THE HYDROGEOCHEMISTRY OF A SAND AQUIFER AFFECTED BY DISCHARGE FROM THE NICKEL RIM TAILINGS, SUDBURY, ONTARIO[1]

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Abstract: Diffusion of atmospheric O_2 into the vadose zone of the pyrrhotite-rich tailings at the abandoned Nickel Rim mine has resulted in sulfide-oxidation reactions. These reactions have produced low pH conditions and have released high concentrations of dissolved metals to infiltrating recharge water for the past 35 years. Dissolution reactions involving carbonate minerals, aluminum and ferric hydroxide phases and aluminosilicate minerals, present in the tailings, neutralize pH resulting in the attenuation of heavy metals. Constituents which remain mobile under high pH conditions (*e.g.* Fe^{2+} and SO_4^{2-}) continue to move through the tailings. Gradual displacement by infiltrating recharge water has resulted in the development of a plume of tailings-derived water in the underlying sand aquifer. This aquifer discharges into a nearby lake. Tritium concentrations suggest that all of the water in the aquifer recharged through the tailings since 1972. Flow modelling indicates that ~50% of the tailings infiltration discharges *via* the aquifer to the nearby lake. The remainder discharges near the toe of the rock dam, becoming surface drainage that flows into the lake. Geochemical modelling indicates that the plume water approaches equilibrium with respect to a number of mineral phases including ferric and Al hydroxides, and carbonates. These results suggest that precipitation and dissolution of these phases control the concentrations of dissolved constituents as the tailings-derived water flows through the aquifer, affecting the movement of the Fe^{2+} and SO_4^{2-}. Upon discharge, the oxidation of Fe^{2+}, subsequent hydrolysis of Fe^{3+} and precipitation of ferric oxyhydroxide and ferric sulfate minerals creates low pH conditions. Based on flow-system interpretation, it is estimated that within 20 years, in the absence of an effective remedial program, water with significantly higher acid generating potential will arrive at the lake.

Key Words: mine tailings, geochemical modelling, MINTEQA2, FLONET, buffering reactions

Introduction

From 1950 to 1958, tailings were deposited in a narrow bedrock valley near the Nickel Rim Cu-Ni mine, 25 km NE of Sudbury (Figure 1). The tailings contain approximately 3 wt.% sulfide sulfur, principally as pyrrhotite ($Fe_{1-x}S$), in a predominantly silicate gangue. Oxidation of pyrrhotite in the vadose zone of the tailings has released high concentrations of Fe^{2+} and SO_4^{2-} to an underlying gravely sand aquifer (1). Ferrous iron is a source of acidity when it enters the surface water environment. There is, however, no offsite impact at this time.

The objective of this study was to use groundwater flow and geochemical modelling to provide an understanding of the mechanisms controlling the composition of the plume as it migrates through the aquifer. From 1992 to 1994 a detailed hydrogeologic and geochemical study was conducted on the aquifer beyond the western dam. Groundwater flow and geochemical modelling assisted in the analysis of field data.

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Background

Pyrrhotite-rich tailings from the Nickel Rim mining operation were deposited up to 10 m thick in a narrow bedrock valley near the mine. The bottom of the valley is filled with glaciofluvial silty fine sand and gravel, forming a 3-8 m thick aquifer which extends towards Moose Lake, 160 m downgradient from the western tailings dam (Figure 1). The upper portion of the aquifer is composed of bouldery road fill, underlain by peat to a depth of ~1.5m.

After cessation of milling operations in 1958, diffusion of atmospheric O_2 into the tailings has caused the oxidation of pyrrhotite. Draining the impoundment in 1976 further lowered the water table in the tailings, creating an unsaturated zone up to 1.2 m thick (1). The position of the watertable and the presence of a goethite-jarosite hardpan layer at the base of the oxidation zone limits the depth of O_2 diffusion and subsequent sulfide oxidation (1). Low pH conditions and high concentrations of dissolved Fe, Al, Ni, Mn, Cu, Cr, Zn and SO_4 are released to infiltrating rain and snowmelt water as a result of sulfide oxidation.

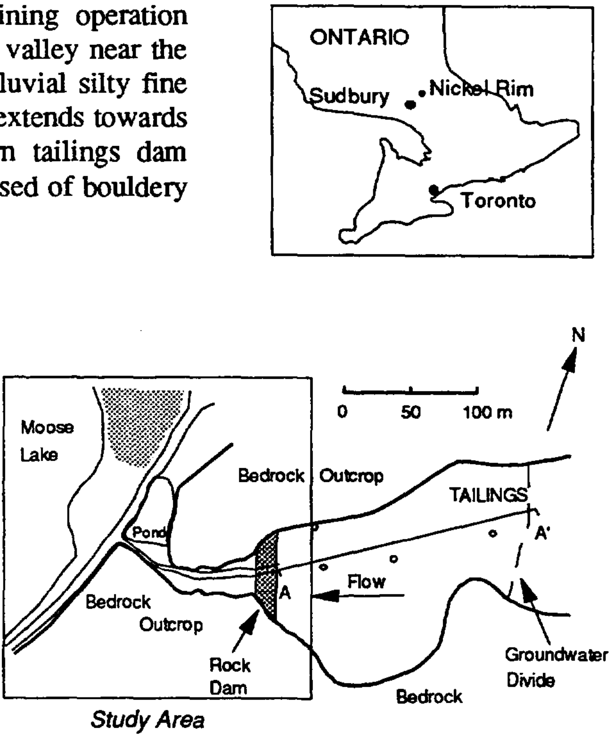

Figure 1. Nickel Rim research location.

Within the vadose zone, and a short distance below the water table, calcite, siderite, *am*-$Al(OH)_3$ and *am*-$Fe(OH)_3$ are successively dissolved from the tailings, buffering the pH of the water affected by sulfide oxidation to near neutral (1). Similar buffering mechanisms have been recognized at other sulfide-rich mine tailings sites (2,3). Most of the heavy metals (Cu, Cr, Al, Co, Ni) are attenuated by precipitation or adsorption reactions as the pH increases. Ferrous iron and SO_4^{2-} remain relatively mobile, however, and high concentrations of these species are displaced into the underlying aquifer (Figure 2). Water entering the aquifer either discharges to surface near the toe of the dam, or migrates toward Moose Lake. Visible red iron staining and sediment encrustation of the lake shore indicates that Fe^{2+} is currently entering the lake. The release of H^+ due to Fe^{2+} oxidation accompanied by *am*-$Fe(OH)_3$ precipitation results in pH values that range from 2.6 to 5 in the surface water near Moose Lake.

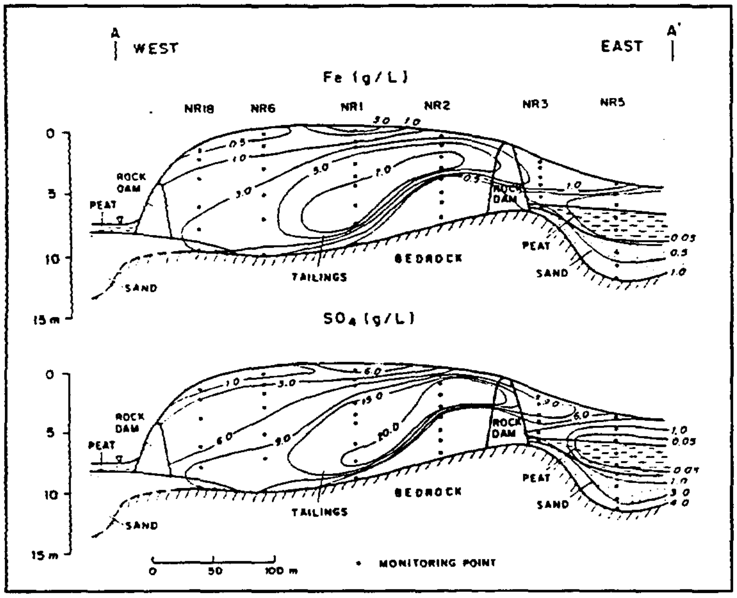

Figure 2. Distribution of Fe^{2+} and SO_4 in the tailings.

Investigative Methods

A network of 16 bundle piezometers and 14 drivepoint piezometer nests was installed into the aquifer (Figure 3). Piezometer placement was aided by EM 31 terrain conductivity analysis which delineated deeper channels of preferred flow and ground of greater electrical conductivity. The piezometer network was sampled several times over a 2 year period (Aug. 1992-June 1994) to obtain representative data and to provide an indication of year to year movement.

Groundwater pH and Eh measurements were made in a sealed flow-through cell that prevented exposure to atmospheric O_2 during measurement. Alkalinity was determined by titration with H_2SO_4 immediately after the sample was collected. Ferrous iron concentrations were determined on site by titration with potassium dichromate (4). Groundwater temperature and electrical conductivity were also measured. Filtered water samples for cation analysis were preserved by acidifying ($pH<1.5$) with 12 N HCl. Samples for anion analysis were refrigerated unpreserved.

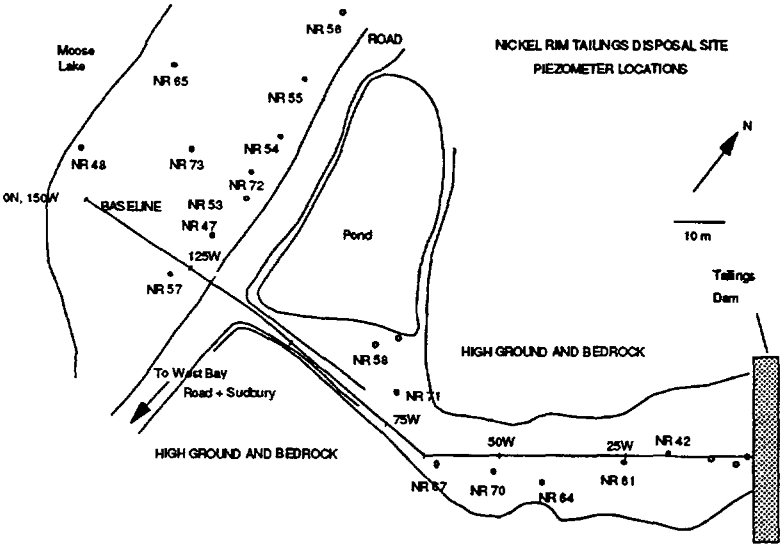

Figure 3. Piezometer locations at the Nickel Rim aquifer.

Total carbonate in the aquifer sediment was determined by the method of Barker and Chatten (5) which was sensitive to 0.002 wt% as $CaCO_3$. Thin sections of sediment were inspected by transmitted light microscopy. Hydraulic conductivity of the aquifer was estimated by a number of methods including: Hvorslev analysis of piezometer response tests; falling head permeameter tests of core material; and grain size analyses of core material.

Results and Interpretation

Hydrogeology

Sediments range from silty fine sand to relatively clean fine sand with occasional pebbles. With depth, the sediments tend to increase in grain size. Based on visual (microscopic) inspection, this type of material should have hydraulic conductivity (K) ranging from 10^{-7} to 10^{-3} cm/s (6). Each of the methods of determining hydraulic conductivity gave similar values, ranging from 10^{-5} to 10^{-3} cm/s. For the purpose of modelling, d_{10} values from the aquifer grain size analyses were used to calculate hydraulic conductivity (Hazen's method). The average hydraulic conductivity values determined for the aquifer using this method are $K_H=8.5\times10^{-4}$ cm/s and $K_v=4.7\times10^{-4}$ cm/s. Johnson (1993) (1) measured $K_H=6\times10^{-4}$ cm/s in the tailings.

Because the sediments are slightly layered, the effects of vertical anisotropy are considered by using the arithmetic and harmonic means of the K values, calculated from the grain-size distribution, to represent equivalent horizontal and vertical conductivities respectively (6). Near the tailings dam, K_H was calculated separately for a shallow sequence of lower K layers ($K_H=4\times10^{-4}$ cm/s) and a deeper sequence of higher K layers ($K_H=1\times10^{-3}$ cm/s) to more accurately estimate linear velocity of groundwater in this portion of the aquifer.

Flow Modelling

The piezometric surface at the site is generally within a few centimeters of the surface, and the hydraulic gradient varies from 0.03 to 0.01. Within 40 m of the dam, flowing artesian conditions are observed. Further downgradient there are local recharge and discharge zones. Groundwater flow was modelled with FLONET (7), a finite-element computer code that solves the hydraulic head and streamfunction forms of the 2D steady-state flow equation to generate flow nets. From the known flow divide in the tailings (Figure 1), flow toward Moose Lake was modelled. The following boundary conditions were used: constant recharge of 0.24 m/a onto the tailings surface and constant head at the lake, at the toe of the dam and at two points on the aquifer where topography changes. The 0.24 m/a recharge value was selected because it is similar to that calculated from tritium profiles at the Inco Copper Cliff tailings site, near Sudbury (1,8). Porosity for the entire system was set at a uniform value of 0.4, slightly lower than the porosity of the tailings (0.45) and higher than that assumed for the aquifer sediments (0.35). FLONET simulations were run until a good fit to measured hydraulic head values was obtained. The resulting flow net, along section A-A' (Figure 1) is shown in Figure 4. Hydraulic conductivity was the only parameter varied to obtain the fit. The finite element grid for the site was set up to incorporate several zones of hydraulic conductivity including the rock dam, tailings, bedrock and two layers in the aquifer.

The measured hydraulic conductivity values generally provided a good fit to aquifer head values when simulated with FLONET. Modelling was quite susceptible to variations in K of the tailings dam. Using the arithmetic and harmonic mean K values for the aquifer, best fit was obtained when $K_H=4.3\times10^{-5}$ cm/s and $K_v=1.4\times10^{-5}$ cm/s were used for the dam. About half of the tailings recharge streamtubes discharge to the surface near the toe of the dam (Figure 4). The remaining streamtubes, which originate away from the dam, discharge at the lake. The pond at the site (Figure 3) fills and drains primarily *via* surface channels but does recharge the aquifer slightly. Groundwater velocities calculated by FLONET are approximately 15 m/a in the lower aquifer layer, 7 m/a in the upper layer of the aquifer and 7 m/a in the tailings. Using Darcy's equation in conjunction with the measured hydraulic gradient (0.02) and $K_x = 1\times10^{-3}$ cm/s yields a similar value of 18 m/a for the lower layer is obtained. Within the tailings the horizontal gradient increases towards the dam. Consequently, horizontal velocities increase with distance from the flow divide and are greatest near the dam.

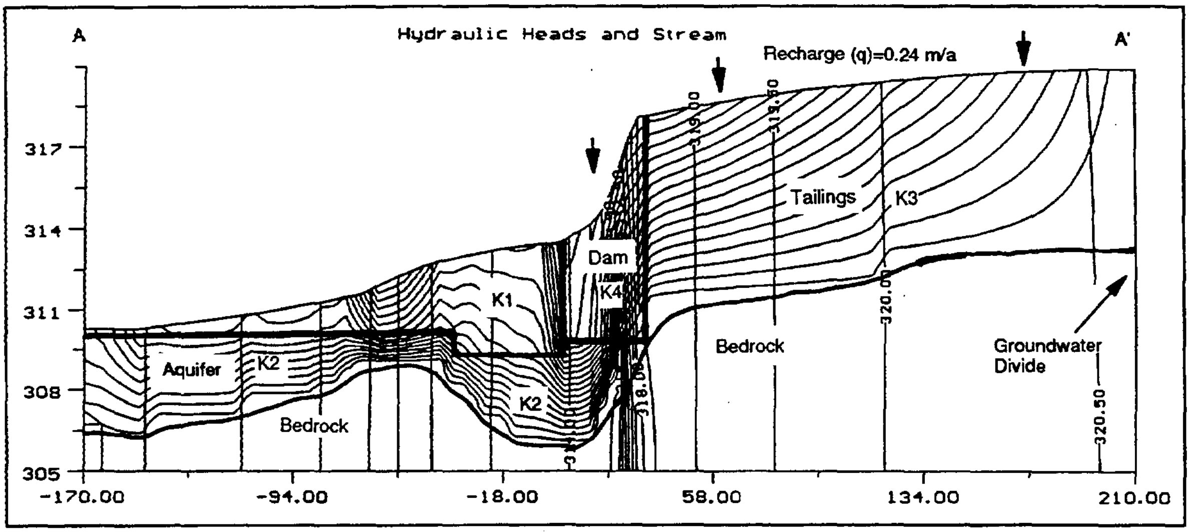

Figure 4. Flow net for the Nickel Rim tailings and aquifer. $K1_H$ (upper aquifer)=0.0004 cm/s; $K2_H$ (lower aquifer)=0.001 cm/s; $K3_H$ (tailings)=0.0006 cm/s; $K4_H$ (dam)=0.00004 cm/s. Distance and elevation (10X vertical exaggeration) in meters.

Tritium concentrations throughout the aquifer are in the range of 10-26 ±8 T.U. This water is interpreted to have been recharged after 1953, and could have recharged through the tailings pre-1961 or post-1972, owing to an absence of higher ^3H values that would be associated with 1960's recharge water. The presence of high dissolved metal concentrations typical of sulfide oxidation-affected water throughout the aquifer suggest that water in the aquifer recharged after 1972. The minimum average groundwater velocity to distribute water less than 23 years old would be about 16 m/a (360m/23a) for a flow path starting near the flow divide and migrating to the lake. This velocity is consistent with the velocities calculated using the steady-state flow model.

Geochemistry and Modelling

Relatively high EM 31 terrain conductivity was found to correlate with zones of deeper bedrock and groundwater with higher specific electrical conductivity and dissolved metal concentrations. Piezometer installations were then focused along the zones of high terrain conductivity.

Acid-neutralization reactions within the tailings induce the precipitation, coprecipitation and adsorption of metals (Al, Ni, Cu, Zn and Co), as the pH of the water increases with increasing depth (1, 2, 9). Cations such as Ca, Na, K, and Mg, are derived from mill process-water, and from the dissolution of carbonate and aluminosilicate minerals within the tailings (1). These cations migrate unattenuated through the tailings at relatively low concentrations. Ferrous iron and SO_4^{2-} also migrate through the tailings, but at much higher concentrations (≤10 g/L Fe^{2+} and ≤24 g/L SO_4^{2-} respectively). Iron and SO_4^{2-} concentrations increase in the tailings with increasing depth below the oxidation zone, and with distance up gradient from the tailings dam (Figure 2). Water in streamtubes originating near the flow divide, which have the longest travel distance and the lowest groundwater velocities in the tailings, takes approximately 50 years to reach the aquifer (1). As a result, high concentrations of Fe^{2+} and SO_4^{2-} released near the divide during the past 36 years remain in the tailings (Figure 4). The high Fe^{2+} (>4000 mg/L) and SO_4^{2-} (>10000 mg/L) concentrations residing deep in the tailings, near the flow divide (Figure 2), should begin to enter the aquifer in about 10 years. Concentrations entering the deep portion of the aquifer then will increase and remain high for about 25 years, as the zone of high concentrations is displaced from the tailings. In contrast, streamtubes originating near the dam have shorter flowpaths and higher velocities. Water in this zone is displaced from the tailings more quickly at lower concentrations due to depletion of oxidizable solids and current low oxidation rates. The concentrations of Fe and SO_4^{2-} present in the bulk of the tailings are representative of the present low oxidation rates.

Water at the outflow of the tailings approaches equilibrium with respect to siderite, *am*-$Fe(OH)_3$ and *am*-$Al(OH)_3$ and is undersaturated with respect to calcite. High Fe^{2+} and SO_4^{2-} concentrations (2000 and 6000 mg/L respectively) form an elongate plume that extends for 75 meters down gradient in the aquifer (Figure 5). Beyond 75 meters, concentration gradients are small and concentrations of Fe^{2+} and SO_4^{2-} become relatively constant at ~500 and ~2500 mg/L respectively. The sediments in the aquifer are composed primarily of quartz (60%), feldspars (35%) and small quantities of mafic minerals (5%).

The water that enters the aquifer is high in pH (pH≈6) as a result of calcite or siderite dissolution in the tailings, and moderately low in Eh (≈200 mV) reflecting the abundance of Fe^{2+} relative to Fe^{3+} (Figure 5). The pH of the plume is generally highest deep in the aquifer, where a pH of about 6 is maintained. The results of calculations conducted with MINTEQA2 (10) indicate that water within 50 meters of the dam approaches equilibrium with respect to siderite, but is undersaturated with respect to calcite ($SI \approx -1.5$) (Figure 6). At the base of the dam carbonate content in the aquifer was near detection limits (0.002 wt%), but at shallower depths up to 0.5 wt% carbonate content was measured. The method of Barker and Chatten is relatively insensitive to primary siderite due to the slow dissolution rate of crystalline siderite (11). This observation implies that any calcite initially present in the deeper portion of the aquifer may have been consumed, or that the calcite dissolution rate is slow relative to groundwater transport rates. Dissolution of any carbonate present, in addition to producing alkalinity, brings the water to saturation with respect to siderite (SI = 0.4 to 0.9). Morin *et al.* (12) inferred the precipitation of secondary siderite under similar conditions at the Nordic uranium tailings impoundment near Elliot Lake, Ontario.

MINTEQA2 calculations also indicate that the water near the dam is supersaturated with respect to *am*-Fe(OH)$_3$ (Figure 6) and goethite, but due to low Fe^{3+} concentrations (<1 mg/L) the precipitation of *am*-Fe(OH)$_3$ and goethite should have little impact on the total iron concentration in the water. Microscopic examination suggests that ferric oxyhydroxides are present in the deep aquifer sediments near the dam. The MINTEQA2 calculations also indicate near-equilibrium with respect to gypsum ($-0.7 < SI < 0.1$) throughout the aquifer. The precipitation and dissolution of gypsum may control SO$_4^{2-}$ concentrations. Sulfate concentrations decrease with increasing distance from the dam until 75 m down gradient, beyond which they remain relatively constant (Figure 5).

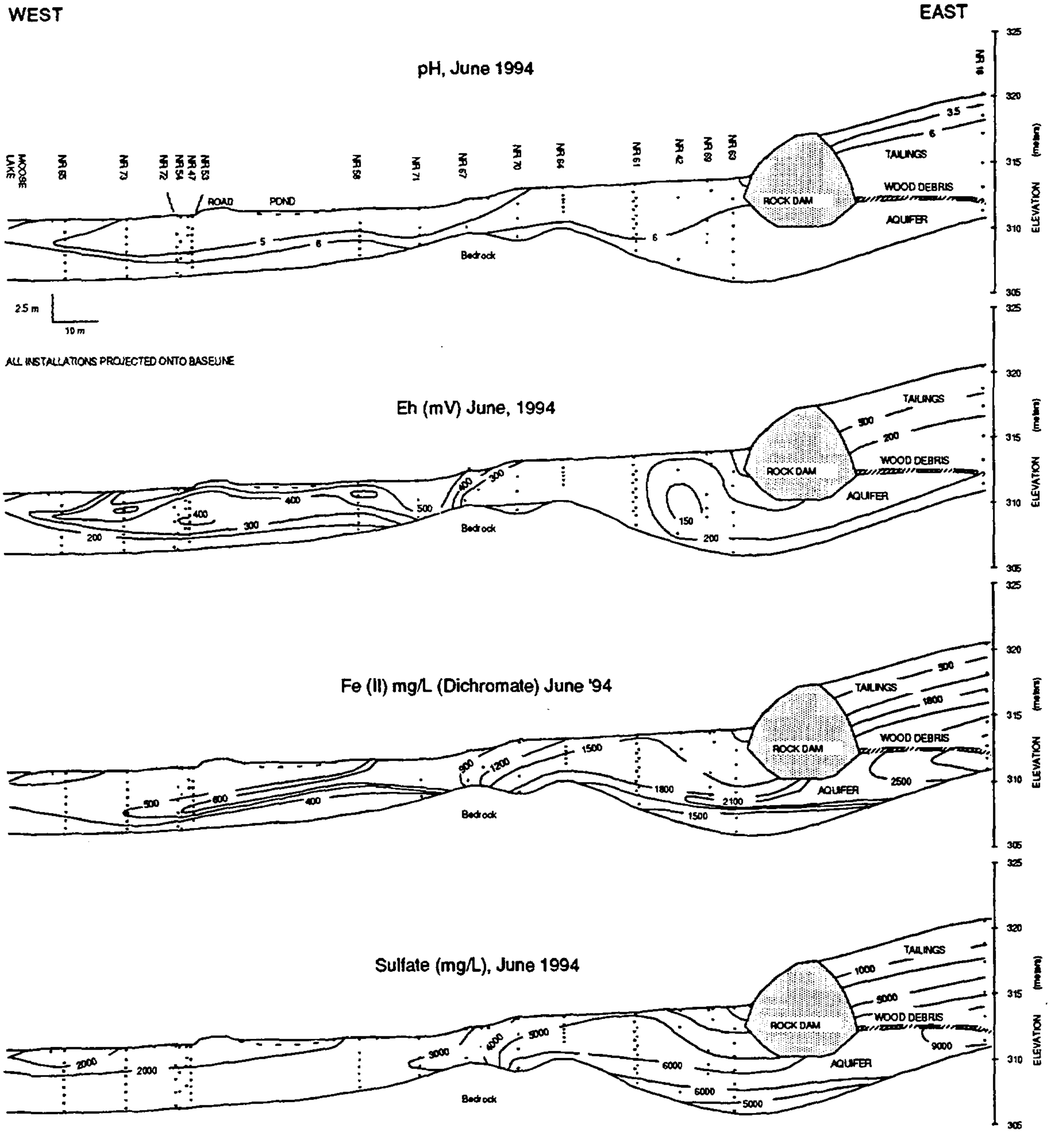

Figure 5. Aquifer geochemical results plotted along the centerline of the plume.

A local zone of recharge exists 50 m down gradient from the dam (Figure 4). Down gradient from this location, the plume water is supersaturated with respect to am-$Fe(OH)_3$, and goethite and has lower Fe^{2+} concentrations. The flow net also indicates that roughly 35% of the water entering the aquifer discharges to surface near the toe of the dam (Figure 4). At 55 meters downgradient from the dam, near piezometer NR 67, the surface of the aquifer undergoes a drop in elevation causing surface discharge of an additional 15 % of the tailings recharge (3 streamtubes) at this location. Most of the water discharged to surface flows *via* surface channels to the pond and then to the lake. At each surface discharge location Fe^{2+} oxidizes, causing the release of H^+ of as Fe^{3+} precipitates as *am*-$Fe(OH)_3$, goethite and jarosite. These processes reduce the pond pH to 2.7, the iron concentration to about 200 mg/L and increase surface-drainage and pond-water Eh up to 660 mV.

A portion of the water from the pond recharges the aquifer. Recharge water derived from the pond is characterized by elevated concentrations of Al (up to 42 mg/L) and Ni (up to 4 mg/L), low pH (~4.3) and Fe^{2+}(<400 mg/L) and high Eh (>300 mV; Figure 5). These Al and Ni concentrations are significantly higher than those present in the aquifer upgradient of the pond, which are near detection limits. The plume of low pH pond water is undersaturated with respect to *am*-$Al(OH)_3$ and near equilibrium with respect to *am*-silica. Dissolution of aluminum hydroxides and aluminosilicates in the aquifer sediments under low pH conditions is likely the primary source of the high dissolved concentrations of Al. The

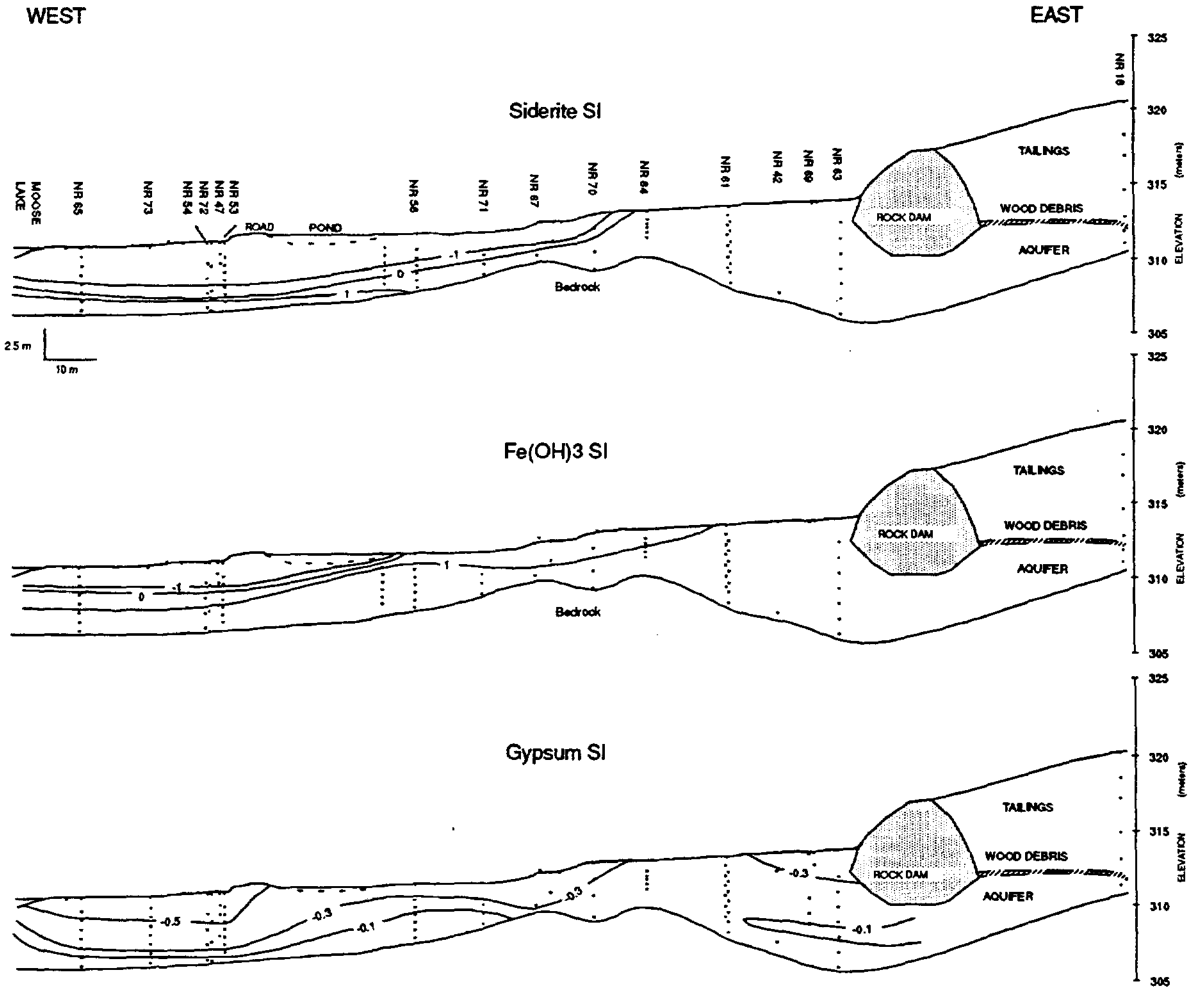

Figure 6. Saturation indices for selected minerals, plotted along the centerline of the plume.

oxidation of Ni bearing sulfides outside of the tailings may be the source of higher Ni concentrations. The low pH of the water allows the Ni to be transported, in solution, to the pond. Low pH dissolution of Ni-bearing aquifer sediments below the pond may also be a source of the dissolved Ni in the plume. MINTEQA2 calculations indicate that the pore water in this zone is slightly supersaturated with respect to gibbsite and the basic aluminum sulfate minerals jurbanite ($AlSO_4OH$) and basaluminite ($Al_4SO_4(OH)_{10}$). Precipitation of these solid phases may limit Al concentrations in solution (2). Aluminum and Ni concentrations in Moose Lake are at 6 and 2 mg/L respectively.

The water underlying the pond plume is near neutral in pH ($pH \approx 6$). The aquifer in this zone contains up to 0.6 wt% carbonate as $CaCO_3$. The water remains undersaturated with respect to calcite ($SI \approx -2$) and near equilibrium with respect to gypsum ($SI \approx -0.2$) but approaches equilibrium with respect to siderite (Figure 6). This observation suggests that the calcite dissolution may be insignificant in this zone, and that siderite dissolution may be the primary pH-buffering mechanism. The water in this zone is supersaturated with respect to jurbanite ($SI \approx 0.8$), basaluminite ($SI > 5$) and gibbsite ($SI \approx 2.5$), and approaches saturation with respect to *am*-$Al(OH)_3$. These results suggest that the aluminum concentrations in this zone are limited by the precipitation of *am*-$Al(OH)_3$. Ferrous iron concentrations are probably controlled by equilibrium with respect to siderite ($-0.3 < SI < +1$). Low Eh values indicate that Fe^{2+} is the dominant iron species at this location, and that moderate supersaturation with respect to ferrihydrite will not significantly affect total iron concentrations.

Conclusions

The ongoing research has indicated several physical and chemical processes which affect the groundwater chemistry of the aquifer at Nickel Rim. Modelling with FLONET illustrates that water infiltrating near the dam has the highest velocity and discharges near the toe of the dam, whereas water which originates near the flow divide has a much lower velocity and will discharge to Moose Lake. High concentrations of Fe^{2+} and SO_4^{2-} from near the divide should reach the aquifer in approximately 10 years. At that time the deeper portions of the aquifer, which discharge to Moose Lake, will receive much higher Fe^{2+} and SO_4^{2-} loading until the zone of water containing high concentrations of Fe^{2+} and SO_4^{2-} is displaced from the impoundment.

High concentrations of Fe^{2+} and now enter the aquifer under neutral pH conditions. Within much of the aquifer, the pore water is at equilibrium with respect to siderite, which serves as a solid phase control on Fe^{2+} concentrations. Ferric iron concentrations are generally low, but supersaturation with respect to *am*-$Fe(OH)_3$ and goethite is common, suggesting that the precipitation of these minerals limits Fe^{3+} concentrations. Throughout the aquifer, SO_4^{2-} concentrations are limited by the solubility of gypsum.

Approximately 50% of the water affected by sulfide oxidation discharges to the surface of the aquifer. Discharge of this water results in the oxidation of dissolved Fe^{2+} and supersaturation with respect to ferric iron-bearing minerals. The resulting low pH, high Eh surface water collects in a small pond prior to draining into Moose Lake. Aquifer recharge through the base of pond creates a plume of high Al and Ni concentrations. Below the pond plume, the water is near equilibrium with respect to siderite and *am*-$Al(OH)_3$. The precipitation and dissolution of these minerals provide solid-phase controls on the concentrations of dissolved Fe and Al.

Acknowledgments

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