture. The final dimensions of the test cell are 1.45 x 1.1 x 1.2 m (length x width x depth). The reactive mixture consisted of composted leaf mulch, pine mulch, and pine bark, as the organic carbon sources, creek sediment, as a source of sulfate-reducing bacteria, agricultural limestone, as a neutralizing agent, and coarse sand and gravel, to increase the permeability of the mixture. The composted leaf mulch was obtained from the Region of Waterloo municipal leaf recycling program. The creek sediment was collected from the bottom of a local Waterloo creek where sulfate-reducing conditions are well established, as indicated by a strong H_2S odor and black color.
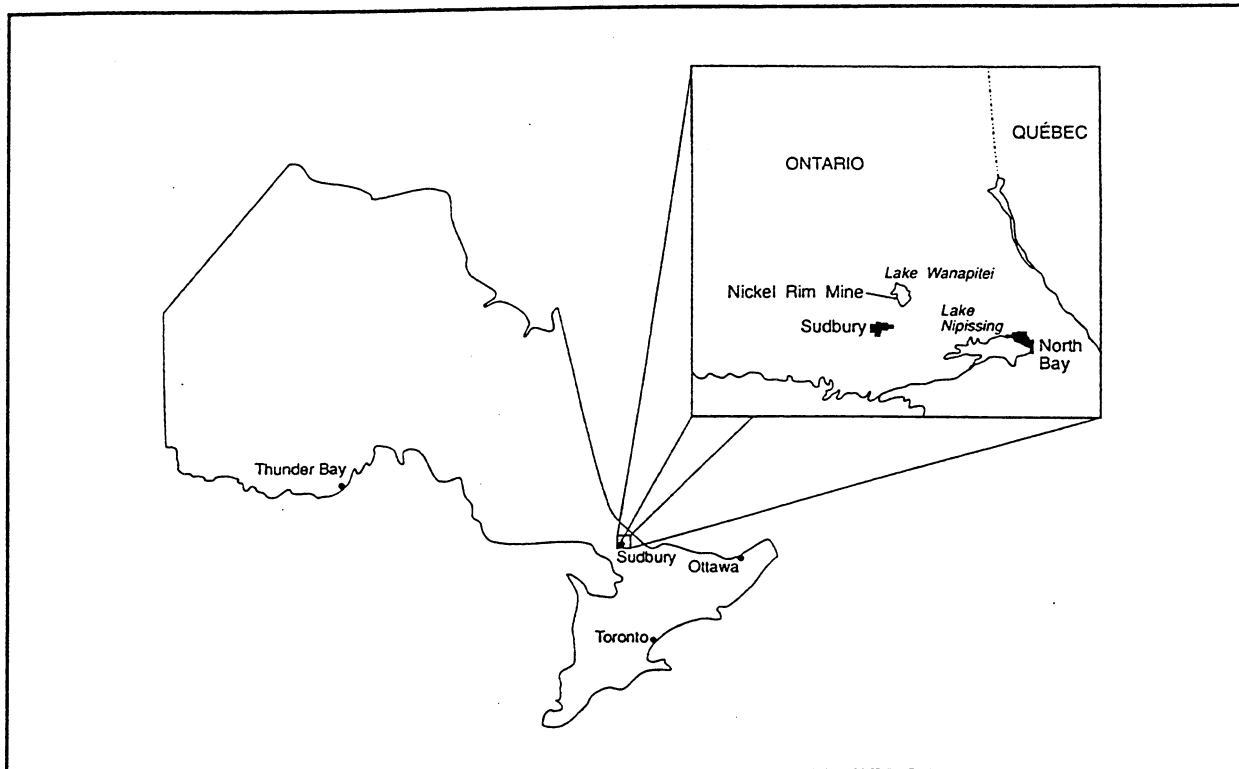
Figure 2. Location of Nickel Rim mine tailings impoundment.

Bundle-style piezometers were used to obtain samples of the groundwater upgradient, within and downgradient of the cell. Samples of groundwater were collected 6, 7 and 12 months after installation of the cell. To collect groundwater samples, groundwater was pumped from the bundle piezometers and filtered in-line through a 0.45 μm cellulose acetate filter. Samples were acidified to a pH < 1.5 using
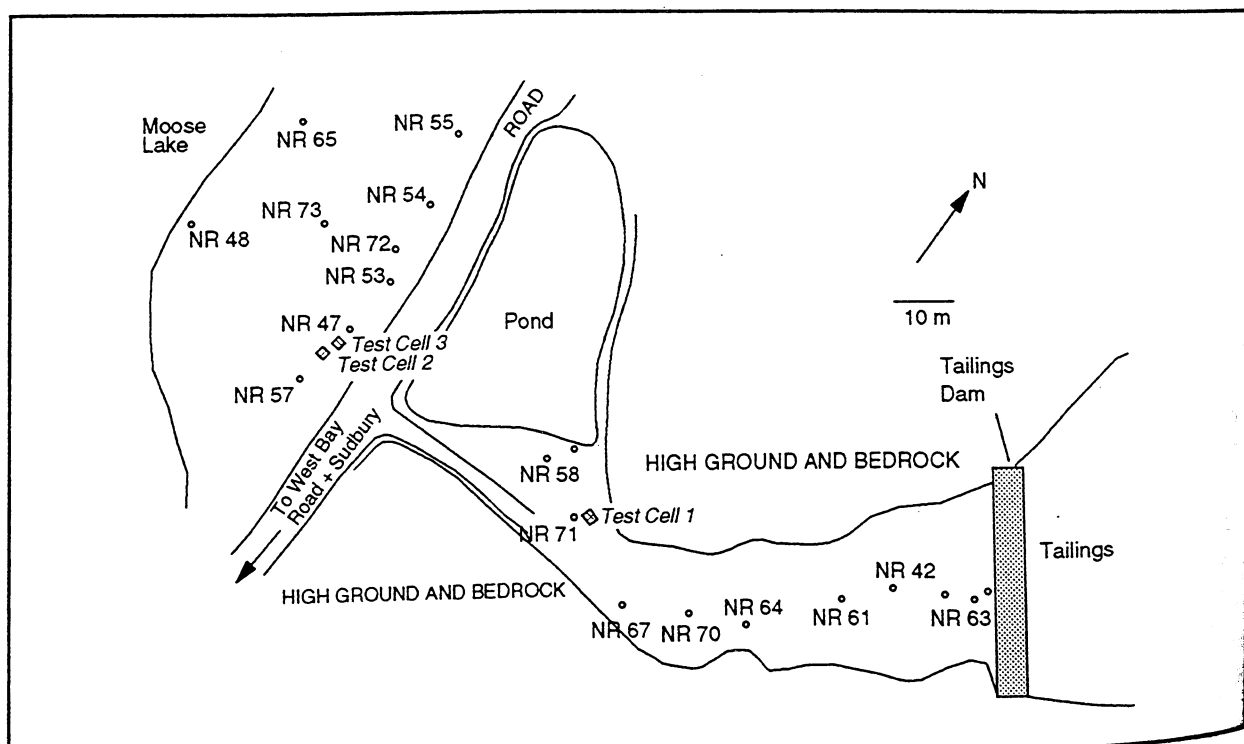

Figure 3. Area map showing location of test cells at the Nickel Rim mine tailings impoundment.
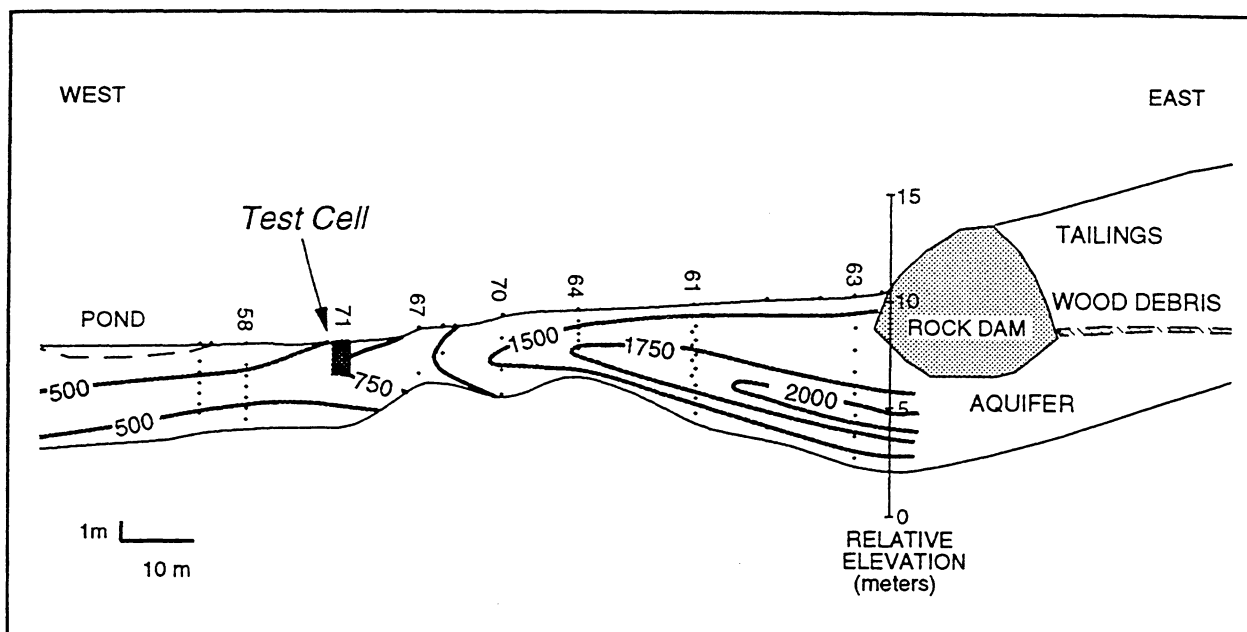
Figure 4. Cross-section map showing plume geochemistry and location of test cell in aquifer downgradient of the Nickel Rim mine tailings impoundment.

metal-free HCl for analysis of Fe, Ca, Mg, Ni, Na, K, Al, Mn, and Zn by flame atomic absorption spectrometry or by inductively coupled plasma atomic emission spectrometry. Unacidified samples were analysed for SO_4, Cl and F by ion chromatography. Determinations of pH and Eh were made in the field, on unfiltered samples, using sealed flow-through cells. Determinations of alkalinity were made in the field on filtered samples.

In September, 1994 two additional cells were installed at the Nickel Rim site (Fig. 3). The purpose of these test cells is to evaluate other reactive mixtures for their ability to promote sulfate-reducing conditions and metal removal.

Results and Discussion

The test cell is excavated into an unconfined sand aquifer, 75 m downgradient from the Nickel Rim tailings impoundment near Sudbury, Ontario (Figs. 3 and 4). Water derived from the Nickel Rim tailings impoundment is currently migrating through the aquifer. A well developed plume has formed downgradient of the impoundment (3). Sulfide oxidation reactions occurring in the shallow tailings have released high concentrations of SO_4, Fe(II), and other metals, to the infiltrating tailings water. These reactions have also generated acidic and oxidized Eh conditions in the shallow tailings. As the pore water migrates through the tailings, the H^+ released by sulfide oxidation is consumed by reactions with pH-buffering minerals, principally carbonate and hydroxide solids. As a result of these reactions, the pH increases from < 3.5 at the tailings surface to > 6.5 at the base of the impoundment. This increase in pH enhances the precipitation of Fe(III) and other dissolved metals. The concentrations of Fe(III), Ni, and other dissolved metals are observed to decrease sharply as the pH increases during flow through the tailings (17, 18). The precipitation of Fe(III) results in a decline in the pore-water Eh. This sequence of reactions results in a change in the pore water as it migrates through the tailings. Water at the base of the impoundment and pore water discharging to the underlying aquifer is typically near neutral in pH (6.2), slightly oxidized in Eh (200 mV), and contains high concentrations of dissolved SO_4 (6000 mg/L) and Fe(II) (2000 mg/L), and moderate to low concentrations of other metals.

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At the location of the test cell, SO_4 concentrations vary from 3000 to 4000 mg/L (Fig. 4) and Fe concentrations vary from 600 to 1000 mg/L. The influent water at this location is affected slightly by surface-water recharge to the aquifer. The Eh is moderately oxidized (300 to 500 mV), the pH is slightly acidic (4.5 < pH < 5.5), and the alkalinity is < 50 mg/L (as $CaCO_3$). The mean annual temperature of the aquifer water, estimated on the basis of periodic measurements, is approximately 10°C. These conditions are suitable for the enhancement of sulfate reduction reactions through the addition of organic carbon to the aquifer material.

Measurements of the composition of the pore water within the test cell, and immediately downgradient of the test cell were made in May, June, and November, 1994, six, seven and twelve months after installation. The pore water in the test cell shows the effect of sulfate-reduction reactions (Fig. 5). The pore water pH increases sharply, from < 5 in the aquifer immediately upgradient of the test cell to > 7 within 0.5 m of the test cell boundary. The pH within the test cell varies from 6.3 to 7.2. The increase in pH is accompanied by a corresponding decline in Eh from in excess of 500 mV to < 150 mV, within 0.5 m of the test cell boundary. The Eh values within the test cell are typically < 250 mV. Sulfate-reduction reactions are also indicated by sharp declines in the concentrations of dissolved SO_4, Fe(II) and other metals. Sulfate concentrations decrease from > 3500 mg/L to typically < 250 mg/L, with concentrations within the central portions of the cell < 10 mg/L. Dissolved Fe(II) concentrations in the aquifer immediately upgradient of the cell vary from 600 to 1000 mg/L. Within the test cell dissolved Fe(II) concentrations are generally < 100 mg/L, with low values in the central portion of the test cell of < 5 mg/L. Sulfate-reduction reactions also produce measurable concentrations of H_2S, varying from 0 to
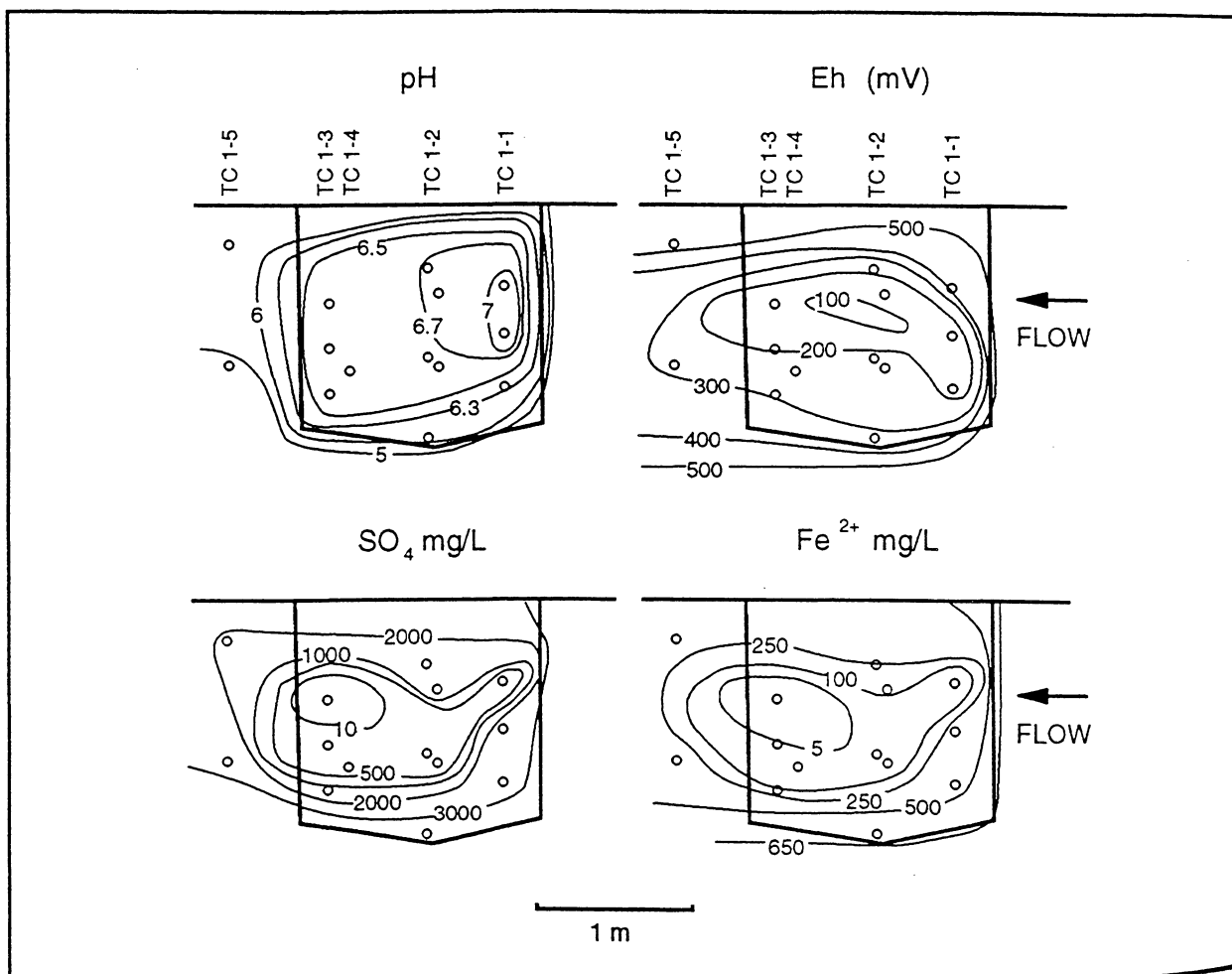

Figure 5. Composition of pore water within test cell installed downgradient of Nickel Rim mine tailings impoundment. Results are for June, 1994, 7 months after installation of test cell.

> 5 mg/L. The production of measurable H_2S suggests that the removal of Fe(II) and SO_4 is through sulfate-reduction and metal-sulfide precipitation reactions.

Sulfate-reduction and carbonate dissolution reactions occurring in the test cell have contributed alkalinity to the pore water. The alkalinity of the water entering the test cell varies from 0 to 30 mg/L (as $CaCO_3$). Within the test cell, the alkalinity increases sharply to maximum values that are in excess of 2000 mg/L. This increase in alkalinity, and the removal of Fe(II) results in a decrease in the acid-generating potential of the water. Ferrous iron is a potential source of acidity when discharged to oxygenated surface water. Release of H^+ accompanies the oxidation of Fe(II) and the precipitation of Fe(III) hydroxides or hydroxysulfates, through reactions of the form:

$$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + 2H^+ \qquad (3)$$
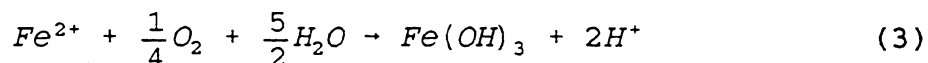
The addition of alkalinity increases the acid-consuming potential of the water through the reaction:

$$2H^+ + CO_3^{2-} \rightleftharpoons H_2CO_3 \qquad (4)$$

Using values typical of the influent water to the test cell, 1000 mg/L Fe(II) and 30 mg/L alkalinity (as $CaCO_3$), the acid generating potential of the influent water is approximately +35 meq/L H^+. The water within the cell has 5 mg/L Fe(II) and 1000 mg/L alkalinity (as $CaCO_3$), resulting in a net acid-generating potential of approximately -20 meq/L H^+. This change in acid-generating potential suggests that although the water influent to the cell has significant potential to generate acidic conditions if released to the surface-water environment, the water within the cell has no potential to generate acidic conditions.

The results of the sampling conducted in May and June of 1994, indicate the potential of reactive walls to remove sulfide-oxidation products from flowing groundwater at velocities that are typical of those observed at many mine-tailings impoundments. An unknown associated with the application of this technology is the longevity of the reactive material and the potential for long-term treatment of tailings-derived water using porous reactive walls. Although the results of a subsequent sampling in November, 1994, are incomplete, the preliminary results indicate dissolved Fe(II) and SO_4 are being removed to concentrations that are similar to those observed in May and June. Successful removal of sulfide-oxidation products from flowing groundwater for more than one year suggests that treatment using porous reactive walls may be viable for longer time periods.

Conclusions

A test-scale permeable reactive wall was installed in an aquifer downgradient from the Nickel Rim mine-tailings impoundment, near Sudbury, Ontario. Preliminary results indicate that interactions between organic carbon, contained in the reactive wall, and the influent tailings-derived water resulted in an increase in pH and decreased Eh conditions and concentrations of SO_4, Fe(II) and other metals. These reactions were sufficiently extensive to result in a change of the acid-generating potential of the tailings-derived water from a net acid-producing water to a net acid-consuming water. As a result, water passing through the barrier is not anticipated to contribute to the production of acidic conditions upon discharge to the surface-water flow system.

Measurements made in May and June, 1994, six and seven months after the installation of the reactive test cell indicate the potential for treatment of tailings-derived groundwaters at velocities that are typical of many inactive tailings areas. The presence of low concentrations of SO_4, Fe(II) and other metals within the test cell and in the downgradient effluent water, observed during a subsequent sampling in November, 1994, one year after installation, suggests that the reactive barrier will remain reactive for at least this period of time. Additional sampling of the test cell, and monitoring of the additional test cells, intended to assess varying sources of organic carbon, will continue in 1995.

The preliminary results of the field study indicate that porous reactive walls are a potential technology for the prevention of acid mine drainage at sites where oxidized tailings are underlain by permeable geological materials. Future assessment of this technology will permit the evaluation of the costs and benefits of this approach to the treatment of tailings-derived water.

Acknowledgments

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