

# A Full-Scale Porous Reactive Wall for Prevention of Acid Mine Drainage

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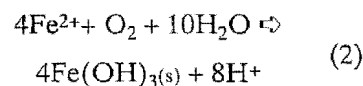
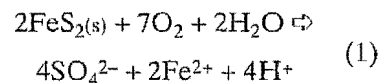
## Abstract

The generation and release of acidic drainage containing high concentrations of dissolved metals from decommissioned mine wastes is an environmental problem of international scale. A potential solution to many acid drainage problems is the installation of permeable reactive walls into aquifers affected by drainage water derived from mine waste materials. A permeable reactive wall installed into an aquifer impacted by low-quality mine drainage waters was installed in August 1995 at the Nickel Rim mine site near Sudbury, Ontario. The reactive mixture, containing organic matter, was designed to promote bacterially mediated sulfate reduction and subsequent metal sulfide precipitation. The reactive wall is installed to an average depth of 12 feet (3.6 m) and is 49 feet (15 m) long perpendicular to ground water flow. The wall thickness (flow path length) is 13 feet (4 m). Initial results, collected nine months after installation, indicate that sulfate reduction and metal sulfide precipitation is occurring. Comparing water entering the wall to treated water exiting the wall, sulfate concentrations decrease from 2400 to 4600 mg/L to 200 to 3600 mg/L; Fe concentrations decrease from 250 to 1300 mg/L to 1.0 to 40 mg/L; pH increases from 5.8 to 7.0; and alkalinity (as  $\text{CaCO}_3$ ) increases from 0 to 50 mg/L to 600 to 2000 mg/L. The reactive wall has effectively removed the capacity of the ground water to generate acidity on discharge to the surface. Calculations based on comparison to previously run laboratory column experiments indicate that the reactive wall has potential to remain effective for at least 15 years.

## Introduction

Acidic metal-rich drainage from mines and mine wastes is the largest environmental problem facing the North American mining industry (Feasby et al. 1991; USDA 1993). On United States Forest Service lands there are between 20,000 and 50,000 mines generating acidic drainage (USDA 1993). In Canada, potential acid-generating sites from base metal mining total more than 37,000 acres (Feasby et al. 1991). In the eastern United States, more than 4000 miles of rivers and streams are adversely impacted by acid mine drainage from coal mining (Kleinmann 1991). In the western United States, between 5000 and 10,000 miles of streams are impacted by metal mining (USDA 1993). Estimated costs for the stabilization of these sites are in the billions of dollars (Feasby et al. 1991).

Production of acidic drainage results from the oxidation of residual sulfide minerals and the subsequent oxidation of dissolved Fe(II) (Boorman and Watson 1976; Nordstrom et al. 1979; Dubrovsky et al. 1984). These reactions can be described as:



Similar reactions, involving other sulfide minerals, can release dissolved As, Cd, Cu, Ni, Pb, and

Zn. The oxidation of sulfide minerals and the oxidation of  $\text{Fe}^{2+}$  are often decoupled in mine tailings impoundments. Sulfide oxidation (Reaction #1) occurs in the unsaturated zone of the tailings releasing  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  to the tailings pore water. At many mine sites, infiltrating precipitation water carries these reaction products downward through the tailings and into underlying aquifers. Mineral phases within the mine waste material and aquifer sediment can buffer acidity, resulting in the formation of a ground water plume containing high concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{2+}$ , and other metals but at near-neutral pH (Morin et al. 1988; Blowes and Jambor 1990; Blowes and Ptacek 1994b). As this contaminated ground water discharges to oxygenated surface water bodies,  $\text{Fe}^{2+}$  oxidizes, releasing a second pulse of acidity to the environment (Reaction #2). Not only are the resulting low pH conditions harmful to biota, but these conditions also increase the mobility of toxic trace metals such as Cd, Cu, Ni, and Pb, greatly enhancing their bioavailability. In many cases, the flux of poor quality water from tailings impoundments will continue for many decades, even centuries (Morin et al. 1988; Blowes and Jambor 1990). It was the objective of this project to significantly decrease the toxicity of mine drainage effluent by preventing the generation of acidity at discharge to the surface by using sulfate reduction in a porous reactive wall.

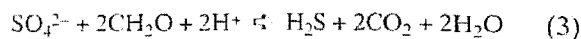
Current methods for the prevention and treatment of acid mine drainage include preventing the infiltration of meteoric water, preventing the oxidation of sulfides, and treating the acidic water discharge (Blowes et al. 1994). Recognition of the significance and causes of acidic drainage has resulted in changes in the approaches used in the design and operation of tailings disposal systems. The objectives of these changes are to prevent the oxidation of sulfides and the mobilization and subsequent release and transport of reaction products. There is often a delay of decades between the oxidation of the sulfides within the tailings and the eventual discharge to surface water bodies. Therefore, even at many tailings impoundments with remedial measures imposed, discharge of poor quality water will continue for many years (Blowes et al. 1994). Conventional treatment of discharge water involves precipitation of Fe-oxyhydroxides by addition of lime. This approach can be effective but often involves high operating costs and produces large volumes of metal-rich sludge from which metals may subsequently leach.

The remediation and prevention of acid mine drainage through the use of permeable, geochemically reactive walls may provide an effective, inexpensive alternative to conventional collection and treatment programs (Blowes 1990; Blowes et al. 1995). This paper describes the design and installation of a full-scale reactive barrier for the treatment of acid mine drainage at the inactive Nickel Rim mine tailings impoundment near Sudbury, Ontario.

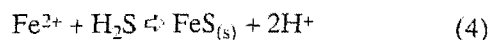
## Sulfate Reduction

Bacterially mediated reduction of sulfate can be

expressed as:



where  $\text{CH}_2\text{O}$  represents a generic organic carbon compound. In the presence of soluble metals, hydrogen sulfide can react to form metal sulfides:



Elements such as As, Cd, Cu, Ni, Pb, and Zn can also react with  $\text{H}_2\text{S}$  to form other sulfide minerals. This reaction sequence results in decreased concentrations of dissolved  $\text{SO}_4^{2-}$ , Fe, and other metals, and an increase in alkalinity and pH. All of these changes are desirable in water affected by mine drainage.

Tuttle et al. (1968) documented naturally occurring sulfate reduction in a stream contaminated by acid mine water. Wakao et al. (1979) suggested that mine water could be treated using sulfate-reducing bacteria. Recently, interest in sulfate reduction has focused on its utility during wetland remediation of acid mine drainage. Wetlands are often designed to treat acid mine drainage using processes of adsorption to solids within the wetland and Fe oxidation and precipitation (Reaction #2). Wetlands are also designed to incorporate anaerobic sulfate reduction (Reactions #3 and 4) (McIntire et al. 1990; Hedin 1989). The primary method of exploiting sulfate reduction has been to force acidic, metal, and sulfate-rich surface water into the subsurface of the wetland by an induced hydraulic gradient (McIntire et al. 1990; Machemer and Wildeman 1992). Others have attempted to use sulfate reduction within bioreactors containing a variety of organic materials (Dvorak et al. 1992; Hammack and Edenborn 1992; Bechard et al. 1993, 1995; Eger and Wagner 1995).

The success of using sulfate reduction for treatment of acidic mine water has been mixed. In many cases, sulfate reduction and metal sulfide precipitation have resulted in improved water quality. However, two factors have hampered this approach. First, high acidity can quickly consume any buffering capacity within the reactive organic material, resulting in a drop in pH. Acidic conditions limit bacterially mediated sulfate reduction (Brock and Madigan 1991), decreasing treatment capacity. Second, where neutral pH conditions have been maintained, the residence times within the reactive mixture are often not sufficient to remove the mass of sulfate and metals entering the system (Eger and Wagner 1995).

## Reactive Wall Technology

Blowes (1990) proposed in situ sulfate reduction to treat water contaminated with mine-related wastes within the saturated zone of tailings or within permeable reaction zones installed into the aquifer downgradient of tailings impoundments. By treating the water prior to the oxidation of  $\text{Fe}^{2+}$  (Reaction #2), the generation of additional acidity and accompanying enhanced

metal mobility is prevented. Because contaminated ground water is treated without pumping, the volume of water that is necessary to treat is smaller. It is also easier to maintain the reduced geochemical conditions necessary for sulfate reduction below the water table within the aquifer. Finally, sulfate reduction is optimized at the near-neutral pH conditions found in many aquifers.

We have attempted to exploit advantages of treatment within the aquifer using the emerging remediation technology of a permeable reactive wall. This method consists of installing an appropriate reactive material into the aquifer, so that contaminated water flows through the material. The reactive material induces chemical reactions that remove the contaminants from the water or otherwise cause a change that decreases the toxicity of the contaminated water. Methods have been developed for the treatment of chromate (Blowes and Ptacek 1992), halogenated organic compounds (Gillham and O'Hannesin 1992, 1994), nitrate (Robertson and Cherry 1995), phosphate (Baker 1993; Ptacek et al. 1994; Baker et al. 1996), and water contaminated by mine wastes (Blowes and Ptacek 1994a; Blowes et al. 1994). For the treatment of ground water affected by leachate derived from mine wastes, the porous reactive wall contains organic carbon to enhance sulfate reduction.

Laboratory and field pilot studies have established the potential utility of this remedial method. Waybrant et al. (1995) and Waybrant (1995) tested a variety of carbon substrates in both batch and column experiments. Batch experiments identified optimal organic carbon substrate materials. Column experiments evaluated the extent and duration of water treatment under dynamic flow conditions. Influent water contained elevated concentrations of  $\text{SO}_4^{2-}$  and  $\text{Fe}^{2+}$  and was similar in composition to aquifer water at the Nickel Rim mine site. The results of these experiments indicate that sulfate reduction and metal sulfide precipitation are the dominant mechanisms responsible for removing  $\text{SO}_4^{2-}$ , Fe, and other metals from the water. An ongoing column experiment continued to remove 1000 mg/L sulfate after more than 24 months. Small-scale field test cells were installed at the Nickel Rim site in the fall of 1993 and 1994. These test cells continue to induce sulfate reduction and metals removal within the aquifer 12 and 24 months after installation, indicating that this technology is transferable to a field setting (Blowes et al. 1995).

## Site Description

The physical and chemical hydrogeology of the site has been well characterized. Johnson (1993), Bain et al. (1995), and Bain (1996) describe the physical hydrogeology and aqueous geochemistry of the tailings impoundment and associated ground water plume. The aquifer is composed of fine-grained, glacio-fluvial quartz-feldspar sand and is 10 to 26 feet (3 to 8 meters) thick. The path length from the tailings dam to where it discharges into Moose Lake is about 425 feet (130 meters) (Figure 1). Bounded on the sides and at the

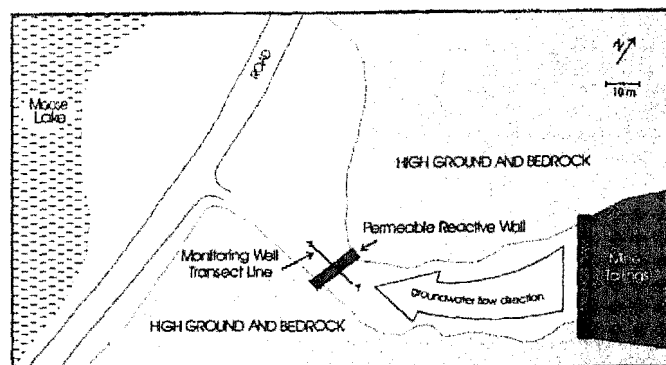


Figure 1. Map view of the Nickel Rim mine site, location of permeable reactive wall installation, and location of monitoring cross section A-A'.

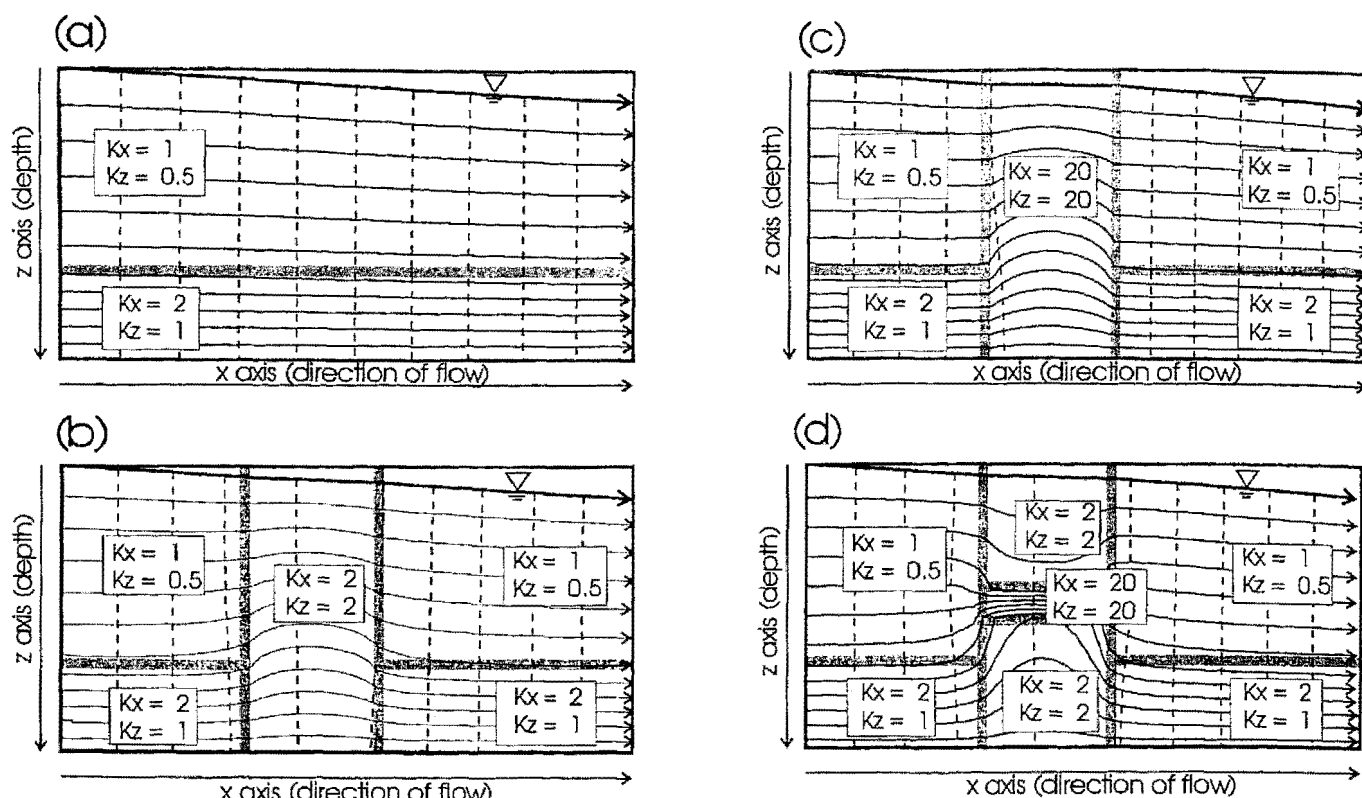
base by bedrock, the aquifer can be thought of as a long, sediment-filled trough in which ground water is flowing. Bain et al. (1995) estimated a ground water velocity in the aquifer of 49 ft./yr. (15 m/a). Residual sulfide minerals contained in the tailings impoundment are being oxidized, and water, migrating downward into the underlying aquifer, is acidic and contains high sulfate and metal concentrations. The chemical composition of the contaminated water is evolving as a result of a sequence of acid neutralization reactions as minerals in the tailings and aquifer sediment are gradually depleted. These reactions result in a progressive increase in pH along the ground water flow path. This increase in pH enhances the attenuation of most metals other than  $\text{Fe}^{2+}$ . The resulting plume contains high Fe and sulfate concentrations (500 to 2000 mg/L Fe and 1000 to 7000 mg/L sulfate) and is slightly acidic (pH 4-6) (Bain 1996). Both Bain (1995) and Johnson (1993) predict that poor quality water will continue to discharge from the tailings for at least 50 years.

## Methods

### Selection of Reactive Material

The material for the porous reactive wall must satisfy five criteria. First, the material must be sufficiently reactive to reduce sulfate concentrations found in the aquifer at Nickel Rim. The material also must be permeable enough to accommodate the ground water flux rates at the site. The material must sustain its permeability and reactivity over a time period of years. Finally, the material must be readily available and affordable with respect to site conditions.

The selection of organic carbon source material for this study was based on laboratory experiments conducted by Waybrant (1995). The results of these experiments indicate that leaf compost is an effective material for promoting sulfate reduction, and that mixtures containing a variety of different carbon sources are most effective. Fresh organic carbon sources are superior to older sources because they likely contain a higher concentration of short-chain, single-carbon-bond aliphatics, the primary substrate of sulfate-reducing bacteria (Brock and Madigan 1991). In addition to an available



**Figure 2.** Results of FLONET modeling showing idealized aquifer in cross section.  $K_x$  and  $K_z$  = hydraulic conductivity in the X and Y directions, respectively. (a) Aquifer with no reactive wall; lower layer is more permeable than upper layer. (b) Same as (a) but with reactive wall with permeability equivalent to lower layer of aquifer. (c) Same as (b) but with reactive wall 10X more permeable than aquifer. (d) Same as (b) but with small layer of higher permeability within reactive wall.

carbon source, sulfate-reducing bacteria also require nitrogen, phosphate, and other trace elements for growth (Brock and Madigan 1991). Based on these considerations, a substrate composed of 40 percent municipal compost, 40 percent leaf compost, and 20 percent wood chips was selected. Municipal compost was selected because it is readily available, is composed of a variety of materials, is rich in nitrogen and phosphate, as well as other trace nutrients, and can be acquired at a point during the composting sequence when only partial decomposition has occurred. Leaf compost was selected because it is readily available and was shown to be effective in long-term column experiments. Wood chips were selected because they are readily available,

are a source of fresh carbon, and their larger size may provide additional longevity.

The reactive mixture must maintain a hydraulic conductivity that is sufficient to accommodate the ground water flow in the aquifer. To increase the hydraulic conductivity of the reactive mixture, pea gravel was mixed with the substrate material. Constant head permeameter tests were conducted to determine an appropriate ratio of pea gravel to organic material. These tests indicate that the hydraulic conductivity of the mixture is sensitive to the ratio of gravel to substrate (Table 1) and that small variations in mixing and packing can have a dramatic impact on hydraulic conductivities. The hydraulic conductivities of all mixture ratios were high enough for use as a reactive wall material in the Nickel Rim aquifer. It was anticipated that dissolution of organics would result in some mass loss of the organic material fraction. To maintain hydraulic conductivity after installation, a ratio of gravel to organics was selected that would be essentially gravel supported (50 percent gravel and 50 percent organic material).

To evaluate the effect of variations in the hydraulic conductivity of the reactive material on the flow regime within the aquifer, ground water flow modeling using the two-dimensional finite element model FLONET was conducted. Parameter representations of the Nickel Rim aquifer were taken from Bain (1996). This modeling suggests that if the hydraulic conductivity of the reactive wall is an order of magnitude greater than the adjacent aquifer, good flow distribution within the

**Table 1**

**Hydraulic Conductivity of Mixtures of Gravel and Reactive Material**

Percentage Gravel	Hydraulic Conductivity (cm/sec)
70 percent	1.0
60 percent	0.5
55 percent	0.5
50 percent	0.4
45 percent	0.05
40 percent	0.02
30 percent	0.0005
Aquifer	0.002

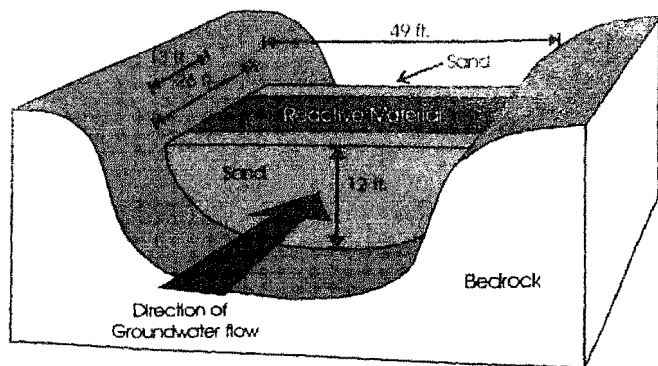


Figure 3. Schematic diagram of porous reactive wall installation.

wall is achieved (Figure 2). There is little change in the flow regime with additional increases in wall hydraulic conductivity (Figure 2). These results are consistent with the observations of Starr and Cherry (1994).

Channeling of flow decreases the contact time between the dissolved contaminants and the reactive material and decreases the total mass of carbon available, potentially leading to reductions in the effectiveness of the reactive wall. Simulations suggest that even small layers of higher hydraulic conductivity material within the wall will result in significant channeling of flow (Figure 2). To avoid preferential flow, the mixture must be homogeneous. To achieve a homogeneous mixture, a 130-foot (40 m) conveyor was used to mix the organic material and pea gravel. Gravel and compost were loaded onto the conveyor simultaneously and dumped into a single pile. This process was repeated with the mixed pile until a uniform mixture was obtained.

### Wall Installation

The reactive wall at Nickel Rim was installed where the bedrock valley narrows to minimize the costs in materials and installation while ensuring that all ground water flowing within the aquifer would pass through the treatment wall (Figure 1). The reactive wall was installed by cut and fill excavation; as the aquifer material was removed to bedrock, the hole was backfilled with the organic carbon and gravel mixture. The resulting structure stretches across the alluvial valley and is in direct contact with the bedrock on both sides and at the base. Sand fill was added at the up- and downgradient sides of the wall to square off the organic mixture with the sloping sides of the trench. These sand zones help to distribute flow evenly through the wall and facilitate sampling of the inflow and the outflow. A 12-inch (30 cm) clay cap was applied on top of the wall to minimize oxygen diffusion into, and water flow out of, the reactive mixture. The installed reactive mixture is approximately 49 feet (15 m) long, 12 feet (3.6 m) deep, and 13 feet (4 m) wide (Figure 3).

### Installation and Sampling of Monitoring Wells

Monitoring wells (2-inch [5 cm] wells and bundle

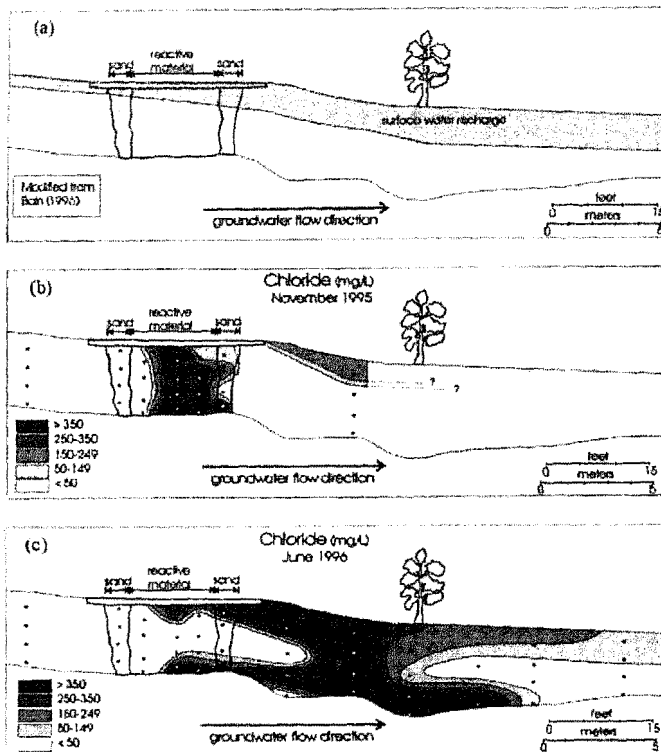


Figure 4. Cross-sectional profiles of reactive wall and adjoining aquifer. Small squares indicate sample locations. (a) Schematic diagram showing zone of aquifer receiving surface water recharge based on head profiles and water chemistry prior to reactive wall installation (From Bain 1996). (b) Profile of chloride concentrations one month after installation. (c) Profile of chloride concentrations nine months after installation.

piezometers) were installed in nests along a transect roughly parallel to ground water flow (Figure 4), establishing monitoring points up- and downgradient of, as well as within, the newly installed porous reactive wall. These wells were installed using a gasoline-powered vibrating hammer (Blair 1981; Dubrovsky 1986).

Samples of ground water were collected approximately one month and nine months after installation. Water samples were collected from installed wells using a peristaltic pump and passed through 0.45- $\mu$ m filters. Samples for cation analyses were acidified to pH < 1 using 12 N HCl. All samples were refrigerated at the field site and stored refrigerated until analyzed at the University of Waterloo or Falconbridge Ltd. Analytical Laboratory. Chemical analyses were conducted to determine the concentrations of Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, S, Sr, Zn by inductively coupled plasma emission spectrometry (ICP) or atomic adsorption spectrometry (AA), and  $\text{SO}_4$ ,  $\text{NO}_3$ , F, and Cl by ion chromatography. Dissolved organic carbon was analyzed by a total organic carbon method using a platinum catalyst and an infrared detector (Eaton et al. 1996). Replicate samples were collected from several locations. Determinations of pH (ORION<sup>®</sup> Ross 815600 Combination Electrode or Accumet<sup>®</sup> Standard 13-620-108 Gel Filled Combination Electrode) and Eh (ORION 9678BN Combination Electrode) were made at each piezometer using sealed cells maintained at ground water temperature. The pH electrode was cali-

brated using pH 4.0 and 7.0 buffer solutions (traceable to NIST). The performance of the Eh electrode was confirmed using prepared Zobell's solution (Zobell 1946; Nordstrom et al. 1977) and Light's solution (Light 1972). Determinations of alkalinity were made in the field by titration with standardized  $\text{H}_2\text{SO}_4$  using a digital titrator (Hach Instruments Ltd.).

## Results and Discussion

### Surface Water Recharge

A cross-sectional view of the flow field at the installation site (Figure 4) provides a physical framework for assessing the impact of the reactive wall on the aquifer. The organic material used in the reactive wall contained high  $\text{Cl}^-$  concentrations compared with the aquifer. The leaching of  $\text{Cl}^-$  from the reactive material resulted in the development of a distinguishable zone of water one month after installation. This zone contained concentrations of dissolved  $\text{Cl}^-$  of up to 6000 mg/L, much greater than the background concentration in the aquifer, approximately 7 mg/L. In addition to ground water flowing through the wall, untreated surface water recharged the aquifer downgradient of the reactive wall. This recharging surface water was acidic, with high concentrations of  $\text{SO}_4^{2-}$  and Fe. Before entering the aquifer, the untreated surface water flowed through a pile of compost material left over from the reactive wall installation and, therefore, also contained high  $\text{Cl}^-$  concentrations. As a result of this recharge, the aquifer downgradient of the reactive wall contained two merging plumes of  $\text{Cl}^-$ . One plume of treated water flowing from the wall occupied the lower portion of the aquifer, and a second plume of untreated water, emanating from the  $\text{Cl}^-$ -rich surface water recharge, occupied the upper portion of the aquifer (Figure 4). This  $\text{Cl}^-$  profile correlates well with the physical flow field profile. It indicates that treated water flowing from the reactive wall will occupy only the lower portion of the downgradient aquifer.

### Ground Water Velocity

The  $\text{Cl}^-$  profile after nine months shows the high- $\text{Cl}^-$  plug was located about 12 meters downgradient, indicating an average ground water velocity of 16 meters a year. This value is in good agreement with estimates of ground water velocities in the aquifer prior to installation of the permeable reactive wall (Bain 1995). The  $\text{Cl}^-$  profile within the wall shows high concentrations along the top and base, suggesting there is some preferential flow through the center of the wall.

### Water Chemistry

Comparing water entering the wall to treated water exiting the wall along transect A-A' (Figure 1) nine months after installation, sulfate concentrations decrease from 2400 to 4800 mg/L to 200 to 3600 mg/L;  $\text{Fe}^{2+}$  concentrations decrease from 250 to 1300 mg/L to 1.0 to 40 mg/L; pH increases from 4 to 6 to 6.6 to 7.0;

and alkalinity (as  $\text{CaCO}_3$ ) increases from 0 to 66 mg/L to 690 to 2300 mg/L (Figures 4 and 5). To assess the objective of preventing the mine effluent from generating acidity on discharge, the capacity of the ground water to generate acidity must be calculated. The acid-producing capacity of the water is a function of the concentration of ions that will generate acidity on discharge. In most mine effluents,  $\text{Fe}^{2+}$ , which forms sparingly soluble oxyhydroxides upon oxidation (Reaction #2), is the dominant acid-generating ion. In addition to acid-producing capacity, the ability of the water to buffer acidity (the alkalinity) must be known. The tendency of the water to produce acidic drainage on discharge can be calculated by subtracting the acid buffering capacity (the molar equivalents of dissolved carbonate alkalinity) from the acid-producing potential (molar equivalents of acid produced by oxidation of dissolved  $\text{Fe}^{2+}$ ):

$$\text{Potential Acidity} = \text{moles/L Alkalinity (as CaCO}_3\text{)} - 2(\text{moles/L Fe}^{2+}\text{)}.$$

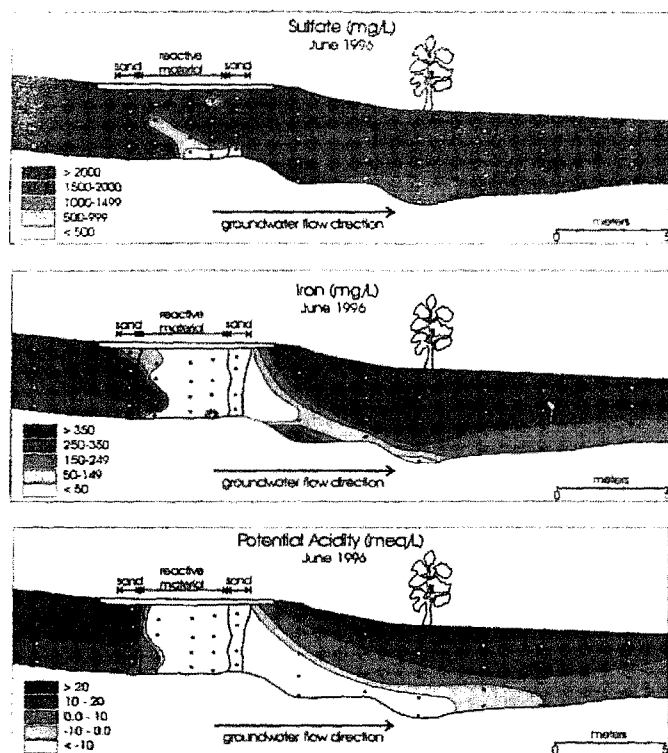
This is called the potential acidity and is a predictive form of mineral acidity as defined by Snoeyink and Jenkins (1980). A positive value indicates a net acid-producing potential and a negative value indicates a net acid-consuming potential. The water entering the wall had net potential acidity of 7.8 to 46 meq/L, while the water exiting the wall had net potential acidity of -16 to -45 meq/L (Figure 5).

Iron and  $\text{SO}_4$  removal occurred at a 1:1 molar ratio, consistent with the precipitation of an Fe mono-sulfide ( $\text{FeS}$ ). This stoichiometric constraint on the removal of Fe and  $\text{SO}_4$  by sulfide mineral precipitation appeared to limit the removal of  $\text{SO}_4$ . Once all of the Fe was removed, approximately half of the  $\text{SO}_4$  remained. Because Fe was the primary acid-generating constituent in the contaminated ground water, a removal ratio that results in excess  $\text{SO}_4$  is preferable to a ratio that results in excess Fe.

### Estimating Reactive Wall Longevity

The ultimate success of the porous reactive wall will be determined by the longevity over which sulfate reduction and metal sulfide precipitation is maintained. The ability of the wall to transform the ground water from acid producing to acid consuming is dependent on the removal of Fe. Therefore, change in Fe concentration as water passes through the wall is a useful measure of the reactive wall effectiveness. It may be assumed that the limiting factor will be the ability of the organic carbon to induce sulfate reduction. Previous work suggests that not all of the carbon is "available" for sulfate reduction (Eger and Wagner 1995). If the total usable carbon for sulfate reduction is limited, the thickness of the porous reactive wall will be proportional to its longevity. In addition, the amount of available organic carbon may also be a function of the amount of time that the sulfate and organic carbon are





**Figure 5.** Cross-sectional view of reactive wall and adjoining aquifer. Small squares indicate sample locations. Concentrations of sulfate and iron in ground water and calculated "potential acidity" nine months after installation are shown.

in contact. Longer residence times may overcome potential kinetic limitations on organic carbon reactivity and may increase the fraction of reactive carbon.

Reactive wall longevity can be estimated by comparison with results of laboratory column experiments conducted by Waybrant et al. (1995). In the laboratory, 300 to 1000 mg/L Fe was removed in a column with a residence time of 15 days and a travel path length of 0.3 m. Assuming a ground water velocity in the Nickel Rim aquifer of 16 meters/year and a wall thickness of 4 meters, the residence time is 90 days. Therefore, the wall residence times are six times longer, and path length is 12 times longer than the laboratory columns. Concentrations of Fe entering the reactive wall are 200 to 1000 mg/L, which is similar to concentrations used in the laboratory columns. Comparison of Fe concentration, path length, and residence time suggests that an estimate of reactive wall longevity based on laboratory column longevity is appropriate.

In the laboratory column (Waybrant et al. 1995), a minimum of 10 percent of the carbon has been consumed by sulfate reduction and metal sulfide precipitation. Assuming that 10 percent of the carbon in the reactive wall at Nickel Rim is available, an estimate of longevity can be made. The wall contains approximately 1,500,000 moles of carbon. Assuming that a minimum of 10 percent of that carbon (~150,000 moles) is available, the minimum amount of Fe that can be precipitated as sulfides by that carbon is 75,000 moles (based on stoichiometry of Reactions #3 and 4). Given a porosity of 0.4, ground water velocity of 16 m/a, and a

cross-sectional area of 45 m<sup>2</sup>, the flux of water through the wall is 288 m<sup>3</sup>/a. With an Fe concentration of 1000 mg/L, the annual flux will be about 5100 moles/yr. This suggests that the reactive wall will be effective for a minimum of 15 years. This estimate neglects potential losses in efficiency due to preferential flow within the wall, variations in the reactive mixtures used, or other differences due to scaling-up from bench-scale column experiments to field application. It is likely that there will be some preferential flow within the wall; this will result in decreased efficiency and a shorter operating lifetime. Plugging of the wall by accumulation of sulfide precipitates is not anticipated. With the reduction of sulfate and precipitation of a sulfide mineral phase, there is a corresponding conversion of organic material to HCO<sub>3</sub><sup>-</sup> (Reactions #3 and 4). Therefore, the process results in the exchange of organic material, with a specific gravity of 1 to 2, for solid phase sulfides which have a specific gravity of 3 to 5. Laboratory column studies indicate no change in hydraulic conductivity after more than 30 pore volumes (Waybrant 1996).

The accumulation of sulfides within the saturated reactive wall provides long-term mineral stability. The reoxidation of the sulfides will be limited by the availability of an electron acceptor to oxidize the sulfide. Possible oxidizers include O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, and Fe<sup>3+</sup>. Assuming that the hydraulic regime does not undergo significant change and the reactive wall remains below the water table, oxygen concentrations are limited to aqueous solubility. Even at saturation, the product of sulfide oxidation by oxygen would be on the order of tens of milligrams per liter. Nitrate is also rarely found in ground water at concentrations greater than 10 mg/L. Ferric iron concentrations are limited by the low solubility of iron oxyhydroxides. Significant concentrations of ferric iron occur at pH of less than 3; pH values less than 3 in ground water are rare, even in mine drainage settings (Blowes and Ptacek 1994b). In addition, all other oxidizable material (e.g., sulfides and organic matter) along the flow path within the tailings material and aquifer must be oxidized before an electron acceptor would become available to oxidize sulfides within the reactive wall.

### Cost of Installation

Materials and installation costs for the porous reactive wall were approximately \$30,000 (U.S. funds). Approximately half of that cost was materials and half was installation. This value does not include costs of monitoring and assessment. Costs will vary from site to site depending on the physical and chemical characteristics of the contaminated ground water plume.

### Conclusions

Installation of a porous reactive wall for prevention of acid mine drainage has resulted in dramatic improvement in downgradient ground water quality. Removal of >90 percent of soluble Fe and a greater than tenfold increase in alkalinity has converted the ground water

system from acid producing to acid consuming. Calculations based on comparison with previous column studies suggest a potential operational life time of >15 years. These results indicate that in situ sulfate reduction is a potentially effective treatment strategy for remediation of ground water plumes impacted by drainage from mining activities. Monitoring of the water quality exiting the wall will continue for a minimum of three years. Studies of the biogeochemical transformations within the wall and the aquifer are under way.

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## References

- Bain, J.G. 1996. The physical and chemical hydrogeology of sand aquifer affected by drainage from the Nickel Rim tailings impoundment, M.Sc. thesis, Dept. of Earth Sciences, University of Waterloo, Waterloo, Ontario.
- Bain, J.G., D.W. Blowes, and W.D. Robertson. 1995. The hydrogeochemistry of a sand aquifer affected by discharge from the Nickel Rim tailings, Sudbury, Ontario. In: *Proceedings of Sudbury '95-Mining and the Environment*, ed. T.P. Hynes and M.C. Blanchette, 715-723. Ottawa: CANMET.
- Baker, M.J. 1993. Laboratory investigations into the potential for solid mixtures containing industrial products to remove phosphate from solution. M.Sc. thesis, Dept. of Earth Sciences, University of Waterloo, Waterloo, Ontario.
- Baker, M.J., D.W. Blowes, and C.J. Ptacek. 1996. Development of a reactive mixture to remove phosphorous from on-site wastewater disposal systems. In: *Waterloo Centre for Groundwater Research Conference Proceedings for Disposal Trenches, Pre-Treatment, and Re-Use of Wastewater*, 51-56, by University of Waterloo. Waterloo, Ontario: University of Waterloo.
- Bechard, G., R.G.L. McCready, D.W. Koren, and S. Rajan. 1995. Microbial treatment of acid mine drainage at Halifax International Airport. In *Proceedings of Sudbury '95- Mining and the Environment*, ed. T.P. Hynes and M.C. Blanchette, 545-554. Ottawa: CANMET.
- Bechard, G., S. Rajan, W.D. Gould, A.E. Torma, M.L. Apel, and C.L. Brierley, eds. 1993. *Characterization of microbiological processes for the treatment of acidic mine drainage*. Warrendale, Pennsylvania: TMS.
- Blair, R.D. 1981. Hydrogeochemistry of an inactive pyritic, uranium tailings basin, nordic mine, Elliot Lake, Ontario. M.Sc. thesis, Dept. of Earth Sciences, University of Waterloo, Waterloo, Ontario.
- Blowes, D.W. 1990. *The geochemistry, hydrogeology and mineralogy of decommissioned sulphide tailings: A comparison study*, Ph.D. thesis, Dept. of Earth Sciences, University of Waterloo, Waterloo, Ontario.
- Blowes, D.W., and J.L. Jambor. 1990. The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings. Waite Amulet, Quebec, Canada. *Appl. Geochem.* 5, 327-346.
- Blowes, D.W., and C.J. Ptacek. 1992. Geochemical remediation of groundwater by permeable reactive walls. Removal of chromate by reduction with iron bearing solids. In *Proceedings of the Subsurface Restoration Conference, Third International Conference on Groundwater Quality Research*, Dallas, Texas, 21-24 June, 214-216.
- Blowes, D.W., and C.J. Ptacek. 1994a. University of Waterloo, W., Canada, assignee. System for Treating Contaminated Groundwater. U.S. 5514279.1994. 329,826. C07F 1/58. 210/617; 210/719; 210/720; 210/721; 210/747.
- Blowes, D.W., and C.J. Ptacek. 1994b. Acid neutralization mechanisms in inactive tailings impoundments. In *Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes*, ed. J.L. Jambor and D.W. Blowes, 271-292. Nepean, Ontario: Mineralogical Association of Canada.
- Blowes, D.W., C.J. Ptacek, J.G. Bain, K.R. Waybrant, and W.D. Robertson. 1995. Treatment of mine drainage water using in situ permeable reactive walls. In *Proceedings of Sudbury '95-Mining and the Environment*, ed. T.P. Hynes and M.C. Blanchette, Vol. 3, 979-987. Ottawa: CANMET.
- Blowes, D.W., C.J. Ptacek, and J.L. Jambor. 1994. Remediation and prevention of low-quality drainage from tailings impoundments. In *Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes*, ed. D.W. Blowes and J.L. Jambor, 22nd edition, 365-379. Nepean, Ontario: Mineralogical Society of Canada.
- Boorman, R.S., and D.M. Watson. 1976. Chemical processes in abandoned sulfide tailings dumps and environmental implication for northeastern New Brunswick. *CIM Bulletin* 69, no. 772: 86-96.
- Brock, T.D., and M.T. Madigan. 1995. *Biology of microorganisms*. 6th ed. Englewood Cliffs, New Jersey: Prentice Hall.
- Dubrovsky, N.M. 1986. Geochemical evolution of inactive pyritic tailings in the Elliot Lake uranium district. Ph.D. thesis, Dept. of Earth Sciences, University of Waterloo, Waterloo, Ontario.
- Dubrovsky, N.M., K.A. Morin, J.A. Cherry, and D.J.A. Smyth. 1984. Uranium tailings acidification and subsurface contaminant migration in a sand aquifer. *Water Poll. Res. J. Canada* 19, no. 2: 55-89.
- Dvorak, D.H., R.S. Hedin, H.M. Edenborn, and P.E. McIntire. 1992. Treatment of metal-contaminated water using bacterial sulphate reduction: Results from pilot-scale reactors. *Biotech. Bioeng.* 40, no. 2: 609-616.
- Eaton, A.D., L.S. Clesceri, and A.E. Greenberg, eds. 1996. *Standard methods for the examination of water and wastewater*. 19th ed. Washington, D.C.: APHA.
- Eger, P., and J. Wagner. 1995. Sulfate reduction for the treatment of acid mine drainage: Long term solution or short term fix? In *Proceedings of Sudbury '95- Mining and the Environment*, ed. T.P. Hynes and M.C. Blanchette, v. 2, 515-524. Ottawa: CANMET.
- Feasby, D.G., M. Blanchette, and G. Tremblay. 1991. The mine environment neutral program. In *Second International Conference on the Abatement of Acidic Drainage*, v. 1, 1-26. Ottawa: MEND, CANMET.
- Gillham, R.W., and S.F. O'Hannesin. 1992. Metal-catalysed abiotic degradation of halogenated organic compounds. In *IAH Conference "Modern Trends in Hydrogeology"*, Hamilton, Ontario, 10-13 May, 94-103.



- Gillham, R.W. and S.F. O'Hannesin. 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* 32, no. 6: 958-967.
- Gillham, R.W., and O'Hannesin, S.F. 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* 32, no. 6: 958-967.
- Hammack, R.W., and H.M. Edenborn. 1992. The removal of nickel from mine waters using bacterial sulphate reduction. *Appl. Microbiol. Biotechnol.* 37, 674-678.
- Hedin, R.S. 1989. Treatment of coal mine drainage with constructed wetlands. In *Wetlands Ecology and Conservation: Emphasis in Pennsylvania*, ed. S.K. Majumdar, R.P. Brooks, F.J. Brenner, R.W. Tiner, 349-362. The Pennsylvania Academy of Science.
- Johnson, R.H. 1993. The physical and chemical hydrogeology of the Nickel Rim mine tailings, Sudbury, Ontario, M.Sc. thesis, University of Waterloo, Waterloo, Ontario.
- Kleinmann, R.L.P. 1991. Acid Mine Drainage: An Overview. In *Proceedings of Conference Energy in the 90s*, ed. B.F. Hobbs, 281-282. New York: American Society of Civil Engineering.
- Light, T.S. 1972. Standard solution for redox measurements. *Anal. Chem.* 44, no. 6: 1038-1039.
- Machemer, S.D., and T.R. Wildeman. 1992. Adsorption compared with sulphide precipitation as metal removal processes from acid mine drainage in a constructed wetland. *J. Contam. Hydro.* 9, 115-131.
- McIntire, P.E., H.M. Edenborn, and R.W. Hammack. 1990. Incorporation of bacterial sulphate reduction into constructed wetlands for the treatment of acid and metal mine drainage. In *National Symposium on Mining*, 207-213. Lexington, Kentucky: University of Kentucky.
- Morin, K.A., J.A. Cherry, N.K. Dave, T.P. Lim, and A.J. Vivyurka. 1988. Migration of acidic groundwater seepage from uranium-tailings impoundments, 1. Field study and conceptual hydrogeochemical model. *J. Contam. Hydro.* 2, 271-303.
- Nordstrom, D.K., E.A. Jenne, and J.W. Ball. 1977. Thermochemical redox equilibria of Zobell's solution. In *Chemical modeling of natural systems*, eds. A.J. Everett and J.W. Ball, 51-79. Washington, D.C.: American Chemical Society.
- Nordstrom, D.K., E.A. Jenne, and J.W. Ball. 1979. Redox equilibria of iron in acid mine waters. In: *Chemical modeling of natural systems*, ed. A.J. Everett and J.W. Ball, 52-79. Washington, D.C.: American Chemical Society.
- Ptacek, C.J., D.W. Blowes, W.D. Robertson, and M.J. Baker. 1994. Adsorption and mineralization of phosphate from septic system effluent on aquifer materials. In *Proceedings of the Waterloo Centre for Groundwater Research Annual Septic System Conference*, 26-44. Waterloo, Ontario: Waterloo Centre for Groundwater Research.
- Robertson, W.D., and J.A. Cherry. 1995. In situ denitrification of septic system nitrate using reactive porous media barriers: Field trials. *Ground Water* 33, no. 1: 99-111.
- Snoeyink, V.L., and D. Jenkins. 1980. *Water chemistry*. New York: John Wiley and Sons.
- Starr, R.C., and J.A. Cherry. 1994. In situ remediation of contaminated groundwater: The funnel-and-gate system. *Ground Water* 32, no. 3: 465-476.
- Tuttle, J.H., C.I. Randles, and P.R. Dugan. 1968. Activity of microorganisms in acid mine water, I. Influence of acid water on aerobic heterotrophs of a normal stream. *J. Bacteriol.* 95, 1495-1503.
- USDA. 1993. Acid drainage from mines on the National Forest: A management challenge. *U.S. Forest Service Publication*, 1505, 1-12.
- Wakao, N., T. Takahashi, Y. Sakurai, and H. Shita. 1979. The treatment of acid mine water using sulphate-reducing bacteria. *J. Ferment. Technol.* 57, 445-452.
- Waybrant, K.R. 1995. The prevention of acid mine drainage using in situ porous reactive walls: A laboratory study. M. Sc. thesis, Dept. of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada.
- Waybrant, K.R., D.W. Blowes, and C.J. Ptacek. 1995. Selection of reactive mixtures for the prevention of acid mine drainage using porous reactive walls. In *Proceedings of Sudbury '95 — Mining and the Environment*, ed. T.P. Hynes and M.C. Blanchette, Vol. 3., 945-953. Ottawa: CANMET.
- Waybrant, K.R., D.W. Blowes, C.J. Ptacek, and S.G. Benner. 1997. A geochemical and mineralogical investigation of porous reactive walls for prevention of acid mine drainage. In *Proceedings of Fourth International Conference on Acid Rock Drainage*, 1645-1658. Ottawa: CANMET.
- Zobell, C.E. 1946. Studies of redox potential of marine sediments. *Bul. Amer. Ass. Petrol. Geol.* 30, no. 4: 477-513.

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