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Metal Mobility and Attenuation in Mine Tailings and a
Mine Drainage Impacted with a Reactive Barrier
(Sudbury, ON)

By:

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ABSTRACT

Concentrations of metals bound in the solid phase of the Nickel Rim tailings impoundment and downgradient aquifer were measured. Chemical extraction techniques and groundwater sampling, among other techniques, were used to assess the mobility of metals in the Nickel Rim impoundment and aquifer. Emphasis was placed on the effects of geology and a reactive barrier on the solid phase geochemistry of the aquifer. Tailings geochemistry determined by extraction techniques was compared to measurements of mineralogy and pore water chemistry made previously. The Tailings geochemistry determined using extraction techniques was in agreement with findings based on groundwater chemistry and optical mineralogy. The order of metal mobility of $Zn > Ni > Co > Al > Cr = Cu$ was determined based on the results of solid phase extractions. The reactive barrier increased the carbonate content of the aquifer. Poorly crystalline Fe and Mn were present in oxidized forms upgradient of the barrier, but as reduced forms, likely carbonates, downgradient of the barrier.

Mobilité des métaux et atténuation par barrière réactive des effets des stériles et des exhaures de mines sur un aquifère (Sudbury, ON)

N.A. Doerr, C.J. Ptacek et D.W. Blowes

RÉSUMÉ

On a mesuré la concentration des métaux dans le bassin de stériles de la mine Nickel Rim (dans la phase solide) et dans l'aquifère situé en aval. On a utilisé les techniques d'extraction chimique et d'échantillonnage de l'eau souterraine, entre autres techniques, pour évaluer la mobilité des métaux dans le bassin et l'aquifère de Nickel Rim. Les efforts ont porté sur les effets des processus géologiques et de la barrière réactive sur le fonctionnement géochimique de la phase solide de l'aquifère. On a comparé les données géochimiques des stériles obtenues à l'aide de techniques d'extraction à des données minéralogiques et des données sur la chimie de l'eau interstitielle qui avaient été recueillies auparavant. Les résultats des analyses géochimiques des stériles réalisées à l'aide de techniques d'extraction concordent avec ceux des analyses de chimie et de minéralogie optique de l'eau souterraine. Les résultats obtenus par l'extraction dans la phase solide ont permis de déterminer l'ordre de mobilité des métaux ($Zn > Ni > Co > Al > Cr = Cu$). La barrière réactive fait augmenter la teneur en carbonate de l'aquifère. On a trouvé, en amont de la barrière, la forme oxydée du fer et du manganèse ordonnés en réseaux peu cristallins, alors qu'en aval, ces métaux se trouvaient sous forme réduite (sans doute sous forme de carbonate).

NWRI RESEARCH SUMMARY

Plain language title

Fate of metals in a mine-drainage impacted aquifer

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

Metals and acid continue to be released from old mine sites for decades, centuries or longer after cessation of mining activities. The duration of release varies from site to site, and is dependent on physical, chemical and microbial processes. Abundant information is available on metal release processes in the early stages of mine waste weathering. Less information is available for the later stages of release.

Why did NWRI do this study?

Elevated concentrations of metals are being released from the Nickel Rim mine tailings near Sudbury, Ontario. These metals are discharging to an adjacent aquifer and directly to the surface. This study was conducted to evaluate the geochemical properties of metals in the aquifer after 30 years of receiving mine drainage. Previous studies indicated a plume of contaminated water is present in the aquifer and a remedial program has been put in place. Various methods were used to evaluate the stability of metals on the aquifer solids and the potential for release over the long term.

What were the results?

The results indicate that the geochemical properties of the aquifer have changed substantially as a result of exposure to 30 years of mine drainage. These changes indicate that some metals have been translocated along the groundwater flow path, and are now present in a relatively labile form in the aquifer solids. Downgradient of the permeable reactive barrier accumulations of beneficial carbonate minerals were observed.

How will these results be used?

The results will be used to predict the potential for long-term release of metals from mine impacted aquifers.

Who were our main partners in the study?

University of Waterloo. Falconbridge Ltd.

Sommaire des recherches de l'INRE

Titre en langage clair

Le devenir des métaux dans un aquifère touché par le drainage minier

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

Après la cessation de leurs activités, durant des décennies, des siècles ou plus, les anciennes exploitations minières libèrent des métaux et des matériaux acides. La durée de ce phénomène varie selon le lieu et dépend de processus physiques, chimiques et microbiens. L'information abonde sur les processus de libération aux premiers stades de météorisation des déchets de mine. Par contre, on possède moins de connaissances sur les stades ultérieurs de libération.

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

Des concentrations élevées de métaux sont libérées à partir des stériles de la mine Nickel Rim, située près de Sudbury (Ontario). Les métaux sont rejetés dans un aquifère adjacent et directement à la surface du sol. Notre étude avait pour but l'évaluation des propriétés géochimiques des métaux dans l'aquifère après l'exposition à des exhaures de mine pendant 30 ans. Des études précédentes indiquaient la présence d'un panache d'eau contaminée dans l'aquifère, et un programme de décontamination a été mis en œuvre. Diverses méthodes ont été utilisées pour l'évaluation de la stabilité des métaux dans la phase solide de l'aquifère et des risques de libération des métaux à long terme.

Quels sont les résultats?

Les résultats indiquent que les propriétés géochimiques de l'aquifère ont été considérablement modifiées par l'exposition à des exhaures de mine pendant 30 ans. Ces modifications indiquent que certains métaux ont été déplacés par l'écoulement de l'eau souterraine et qu'ils sont maintenant présents sous une forme relativement instable dans la phase solide de l'aquifère. En aval de la barrière réactive perméable, on a observé une accumulation de carbonates (dont l'effet est bénéfique).

Comment ces résultats seront-ils utilisés?

Les résultats serviront à des prévisions sur les risques d'une libération à long terme de métaux provenant d'aquifères touchés par les mines.

Quels étaient nos principaux partenaires dans cette étude?

Université de Waterloo. Falconbridge Ltée.

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Metal Mobility and Attenuation in Mine Tailings and a Mine Drainage Impacted Aquifer with a Reactive Barrier (Sudbury, ON)

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Abstract:

Concentrations of metals bound in the solid phase of the Nickel Rim tailings impoundment and downgradient aquifer were measured. Chemical extraction techniques and groundwater sampling, among other techniques, were used to assess the mobility of metals in the Nickel Rim impoundment and aquifer. Emphasis was placed on the effects of geology and a reactive barrier on the solid phase geochemistry of the aquifer. Tailings geochemistry determined by extraction techniques was compared to measurements of mineralogy and pore water chemistry made previously. The tailings geochemistry determined using extraction techniques was in agreement with findings based on groundwater chemistry and optical mineralogy. The order of metal mobility of $Zn > Ni > Co > Al > Cr = Cu$ was determined based on the results of solid phase extractions. The reactive barrier increased the carbonate content of the aquifer. Poorly crystalline Fe and Mn were present in oxidized forms upgradient of the barrier, but as reduced forms, likely carbonates, downgradient of the barrier.

Key Words: mine tailings, metals, extraction, aquifer, mine drainage, reactive barrier, geochemistry, solid phase, mobility, buffer, redox.

Introduction:

The release of metals and the generation of acid by the oxidation of sulfide minerals in mine waste represents an environmental risk worldwide. Metal-rich mine drainage can impact groundwater and surface water for centuries after mine-waste decommissioning (Blowes and Cherry, 1991). Furthermore, metals initially attenuated by acid neutralization reactions, have the potential to be released by changing geochemical conditions. Thus metals bound in the solid phase of tailings impoundments, waste rock piles, and aquifers impacted by mine drainage, may represent a latent risk to the surrounding environment.

The Nickel Rim tailings impoundment has been a site of active sulfide mineral oxidation and metal release since decommissioning in 1958. High concentrations of Fe and SO_4 have impacted a downgradient aquifer for several decades. In 1995, a reactive barrier, which remediates mine drainage by

reducing SO_4 and precipitating metal sulfides, was installed. Several studies have been conducted to assess the evolution of the tailings (Ribet et al., 1995; Johnson et al., 2000) and aquifer (Bain et al., 2000) geochemistry, and the effectiveness of a reactive barrier (Benner et al., 1999; Benner et al., 2000). With the exception of Ribet et al. (1995), these studies largely make use of the pore water chemistry to assess the impact of mine drainage and the mobility of metals within the tailings and aquifer. As the solid phase chemistry represents a major control on groundwater chemistry, both as a source of metals and as a buffer against acidic and reducing plumes, a greater understanding of the solid phase geochemistry of the Nickel Rim tailings impoundment and downgradient aquifer is the focus of this study.

The overall objective of this study was to assess metal mobility in the Nickel Rim tailings impoundment and downgradient aquifer based on the solid phase geochemistry. Within

the tailings impoundment, emphasis was placed on comparing interpretations based on the solid phase chemistry to those developed by other researchers based on mineralogy and porewater chemistry. Within the aquifer, the study focused on the effects of geology and the reactive barrier on the solid phase geochemistry and on metal mobility.

Site Description:

The Nickel Rim mine is located on the east rim of the Sudbury eruptive, near Sudbury, Ontario, Canada, within a band of quartz diorite breccia. Mine exploration and development began in 1928 and was continued, by various companies, until 1958. At its peak, the Nickel Rim mine produced 1 350 000 tons of Cu and 3 370 000 tons of Ni in one year

Tailings from the milling of ore from the Nickel Rim deposit were deposited in a 9.4 hectare impoundment, and have been exposed to the atmosphere since 1958. The unaltered tailings are comprised of aluminosilicate minerals and 8% sulfide minerals, mainly pyrrhotite (Jambor and Owens, 1993). The predominant silicates are anorthite, albite, augite, and quartz, with smaller quantities of amphibole, biotite, chlorite, enstatite, and talc.

Secondary phases precipitated over time in the oxidation zone of the tailings include goethite, jarosite, and ferrihydrite. Covellite has precipitated at the depth of a hardpan layer, and gypsum is present throughout the impoundment (Jambor and Owens, 1993). The tailings contain up to 0.2 wt% carbonate minerals, principally as dolomite (Johnson et al., 2000). The oxidation of tailings in the Nickel Rim impoundment has generated H^+ (pH <4.5) and released high concentrations of dissolved metals such as Fe (up to 9.8 g/L) and dissolved SO_4 (up to 24 g/L) to infiltrating water.

Water migrating through the tailings discharges to surface or flows into a glacial outwash aquifer, composed primarily of sand and gravel (Fig. 1). The entire aquifer has been impacted by mine drainage generated in the upgradient tailings (Johnson et al., 2000; Bain et al., 2000). A reactive barrier which treats mine drainage was installed at the narrowest part of the aquifer in 1995 (Benner et al., 1999). The

barrier is composed of gravel, organic matter, and a small amount of limestone, and was designed to reduce sulfate and precipitate metal sulfides. Groundwater 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. 2).

Methods:

Pore Water Sampling:

Pore water samples were taken from drive-point piezometers installed by Johnson et al. (2000) and Bain et al. (2000) at the locations shown in Figure 1. Samples were collected using a peristaltic pump and 0.64 cm polyethylene tubing. For Eh and pH measurements, flow through cells were used to isolate pore water from the atmosphere and mitigate oxidation. The pH was measured using an ORION Ross pH electrode calibrated using pH 4 and 7 buffers, and 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. Buffers and solutions used to check the pH and Eh were maintained at groundwater temperatures. Performance checks for Eh and pH were carried out before and after each measurement, and the pH electrode was recalibrated when values varied by a pH of 0.02 or more from the temperature-corrected pH of the buffered solutions. Alkalinity was determined in the field by titration against standardized sulfuric acid, using freshly filtered samples of pore water. Titration against potassium dichromate was used to analyze for Fe^{+2} (Waser, 1966).

Water for cation and anion analyses was filtered through 0.45 μm filters, and samples for cation analyses were acidified to a pH of less than 1 using trace hydrochloric acid. Samples

were kept cool until analysis at the National Laboratory for Environmental Testing, Environment Canada. Cations Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). Anions SO_4 , Cl, and Si were analyzed by automatic colorimetric techniques. Blanks, standards, and duplicates were analyzed as part of the quality analysis/quality control procedure. Charge balance errors were calculated and were generally less than 10%.

Solid Phase Chemical Analyses:

Cores of tailings and aquifer material were collected from the Nickel Rim impoundment and aquifer at the locations shown in Figure 2. A piston coring device (Starr and Ingleton, 1992) was used to collect continuous cores, which were capped and frozen until analysis, to prevent oxidation. Analyses were performed on homogenized subsamples of cores, which were cut while still partially frozen, and homogenized in an anaerobic chamber.

The carbonate content of the solids was measured using the method of Barker and Chatten (1982), which involves allowing the solids to react with sulfuric acid and measuring the CO_2 produced by the reaction. Total reduced sulfides (TRS) and acid volatile sulfides (AVS) were determined by the methods of Canfield et al. (1986), and Morse and Cornwell (1987), respectively. Argon purged deionized (DI) water was used to extract water-soluble anions and cations from the tailings material. The solid phase concentrations of oxidized phases were determined using three reductants. A pH-neutral solution of Na-ascorbate, bicarbonate and citrate (Amirbahman et al., 1998) was used to target poorly crystalline, reducible phases. Ti-EDTA (Amirbahman et al., 1998) targeted total reducible phases, and was also buffered to a circumneutral pH so that it did not target siderite. A method using separate extractions with HHCl and HCl (Lovley and Phillips, 1987), was used to target microbially reducible Fe(III) . A 0.5 M HCl extraction method (Heron et al., 1994) was used to target poorly crystalline

phases, adsorbed metals, and carbonate phases. A 5 M HCl extraction (Heron et al., 1994) was used to target total acid soluble metal phases, including crystalline metal oxides. The Fe extracted by DI water, 0.5 M HCl , and 5 M HCl was speciated by the method of Gibbs (1979). Lastly, dried solids were digested using an HF/aqua regia solution, for the determination of the total metal content of the solid phase. Cations extracted using all methods were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES). Anions extracted by deionized water were determined using automatic colorimetric techniques.

Geochemical Modelling:

The geochemical speciation model MINTEQA2 (Allison et al., 1990) was used to calculate saturation indices for groundwater sampling locations throughout the impoundment and aquifer. The database was modified to be consistent with the WATEQ4F database (Ball and Nordstrom, 1991). The Eh measured in the field was used to specify redox conditions for the calculation of the saturation indices.

Results and Discussion:

Tailings Impoundment Geochemistry:

Oxidation reactions in the unsaturated zone have caused major changes in the solid phase geochemistry. Total reduced sulfide extractions indicate that the sulfide mineral content of the tailings material is depleted in the unsaturated zone, decreasing from 2 wt % S in the saturated zone to 0.1 wt % S in the unsaturated zone. The depletion of total, HF digestible Cu, Ni, and Co is concurrent with the depletion of total sulfides. Cu occurs primarily as chalcopyrite (CuFeS_2), and Ni as pentlandite ($(\text{Fe, Ni})_9\text{S}_8$), and Co is associated with pyrrhotite (Jambor and Owens, 1993). Thus, as sulfide phases are depleted by oxidation reactions, trace metals Cu, Ni, and Co are released to the aqueous phase. Na-ascorbate extractions suggest that poorly crystalline, oxidized Fe has accumulated in the unsaturated zone. Jambor and Owens determined that Fe(III) precipitation was extensive in the unsaturated zone, although they found

predominantly crystalline goethite ($\text{FeO}(\text{OH})$) and smaller quantities of poorly crystalline ferrihydrite ($\text{Fe}_3(\text{OH})_8 \cdot 4\text{H}_2\text{O}$). Na-ascorbate extractable Cr is also abundant in the oxidation zone. Na-ascorbate extractable Cr is likely Cr(III) associated with Fe oxyhydroxide phases. Oxidation reactions which generate acid have also caused the depletion of carbonate minerals through neutralization reactions in the unsaturated zone. The carbonate content of the tailings material decreases from 0.1 wt % in the saturated zone to <0.01 wt% in the unsaturated zone of the tailings impoundment.

The hardpan is the zone where metals accumulate as the tailings pore water migrates from the unsaturated zone to the saturated zone, and where conditions become more reducing and the pH increases. 0.5 M HCl extractable Fe, Ca, and Cu accumulate in the hardpan; 0.5 M HCl extractable Al accumulates just below the hardpan. Deionized water extractable SO_4 also accumulates in the hardpan. Jambor and Owens (1993) determined that the hardpan is cemented mainly by goethite ($\text{FeO}(\text{OH})$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$). These Fe(III) mineral phases are likely the main source of 0.5 M HCl extractable Fe in the hardpan, and are present in the reddish-colored bands of material observed in the field. Extracted Ca and SO_4 are likely released by gypsum dissolution. Whereas extractions indicate that gypsum occurs primarily in the hardpan, saturation indices suggest that it may be present throughout the saturated zone. Jambor and Owens (1993) found gypsum in the hardpan but also in other parts of the saturated zone. The 0.5 M HCl extractable Cu concentrations, which reach a maximum in the hardpan, are likely the result of Cu precipitation. Jambor and Owens (1993) observed covellite precipitation at the boundary between the unsaturated and saturated zones, and the presence of green bands of material in the field also suggests the precipitation of a Cu sulfide phase in the hardpan. The 0.5 M HCl extractable Al concentrations increase just below the hardpan, where the porewater attains supersaturation with respect to gibbsite. Johnson et al. (2000) hypothesized that gibbsite precipitates between 2 and 4 m depth in the tailings, as the pH exceeds 3.8 and Al released

by the dissolution of aluminosilicates in the oxidation zone precipitates. The extraction of high concentrations of Al between a depth of 1.5 m and 4 m (Fig. 3) is consistent with the hypothesis of Johnson et al. (2000).

In the saturated zone, the pH is generally greater than 5, and reduced Eh conditions predominate. Carbonate extractions indicate that approximately 0.1 wt % carbonate phases are present; Johnson et al. (2000) suggested that the carbonates are predominantly dolomite and calcite. Saturation indices for dolomite and calcite are below zero in the unsaturated zone, suggesting that dolomite dissolution is controlled by slow dissolution rates, a finding consistent with those of Al et al. (2000). Saturation indices for siderite are greater than zero, implying that siderite precipitation is likely, although it has not been observed by optical microscopy. The contribution of acid volatile sulfide minerals to the Fe(II) extracted by 0.5 M HCl is only 35-85 %. The remaining Fe(II) extracted by 0.5 M HCl may be derived from siderite. Several trace metals, such as Co, Ni, and Zn, accumulate in the saturated zone. These metals are likely adsorbed to other phases, co-precipitated with ferric oxyhydroxides, or exist as hydroxide phases. The secondary accumulations of trace metals are generally extractable by 0.5 M HCl. Thus, the peaks in 0.5 M HCl extractable metals, can be inferred to represent zones of accumulation (Fig. 3). The zones of accumulation can be used to determine an order of metal mobility; more mobile metals travel further into the tailings impoundment before being attenuated, while less mobile metals precipitate or adsorb closer to the surface of the impoundment. Thus the order of mobility of trace metals in the Nickel Rim tailings was found to be: $\text{Zn} > \text{Ni} > \text{Co} > \text{Al} > \text{Cr} = \text{Cu}$ (Fig. 3). This mobility hierarchy is very similar to the order of mobility of $\text{Fe} = \text{Mn} > \text{Zn} > \text{Ni} > \text{Co} > \text{Pb} > \text{Cu}$ found by Blowes and Jambor (1990) for the Waite Amulet tailings impoundment, to the order of mobility of $\text{Co} = \text{Ni} > \text{Zn} > \text{Pb} > \text{Cu}$ observed by Dubrovsky (1985) for the Nordic Uranium tailings impoundment, and to the order of mobility of $\text{Fe} = \text{Mn} > \text{Co} = \text{Ni} = \text{Zn} > \text{Cr} = \text{Al} > \text{Cu}$ found by

Johnson et al. (2000) for the Nickel Rim tailings impoundment. Jurjovec et al. (2002) also found Ni, Zn and Co to be more mobile than Cr and Al.

Aquifer Geochemistry:

The acid buffering capacity of the Nickel Rim aquifer is dependent on the carbonate content of the aquifer solids. The carbonate content of the aquifer solids is highest downgradient of the reactive barrier, with a total carbonate content of > 1%. The groundwater reaches saturation with respect to calcite, siderite, and rhodocrosite downgradient of the barrier. The pH is higher downgradient of the barrier than upgradient, and the alkalinity of the groundwater is 10 times higher immediately downgradient of the barrier than upgradient. Benner et al. (1999) suggested that reducing reactions occurring in the barrier generated alkalinity. Furthermore, Benner et al. (1999) indicated that the barrier contains 1 % limestone, which may also increase the pH and alkalinity of the groundwater. Carbonate extraction data and carbonate mineral saturation indices suggest that the increase in alkalinity downgradient of the reactive barrier is leading to the precipitation of carbonate mineral phases. By increasing the carbonate content of the aquifer solids, the barrier is not only treating the current mine drainage problem, but is mitigating the future impacts of acid mine drainage on the groundwater and on surrounding bodies of water by increasing the buffering capacity of the aquifer.

The reduction of SO_4 by organic carbon in the reactive barrier leads to the precipitation of metal sulfides, thereby removing both metals and SO_4 from solution. Our analyses indicate that solid phase concentrations of acid volatile sulfides increase downgradient from the reactive barrier. Benner et al. (2000) 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 the barrier, and that AVS accounted for the majority of the sulfide minerals accumulating in the barrier. The flow system determined by Benner et al.

(2000) suggests that both the reactive barrier and a thin layer of tailings overlying the aquifer are contributing to the increase in acid volatile sulfides in the aquifer downgradient of the reactive barrier. It is unlikely that these secondary sulfide phases will be released by future oxidation, as the aquifer is confined, and only small quantities (<10 mg/L) of O_2 are soluble in water; furthermore, Fe(III) is not soluble unless the pH decreases severely.

Certain fractions of extractable metals in the aquifer solids appear to be affected by the reactive barrier and by aquifer geology. Na-ascorbate extractable Fe, Mn, and Cr decrease downgradient of the reactive barrier (Fig. 4). With respect to Fe and Mn, the Na-ascorbate extractable fraction likely represents amorphous, oxidized Fe and Mn phases. Cr extracted with Na-ascorbate is likely Cr(III) associated with the poorly crystalline, oxidized Fe phases. Although the oxidized fractions of poorly crystalline Fe and Mn decrease downgradient of the barrier, concentrations extracted by 0.5 M HCl, do not change. Therefore, there is an increase in the reduced, easily soluble Fe and Mn phases downgradient of the reactive barrier. The groundwater is supersaturated with respect to siderite, and saturated with respect to rhodocrosite, and given that carbonate extractions show an increase in the total solid phase carbonate content of the aquifer solids, it is likely that Fe and Mn are precipitating as carbonate phases downgradient of the barrier. Oxidized phases likely precipitate to a greater extent upgradient, where the aquifer is impacted by mine drainage, but reducing conditions generated by the barrier may make the precipitation of Fe and Mn oxyhydroxides unfavorable downgradient. The 0.5 M HCl extractable Fe downgradient of the barrier likely also exists as FeS, as acid volatile sulfides were detected. Na-ascorbate extractable Fe and Mn are present throughout the upgradient aquifer but accumulate especially in a peat layer, where natural organic matter may stabilize Fe and Mn oxyhydroxide phases (Pfeiffer et al., 1999). The 0.5 M HCl extractable Zn concentrations are higher upgradient of the barrier than downgradient. By preventing the accumulation of reducible Fe and

Mn, Cr(III) associated with reducible Fe, and acid-soluble Zn, the reactive barrier is not only remediating the current mine drainage problem, but is also diminishing potential future impacts on the environment.

Conclusions:

Oxidation reactions in the Nickel Rim tailings impoundment have lead to the nearly complete depletion of the sulfide mineral pyrrhotite above the water table, and also to the depletion of carbonates phases above and 1 m below the water table. Metals released by oxidation and acid neutralization reactions have accumulated throughout the impoundment, where they could potentially be released if more reduced conditions are imposed on the impoundment. Solid phase Fe could be dissolved by a reducing plume, and trace metals could be released by an acidic plume, with the order of mobility being $Zn > Ni > Co > Al > Cr = Cu$.

Analyses of the solid phase geochemistry of the Nickel Rim aquifer indicate

that the reactive barrier installed in the aquifer to remediate mine drainage is having an impact on the aquifer solids as well as groundwater chemistry. Na-ascorbate extractable Fe, Mn and Cr concentrations are lower downgradient of the barrier than elsewhere in the aquifer, although the acid soluble fractions remain constant. The 0.5 M HCl extractable Mn and Fe likely exist primarily as oxyhydroxide phases upgradient of the barrier, but as carbonate and, in the case of Fe, secondary sulfide phases downgradient. Solid phase carbonate analyses indicate that the barrier leads to an increase in the total solid phase carbonate content of the aquifer, thereby increasing the acid buffering capacity; saturation indices also suggest carbonate precipitation downgradient of the barrier. Reducing reactions within the barrier have lead to the precipitation of acid volatile sulfides not only within the barrier, but also downgradient of the barrier.

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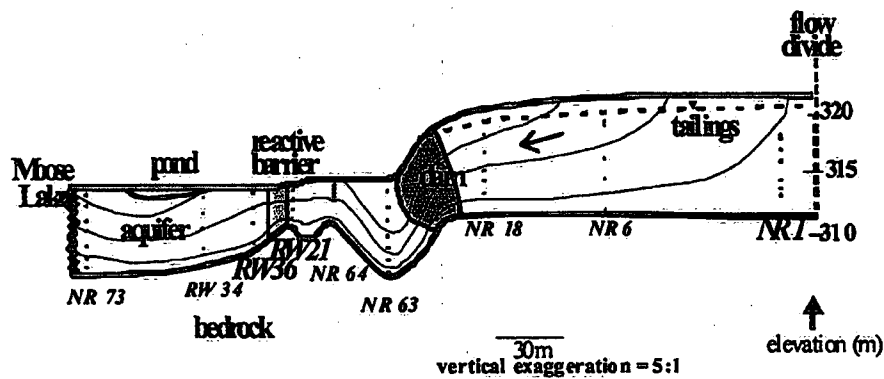


Figure 1. Flow of water through the Nickel Rim tailings impoundment and downgradient aquifer, showing groundwater sampling points.

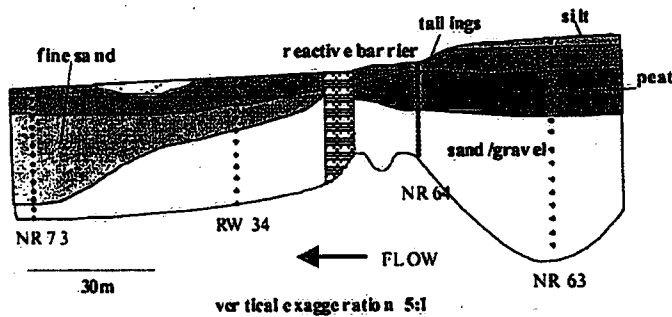


Figure 2. Geology of the Nickel Rim aquifer, showing sample points for solid phase extractions.

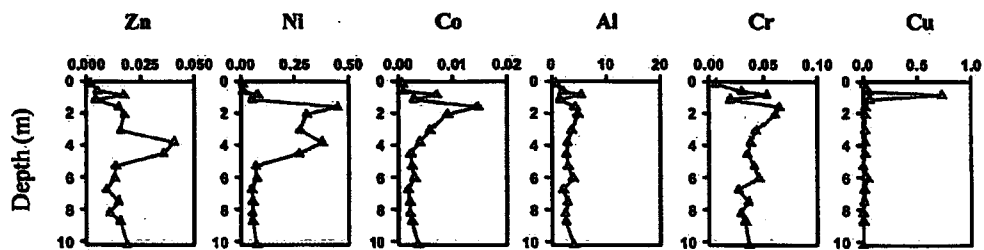


Figure 3. 0.5 M HCl extractable metals (mg/g dry sediment) in Nickel Rim tailings solids (NR 6).

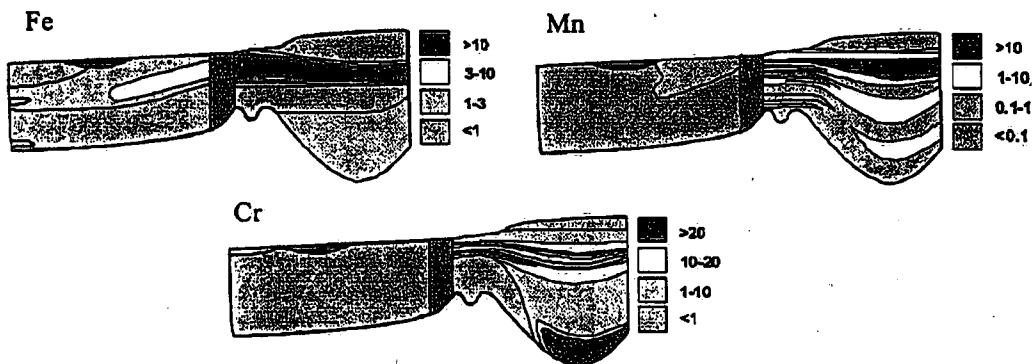


Figure 4. Na-ascorbate extractable Fe, Mn, and Cr, in the Nickel Rim aquifer, as a percentage of total, HF digestible Fe, Mn and Cr.

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