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Effects of a Reactive Barrier and Aquifer Geology on Metal Distribution and Mobility in a Mine Drainage Impacted Aquifer 04-159

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Abstract

The Nickel Rim aguifer has been impacted for five decades by a metal-rich plume generated from the Nickel Rim mine tailings impoundment. Metals released by the oxidation of pyrrhotite in the unsaturated zone of the tailings migrate into the downgradient aquifer, affecting both the groundwater and the aquifer solids. A reactive barrier has been installed in the aquifer to remove sulfate and metals from the groundwater. The effect of the reactive barrier on metal concentrations in the aquifer solids has not previously been studied, nor have other controls on metal distribution in the solid phase. In this study, a range of chemical extraction methods was applied to cores of aquifer sediment, to ascertain the distribution of metals among various solid phases present in the aquifer solids. Extraction results were combined with groundwater chemistry, geochemical modelling, and solid-phase microanalyses, to assess the potential mobility of metals under changing geochemical conditions. Reactions within the reactive barrier caused an increase in the solid phase carbonate content downgradient of the barrier. The concentrations of poorly crystalline, oxidized phases of Mn, Fe, Cr(III) associated with oxidized Fe, and poorly crystalline Zn, are lower downgradient of the barrier, whereas total solid-phase metal concentrations remain constant. Iron and Mn accumulate as oxidized, poorly crystalline forms in a peat layer overlying the aquifer. Although these oxides may buffer reducing plumes, they also have the potential to release metals to the groundwater, should a reduced condition be imposed on the aquifer by remedial actions.

Effets d'une barrière réactive et de la géologie de l'aquifère sur la distribution et la mobilité des métaux dans un aquifère perturbé par des exhaures de mines 04-160

Doerr, Nora A., Ptacek, Carol J., et Blowes, David W.

Résumé

Depuis cinq décennies, l'aquifère de Nickel Rim est perturbé par un panache riche en métaux produit par un bassin de stériles de la mine du même nom. Les métaux libérés par l'oxydation de la pyrrhotite dans la zone non saturée des résidus migrent dans l'aquifère situé en aval et perturbent les eaux souterraines et la phase solide de l'aquifère. Pour éliminer les sulfates et les métaux contenus dans les eaux souterraines, on a installé dans l'aquifère une barrière réactive. L'effet de cette barrière sur les concentrations de métaux dans la phase solide de l'aquifère n'a jamais été étudié, ni ceux d'autres mesures de contrôle sur la distribution des métaux dans la phase solide. Dans la présente étude, nous avons utilisé un éventail de méthodes d'extraction chimique pour étudier des carottes de sédiments de l'aquifère afin de préciser la distribution des métaux dans les diverses phases solides présentes dans les solides de l'aquifère. Les résultats obtenus ont été combinés à ceux de la détermination des caractéristiques chimiques des eaux souterraines, de la modélisation géochimique et des microanalyses en phase solide afin d'évaluer la mobilité potentielle des métaux en présence de conditions géochimiques changeantes. Les réactions dans la barrière réactive ont fait augmenter la teneur en carbonate de la phase solide en aval de la barrière. Les concentrations des phases oxydées à structure faiblement cristalline de Mn, de Fe et de Cr(III) associées au Fe oxydé et la concentration de Zn à structure faiblement cristalline sont moins élevées en aval de la barrière, tandis que les concentrations de métaux totaux en phase solide demeurent constantes. Le fer et le manganèse s'accumulent sous des formes oxydées à structure faiblement cristalline dans une couche de tourbe recouvrant l'aquifère. Bien que ces oxydes puissent tamponner et réduire ainsi les panaches, ils pourraient également libérer des métaux dans les eaux souterraines si une réduction était imposée à l'aquifère dans le cadre de mesures d'assainissement.

NWRI RESEARCH SUMMARY

Plain language title

Long-term evolution of a mine-impacted groundwater plume.

What is the problem and what do scientists already know about it?

There are thousands of abandoned mine sites in Canada requiring remediation. As mine wastes weather, large plumes of contaminated groundwater can develop in adjacent aquifers. As the plumes enter the aquifers, a series of reactions takes place that influence the distribution of dissolved metals, including partitioning onto the aquifer solids and modification of other aquifer properties. Basic information is available on the initial metal attenuation reactions, but less is known about long-term changes in the aquifer properties.

Why did NWRI do this study?

This study was conducted at the Nickel River tailings disposal area near Sudbury as part of a much larger study to evaluate the long-term release of metals from mine sites. The specific study focused on evaluating long-term reactions that control plume migration. Mine wastes have been weathering at the study area for over 40 years, and a large plume of contaminated groundwater has developed in the adjacent aquifer. This study focused on defining changes in the aquifer properties as the result of the plume evolution. Remediation efforts have been underway at the site, and the effects of this remediation on aquifer properties were also evaluated. This information can be used to assess to what extent metals are accumulating in the aquifer, and what reactions are controlling the long-term evolution of the plume.

What were the results?

The results indicate that certain metals are accumulating in different zones of the aquifer as the result of many years of contaminated groundwater passing through the aquifer. The aquifer is gradually becoming more oxidized, and the attenuation of metals is expected to change as a result of the gradual changes in aquifer properties. These results can be used to predict the overall evolution of the plume.

How will these results be used?

The results will be used by the property owner to plan long-term remediation strategies for the site. The results can be used more broadly to understand the longterm evolution of groundwater plumes emanating from mine waste facilities.

Who were our main partners in the study?

University of Waterloo and Falconbridge Inc.

Sommaire des recherches de l'INRE

Titre en langage clair

Évolution à long terme d'une mine touchée par un panache d'eaux souterraines.

Quel est le problème et que savent les chercheurs à ce sujet?

Il y a au Canada des milliers de mines abandonnées qui auraient besoin d'être assainies. À mesure que les déchets miniers se météorisent, de larges panaches d'eaux souterraines contaminées peuvent se former dans les aquifères adjacents. Lorsque ces panaches pénètrent dans les aquifères, une série de réactions influant sur la distribution des métaux dissous a lieu, notamment une séparation dans les matières solides de l'aquifère et la modification des autres propriétés de l'aquifère. On possède des données de base sur les premières réactions d'atténuation des métaux, mais on en sait moins sur les changements à long terme dans les propriétés de l'aquifère.

Pourquoi l'INRE a-t-il effectué cette étude?

Cette étude a été réalisée au site d'élimination des stériles de Nickel River près de Sudbury dans le cadre d'une étude plus vaste visant à évaluer la libération à long terme des métaux depuis les sites miniers. L'étude en question visait à évaluer les réactions à long terme régissant la migration du panache. Les déchets de mine se météorisent depuis plus de 40 ans sur le site d'étude, et un large panache d'eaux souterraines contaminées s'est formé dans l'aquifère adjacent. Il s'agissait donc d'évaluer les changements survenus dans les propriétés de l'aquifère par suite de l'évolution du panache. Des mesures d'assainissement ont été mises en œuvre sur le site, et leurs effets sur les propriétés de l'aquifère ont également été mesurés. Ces informations peuvent servir à évaluer dans quelle mesure les métaux s'accumulent dans l'aquifère et quelles réactions régissent l'évolution à long terme du panache.

Quels sont les résultats?

D'après les résultats obtenus, certains métaux s'accumulent dans différentes zones de l'aquifère par suite du passage des eaux souterraines contaminées depuis de nombreuses années. L'aquifère s'oxyde de plus en plus, et l'atténuation des métaux devrait changer par suite des changements graduels des propriétés de l'aquifère. Ces résultats peuvent servir à prévoir l'évolution globale du panache.

Comment ces résultats seront-ils utilisés?

Ces résultats aideront le propriétaire du lieu à formuler des stratégies d'assainissement à long terme. Ils peuvent aussi aider de façon plus générale à comprendre l'évolution à long terme des panaches d'eaux souterraines libérés des installations de stockage de résidus de mine.

Quels étaient nos principaux partenaires dans cette étude?

Université de Waterloo et Falconbridge Inc.



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Effects of a reactive barrier and aquifer geology on metal distribution and mobility in a mine drainage impacted aquifer

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Abstract

The Nickel Rim aquifer has been impacted for five decades by a metal-rich plume generated from the Nickel Rim mine tailings impoundment. Metals released by the oxidation of pyrrhotite in the unsaturated zone of the tailings migrate into the downgradient aquifer, affecting both the groundwater and the aquifer solids. A reactive barrier has been installed in the aquifer to remove sulfate and metals from the groundwater. The effect of the reactive barrier on metal concentrations in the aquifer solids has not previously been studied. In this study, a series of selective extraction procedures was applied to cores of aquifer sediment, to ascertain the distribution of metals among various solid phases present in the aquifer. Extraction results were combined with groundwater chemistry, geochemical modelling and solid-phase microanalyses, to assess the potential mobility of metals under changing geochemical conditions. Reactions within the reactive barrier caused an increase in the solid-phase carbonate content downgradient from the barrier. The concentrations of poorly crystalline, oxidized phases of Mn and Fe, as well as concentrations of Cr(III) associated with oxidized Fe, and poorly crystalline Zn, are lower downgradient from the barrier, whereas total solidphase metal concentrations remain constant. Iron and Mn accumulate as oxidized, easily extractable forms in a peat layer overlying the aquifer. Although these oxides may buffer reducing plumes, they

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also have the potential to release metals to the groundwater, should a reduced condition be imposed on the aquifer by remedial actions. © 2005 Elsevier B.V. All rights reserved.

Keywords: Aquifer; Mine drainage; Reactive barrier; Metals; Chemical extractions; Redox

1. Introduction

The release of dissolved metals from sulfide-mineral oxidation within mine wastes affects the water quality at mine sites worldwide. Sulfide-bearing mine tailings contribute significantly to the generation of acid and the release of metals to the environment. Acidic water generated by sulfide oxidation is neutralized by the dissolution of carbonate, (oxy)hydroxide and aluminosilicate minerals within tailings. As the pH increases, many metals precipitate or are adsorbed. The attenuation of metals occurs in tailings impoundments, and in aquifers, streams and lakes downgradient from impoundments (Morin et al., 1988; Blowes and Ptacek, 1994; Williams and Smith, 2000; Kimball et al., 2002).

Sulfide oxidation at some mine sites has generated acid for decades (Wood et al., 1999; Johnson et al., 2000; Moncur et al., 2003), as the buffering capacity of the mine wastes and adjoining aquifers has been exceeded. The depletion of the primary buffering capacity of the tailings and aquifer materials can result in the development of a plume of acidic, metalbearing groundwater (Dubrovsky et al., 1985). As low-pH groundwater moves through the aquifer and tailings, it may re-dissolve metals that precipitated previously (e.g., Bain et al., 2001). Flooding or the addition of organic carbon covers to tailings impoundments is employed as means of preventing sulfide oxidation and the generation of acid. When applied to oxidized tailings, flooding or the addition of organic carbon may induce reducing conditions in the tailings resulting in the potential for the release of metals by reductive dissolution (Ribet et al., 1995). To assess the potential impact of mine wastes on surrounding waters over several decades or even a century, and to evaluate the potential effects of mitigative measures, it is necessary to understand the distribution and binding of metals in tailings and aquifers.

Most studies of the impact of mine drainage on the Nickel Rim tailings and aquifer have focused on pore water quality (Bain et al., 2000; Benner et al., 2000; Johnson et al., 2000), with the exception of Ribet et al. (1995) who studied the solid-phase geochemistry of the oxidized tailings. Less information, however, is available with respect to the solidphase composition of the Nickel Rim aquifer. The purpose of this study was to determine the effects of a reactive barrier and aquifer geology on the solid-phase geochemistry of the aquifer, using solid-phase extraction techniques. Based on the groundwater chemistry and the solid-phase chemistry, inferences are made with respect to solid-phase controls on metal mobility, the potential for future metal release, and redox and pH buffering capacity. Geochemical modelling is used to enhance the understanding of the effects of a reactive barrier installed in the aquifer in 1995 and of the aquifer geology, on the solid-phase chemistry and on metal mobility.

2. Background

2.1. Site location, geology and previous characterization

The Nickel Rim tailings disposal area is located near the city of Sudbury, Ontario, on the outer rim of the Sudbury Igneous Complex (Fig. 1). The Nickel Rim tailings were deposited in an existing narrow glacial valley, between 1953 and 1958. An unconfined aquifer underlying and downgradient from the Nickel Rim impoundment is composed of glacial outwash. This aquifer has been impacted by mine drainage generated upgradient in the tailings (Johnson et al., 2000; Bain et al., 2000). In 1994, the core of the mine drainage plume had migrated 60 m downgradient into the aquifer (Fig. 2) (Bain, 1996). Bain (1996) determined that water moving through the upper



Fig. 1. Plan view of the Nickel Rim tailings impoundment and downgradient aquifer showing sections A-B and A-A'.



Fig. 2. Diagram from Bain (1996), showing that, in 1994, the core of the mine drainage plume had migrated approximately 60 m into the aquifer. (Note: Reactive barrier had not yet been installed.)

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Fig. 4. Geology of the Nickel Rim aquifer and core sampling locations through section A-B.

portion of the aquifer at NR 63 discharges to surface (Fig. 3), where Fe(II) oxidizes, causing the pH of the discharging water to decrease to ~3.3. Low pH water containing elevated concentrations of Fe, Al and Ni flows overland, and accumulates in a pond downgradient from the reactive barrier, where it recharges the aquifer.

A permeable reactive barrier was installed in the Nickel Rim aquifer, approximately 70 m downgradient from the tailings dam, in 1995 (Figs. 1, 3 and 4); Benner et al., 1997, 2000). The barrier is composed of gravel, organic matter and limestone. The barrier was designed to promote bacterially mediated sulphate reduction and the precipitation of metal sulfides, to remediate the low-quality drainage waters. Ground-water concentrations of SO_4 , Fe and other metals are lower downgradient from the reactive barrier than upgradient from the barrier (Benner et al., 1999). Upgradient from the reactive barrier, the aquifer is composed mainly of sand and gravel, overlain by a thick peat layer and thinner layers of tailings, and at NR 63, silt. Downgradient from the reactive barrier, a thick layer of sand and gravel is overlain by sand, which is in turn overlain by tailings (Fig. 4).

3. Methods

3.1. Field methods

3.1.1. Core collection

Core samples were collected from the aquifer at the locations shown in Figs. 1, 3 and 4, in the fall of 1999 and the summer of 2000. Continuous cores were collected using a piston coring device (Starr and Ingleton, 1992). Sections of core were capped to isolate them from the atmosphere and were frozen until they were analyzed.

3.1.2. Groundwater sampling

Groundwater samples were collected in August 2000 from drive-point piezometers installed adjacent to the locations from which the core samples were taken in the aquifer and in the tailings impoundment (Figs. 1 and 3). Pore water samples for cation and anion analysis were collected using the methods of Johnson et al. (2000). Cations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Anions were analyzed by automatic colorimetric techniques. Quality control and analysis procedures included the analysis of blanks and duplicates, as well as laboratory standard addition methods and laboratory replicates. Charge balance errors were calculated and were generally less than 10%.

Oxidation-reduction potential (Eh), pH and alkalinity were determined in the field, using the methods of Johnson et al. (2000). Specifically, pH and Eh were measured using combination electrodes (Orion Ross and Orion 96-7800). The electrode measurements were conducted in sealed flow-through cells, to isolate the water from the atmosphere and thereby prevent oxidation. The pH electrode was calibrated using pH 4 and 7 buffers, and was checked against a pH 10 buffer to ensure accurate measurements. Eh measurements were checked against Light's (Light, 1972) and Zobell's (Nordstrom, 1977) solutions. The solutions and buffers used to calibrate and check the pH and Eh were maintained at groundwater temperature. Eh and pH electrode performance checks were carried out before and after each measurement. The pH electrode was recalibrated when measured values varied from temperature-corrected buffer values by more than 0.02. Alkalinity was determined in the field by titration against standardized sulfuric acid, using freshly filtered water samples.

3.2. Geochemical modelling

Geochemical speciation model calculations of saturation indices for groundwater samples were performed using MINTEQA2 (Allison et al., 1990). The database was modified to be consistent with the WATEQ4F database (Ball and Nordstrom, 1991). The field-measured Eh was used in the calculations.

3.3. Solid-phase chemical analyses

Solid-phase analyses were performed on subsamples of cores NR 63, NR 64, RW 34 and NR 73. Cores were cut and sampled while still partly frozen.

3.3.1. Carbonate and sulfide content

The carbonate content of the aquifer material was determined using the method of Barker and Chatten (1982). Acid volatile sulfides (AVS) and total (inorganic) reduced sulphur contents were determined using the techniques of Morse and Corriwell (1987) and Canfield et al. (1986), respectively.

3.3.2. Selective extractions

Selective extractions were performed on samples thawed in an anaerobic glovebox (Coy^{TM}). Reagents were added to the sample vials in the anaerobic glovebox, and the

vials were sealed before being placed on a shaker in the dark. After shaking for the times listed in Table 1, the extracts were filtered through 0.45 μ m filters in the anaerobic chamber. Extracts were analyzed for total Fe and Fe(II) using the Ferrozine technique (Gibbs, 1979). Samples were also analyzed for a suite of cations (Al, Ca, Cd, Co, Cr, Cu, K, Fe, Mn, Mg, Mn, Na, Ni, Pb, Zn) by ICP-OES. For the deionized water extractions, the water was purged with Ar, samples for cation analyzed using automatic colorimetric techniques.

Different extraction methods were used to distinguish the metal content of various phases present in the aquifer material (Table 1). Argon purged, deionized water was used to target water soluble phases, e.g., sulfate salts, in the aquifer sediment (Ribet et al., 1995). Three reductants were used to target oxidized phases. In accordance with the method of Lovley and Phillips (1987), Fe(II) extracted by 0.5 M HCl was subtracted from Fe(II) extracted by 0.25 M hydroxylamine hydrochloride in 0.25 M HCl, to yield Fe(III) concentrations originally defined as being microbially extractable. A buffered, Na-ascorbate/citrate/bicarbonate extract was used to target poorly crystalline, reducible metals (Amirbahman et al., 1998). The hydroxylamine hydrochloride (Lovley and Phillips, 1987) and Na-ascorbate (Amirbahman et al., 1998) methods were used to give an indication of the potential for metal release if water containing a reductant (e.g., dissolved organic carbon) were to migrate through the aquifer. Ti-EDTA was used to reduce Fe(III) and target total Fe(III), representing the total oxidation capacity of the aquifer (Amirbahman et al., 1998). The oxidation capacity (OXC) is operationally defined, in accordance with Amirbahman et al. (1998) and Heron et al. (1994a). It is the capacity of the aquifer solids to oxidize Ti³⁺ in the Ti-EDTA complex. The purpose of the Ti-EDTA method was to determine the overall oxidation capacity of the aquifer solids, to allow the total oxidation capacity of the solids from different parts of the aquifer to be compared and to allow comparison with other studies which have assessed aquifer oxidation capacity using the Ti-EDTA method. The HHCl and Na-ascorbate methods were used to obtain more realistic evaluations of the ability of the aquifer solids to oxidise dissolved reduced species; the Na-ascorbate extractable Fe and Mn can be viewed as the available oxidation capacity of the aquifer solids.

Table 1

Extraction methods used to assess the distribution of metals in the Nickel Rim aquifer and target phases

Target	Reagent	Time	Source	
Water soluble phases	Deionized water	24 h	after Ribet et al. (1995)	
Microbially reducible Fe(III)	Hydroxylamine 1 h		Lovley and Phillips (1987)	
Poorly crystalline oxyhydroxides	Na-ascorbate 24 h Amirbahman ei Na-bicarbonate		Amirbahman et al. (1998)	
	Na-citrate			
Total oxidation capacity	Ti-EDTA	24 h	Amirbahman et al. (1998)	
Poorly crystalline phases, adsorbed phases, carbonates	0.5 M HCl	24 h	Heron et al. (1994a,b)	
Total acid-extractable phases	5 M HCl	21 days	Heron et al. (1994a,b)	

Several acids were used to extract metals belonging to different phases. 0.5 M HCl was used to target metals associated with poorly crystalline phases, adsorbed metals and metals associated with carbonate phases (Heron et al., 1994b). Metals retained in these phases have the potential to be released if low pH water migrates through the aquifer. 5 M HCl was used to target the metals extracted by 0.5 M HCl, as well as crystalline metals oxides. An HF/agua regia digestion was used to completely dissolve the aquifer solids, so that total metal concentrations could be determined. The 5 M HCl and HF extractions were used to calculate ratios of easily extractable metals to total acid extractable metals or to the total solid-phase metal content. These ratios were used to account for natural background variation in the primary mineral phases. For example, if the ratio of 0.5 M HCl/5 M HCl extractable metals remains constant while the total 0.5 M HCl extractable metal quantifies change, it is likely that the variation in 0.5 M HCl extractable metals reflects variations in the primary phases present in the aquifer solids. However, if the ratio of 0.5 M HCl/5 M HCl varies, it is likely that the solid-phase concentrations of secondary phases are changing due to geochemical processes occurring in the aquifer, rather than because of variation in the primary mineral phases. Furthermore, 0.5 M HCl and 5 M HCl extractable Fe(II) are used to operationally define available reduction capacity and total reduction capacity, respectively, in Section 4.6.

3.4. Optical and electron microscope, and X-ray photoelectron spectroscopy

Samples of aquifer material for optical microscope and scanning electron microscope/ energy dispersive X-ray (SEM/EDX) analyses were dried under vacuum in an anaerobic chamber, and cut into thin sections in the absence of water. Samples from NR 63 were examined under reflected and transmitted light. Thin sections were coated with 15 μ m of Au for SEM/EDX analyses. SEM images were collected using a LEO 1530 field emission scanning electron microscope (FE-SEM), and EDX analyses were conducted using an EDAX Pegasus 1200 integrated energy dispersive X-ray/orientation imaging microscope (EDX/IOM).

Samples for X-ray photoelectron spectroscopic analyses were prepared as grain mounts. XPS analyses were conducted using a VG ESCALab 250 instrument. The base chamber pressure was 2×10^{-10} mbar and the working pressure was 1×10^{-8} mbar. Monochromatized Al K α X-rays (1486.6 eV) were used to obtain spectra. The instrument work function was set so that a binding energy of 84.00 eV was measured for metallic Au, Au(4_{7/2}). The analyzer pass energy was 20 eV and the focus of the X-ray beams was 500 μ m². Spectra were analyzed using a Gaussian–Laurentian model and a Shirley background subtraction (Shirley, 1972). Semiquantitative surface compositions were determined using peak areas and theoretical cross-sections. Carbon peaks were separated into carbonate (290.1 eV) and adventitious carbon (284.8 eV) peaks (Stipp and Hochella, 1991). The ferric iron peak was not separated into multiplets, but the whole peak at 712 eV as well as the orbital peak at 726 eV were included in data analyses. Oxygen was separated into three peaks representing oxides (530.3 eV), hydroxides (531.4 eV) and water (533.8 eV), after Pratt et al. (1994). Only one sulfur peak was present in all spectra, representing sulfate, at 168.5 eV (Jones et al., 1992).

4. Results and discussion

4.1. Carbonates, pH, alkalinity and acid-buffering capacity

Contour diagrams showing solute concentrations are used as the main method of displaying water chemistry, as they allow the reader to visualize the movement of the mine drainage plume through the tailings and aquifer (Fig. 5). The contour diagrams were drawn by hand, based on water quality data (see Appendix) obtained at the sampling points shown in Figs. 3 and 5, using groundwater flow (Fig. 3) as an aid to interpretation. The contour diagrams, drawn by hand, based on solid-phase chemical analyses at subsampling points are illustrated in Fig. 6a-d. Aquifer geology (Fig. 4) was used as an additional guide in drawing contours.



Fig. 5. Groundwater chemistry contours for the Nickel Rim mine tailings and aquifer, both upgradient and downgradient of the reactive barrier, corresponding to section shown in Fig. 3.



Fig. 6. Solid-phase concentrations of (a) carbonates and sulfides, (b) Fe(III), (c) Na-ascorbate extractable metals, (d) 0.5 M HCl extractable Zn, in the Nickel Rim aquifer.

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In acid mine waters, high Fe(II) and Fe(III) activities allow Fe(II)/Fe(III) to act as the prevailing, reversible redox couple to which platinum Eh electrodes are responsive (Nordstrom et al., 1979). Thus, Eh measurements are representative of redox state in acid mine waters and were used as the basis for speciation calculations by MINTEQA2 (Allison et al., 1990).

Regions of low pH are present in the tailings impoundment (Fig. 5); some of this low-pH water, migrating through the tailings and into the aquifer, is likely being neutralized to a near-neutral pH by reacting with carbonate minerals initially present in the aquifer, dissolving the carbonate minerals. The pH of the groundwater in the Nickel Rim aquifer is approximately 6 (Fig. 5). Although the pH is similar upgradient and immediately downgradient from the reactive barrier, the alkalinity increases by an order of magnitude downgradient from the reactive barrier, indicating that reactions within the barrier are generating alkalinity. Furthermore, the solid-phase carbonate content of the aquifer is highest downgradient from the reactive barrier (Fig. 6a). Geochemical modelling indicates that the groundwater reaches saturation with respect to siderite, calcite, rhodocrosite and dolomite immediately downgradient from the reactive barrier (Fig. 7). These findings suggest that carbonate phases may be precipitating downgradient from the barrier. XPS analyses indicate that the abundance of carbonate on the surface of the aquifer material is up to six times higher in the aquifer samples from downgradient of the barrier than from samples collected upgradient of the barrier (Table 2). It should be noted that the CS1 (S) peaks at 288.2 eV (Table 2) in the peat are probably indicative of the presence of oxidized organic



Fig. 7. Saturation indices for carbonate, sulfate and hydroxide minerals in the Nickel Rim aquifer.

Table 2

X-ray photoelectron spectroscopy results indicating the relative abundance of key species on the surface of solids collected from the Nickel Rim aquifer, downgradient from the Nickel Rim tailings impoundment

Peak	Component	Average energy (eV)	Pre-barrier aquifer (% conc.)	Pre-barrier peat (% conc.)	Post-barrier aquifer (% conc.)
C1S total	Total carbon		4.0	19.2	6.6
C1S (1)	Carbonate ^a	288.2	0.7	14.4	4.2
C1S (2)	Adventitious carbon ^b	284.8	3.3	4.5	2.2
Fep	Ferric iron ^c	712.2	4.2	1.9	3.0
O1S total	Total oxygen		44.5	29.7	43.4
OIS (1)	Oxide ^d	530.3	3.7	11.5	6.4
O1S (2)	Hydroxide	531.8	13.7	17.2	10.7
O1S (3)	Water ^f	533.8	25.9	1.6	23.5
S2p	Sulfate ^g	171.7	0.0	0.0	0.0
Total	Total of major components		100.0	100.0	100.0

^a Carbonate binding energy=290.1 eV (Stipp and Hochella, 1991).

^b Adventitious carbon binding energy=284.8 eV (Swift, 1982).

^c Ferric iron binding energies=711.0-711.9 (Pratt et al., 1994).

^d Oxide binding energies=530.0-530.3 (Pratt et al., 1994).

^e Hydroxide binding energy=531.4 (Mills and Sullivan, 1983).

^f Water binding energy=533.8 (Jones et al., 1992).

^g Sulfate binding energy=168.5 (Jones et al., 1992).

carbon phases such as carboxylates, ketones, diols and alcohols (Stipp and Hochella, 1991), rather than of the presence of carbonate phases. The observed increase in alkalinity, the degree of saturation of the groundwater with respect to carbonate phases and the increase in solid-phase carbonate content downgradient from the barrier are due to the release of alkalinity by oxidation of organic carbon coupled with sulfate reduction and other reduction reactions occurring within the barrier (Benner et al., 1999). The increase in alkalinity may be leading to the precipitation of carbonates and an increase in the acid-buffering capacity of the aquifer; however, carbonate minerals were not seen.

The degree of saturation of the groundwater with respect to carbonate minerals is dependent upon the pH. At NR 73, the pH is low due to the infiltration of oxidized pond water (Fig. 5). The alkalinity, the solid-phase carbonate content and the carbonate mineral saturation indices are also low (Figs. 5–7). The water is undersaturated with respect to calcite and rhodocrosite in most of the aquifer, aside from the area immediately downgradient from the reactive barrier. The water is supersaturated with respect to siderite throughout most of the aquifer. In Fe(II)-rich mine waters, carbonate species released by calcite dissolution react with Fe(II) to form siderite (Dubrovsky et al., 1984; Al et al., 2000); similar reactions may be occurring in the Nickel Rim aquifer, although siderite has not been seen in the aquifer material. If siderite is precipitating in the aquifer. However, acid-neutralizing reactions involving siderite will release Fe(II) to the groundwater, and the Fe(II) may be oxidized to Fe(III) when the groundwater is discharged to surface water at Moose Lake.

4.2. Sulfides

Analyses of the total reduced sulfide content and acid volatile sulfide content indicate that low levels of total sulfides are present throughout the Nickel Rim aquifer. and that up to 3% total reduced sulfides, and 0.2% acid volatile sulfides, are present within the upper portion (1-2 m, depending on the exact location) of the aquifer (Fig. 6a). Examination of the aquifer material with a reflected light microscope revealed the presence of 0.3% pyrrhotite (Fe_{1-x}S) within the sand and gravel portion of the aquifer at NR 63 and up to 5% pyrrhotite in the top 1.5 m of NR 63. SEM/EDX analyses also suggest the presence of pyrrhotite as well as pentlandite ((Fe.Ni) $_{0}S_{8}$) within the top 1.5 m of NR 63, but not in the sand and gravel portion of the aquifer. Fig. 8 illustrates the presence of a high-Fe, -Ni and -S grain, which is likely pentlandite. Furthermore, it was observed that metal concentrations in the solid-phase aquifer material are up to 10 times higher in the top 1-2 m of the aquifer than in the rest of the aquifer. These results suggest that the aquifer is overlain by 1-2 m of mill tailings derived from the tailings impoundment (Fig. 4). The presence of tailings has important implications for the portion of the aquifer near and downgradient from the pond, where water infiltrates from the surface, through the tailings layer, into the aquifer. Here, the primary sulfides in the tailings may be contributing to an increase in the acid volatile sulfide content of the solids. Whereas these tailings generally contain primary sulfides, such as pyrrhotite, it is possible that secondary, acid volatile sulfides are nucleating and precipitating in small quantities on the primary sulfides. Although the presence of secondary sulfides was not confirmed by SEM/EDX or by optical microscopy, Benner et al. (2000) found that sulfate reducing bacteria increased in population near the surface of the aquifer at two locations, suggesting the potential for the bacterially mediated generation of secondary sulfides.

Benner et al. (2000) also found elevated numbers of sulfate reducing bacteria within the reactive barrier, as well as immediately downgradient from the reactive barrier. Herbert et al. (2000) found that acid volatile sulfide concentrations were high within



Fig. 8. EDX images and spectra and SEM backscatter electron image of a Ni-Fe sulfide grain. The grain may be composed of pentlandite.

the barrier and that AVS accounted for the majority of the sulfide minerals accumulating in the barrier. The solid-phase concentrations of acid volatile sulfides increase behind the reactive barrier. The increase in acid volatile sulfide content immediately downgradient from the reactive barrier is consistent with the observations of Benner et al. (2000) and Herbert et al. (2000), and suggests that the reactions within the barrier are generating strongly reduced conditions, not only within the groundwater, but also in the solid phase. These changes to the solid phase are of note because they may influence the groundwater chemistry at a later time. For instance, the secondary sulfide phases could be dissolved if a low pH plume migrates through the aquifer in the future.

4.3. Iron

The oxidation of the sulfide content of the top meter of the Nickel Rim tailings impoundment has lead to the release of iron from pyrrhotite and the generation of Ferich water, which is migrating through the tailings and into the downgradient aquifer (Fig. 5). The iron is present mainly as Fe(II), because Fe(III) precipitates from solution to form goethite (FeO(OH)) under neutral pH conditions (Jambor and Owens, 1993), or is consumed by further reactions with the sulfide minerals (Johnson et al., 2000). Goethite is abundant in the central portion of the tailings impoundment and in the aquifer. Iron concentrations in the aquifer upgradient from the reactive barrier reach 1.8 g/L, but decrease to as little as 0.2 g/L downgradient from the reactive barrier. Iron is being removed from the groundwater by reactions with dissolved sulfide species generated by SO_4^{2-} reduction within the reactive barrier. The Fe precipitates as secondary Fe-S phases (Benner et al., 1999).

The solid-phase distribution of Fe in the Nickel Rim aquifer was assessed based on the results of the chemical extractions. Comparisons between the DI water extractable metals and the concentrations of metals contained in the groundwater suggest that Fe and other metal concentrations extracted from the aquifer by DI water correspond only to pore water metal concentrations; no additional metals were extracted from the solid phase. In other words, no water soluble phases appear to be present. Iron concentrations extracted by most methods are high in the tailings layer overlying the aquifer (Fig. 6b,c). Speciation of the iron extracted by 0.5 M and 5 M HCl indicates that, in both cases, the iron in the tailings is predominantly as Fe(II) and that the highest solid-phase Fe(II) concentrations are confined to the tailings.

The 5 M HCl extractable Fe(III) is not present in the tailings to the same extent as Fe(II) and extends below the tailings at RW 34, where infiltrating, oxidized water is reacting with sulfides in the tailings layer, releasing Fe(II) and carrying it further down into the aquifer. Poorly crystalline, 0.5 M HCl extractable Fe(III) is absent from much of the clay and tailings layer upgradient from the reactive barrier, but is found in the peat layer underlying the tailings layer. The same is observed for the HHCl extractable Fe(III). Ti-EDTA extractable Fe(III) is found at the base of the peat and also within the tailings (Fig. 6b).

The XPS analyses do not indicate the presence of more Fe(III) in the peat than elsewhere. These analyses, however, do indicate an increase in the abundance of

oxides and hydroxides compared to the oxide and hydroxide content in the sand and gravel portions of the aquifer (Table 2). Pfeiffer et al. (1999) found that natural organic matter (NOM) can stabilize ferric iron colloids; the stabilization of Fe(III) solids by NOM may explain the accumulation of Fe(III) phase in the peat. While organic matter is often associated with reducing capacity (Christensen et al., 2000), the peat at this site does not seem to exert significant reducing potential. The presence of this zone of elevated Fe(III) within the aquifer has implications with respect to the poise, or the oxidation-reduction capacity, of the aquifer. Because the Fe(III) found in the peat is largely extracted by weak reductants and is probably poorly crystalline, it will probably react relatively easily with reduced waters. Amorphous Fe(III) phases are more easily reduced via microbially catalyzed reactions than crystalline phases (Lovley and Phillips, 1986). If, for instance, the tailings are capped with organic material and reducing conditions are imposed on the tailings and aquifer, the poorly crystalline Fe(III) hydroxide phases in the peat will likely be susceptible to reduction and dissolution, increasing the total Fe concentrations in the groundwater. Furthermore, amorphous Fe oxides are important surfaces for sorption of both anions and cations within aquifers, and their depletion can lead to the migration of higher concentrations of dissolved constituents through aquifers (Knapp et al., 2002).

In addition to assessing metal concentrations with respect to total solid-phase material, it is also useful to examine the metals contained in various phases and extracted by different reagents as a percentage of the total metals. With respect to Fe, the percentage of the total aquifer Fe represented by Na-ascorbate extractable Fe decreases downgradient from the reactive barrier (Fig. 6c). The HHCl extractions indicate that the abundances of poorly crystalline, microbially reducible Fe(III) are higher in most of the aquifer upgradient from the barrier than downgradient (Fig. 6b), suggesting that the presence of the reactive barrier has resulted in a decreased percentage of Na-ascorbate extractable Fe(III) downgradient from the barrier. Despite the decline in Na-ascorbate extractable Fe, or poorly crystalline Fe(III), downgradient from the barrier, the 0.5 M HCl extractable Fe, or total poorly crystalline Fe, does not display a similar trend and instead remains relatively constant. The percentage of Fe(III) making up the 0.5 M HCl extractable Fe remains the same upgradient and downgradient of the barrier, although it is highest at the center of the peat layer. The accumulation of carbonate and secondary sulfide phases, which likely contain Fe(II), downgradient of the barrier, combined with the results of the Na-ascorbate and HHCl extractions, suggests that the reactive barrier is causing a decrease in poorly crystalline, oxidized Fe, favouring the precipitation of Fe(II)-bearing solids downgradient.

The Nickel Rim aquifer has an iron content similar to that documented for several other aquifers (Tables 3a and b). Total 5 M HCl extractable Fe concentrations in the sand and gravel portion of the Nickel Rim aquifer are similar to those found in uncontaminated portions of the Bemidji (Tucillo et al., 1999), Vejen (Heron and Christensen, 1995) and Winterthur (Amirbahman et al., 1998) aquifers. Total oxidized iron concentrations (Ti-EDTA extractable iron) in the Nickel Rim sand and gravel are similar to concentrations in the Bemidji and Vejen aquifers, although 0.5 M HCl extractable Fe(III) concentrations are lower than in other aquifers. These results suggest

Table 3a

Comparison of the iron content (mg/g) of the sand and gravel portion of the Nickel Rim aquifer and in the uncontaminated portion of three other aquifers

Iron fraction	Nickel Rim	Bemidji ^a	Vejen ^b	Winterthur
0.5 M HCl Fe(II)	1-3	0.26	< 0.2	n/a
0.5 M HCl Fe(III)	0.1-0.5	1.3	0.5-3	n/a
5 M HCl Fe(II)	0.1-10	n/a	0.3	n/a
5 M HCl Fe(III)	0.2-10	n/a	3-10	n/a
Ti-EDTA Fe(III)	1-3	1.9	1–7	5.5-8.25
Na-ascorbate Fe(III)	0.1-1	n/a	n/a	0.57

Data represent ranges or, where single values are given, averages. Nickel Rim ranges include data collected from NR 63 and NR 64, upgradient from the reactive barrier.

^a Tucillo et al. (1999).

^b Heron and Christensen (1995) (note: some values interpreted from graphs).

^c Amirbahman et al. (1998) (note: some values interpreted from graphs).

that the iron in the sand and gravel portion of the Nickel Rim aquifer is present in a less easily extractable form than in other aquifers; in other words, that a greater fraction of Fe(III) is in a crystalline form. The relatively low levels of 0.5 M HCl extractable Fe(III) may be a result of reactions depleting easily acid extractable Fe(III) in the Nickel Rim aquifer. Concentrations of Ti-EDTA extractable Fe(III) in the Nickel Rim peat are similar to the higher concentrations in the uncontaminated Winterthur aquifer. Na-ascorbate extractable Fe(III) concentrations in the Nickel Rim peat are higher than those of the Winterthur aquifer. These findings suggest that easily extractable Fe(III) has accumulated in the Nickel Rim peat.

4.4. Manganese

The mine drainage migrating from the tailings into the aquifer carries high dissolved Mn concentrations. At this time, however, concentrations of only 5-10 mg/L have reached the aquifer (Fig. 5). The reactive barrier seems to have a minimal impact on

Table 3b

Comparison of the iron content (mg/g) of the peat portion of the Nickel Rim aquifer, an oil-contaminated aquifer (Bemidji) and two landfill-leachate contaminated aquifers (Vejen and Winterthur)

Iron fraction	Nickel Rim	Bemidji ^a	Vejen ^b	Winterthur ^c
0.5 M HCl Fe(II)	18	1.0	~ 0.4	n/a
0.5 M HCl Fe(III)	1-4	0.90	< 0.1	n/a
5 M HCl Fe(II)	0.1-1	n/a	0.4-1.6	n/a
5 M HCl Fe(III)	0.2-10	n/a	< 3	n/a
Ti-EDTA Fe(III)	4–5	1.2	< 0.5	2.8-4.4
Na-ascorbate Fe(III)	3-8	n/a	n/a	0.17

Data represent ranges or, where single values are given, averages. Nickel Rim ranges include data collected from NR 63 and NR 64, upgradient from the reactive barrier.

^a Tucillo et al. (1999).

^b Heron and Christensen (1995).

^c Amirbahman et al. (1998).

dissolved Mn concentrations. Groundwater Mn concentrations increase downgradient from the reactive barrier, where surface water infiltrates into the aquifer. Total, HF digestible Mn concentrations are much higher in the tailings layer than in the rest of the aquifer, as is the case for all the metals. The 0.5 M HCl extractable Mn content of the aquifer, and the fraction of the total solid-phase Mn represented by the 0.5 M HCl extractable fraction, do not appear to be affected by the barrier. However, the Naascorbate extractable Mn, and the percentage of total Mn that is Na-ascorbate extractable, decrease downgradient from the barrier (Fig. 6c). It is likely that the total Mn is comprised mainly of Mn(IV) upgradient from the barrier, and of Mn(II) downgradient from the reactive barrier. Manganese(IV) is likely present as an oxyhydroxide phase, whereas Mn(II) is present as a carbonate phase. Potential carbonate minerals include rhodocrosite and siderite. The saturation indices for rhodocrosite (Fig. 7) indicate that geochemical conditions favour rhodocrosite precipitation downgradient from the barrier to a greater extent than upgradient from the barrier. Rhodocrosite was not detected in core sections, however. Immediately downgradient from the barrier, saturation indices indicate that the groundwater is supersaturated or near saturation with respect to rhodocrosite, but upgradient and further downgradient from the barrier, the rhodocrosite saturation indices all indicate undersaturation. Redox conditions within the reactive barrier favor the reduction of Mn(IV) to Mn(II), and the barrier also generates alkalinity, favoring rhodocrosite precipitation.

Poorly crystalline, oxidized Mn accumulates in the peat layer in the Nickel Rim aquifer, similar to Fe (Fig. 6c). In the peat, the fraction of total Mn comprised by Naascorbate extractable Mn is greater than anywhere else in the aquifer. The 0.5 M HCl extractable Mn, or total poorly crystalline Mn, can also be seen to accumulate at the bottom of the peat, but less near the top.

Manganese is present as a poorly crystalline, oxidized phase upgradient from the reactive barrier. This form of Mn oxide is much more likely to be released if reducing conditions develop. Manganese could be released from the downgradient aquifer, and, to a lesser degree, from the upgradient aquifer, by low pH water, which may reach the aquifer if the buffering capacity of the upgradient tailings material is exceeded.

4.5. Trace metals Co, Cr, Cu, Ni and Zn

Trace metals Co, Cr, Cu, Ni and Zn are being released by oxidation and dissolution reactions in the tailings, and are migrating into the aquifer, although they are attenuated to some degree by precipitation and adsorption reactions within the tailings impoundment and the aquifer (Fig. 5). The reactive barrier removes Ni and Zn from the groundwater, although infiltrating surface water leads to high Ni concentrations downgradient from the barrier. The barrier only has a noticeable impact on the solid-phase abundance of some metals. The 0.5 M HCl extractable Zn concentrations decrease downgradient from the reactive barrier (Fig. 6d). The percentage of total Zn comprised by the 0.5 M HCl extractable Zn does not decrease, due to corresponding low HF digestible Zn concentrations downgradient from the barrier.

chromium in the Na-ascorbate extractable form decrease downgradient from the barrier (Fig. 6c). With respect to Zn, the reactive barrier is not only remediating the current groundwater impacts of mine water, but it is potentially mitigating the future release of Zn to the environment by limiting its accumulation in the aquifer.

Most of these trace metals, with the exception of Cu, are most abundant in their Na-ascorbate extractable forms at NR 63. NR 63 has been impacted by the oxidized. metal-rich water from the tailings to a greater extent than other locations. These metals are probably bound to oxidized iron phases and are released when these iron (oxy)hydroxides are dissolved by the Na-ascorbate extractant. Nickel and Zn are extracted to a greater degree by Na-ascorbate than by 0.5 M HCl at NR 63. This observation may be an indication that these metals are strongly associated with Fe and Mn (oxy)hydroxides, and that the Na-ascorbate is more efficient at releasing metals coprecipitated with or adsorbed to Fe and Mn (oxy)hydroxides than 0.5 M HCl. The 0.5 M HCl extractable concentrations of all of these trace metals are least abundant towards the top of the sand and gravel portion of the aquifer at NR 63. Zinc and Cu accumulate in the peat, but Co, Cr and Ni are largely absent from the peat. The explanation for the low abundance of 0.5 M HCl extractable metals towards the center and top of the NR 63 sand and gravel may be that this zone has been impacted to the greatest degree by tailings discharge water from the impoundment. Although the pH is not overly acidic in the aquifer (mainly pH 5-7), it is acidic at the top and bottom of the proximal tailings, as well as in throughout most of the distal tailings (pH<5). The near-neutral pH in the aquifer is maintained at the expense of carbonate minerals which neutralize the infiltrating acid water and are dissolved. Some of the metals extracted by 0.5 M HCl are probably associated with these carbonate minerals, which have probably been partly dissolved by incoming tailings discharge water.

4.6. Poise of the Nickel Rim aquifer

The poise or redox-buffering capacity of an aquifer is comprised of two main factors: its oxidation capacity (OXC) and its total reduction capacity (TRC). The oxidation capacity represents the reservoir of oxidized species available to oxidize dissolved reduced species entering the aquifer (Heron et al., 1994a; Christensen et al., 2000). Oxidized solid phases, such as Fe and Mn oxides, are among the major contributors to the OXC of an aquifer (Christensen et al., 2000). At Nickel Rim, the Mn content of the aquifer is low in comparison with the Fe content. Therefore, oxidized Fe phases are likely the principal source of the bulk of the oxidation capacity of the Nickel Rim aquifer, and Fe(III) measured by Ti-EDTA extractions can be used to operationally define total oxidation capacity (OXC). While the total Fe(III) content at Nickel Rim is similar to the total Fe(III) content of other aquifers (Tables 3a and b), the poorly crystalline Fe(III) content throughout most of the aquifer is low. Iron reducing bacteria preferentially target poorly crystalline iron (Lovley and Phillips, 1986). Thus, the available oxidation capacity of the Nickel Rim aquifer is comprised mainly of this poorly crystalline, labile Fe(III), and can be defined operationally as Na-ascorbate extractable Fe(III). Because of the low Na-ascorbate extractable Fe(III)

concentrations in the Nickel Rim aquifer, the capacity of the aquifer solids to react with incoming reducing species will be limited, especially downgradient from the reactive barrier. In the Nickel Rim peat, however, the poorly crystalline Fe(III) content was found to be high. This finding suggests that the peat will have a greater oxidation capacity than the rest of the Nickel Rim aquifer. The capacity of the peat to buffer reducing water will not necessarily be a benefit to the adjacent environment. If water containing reduced species enters the aquifer, Fe in the peat may be released to the groundwater by reductive dissolution, increasing the Fe loading to the surrounding environment.

The total reducing capacity of an aquifer is comprised mainly of sulfides, Fe(II) and Mn(II) carbonates, and organic matter. The reactivity of sediment-bound organic matter is usually low (Christensen et al., 2000), and the Mn content of the Nickel Rim aquifer substantially lower than the iron content. The main contributors to the total reducing capacity of the Nickel Rim aquifer, therefore, are Fe(II) phases such as siderite, pyrrhotite and acid volatile Fe(II) sulfides. Thus, Fe(II) concentrations measured by the extractions can be used to provide an estimate of the aquifer reduction capacity. Total reduction capacity can be operationally defined as 5 M HCl extractable Fe(II); available reduction capacity can be operationally defined as 0.5 M HCl extractable Fe(II).

Both 0.5 M HCl and 5 M HCl extractable Fe(II) were much higher in the Nickel Rim aquifer than in the uncontaminated portion of other typical aquifers (Tables 3a and b). The source of most of this Fe(II) is likely siderite; the Nickel Rim aquifer has a high dissolved Fe(II) content and the groundwater is largely supersaturated with respect to siderite (Figs. 5 and 7). AVS and TRS extractions, as well as optical microscopy, indicate that low concentrations of sulfides, which are found throughout the aquifer, likely also contribute some Fe(II), as well as reduced S, to the total reduction capacity





of the aquifer (Fig. 6a). Because of its high solid-phase Fe(II) content, the Nickel Rim aquifer has a high reduction capacity, or an ability to reduce oxidized species contained in water infiltrating into the aquifer. As oxidized species enter an aquifer with less capacity for reduction, redox buffering will initially allow a moderate Eh to be maintained, but the Eh will quickly rise as the capacity of the aquifer material to oxidize dissolved species is exceeded. If a similarly oxidized water enters the Nickel Rim aquifer, the oxidized species will be rapidly reduced and a low Eh will be maintained (Fig. 9).

5. Conclusions

The geological materials of the aquifer and the reactive barrier represent important controls on the distribution of metals within the aquifer, as well as the poise and pH buffering capacity of the aquifer. The peat layer provides an environment for the accumulation of poorly crystalline Fe and Mn oxides, from which Fe and Mn could potentially be released by reductive dissolution. For instance, if the tailings are covered with organic material to prevent further oxidation, a plume of highly reduced species (e.g., dissolved organic carbon) could migrate through the aquifer, potentially reducing Fe(III) and Mn(IV) oxides and releasing Fe(II) and Mn(II). Reactions within the reactive barrier generate alkalinity, apparently resulting in an accumulation of carbonate minerals downgradient from the barrier, increasing the acid buffering capacity of the aquifer. The barrier also appears to diminish, to some degree, the accumulation poorly crystalline Mn and Fe (hydr)oxides, as well as Cr(III) and Zn associated with these Fe (hydr)oxides. Thus, the barrier not only remediates tailings drainage water currently flowing through the aquifer, but limits the availability of some metals for release from the aquifer solids in the future. These findings indicate that reactive barriers for remediation of mine drainage can play a dual role in averting the release of acidity and metals to the environment; firstly, by remediating already contaminated water and, secondly, by buffering acidic plumes and preventing metal release in the future.

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Appendix

Pore water chemistry data for samples	collected from piezometer	nests in the Nickel	Rim tailings impoundment
and aquifer in the summer of 2000			

Depth below surface (m)	рН	Alkalinity	Fe	SO₄	Zn
	· · ·	(mg/L)	(mg/L)	(mg/L)	(mg/L)
NR 1 (tailings impoundment)					
1.54	5.31	2.3	4436	16,400	4.20
3.86	4.06	< 1	n/a	15,000	n/a
3.91	3.81	< 1	4812	16,800	2.33
4.94	4.42	< 1	3846	14,600	2.65
5.69	5.40	< 1	n/a	n/a	n/a
7.98	4.85	< 1	5114	16,300	0.589
8.48	4.80	< 1	n/a	n/a	n/a
9.19	5.22	< 1	2290	1640	0.021
NR 6 (tailings impoundment)	,				
2.84	6.02	<1	n/a	n/a	n/a
3.50	5.05	< 1	405	2140	0.143
5.69	5.89	3.6	2127	6120	0.143
7.56	6.25	1.8	2767	8160	0.043
10.43	6.23	17	2616	11,500	0.187
NR 18 (tailings impoundment)					
3.05	2.93	< 1	523	2220	0.223
5.25	6.32	4.9	699	2840	0.043
7.01	6.10	< 1	1923	7800	0.097
7.92	6.03	9.7	3695	13,200	0.258
8.70	2.41	< 1	3319	11,900	0.483
NR 63 (aquifer)					
1,76	6.12	66	n/a	3320	0.081
2.76	6.13	70	1221	3960	0.077
3.76	6.49	73	1294	4160	0.075
4.76	6.09	79	n/a	4520	n/a
5.76	6.23	40	1564	6490	0.113
6.76	6.16	106	1432	.4000	0.100
7.77	6.17	71	1212	3990	0.081
NR 64 (aquifer)					
0.67	5.66	42	1262	4410	0.102
0.97	6.00	98	1277	4200	0.083
1.27	5.90	86	1151	4460	0.087
1.57	6.04	n/a	1076	4090	0.084
1.87	5.46	17	1296	4550	0.094
RW 21 (aquifer)					
1.19	5.11	7	425	6997	0.13
2.20	5.62	53	87.8	3458	0.03
3.05	5.92	50	39	278	< 0.01
3.93	5.81	27	8	2571	0.01

Appendix (continued)						
Depth below surface (m)	рН	Alkalinity (mg/L)	Fe (mg/L)	SO₄ (mg/L)	Zn (mg/L)	
RW 34 (aquifer)						
0.5	6.23	500	132	1872	< 0.01	
1,5	6.67	1260	200	1652	< 0.01	
2.5	6.42	762	166	2823	< 0.01	
3.75	6.43	620	113	2147	0.01	
NR 73 (aquifer)						
0.7	4.25	< 1	183	1320	0.078	
1.3	4.05	< 1	126	1230	0.04	
2.5	4.13	< 1	226	n/a	0.04	
3.1	4.15	< 1	259	964	0.061	
3.7	6.15	52	282	1350	0.028	
4.3	6.33	124	282	1610	0.022	

Contour diagrams for pore water chemistry (Fig. 5) are based on these data.

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