CHAPTER 17. TREATMENT OF MINE DRAINAGE USING PERMEABLE REACTIVE MATERIALS

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INTRODUCTION

The disposal of sulfide-bearing waste rock and tailings in surface facilities has the potential to create environmental concerns. At active minesites, the waste-management operations can be closely controlled. Environmental management programs are complex because of the large quantities of waste rock, mill tailings, and wastewater generated by an active mining operation. At decommissioned and inactive minesites, often the mine-waste materials extend beyond the limits of the original disposal areas because of material transport by wind and water. The oxidation of sulfide minerals within mine wastes has the potential to damage terrestrial and aquatic ecosystems as a consequence of the release of acidic solutions, possibly containing elevated concentrations of metals and metalloids, to surface-water and groundwater systems. The oxidation of sulfide minerals, such as pyrite [FeS_2] in the presence of oxygen and water in the vadose zone of tailings or waste-rock impoundments can be represented by the reaction:

$$2\,FeS_{2(s)} + 7\,O_2 + 2\,H_2O \rightarrow 4\,SO_4^{2-} + 2\,Fe^{2+} + 4\,H^+ \quad (1)$$

The effluent derived from mine waste undergoing sulfide oxidation has a low pH and contains elevated concentrations of sulfate, ferrous iron, and dissolved heavy metals or metalloids. The heavy metals can originate as the principal components of mineral species, or as the solid-solution trace components of other minerals, especially Fe-sulfide minerals. The effluent water can migrate with infiltrating recharge water through the tailings or waste rock along the groundwater-flow system within and adjacent to the impoundments. Effluent water may move laterally and discharge to streams or ponds within and adjacent to the waste impoundment, or the water may move vertically through the impoundment to underlying aquifer systems (Fig. 1).

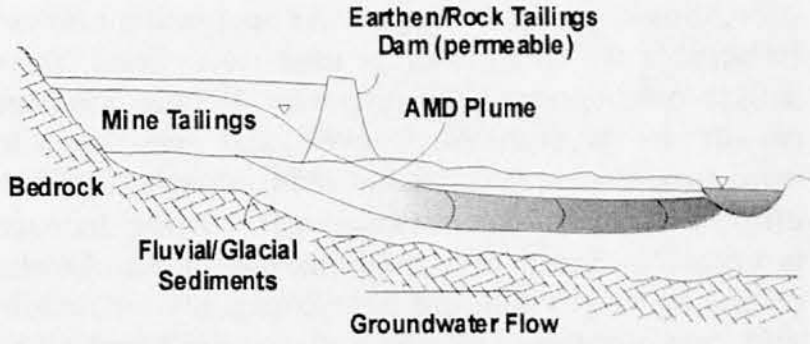

FIG. 1. Schematic section of a mine-tailings impoundment. Sulfate and metals released by sulfide oxidation in the vadose zone of the tailings move downward and laterally through the tailings and the underlying aquifer. When these oxidation products discharge to surface-water systems, the oxidation of ferrous iron causes pH to decrease.

The geochemical evolution of the groundwater as it moves through the waste and underlying geological materials is controlled by a complex series of acid-neutralization and chemical-precipitation reactions (Blowes & Ptacek 1994a, Blowes *et al.* Chapter 5 in this Volume). At many minesites, effluent from sulfide mine-waste has neutral pH. Although the pH of the groundwater can range from <3 to neutral within and beneath the impoundments, Fe(II) and SO_4 concentrations typically remain high. Discharge of the groundwater to surface water releases dissolved metals to aquatic systems, and the Fe(II) oxidizes to Fe(III). This can be represented as:

$$4\,Fe^{2+} + O_2 + 10\,H_2O \rightarrow 4\,Fe(OH)_{3(s)} + 8\,H^+ \quad (2)$$

The reaction results in the precipitation of ferric oxyhydroxides and the generation of additional acidity in the surface water.

Arsenic is commonly associated with the sulfide minerals that are present in gold ores and coal. In mine wastes, the As may be present as a distinct sulfide mineral, such as arsenopyrite [FeAsS], or may be a trace component of other sulfide minerals. Arsenic may be released from mine wastes by sulfide oxidation. Oxyanion-forming metals such as As behave differently than cation-forming metals released in mine drainage. Unlike many other heavy metals, As is mobile in groundwater under a wide range of pH conditions: acidic, neutral, and alkaline. Under typical neutral-pH conditions, As is mobile in groundwater in both the As(III) and As(V) oxidation states.

MANAGEMENT OF MINE DRAINAGE

Management of mining waste areas is required to maintain the physical stability of the waste impoundment, and to control and treat surface runoff and groundwater derived from waste disposal sites. Covers have been used to prevent sulfide oxidation, to limit water flow through waste piles, and to minimize the potential for erosion and sedimentation (Wireman 2001, Wilson in Chapter 18 of this Volume, Ritchie & Bennett in Chapter 19 of this Volume).

Although several alternatives exist for the prevention of acidic drainage, these approaches may not be suitable for remediation at mine-waste areas where sulfide oxidation and the migration of mine drainage off-site are in progress. Conventional approaches to management include collection and treatment of surface effluent. At sites where acidic, metal-bearing drainage is a problem, practices to minimize the impact of metal release to the environment have commonly focused on acid neutralization and metal attenuation through the addition of lime at discharge points (Jambor *et al.* 2000). The water-treatment facilities for this type of activity may be large and require on-going maintenance and expenditures. Limestone drains are a passive, alternative treatment for acidic mine drainage. The performance of anoxic limestone drains can be complicated by encrustation, and thus passivation, of the 'reactive' limestone by dissolved metals contained in the drainage (Cravotta & Trahan 1999). Wetlands have also been used to treat the effluent from mines and mine wastes (Eger *et al.* 1994, Sobelewski *et al.* 1995, Walton-Day in Chapter 16 of this Volume).

In-situ treatment of mine drainage

Sulfate reduction. Passive interception and *in-situ* treatment of groundwater affected by mine-waste leachate have been suggested as a control for the subsurface drainage component of environmental mine-waste management programs (Blowes & Ptacek 1991, Blowes *et al.* 1994). Treatment can occur below the water table within the mine wastes, or in groundwater seepage paths emanating from the waste impoundments. Treatment is achieved through the addition, to the subsurface, of reactive materials that promote the removal of sulfate, Fe, or other contaminants from groundwater by geochemical reactions. Tuttle *et al.* (1969) used a batch reactor containing wood-dust cellulose to promote sulfate reduction by a mixed culture of anaerobic bacteria, and noted removal of sulfate and a net increase of pH in AMD and sulfate salt solutions. Grinenko & Ivanhoff (1983) identified sulfate-reducing bacteria as a group of obligate anaerobic bacteria that utilize organic carbon. Organic carbon has been used as a reactive medium for supporting bacterially mediated sulfate reduction and the removal of divalent metals (*e.g.*, Cd, Co, Cu, Fe, Ni, Pb, Zn) contained in mine drainage (Dvorak *et al.* 1992, Eger 1992, Eger & Wagner 1995, Waybrant *et al.* 2002).

Sulfate-reducing bacteria (SRB) are ubiquitous in the environment. These are heterotrophic bacteria that reduce sulfate to sulfide in the absence of oxygen (*e.g.*, *Desulfovibrio desulfuricans*). Using a general form of a carbohydrate, microbially mediated sulfate reduction results in the generation of H_2S and bicarbonate ion (Berner 1971) as represented by the reaction:

$$SO_4^{2-} + 2\,CH_2O \rightarrow H_2S + 2\,HCO_3^- \qquad (3)$$

In the presence of hydrogen sulfide, soluble metals or metalloids may precipitate as low-solubility sulfide minerals through the reaction:

$$Me^{2+} + H_2S \rightarrow MeS + 2\,H^+ \qquad (4)$$

where *Me* represents a variety of divalent metals or metalloids, such as Fe, Cd, Cu, Co, Ni, Zn, As, or Se. In combination, the sulfate-reduction and sulfide-precipitation reactions have the potential effect of decreasing the concentrations of sulfate, Fe, and other metals and metalloids, and of increasing the alkalinity and pH.

Although this process occurs naturally in many subsurface environments, the addition of solid-phase organic material to mine-waste materials within impoundments, or in the groundwater-flow system external to the impoundments, provides the SRB with a rich supply of electron-donating material, thereby promoting sulfate reduction, sulfide precipitation, and the improvement of water quality. Sulfate-reducing bacteria require anaerobic conditions and consequently are more likely to be active below the water table, where concentrations of dissolved oxygen are low, and gas-phase O_2 is absent. Under water-saturated conditions, the oxidation of sulfide precipitates in the reactive materials is limited by the low solubility of oxygen in water (~10 mg L^{-1} O_2 solubility at 15 °C). The sulfide minerals will remain stable because they are protected from any influx of oxidizing water, due to the high capacity for the organic carbon to consume oxygen.

A variety of forms of organic carbon is widely available and is inexpensive for use in *in-situ* treatment systems. Examples of suitable material include municipal compost, forestry waste, leaf mulch, and manure (Eger & Wagner 1995, Waybrant *et al.* 1998). Many of these are waste products or low-cost materials.

Other reactive materials have been investigated for the treatment of metal-bearing water, and potentially for the treatment of mine drainage. Mixtures containing zero-valent iron [Fe^0] have been used to remove dissolved electroactive metals (*e.g.*, Cr, Hg, U, Cu, Se) from contaminated water (Blowes *et al.* 1997, 1999a,b, Benner *et al.* 1999, McRae *et al.* 1999, Morrison *et al.* 2001, Bain *et al.* 2002). McRae *et al.* (1999) used iron

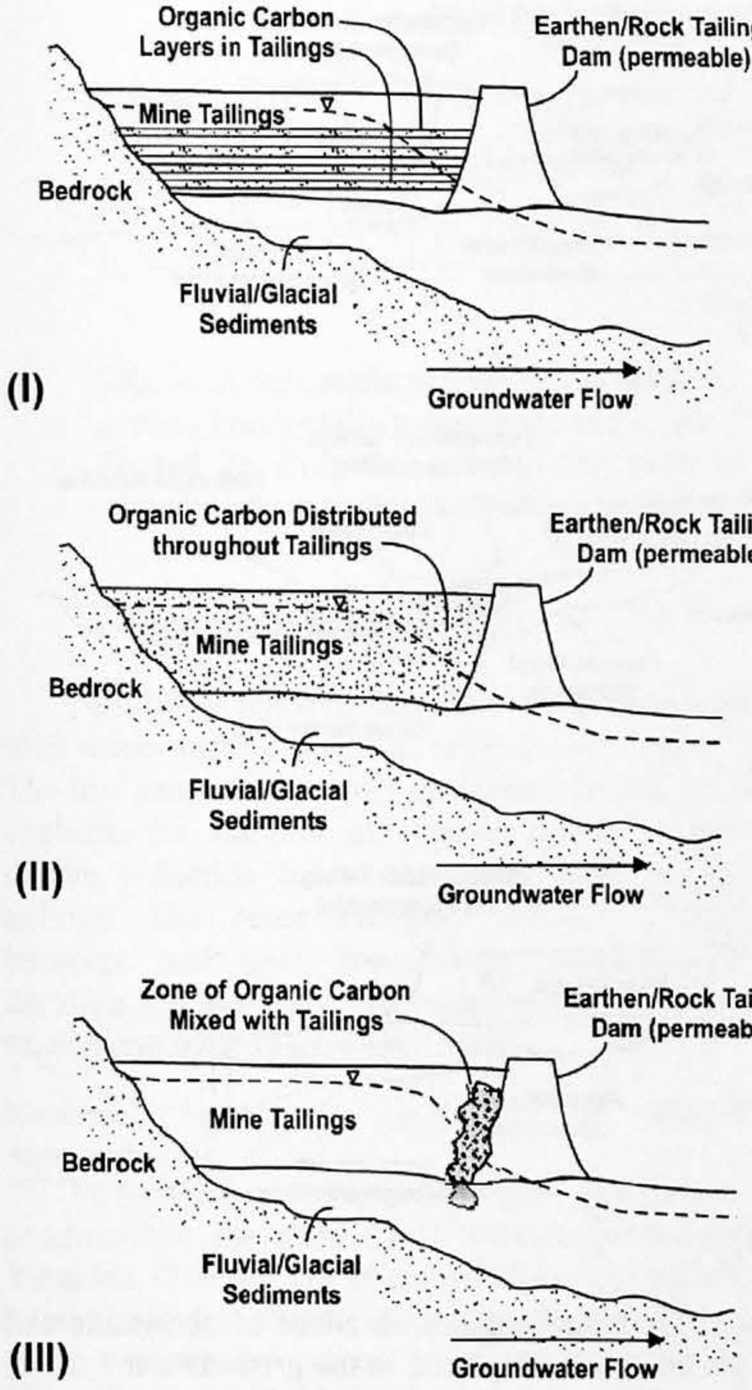

FIG. 2. As porewater moves through the tailings impoundment, organic carbon added below the water table promotes sulfate reduction and the precipitation of sulfide minerals. The organic material could be: **(I)** in the form of horizontal layers across the impoundment, emplaced as the tailings are deposited; **(II)** dispersed throughout the tailings by mixing during deposition; or **(III)**, added by mechanical mixing to zones that intercept the migration of AMD-impacted groundwater in the tailings.

oxides, activated alumina, and Fe^0 successfully for the removal of As(III) and As(V), and Fe^0 for the removal of Se(VI).

CONCEPTUAL APPROACHES TO *IN-SITU* TREATMENT

Reactive layers or mixtures in tailings

Blowes & Ptacek (1991) described incorporating organic carbon below the water table in mine tailings to promote the treatment of tailings porewaters. Sulfide-oxidation products are generated in the vadose zone in the tailings, consistent with Figure 2, and are transported to the groundwater zone with infiltration. Although acid-neutralization reactions provide some attenuation, the migration of sulfate and Fe with groundwater flow below the water table beyond the limits of the impoundment can be expected to occur. If organic carbon materials are available in the tailings material below the water table, conditions favorable for sulfate reduction and the precipitation of Fe-sulfide and other metal-sulfide minerals will be generated. The primary benefit of the removal of sulfate, Fe, and other metals from the groundwater within the mine-waste impoundment is that seepage-water quality will improve and the demands for control of off-site drainage can be expected to decrease.

At active mines, the organic carbon amendments can be distributed throughout the tailings at the time of disposal, or can be placed as horizontal layers periodically during disposal. Regardless of the emplacement technique, a volume of organic carbon sufficient to sustain the remedial geochemical reactions for the duration of sulfide oxidation in the vadose zone is required.

The use of organic materials to minimize the migration of contaminants away from inactive waste impoundments may also be possible. Emplacement of the organic materials within the tailings is likely to be more challenging. The organic material would need to be added below the water table in a manner to intercept a significant portion of the impoundment drainage so that sulfate reduction and sulfide precipitation can occur. Possible methods of emplacement include deep soil mixing of organic material with tailings, or the construction of permeable zones of organic material within the tailings adjacent to primary seepage pathways from the impoundment.

Permeable reactive barriers

The migration of dissolved contaminants along groundwater flowpaths from mine-waste impoundments releases tailings-derived constituents to adjacent watersheds at many minesites. Remedial goals at these sites commonly are achieved by collecting contaminated groundwater by pumping and treating the recovered water prior to discharge. Interception and treatment of contaminated groundwater is a conventional approach to remediation. However, because of the large areal extent of many tailings impoundments, containment of the mine-drainage plume by groundwater pumping, and treating that water prior to release, is a costly option that will require ongoing maintenance for years or decades. Capital, operational, and maintenance costs for pumping and wastewater-treatment systems can be significant.

Blowes & Ptacek (1994b, 1996) described the passive interception and *in-situ* treatment of groundwater containing metals and other inorganic contaminants by using permeable reactive barriers (PRBs). PRBs are designed to intercept and passively treat plumes of contaminated groundwater. PRBs typically consist of reactive material that has been installed in an excavated trench or cavity, thereby replacing the native aquifer material. As groundwater flows through the reactive material, contaminants are degraded or removed within or downgradient of the PRB by physical, chemical, or biological processes. PRBs are a remedial option that potentially offers relief from constant long-term maintenance.

Possible methods for installation of PRBs include continuous trenching (Blowes *et al.* 1999a), excavation and backfill (Benner *et al.* 1997), slurry trenching (Mountjoy & Blowes 2002), or temporary sheet-piling or trench box (O'Hannesin & Gillham 1998). Slurry trenching has been used to install PRBs to depths of more than 15 m (Mountjoy & Blowes 2002) and is likely appropriate for installations of up to 25 m.

The removal of electroactive metals, metalloids, and radionuclides from groundwater has been achieved by reductive precipitation using zero-valent iron, by microbially mediated sulfate reduction using organic carbon mixtures, and by sorption and precipitation using Basic Oxygen Furnace (BOF) slag. The use of mixtures containing organic carbon is generally the most appropriate for PRBs to treat mine drainage. A key design feature of a PRB is that groundwater should flow uniformly and unimpeded through the reactive material under the natural hydraulic gradient. To meet this condition, the mixture should have a hydraulic conductivity that at least equals or is greater than that of the surrounding formation. Organic carbon is commonly the least permeable component in a reactive mixture. In some cases it is necessary to increase the hydraulic conductivity of the mixture by including a coarse-grained material, such as pea gravel.

As indicated in Figure 1, mine-waste seepage can migrate with groundwater flow away from mine-waste impoundments, toward the receiving surface-water systems. Formation of the seepage plume begins shortly after deposition of the mine wastes, and the leading edge of the plume advances farther from the impoundment with increasing time. For a plume that is increasing in extent, a PRB could be installed across the path but in advance of the plume (Fig. 3(I)). If the plume of AMD-impacted groundwater is already discharging to a receiving surface-water body (Fig. 3(II)), PRB installation could occur near the surface-water body. Another consideration for the position of a PRB relative to a mine-waste impoundment is the depth interval over which the plume occurs. If the bottom of the plume is confined by low-permeability bedrock or a silt or clay aquitard, it may be feasible to construct a PRB through the aquifer to the confining unit (Fig. 3(III)). On the other hand, the vertical extent of the contaminant plume in a thick aquifer may be constrained by hydraulic gradients in the vicinity of the receiving surface water. In this case, the PRB could be constructed to a depth slightly deeper than the base of the plume, but need not intercept an underlying confining unit.

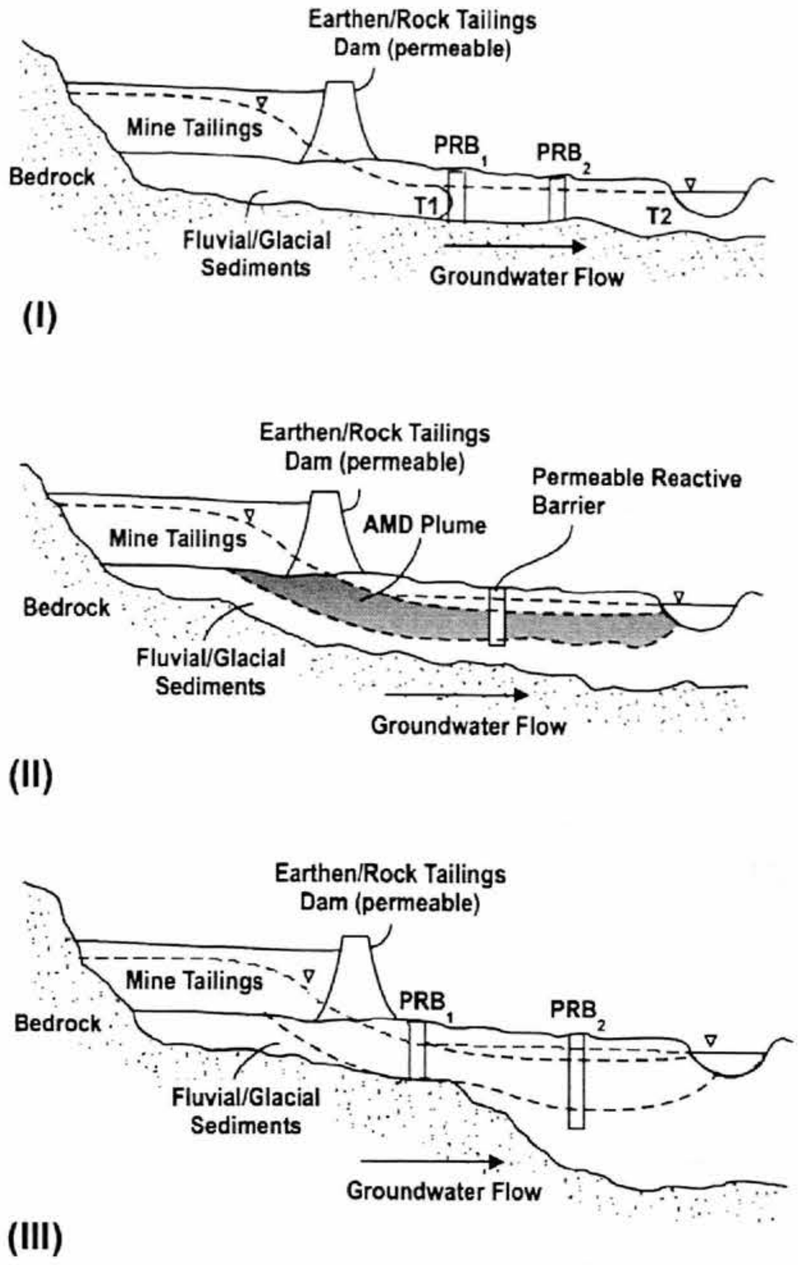

FIG. 3. PRBs are engineered zones of permeable and reactive materials emplaced in the groundwater system. PRBs provide passive interception and *in-situ* treatment of contaminated groundwater. For groundwater impacted by mine wastes, sulfate-reduction PRBs can remove metals and metalloids and decrease the acid-generating potential of the groundwater. PRBs can be installed: **(I)** in advance of the leading edge of contaminant plumes; or **(II)** across existing plumes to decrease future impacts of AMD on receiving surface waters or other receptors. A PRB may extend through the entire depth of an aquifer, or extend to depths slightly greater than the base of the plume **(III)**.

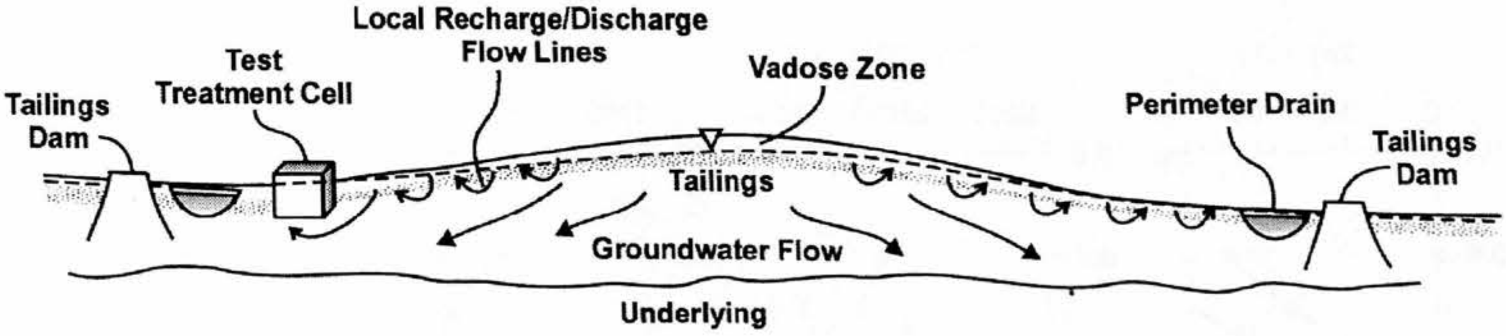

FIG. 4. A schematic section of the Kidd Creek impoundment. Groundwater flow is from the central portion horizontally towards the perimeter of the impoundment. A field trial evaluated the removal of Fe and Zn from the groundwater, prior to its discharge to the perimeter drain, by using organic amendments to promote sulfate reduction and the precipitation of metal sulfides.

CASE STUDIES

Permeable reactive materials have been used to treat mine-waste effluent in several field applications. The first example describes an experiment conducted to evaluate the addition of organic carbon to promote sulfate reduction below the water table in sulfidic tailings. The other examples describe PRBs that intercept and treat groundwater containing mine-drainage water, metals, and metalloids by using organic carbon and other reactive materials.

Reactive layers or mixtures in mine-waste impoundments

In September 1999, a field-scale experiment was conducted at the Kidd Creek Metallurgical Site near Timmins, Ontario. The objective of the experiment was to evaluate the extent of *in situ* treatment achieved using two organic carbon amendments to the tailings (Fig. 4). At the Kidd Creek site, concentrator tailings are deposited from a series of central spigot points as a thickened tailings slurry that contains 62 wt% solids. The tailings are deposited in a conical pile that covers an area of approximately 1200 ha. The conical pile is 15 m in depth at its peak, and is several thousand metres in diameter. Sulfide minerals account for as much as 25% of the tailings solids, and include pyrite, pyrrhotite, chalcopyrite and sphalerite. Synthetic Na jarosite ('natrojarosite') residue, a by-product of the zinc refining process, has been co-disposed with the tailings since 1985. The process residue contains zinc ferrite, gypsum [$CaSO_4{\cdot}2H_2O$], 'natrojarosite' [$(Na_{0.75}K_{0.01}(H_3O)_{0.24})Fe_3(SO_4)_2(OH)_6$], goethite [$\alpha$-FeOOH], and other phases (Al *et al.* 1994). Al *et al.* (1994) indicated that As, Pb and, in particular, Zn are present at significant concentrations in the natrojarosite. The dissolution of the natrojarosite residue releases SO_4, Fe, Na, Zn, As, and other metals to the tailings porewater in the central part of the tailings cone (Al *et al.* 1994). The depth to the water table in the central portion of the tailings impoundment is several metres. Sulfide oxidation in the shallow portion of the vadose zone also releases H^+, SO_4, Fe, Zn, and other metals to the tailings porewater. Groundwater flows vertically downward through the vadose zone to the water table in the central area of the tailings, and laterally toward the perimeter ditches that surround the tailings cone. In proximity to the perimeter ditch, there is an upward component to groundwater flow, and the water table occurs within several tens of centimetres of the surface of the tailings. The groundwater discharges to the perimeter ditches that surround the impoundment.

For the treatment trial, three cells were installed within 50 m of the perimeter drain in an area of upward hydraulic gradients (Hulshof 2001). The cells were three metres square, and were constructed of steel-sheet piles driven to a depth of 2 m. In two of the cells, organic-rich waste materials were mixed within the upper metre of tailings by using a backhoe bucket. The resulting mixtures contain approximately 15% organic material by volume. The organic-rich materials included wood chips and pulp waste derived from the forestry industry. No reactive materials were added to the third cell, but the upper metre of tailings was physically disturbed with the backhoe bucket, similar to what had been done to the other cells. Two sets of multi-level standpipe piezometers were installed at depths from 0.5 to 2 m below ground surface in each cell and at two locations in undisturbed tailings adjacent to the cells. The objective of the trial was to observe changes in porewater chemistry in the cells as a function of time. As noted, groundwater in the tailings in the vicinity of the cells was generally moving upward to discharge at the surface. Al & Blowes (1996) estimated the groundwater velocity to be approximately 0.1 m a^{-1} in this area of the tailings. This estimate suggests that porewater in the test cells could reside in the zone containing the organic amendments for as long as ten years.

The tailings porewater was monitored by sampling the piezometers and by the collection and squeezing of soil cores in and adjacent to the cells (Hulshof 2001).

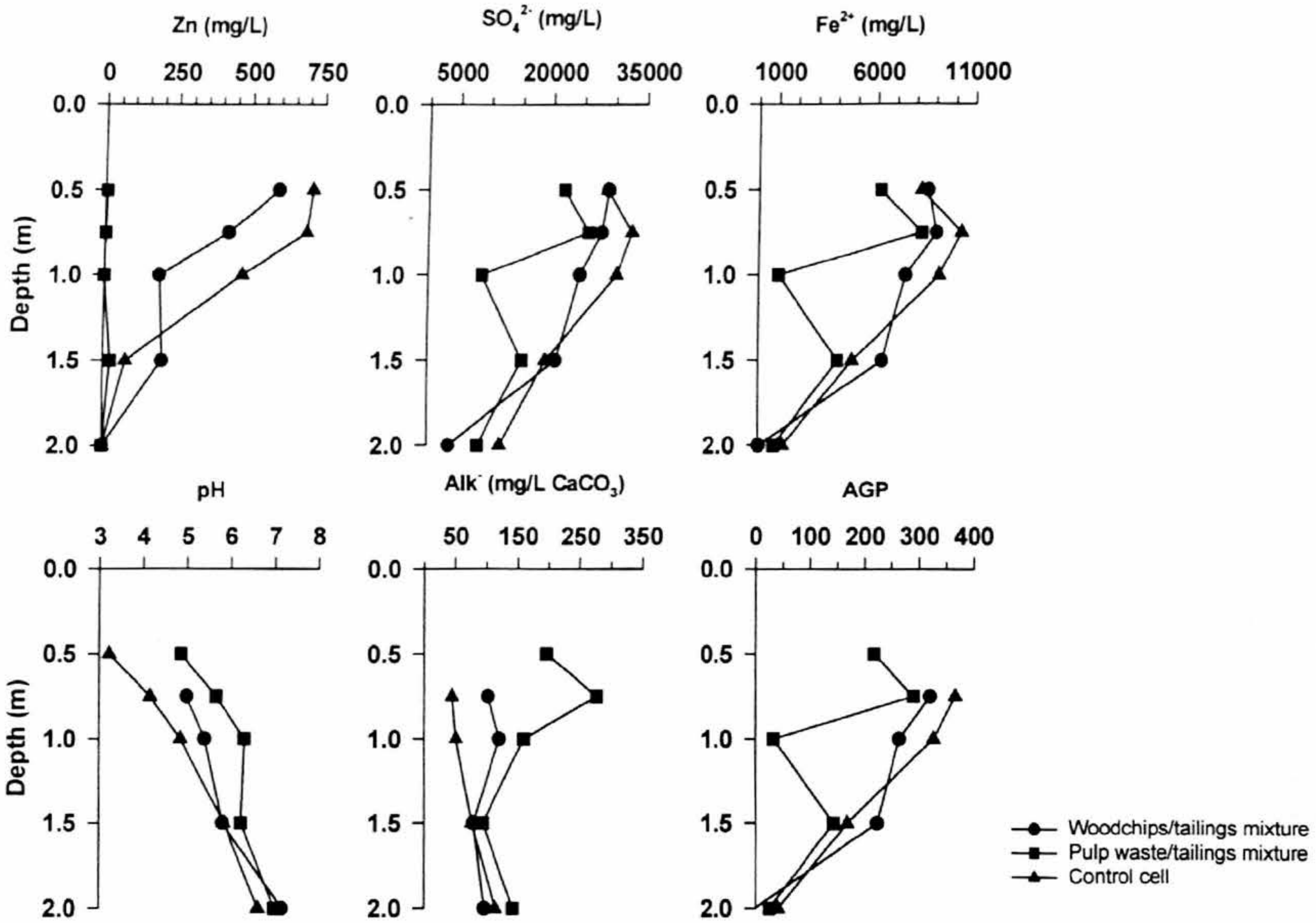

FIG. 5. Profiles of Zn, SO_4, Fe(II), pH, alkalinity, and acid-generating potential in porewater as a function of depth in tailings in the treatment and control cells at the Kidd Creek site in September 2000, approximately 13 months after the cells were installed (after Hulshof 2001). Acid-generating potential is calculated by subtracting acid-consuming potential (molar equivalents of carbonate alkalinity) from acid-producing potential (molar equivalents of acid released by oxidation of Fe^{2+}).

Core samples were also collected for solid-phase and microbiological analysis. Under late-summer conditions, the water table in the vicinity of the cells was 0.6 m below the tailings surface, but the tension-saturated zone extended to approximately 0.2 m below the surface. The shallow porewater in the vicinity of the cells is characterized by very high concentrations of sulfate (15,000 to 35,000 mg L^{-1}), Fe (6000 to 10,000 mg L^{-1}), and Zn (500 to 800 mg L^{-1}). The pH decreases from above pH 6 at 2 m below the tailings surface, to pH 4 within 0.5 m of the ground surface. The lower pH conditions at shallow depth likely reflect oxidation of Fe^{2+} by oxygen as the Fe(II)-rich porewater contacts O_2 at the tailings surface.

Profiles of porewater chemistry within the cells, measured 13 months following installation, are shown in Figure 5 (Hulshof 2001). Relative to the tailings control cell, concentrations of sulfate, Fe(II), and Zn were lower, and pH and alkalinity measurements higher, in the organic-amended tailings cells. The differences were greater for the cell containing the pulp waste than for the cell containing the wood chips. In the cell amended with pulp waste, porewater concentrations of SO_4, Fe(II), and Zn were much lower than in the control cell. Concentrations declined by up to 20,000 mg L^{-1} SO_4, up to 10,000 mg L^{-1} Fe, and as much as 700 mg L^{-1} Zn. In the pulp-waste cell the alkalinity decreased by up to 200 mg L^{-1}. The $\delta^{13}C_{DIC}$ of the water collected from the cells was depleted in porewater from both the wood-chip and pulp-waste cells. The degree of depletion indicated microbially mediated oxidation of organic carbon. Bacterial enumerations using the MPN method indicated the presence of one to two orders of magnitude more of sulfate-reducing bacteria within the upper metre of the pulp-waste cell relative to the tailings cell. Black precipitates, possibly sulfides, were detected on monitoring instrumentation within the pulp-waste cell.

The field trial indicated good potential for the *in-situ* treatment of AMD contaminants directly within mine wastes. The *in-situ* removal of contaminants by reactive organic mixtures in the tailings could decrease

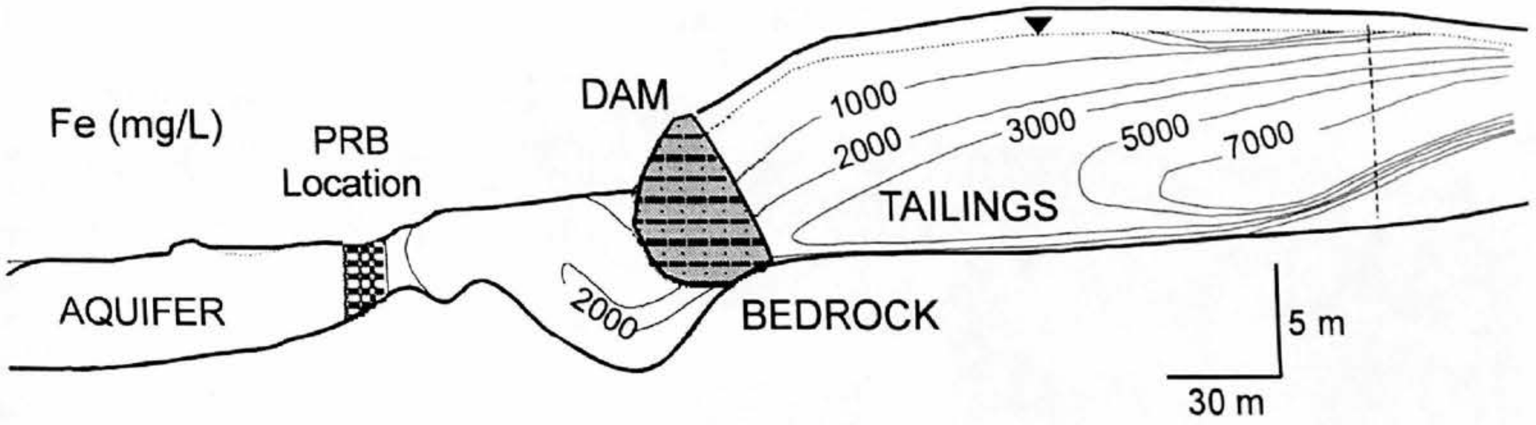

FIG. 6. Location of the full-scale PRB, relative to the Fe plume in the Nickel Rim aquifer.

demands on, and the costs for, conventional water-treatment and long-term environmental management.

Permeable reactive barriers

Sudbury, Ontario. Nickel and Cu were mined at the Nickel Rim minesite until 1958. During the decades since decommissioning, sulfide oxidation in the vadose zone of an elevated tailings impoundment at the site has released high concentrations of dissolved Fe and SO_4 to an aquifer below and adjacent to the impoundment. Drainage from the impoundment follows a narrow (<40 m wide), shallow (<6 m deep) aquifer. The aquifer discharges to a small lake 160 m downgradient from the impoundment (Bain *et al.* 2000). High concentrations of SO_4, Fe, Ni, and other metals (~15,000 mg L^{-1} SO_4, 5000 mg L^{-1} Fe), released during the period of peak sulfide oxidation, are observed at the base of the tailings impoundment. This water is moving through the impoundment and will discharge into the aquifer (Johnson *et al.* 2000). Groundwater in the plume currently contains 500–2000 mg L^{-1} Fe and 2000–4000 mg L^{-1} SO_4 (Fig. 6). The pH of the aquifer water is 5 to 6. High concentrations of dissolved metals, such as Al and Ni, are present in the aquifer.

In 1995, a full-scale PRB was installed across the full width of the aquifer, 60 m downgradient of the tailings impoundment (Benner *et al.* 1997). This installation is the first full-scale PRB to employ sulfate reduction to treat dissolved metals. The barrier contains a mixture of municipal (mixed composition) compost (20 vol.%), leaf compost (20 vol.%), wood chips (9 vol.%), and gravel (50%) plus a small amount of limestone (1 vol.%). These materials were mixed together by repeatedly being dumped into large piles with a portable belt-conveyor. The barrier was installed by cut-and-fill excavation over a two-day period. The barrier extends in depth and laterally to bedrock, and is designed to intercept all of the groundwater flow in the aquifer (Fig. 6). The bedrock valley is 15 m wide and 3.6 m deep at the location of the barrier. The reactive zone of the barrier is 4 m thick. A zone composed of sand, 2 m in thickness, was placed on the upgradient side, and another on the downgradient side, of the reactive zone.

Regular monitoring of the groundwater chemistry upgradient, within, and downgradient of the PRB over the past seven years indicates that the barrier decreases the concentrations of Fe by >250 mg L^{-1} and SO_4 by >1500 mg L^{-1} (Fig. 7). In addition, because of the removal of Fe and the production of alkalinity, the water that exits the barrier has an excess acid-neutralizing capacity (Benner *et al.* 1999). Influent Ni concentrations of up to 15 mg L^{-1} are consistently removed to ~0.1 mg L^{-1}.

Several indicators confirm that bacterially mediated sulfate reduction is responsible for the improvements in water quality. Microbiological enumeration of core materials indicates sharp increases in the number and in the activity of sulfate-reducing bacteria within the PRB (Benner *et al.* 2000). The observed enrichment of sulfate $\delta^{34}S$ (Benner *et al.* 1999) is consistent with bacterially mediated sulfate reduction. Dissolved HS^- concentrations within the barrier are commonly >1 mg L^{-1}, and alkalinity is >1000 mg L^{-1} $CaCO_3$. Examination of the solid material from the barrier indicates that dissolved HS^{-1} is precipitating as poorly crystalline Fe monosulfides (Herbert *et al.* 1998, 2000).

Recent monitoring data confirm that the efficiency of the barrier, as a full-scale treatment system, is gradually declining (Benner *et al.* 2002). In spite of this gradual decrease in the rate of SO_4 and Fe removal, as recently as 2001 the barrier was continuing to remove >1000 mg L^{-1} SO_4 and >250 mg L^{-1} Fe (Fig. 7). Water exiting the barrier continues to have an excess of alkalinity and will consume acidity when it discharges at the acidic lake at the site.

The evaluation of the PRB performance is affected by the uncertainty associated with estimating the spatial variability of groundwater velocity within the barrier.

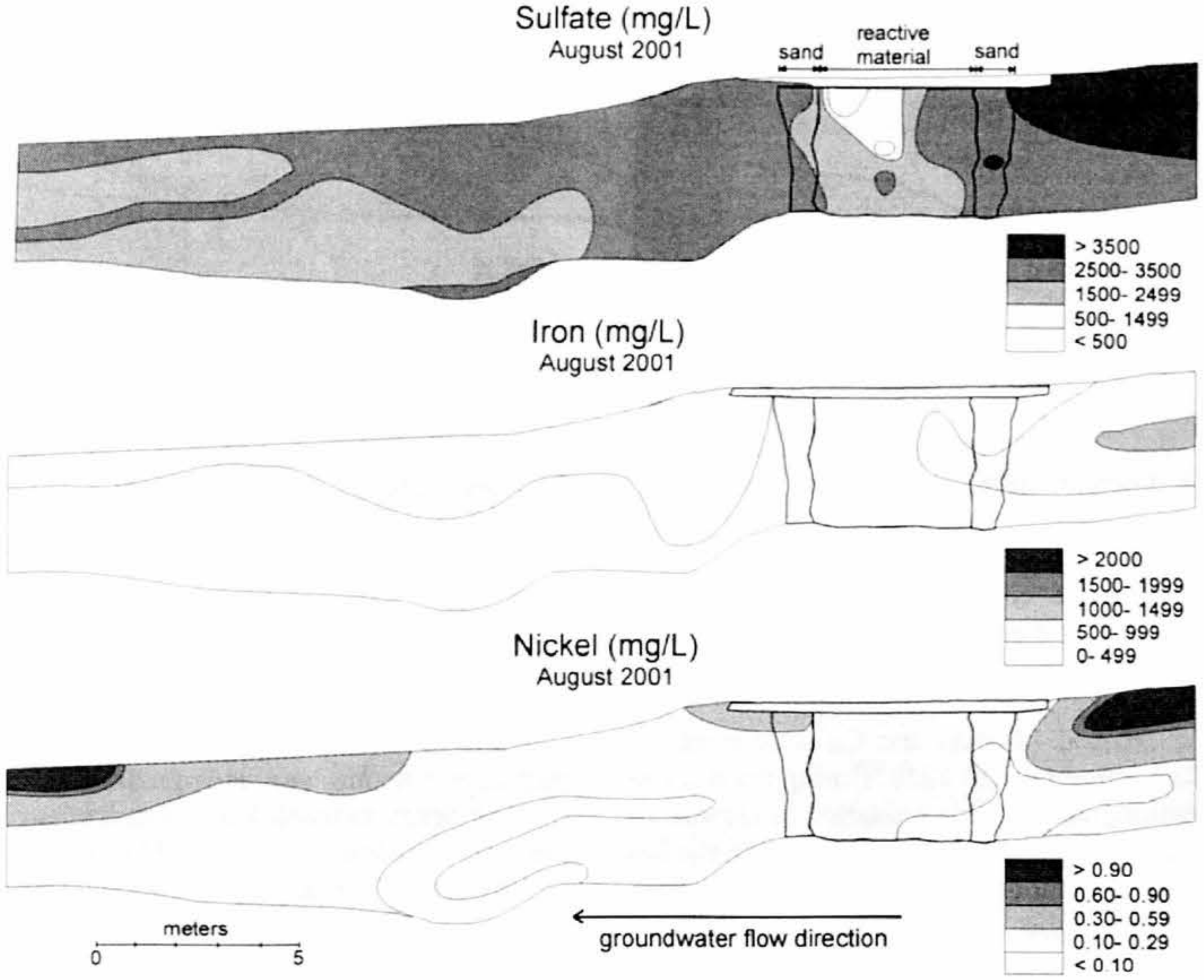

FIG. 7. Profiles of SO_4, Fe, and Ni concentrations in the Nickel Rim PRB and adjacent aquifer, six years after installation.

Based on the movement of a conservative tracer (Cl), groundwater flow through the barrier averages 16 m a^{-1}, resulting in an average residence time of 3 months. However, the tracer-movement data also indicate that preferential flow channels are present in the central portion of the barrier (Benner *et al.* 1997). The groundwater velocity in this zone is not easily defined. Benner *et al.* (1997, 2001) concluded that heterogeneities in the permeability of the PRB and aquifer strongly affect the degree of water treatment. Parts of the PRB consistently show almost complete removal of dissolved metals and sulfate, whereas other areas consistently show only partial removal. These results suggest that contact time between the water and reactive material is insufficient for complete treatment in zones of preferential flow.

At Nickel Rim, the reactive mixture contained 50% gravel by volume. Considerable care was taken to thoroughly mix this material before emplacement in the excavated trench (Benner *et al.* 1997). Although the reactive materials were mixed carefully, the field results suggest that the heterogeneities in hydraulic conductivity were formed during placement of the reactive material into the trench; thus, the construction technique has had a strong influence on the hydraulic performance, which directly affects the geochemical performance and longevity of the PRB. A flow-modelling study conducted by Benner *et al.* (2001), based on the Nickel Rim observations, indicated that the spatial distribution of hydraulic conductivity and contaminants in the aquifer strongly affects the distribution of inflow contaminant within the reactive material. Further, the results emphasized the value of collecting detailed hydrogeochemical data from the site, and of performing numerical studies as part of the PRB design process.

The total cost of the PRB at Nickel Rim was less than $45,000 CAD. Approximately half of the cost was for installation. The purchase and delivery of the reactive mixture materials (compost, wood chips, gravel, and limestone) were the remaining expenses. Because of the low material costs, it is foreseeable that future PRB installations using similar materials will have a similar cost structure, with installation accounting for 50 percent or more of the total. With improvements based on what has been learned at Nickel Rim, future reactive-barrier installations can provide effective long-term treatment of groundwater containing elevated concentrations of SO_4, Fe, and other metals.

Vancouver, British Columbia. A sulfate-reduction PRB was used in a field-scale demonstration at an industrial site in Vancouver, Canada. The historical storage of metal-sulfide ore concentrate introduced Fe-sulfide minerals to the shallow soil. The oxidation of the sulfide ores resulted in the contamination of groundwater, with high concentrations of sulfate, Fe, and other heavy metals, including Cu, Zn, Ni, Cd, and Pb. As a consequence of the characteristics of the ore concentrate and the buffering capacity of the aquifer, concentrations of Fe in the groundwater are low relative to those at many mine-waste sites. Sulfate concentrations are approximately 1000 mg L^{-1}. The reactive media for the trial PRB consisted of municipal compost mixed with gravel. The trial PRB was installed in a guar-gum slurry trench 10 m long, 6.7 m deep, and approximately 2.5 m thick, in the general direction of groundwater flow (Ludwig *et al.* 2002). The site is adjacent to a tidal channel, and tidal influences on hydraulic-head measurements caused difficulty in estimating groundwater velocity. The aquifer material includes sand, gravel, and cobbles.

The distribution of metals in groundwater within and near the PRB cell is shown in Figure 8. Concentrations of dissolved metals within the test wall remained low for the three years following installation. Concentrations of Zn decreased from >2 mg L^{-1} in the influent water to <0.1 mg L^{-1} (typically <0.05 mg L^{-1}) within the trial PRB. After seven months of operation, concentrations of Cu decreased from >2 mg L^{-1} in the influent to <0.05 mg L^{-1} in the effluent (Ludwig *et al.* 2002). Mineralogical study confirmed the removal of Cu as a sulfide precipitate. Concentrations of dissolved HS^{-1} averaged 0.7 mg L^{-1} within the PRB, up to 0.5 mg L^{-1} at 1 m downgradient of the PRB, and were <0.001 mg L^{-1} at 3 m from the PRB (Ludwig *et al.* 2002).

As part of the overall environmental management plan for the site, which included removal of remnant sulfide ores from the shallow soil, a full-scale PRB was constructed during November 2000 – February 2001 in the vicinity of the test cell (Mountjoy & Blowes 2002). The full-scale PRB is approximately 400 m long, as much as 15 m deep and 2.5 to 5 m thick. Guar gum slurry trenching was also used for the full-scale installation.

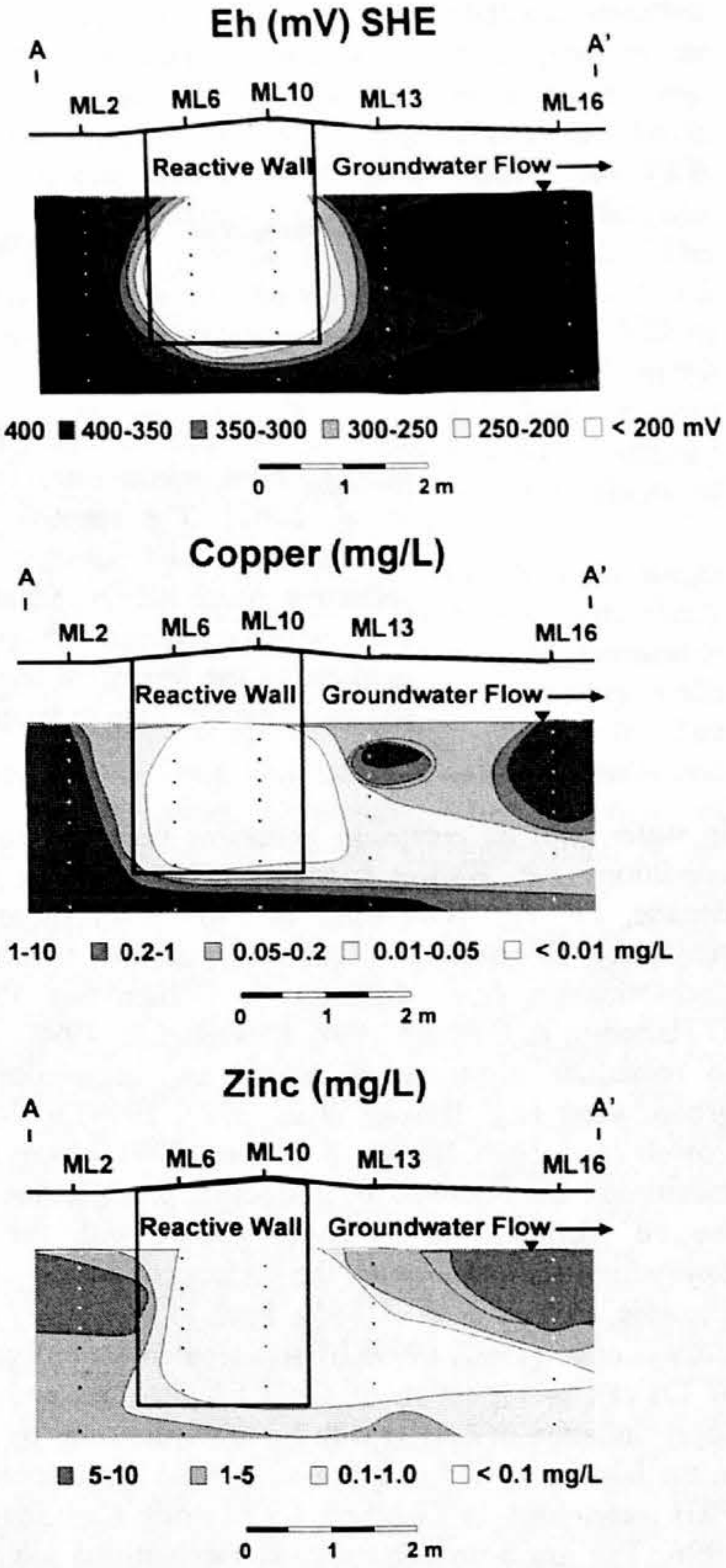

FIG. 8. Concentrations of Cu and Zn in groundwater in the trial PRB at the Vancouver site (after Ludwig *et al.* 2002). Groundwater flow is from the left to right. Organic carbon promotes sulfate reduction. The Eh decreased in the PRB, and the precipitation of metal-sulfide minerals decreased the concentrations of metals to very low levels.

Monticello, Utah. At Monticello Canyon, Utah, groundwater has been contaminated by seepage from a uranium mill-tailings impoundment. Although the mill wastes were removed from the site in 1999, elevated concentrations of U, As, Se, Mo, V, Mn, and nitrate continue to migrate through an alluvial valley (Morrison *et al.* 2001, 2002, Morrison 2003). Infiltration of precipitation was responsible for leaching the metals, metalloids, and nitrate from the mill wastes. The valley is underlain by a shale aquitard at a depth of 4.5 to 6 m below ground surface. A PRB system was installed in June 1999 to treat the groundwater.

The reactive medium for the PRB is granular zero-valent iron [Fe^0]. Zero-valent iron is a strong reductant

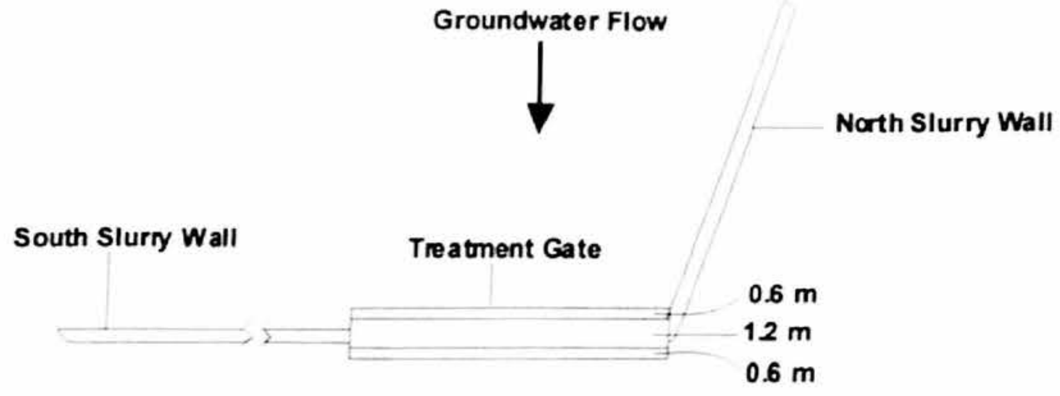

FIG. 9. The funnel-and-gate PRB system installed in 1999 to remediate seepage from uranium-mill wastes at Monticello, Utah (after Morrison *et al.* 2002). The reactive medium is zero-valent iron. Excellent removal of U and selected metals and metalloids was achieved by reductive precipitation. Significant treatment occurred in the gravel zone, which contained 13% (volume) zero-valent iron, immediately up-gradient of the treatment zone containing 100% zero-valent iron. The treatment gate is 30 m in length.

in water, and its corrosion generates very low redox conditions (*e.g.*, Blowes & Mayer 1999). Over the past decade, Fe^0 has been used in PRB applications to remediate chlorinated solvents by abiotic reductive dechlorination (*e.g.*, Gillham & O'Hannesin 1994, O'Hannesin & Gillham 1998, Powell *et al.* 1998), and to remediate electroactive metals and metalloids in groundwater (*e.g.* Blowes *et al.* 1997, 1999a,b, 2000, Powell *et al.* 1998, Blowes & Mayer 1999). Metals and metalloids are removed by reductive precipitation on the Fe^0 surfaces, or as coprecipitates with the Fe oxyhydroxides that form on the surfaces of the iron. For example, Powell *et al.* (1995), Pratt *et al.* (1997) and Blowes *et al.* (1997, 1999a,b) investigated the reduction of Cr(VI), precipitation of Cr(III) hydroxide, and the coprecipitation of Cr(III) with Fe oxyhydroxides by Fe^0 in the laboratory and in a full-scale field application of PRB technology in Elizabeth City (North Carolina) in 1996. The grain-surface removal mechanisms suggest that Fe^0 has a finite treatment capacity for metals and metalloids.

The PRB at Monticello Canyon is a funnel-and-gate system. The system includes two low-permeability slurry walls to direct the flow of contaminated groundwater through a central permeable treatment zone or gate. The treatment gate is 30 m long, 2.4 m thick in the direction of groundwater flow, and extends to the base of the aquifer. The treatment gate has three components: an up-gradient gravel pack 0.6 m thick containing 13% zero-valent iron, a central zone of zero-valent iron 1.2 m thick, and a down-gradient gravel pack, 0.6 m thick, containing 10% zero-valent iron. The treatment gate was installed in a temporary trench excavation supported by steel-sheet piling (Fig. 9). A total of 251 tonnes of Fe^0 was used in the treatment gate. Groundwater velocity in the treatment gate was estimated, by using flow sensors and tracers, to be 5.7 m day^{-1} (Morrison *et al.* 2002). Thus, residence time of groundwater in the 100 % zero-valent iron portion of the PRB is approximately 5 h. After installation, groundwater mounding immediately up-gradient of the PRB caused the water-table elevation to increase by approximately 0.75 m (Morrison *et al.* 2002). On the basis of solid-phase mineral accumulations in the PRB, Morrison (2003) suggested that groundwater flux might actually be about 10% of that determined by flow sensors and tracer tests.

Using influent data from five wells located 1 m up-gradient of the treatment zone, and effluent data from five wells in the down-gradient portion of the treatment zone, Morrison *et al.* (2002) demonstrated excellent treatment of all contaminants except Mn within the PRB. Uranium decreased from 396 $\mu g\ L^{-1}$ in the influent to <0.24 $\mu g\ L^{-1}$ in the effluent from the PRB; As decreased from 10.3 $\mu g\ L^{-1}$ to <0.2 $\mu g\ L^{-1}$; Se decreased from 18.2 $\mu g\ L^{-1}$ to 0.1 $\mu g\ L^{-1}$; Mo decreased from 62.8 $\mu g\ L^{-1}$ to 17.5 $\mu g\ L^{-1}$; V decreased from 395 $\mu g\ L^{-1}$ to 1.2 $\mu g\ L^{-1}$; nitrate decreased from 60.7 mg L^{-1} to <65.1 $\mu g\ L^{-1}$; and Mn decreased from 308 $\mu g\ L^{-1}$ to 177 $\mu g\ L^{-1}$. Consistent with observations of other Fe^0 PRB systems, the pH of the groundwater within the Fe^0 increased from a maximum of 6.8 in the influent to 10. Although nitrate concentrations were observed to decrease, the form of treatment was not clear. It is possible that the nitrate was reduced to ammonia abiotically, or it is possible that some microbially mediated denitrification within the Fe^0 may have occurred.

Seventy cores of the PRB solids were collected in February 2002 (Morrison 2003). Concentrations of U, V, and Ca were determined in groundwater and on the solid-phase materials within and near the PRB. Mean concentrations in solids from the up-gradient gravel and Fe^0 zone were 15.1 to 46.8 g kg^{-1} of Ca, 70 to 596.9 mg kg^{-1} of U, and 30.2 to 1168.3 mg kg^{-1} of V. Within the Fe^0 zone, mean concentrations of Ca ranged from 0.8 to 33.5 g kg^{-1}, and U (0.06 mg kg^{-1}) and V (60.7 mg kg^{-1}) were similar to those in a control sample of zero-valent iron that was retained at the time of installation of the PRB. The data suggest that most of the U and V had been removed in the up-gradient gravel and Fe^0 zone. Mechanisms for removal of U and V could include reductive precipitation, *e.g.*, U(VI) → U(IV) and precipitation as UO_2, and adsorption on the Fe-oxyhydroxide coatings and surfaces of the iron (Cantrell *et al.* 1995, Morrison *et al.* 2002). As has been observed in other Fe^0 PRB systems, the removal of Ca and other constituents as carbonate or other secondary (*i.e.*, not primary contaminant) precipitates has the potential to reduce hydraulic performance and the reactivity of the Fe^0 (Morrison 2003).

Morrison (2003) indicated that the concentration of U exiting the up-gradient gravel and Fe^0 zone increased from <0.2 μg L^{-1} at early time to 185 μg L^{-1} after 2.7 years. This increase reflects consumption of available contaminant-removal sites on the Fe^0, but may also reflect loss of reactivity as a consequence of the precipitation of secondary carbonate minerals on grain surfaces. Additional precipitation of carbonate material had occurred within the Fe^0 zone after 2.7 years of operation, but the evidence suggested that excellent treatment of U and V continued to occur. Furthermore, Morrison (2003) could not detect any decrease in the hydraulic conductivity of the PRB as a consequence of the formation of the precipitates. This work is consistent with evaluations of the 100% Fe^0 PRB in Elizabeth City. Blowes & Mayer (1999), on the basis of monitoring and numerical modelling, evaluated the potential influence of secondary precipitates on long-term PRB performance. It was suggested that the precipitation of secondary carbonate and sulfide minerals could result in the reduction of the porosity from the initial 0.5 to approximately 0.4 after 20 years of operation, but that hydraulic performance of the PRB will not be compromised with this loss of porosity. After five years, with influent concentrations of Cr(VI) between 5 and 10 mg L^{-1} and a groundwater velocity of approximately 0.1 m day^{-1}, Cr(VI) remained non-detectable at 0.1 m into the Fe^0 zone. As indicated by the investigations at Monticello and Elizabeth City, formation of secondary precipitates may limit long-term performance of PRBs in groundwater with high total dissolved solids or alkalinity.

Fry Canyon, Utah. At a former uranium up-grading site in southeastern Utah that received ores from three mines, a funnel-and-gate PRB was installed in 1997 to evaluate the removal of U from groundwater by using three reactive materials: bone-char pellets, granular zero-valent iron, and amorphous ferric oxyhydroxide (Naftz *et al.* 2000; 2002). The PRB system was installed in a shallow colluvial aquifer (silt- to gravel-size particles) overlying bedrock. The saturated thickness of the aquifer ranged from 0.6 to 1.2 m. Groundwater velocity was estimated to be 0.23 m day^{-1} (Naftz *et al.* 2000). The concentration of U in the groundwater exceeded 20,000 μg L^{-1}, likely present primarily as U(VI). The groundwater contained measurable dissolved oxygen and had an alkalinity of approximately 400 mg L^{-1} (as $CaCO_3$).

The funnel-and-gate system consisted of two wings in a v-shape. One wing was a low-permeability slurry wall. The second wing contained three permeable treatment gates separated by low-permeability walls that contained steel-sheet piling (Fig. 10). The treatment-gate wing was installed using a trench box and track-mounted excavator. The direction of groundwater flow was toward the intersection of the two wings, and was approximately 35° from perpendicular to the wing with the treatment gates. Each treatment gate was 0.9 m in thickness and 2.1 m in length. The treatment gates extended to depths ranging from 0.97 to 1.1 m, and were separated by low-permeability barriers 1 m in length (Fig. 10). A zone of pea gravel 0.46 m in thickness was installed immediately up-gradient of the treatment-gate wing along its entire length and depth (Naftz *et al.* 2002).

Conservative tracer tests and heat-pulse flow meters were used to estimate the velocities of groundwater flow in the vicinity of the PRB system and within each treatment gate (Naftz *et al.* 2002). Measurements were complicated because of the oblique orientation of the treatment-gate wing to the direction of groundwater flow and the high hydraulic conductivity of the zone of gravel immediately up-gradient of the wing. Tracer tests indicated groundwater velocities ranging from 0.14 m day^{-1} in the bone-char gate to 2.7 m day^{-1} in the amorphous ferric oxyhydroxide gate. Flow-meter measurements in the Fe^0 gate indicated that the groundwater velocity ranged from <1 to >5 m day^{-1}. Higher velocities were measured when groundwater levels were highest, which generally occurred following significant precipitation events. Thus, residence time of groundwater within the treatment zones could have ranged from several hours to several days.

Monitoring during the first three years of operation indicated an attenuation of U by each of the treatment media (Naftz *et al.* 2000, 2002). Treatment performance varied among the media, and within individual treatment gates. The influent concentrations of U for each of the treatment gates were also variable for any

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