URANIUM TAILINGS ACIDIFICATION AND SUBSURFACE CONTAMINANT MIGRATION IN A SAND AQUIFER

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ABSTRACT

Investigations of the geochemistry of inactive pyritic uranium tailings in the Elliot Lake Mining district of Ontario have focused on the Nordic tailings management area, where two impoundments are located in natural bedrock basins. The tailings are 8-12 m thick and overlie a localized deposit of glaciofluvial sands. Analyses of the solid, liquid, and gas phases of the vadose zone of the tailings show that gas-phase oxygen levels drop rapidly within 0.7 to 1.5 m of the surface, indicating rapid oxygen consumption during pyrite oxidation. Oxidation during the past 15 to 20 years has caused a marked depletion of near-surface pyrite.

The oxidation of pyrite in the vadose zone impacts to infiltrating precipitation high concentrations of Fe, SO₄²⁻, various heavy metals, and a pH generally between 1.5 and 4. The acidic infiltration moves downward at a rate of 0.2 to 2.0 m/yr, displacing high-pH groundwater that originated as process water discharged from the mill. It now occupies the entire tailings thickness over a small area of the tailings.

At one location a well-defined plume of high-Fe²⁺ tailings-derived groundwater has developed in the sand aquifer adjacent to the tailings. The plume consists of three zones: an inner core characterized by Fe > 5000 mg/L, pH < 4.8, and elevated concentrations of several heavy metals and radionuclides; an outer zone with Fe < 2500 mg/L, pH > 5.5, and relatively low concentrations of heavy metals and radionuclides; and a transition zone separating the two. Although the average linear groundwater velocity is about 440 m/yr near the dam, reactions such as mineral dissolution, precipitation, and coprecipitation retard the migration of the front of the inner core, producing an observed frontal migration rate of approximately 1 m/yr.

Groundwater from the outer zone of the plume flows laterally towards a small stream, where a portion of it is now discharging into the stream bed. The discharge results in the precipitation of amorphous ferric hydroxide on the stream bed. Most of the H⁺ produced by Fe precipitation is buffered, and only a moderate decrease in stream pH is observed. Inner zone conditions will not reach the stream unless input of low-pH groundwater from the tailings continues for several hundred years.

Although the rate of pyrite oxidation in the Nordic Main tailings has been decreasing, there is sufficient pyrite in the tailings to generate high-Fe groundwater for several decades or more. Calculated groundwater migration rates indicate that in the next few decades acidic, low-pH groundwater will occupy the entire tailings thickness over most of the tailings area, causing an increase in the total flux of contaminated groundwater into the underlying aquifer. The outer zone of the plume has already arrived at a small stream, and acidification of the surface waters may increase if the Fe concentration in the groundwater seepage increases.
INTRODUCTION

The large-scale mining of uranium in the Elliot Lake district of Ontario has been ongoing since 1956 (Fig. 1). The ore body is an Archean quartz pebble conglomerate that contains from 3 to 8% pyrite. The uranium is recovered by first grinding the ore until 50% is finer than 75 μm, and solubilizing it by leaching it in hot dilute sulfuric acid. The acidic liquid and solid wastes are then neutralized with limestone and lime to a pH of between 8 and 10 and discharged as a slurry to a tailings impoundment. These tailings impoundments are constructed in natural bedrock-enclosed topographic depressions. The tailings areas are allowed to drain after discharge from the mill ceases. To date more than 100 million tonnes of tailings have been discharged to 10 tailing impoundments, three of which are currently in use. Approximately one billion tonnes of tailings will have been produced by the time the ore bodies are exhausted.

Figure 1 Location map showing inactive tailings areas. The area drains to Lake Huron via the Serpent River system. The insert shows the location of the Elliot Lake uranium mining district.

Current reclamation practice for inactive tailings in the Elliot Lake district is to grow vegetation on the tailings surface. Precipitation infiltrates the vegetation and tailings and maintains a water table generally within a few metres of the surface. As the neutralized process water is displaced by infiltrating precipitation, the water and oxygen react with pyrite, generating acidic conditions and causing a deterioration of the quality of the porewater in the tailings.

Potential environmental problems are posed by the acidified water generated by pyrite oxidation at shallow depths in the tailings. The
Acidified porowater can exit the tailings areas through two pathways: by seepage downward into the underlying groundwater flow system, or by groundwater discharge to small surface water courses on the tailings. To maintain acceptable effluent water quality, surface drainage from inactive tailings areas is treated with NaCl for removal of Ra and time for removal of acidity and metals. This treatment will be maintained for as long as the quality of this water is below Ontario Provincial water quality objectives.

The geochemical behavior and rates of migration of the acidic water in the groundwater flow system must be evaluated if the long-term effects of tailings disposal on the aquatic environment are to be determined. When the acidic pore water from the tailings enters the geological domain beneath the tailings, it travels along the groundwater flow paths towards streams, lakes, or marshes. During this period of travel, it is not an environmental problem because only surface water is used for water supply in the Elliot Lake region. When the acidic water passes all the way through the groundwater flow system and discharges into streams and lakes, it has potential to cause an adverse impact on surface-water quality.

To acquire insight into the chemical nature and rates of migration of tailings-derived solutions within inactive tailings and within the groundwater zone containing pathways for solute migration from the tailings to surface waters, two tailings impoundments in an inactive tailings management area in the Elliot Lake district were selected in 1979 for detailed investigations. These tailings areas, the Nordic Main and Nordic West Arm impoundments, were chosen for study because they are underlain by a local sand aquifer which discharges into nearby surface water bodies, therefore providing a groundwater flow path with all of the above-mentioned components. Most other tailings impoundments in the Elliot Lake area are underlain by fractured bedrock, in which groundwater monitoring is much more difficult. All of the inactive tailings areas have a vadose zone of varying thickness in which pyrite oxidation occurs, underlain by a groundwater zone.

Tailings were discharged to the Nordic West Arm tailings between 1952 and 1957. The Nordic Main impoundment received tailings during the period from 1957 to 1968, then the tailings were used for sand and gravel until 1970. In 1970, the surface of the tailings was seeded with grass, and between 1973 and 1980 vegetation cover was established over most of the surface of both the tailings areas.

This paper describes the hydrogeochemical conditions that occur along a migration pathway that leads from the surface soil zone on the tailings, downward through the tailings into the sand aquifer and then outward from the tailings in the groundwater zone to a small stream that is the exit zone for some of the tailings-derived water. This pathway from input area to output area is several hundred metres or more in length and is characterized by a groundwater residence time of more than a decade.

**PREVIOUS WORK**

In the first study of the chemistry of tailings groundwaters in the Elliot Lake district, Moffett and Tellier (1978) found that much of the shallow groundwater in the Nordic West Arm tailings had become acidic due to pyrite oxidation. The acidic groundwaters were found to contain high concentrations of Fe and SO$_4^{2-}$, as well as uranium, $^{210}$Po, thorium isotopes, and heavy metals.

Beginning in late 1978, the Department of Earth Sciences of the University of Waterloo, in association with Rio Algom and the Elliot Lake Laboratory of CANMET (Energy, Mines, and Resources Canada), initiated a detailed hydrogeologic study of the Nordic Main tailings and the surrounding area. In the first phase of this study, Blair et al. (1980) and Blair (1981) found that acidic, low-pH groundwater with high concentrations of Fe, S, and heavy metals occupies the upper 6 to 12 m of the groundwater zone of the tailings. These authors identified the acidic groundwater as infiltrated to the tailings since tailings deposition ceased. Deeper alkaline groundwaters...
were considered to be mill process water originally discharged with the tailings. Further studies of the saturated zone of the Nordic Main and other impoundments in the Elliot Lake district are reported on by Cherry et al., 1980; Blackport and Cherry, 1980; Dave et al., 1982; Feenstra et al., 1981; and Dubrovsky et al., 1983. Other aspects of Elliot Lake tailings were investigated by Blouwe and Gillham (in preparation) and Abdul and Gillham (1984) who examined surface water/groundwater interactions in the Nordic West Arm tailings, and Smyth (1981) who examined the gaseous, aqueous, and solid phases of the unsaturated zone of the Nordic Main tailings. In addition, microbiological studies of the Nordic Main and Nordic West Arm have also been performed (McCready, 1976; Silver and Taylor, 1981).

Blair et al. (1980) also established a network of piezometers in the aquifer adjacent to the Nordic Main tailings and identified a zone where low-pH water with high Fe and SO$_4^{2-}$ enters the underlying sand. This contaminant plume extends several hundred meters southward from the tailings dam. The sampling network in the aquifer has since been expanded, and contaminant migration in subsurface seepage from the Nordic Main and other impoundments is the subject of an on-going study (Morin et al., 1982; Morin, 1983; Morin, in progress; Morin and Cherry, submitted; Cherry et al., 1984).

No attempt was made in the literature cited above to integrate the findings obtained from the various parts of the system. By synthesizing information from all of these studies as well as additional new material, this paper presents an integrated description and hydrochemical interpretation of a subsurface pathway that connects the tailings, which are undergoing major geochemical changes, to the surface-water environment. Based on this interpretation, a prognosis for hydrochemical changes in the system in future decades is developed.

HYDROGEOLOGICAL SETTING

The Nordic Main and West Arm tailings areas are situated in an east-west trending valley formed by the dip and scarp topography of the northward-dipping Lower Proterozoic bedrock. The valley is partially filled with Pleistocene deposits which consist of a basal till unit overlain by very permeable glaciofluvial sands (Fig. 2). Prior to tailings deposition, much of the valley was occupied by spruce bog and a discontinuous layer of peat 0.5 to 1.0 m thick formed on the glaciofluvial aquifer. The peat layer was removed along the east and southeast edges of the Nordic Main tailings area before the deposition of tailings, and may also be absent from areas that were formerly topographic highs (Blair, 1981).

The detailed stratigraphy of the plume area consists of four to six distinct layers. The surficial layer is a 1 m thick deposit of unsorted, cobbly fill emplaced during construction of the tailings dam in the late 1960s. This fill is discontinuously underlain by 1 m of peat. The next two layers comprise the glaciofluvial sand aquifer. The upper layer consists of 4 to 8 m of dark tan medium-grained sand with a porosity of 0.36. The lower sand is a light gray, very fine-grained sand ranging from 3 m to greater than 8 m in thickness. The aquifer is underlain by a sandy till or bedrock.

Tailings were deposited as a slurry with a water content of approximately 66%. The thickness of the tailings in the Nordic Main impoundment varies from approximately 8 to 15 m. Substantial grain-size segregation occurs during settling of the suspended solids from the slurry. In areas close to the discharge point coarser grained components of the tailings are deposited. Finer-grained fractions are transported to areas of ponded water. The process of grain-size segregation and the frequent relocation of the slurry discharge point produced a deposit with complex layering.
The depth below ground surface of the water table in the Nordic Main tailings measured in the summer of 1980 increased from less than a meter in the north where the tailings are bounded by bedrock, to a depth of 6 to 10 meters along the southern edge where the tailings are bounded by a permeable dam and bedrock knobs (Fig. 3). Seasonal changes in the depth to the water table in the tailings are substantial, and fall and spring recharge increase groundwater elevations by up to 1.5 m. The elevation of the water table in the glaciofluvial aquifer is generally within 1 to 3 m of ground surface, and annual fluctuations in the elevation of the water table are less than 0.2 m.

METHODS

The groundwater sampling network in the Nordic Main tailings consists of 12 piezometer nests, including three nests installed by Blair (1981). Most of the piezometers are a modified Casagrande drive-point type, consisting of a 3.18 cm (1-1/4") diameter PVC pipe with an intake screen of porous polyethylene (Vyon) (Fig. 4). The piezometers were installed by augering to within 1 m of the depth desired, and then hand-driving the piezometer the final distance in order to minimize the disturbance around the screen.

Piezometer bundles of the type described by Cherry et al. (1983) were installed in the plume area of the glaciofluvial aquifer (Fig. 3). The piezometer bundles were installed by insertion through the stem of hollow-stem augers. Piezometer bundles were also installed in the aquifer underlying the Nordic Main tailings at sites T1, T3, T4, T5, and T7. A schematic of a piezometer nest and piezometer bundle is shown in Figure 4. Details of piezometer bundle installation are given in Morin et al. (1982).

Groundwater samples from the tailings piezometers were collected for chemical analysis using a syringe sampling technique (Gillham, 1982). Samples from the piezometer bundles in the glaciofluvial aquifer were taken by means of a peristaltic pump. Water samples were filtered through 0.45 μm membrane filters; samples for cation analysis were acidified with concentrated HCl, while samples for anion analysis were refrigerated without treatment. In addition, samples from one piezometer nest, T6, were analysed for 226Ra, 210Po, 228Th, 230Th, 232Th, and total uranium.
Figure 3 Map of the Nordic Main tailings impoundment showing the locations of piezometer nests and the depth-to-water table. The locations of sampling points in the plume and Buckles Creek study areas are shown in details A and B respectively. (adapted from Cherry et al., 1980; detail A from Morin et al., 1982).
The pH and redox potential of the unfiltered groundwaters were measured in the field in a flow-through cell maintained at groundwater temperature. The redox potential measurements were made with a platinum electrode and were used to calculate pE values. Alkalinity titrations on filtered samples were performed in the field immediately after sampling, and the electrical conductance of unfiltered samples was measured. Ferrous iron was determined in the field by redox titration with potassium dichromate (Waser, 1966), total Fe was determined by atomic adsorption spectrophotometry, and ferric iron was determined by difference.

Samples of pore waters from the zone above the water table were obtained at piezometer nests T5 by coring with 7.62 cm (3 in) thin-walled aluminum tubing. The cores were taken in 1 m sections to maximize recovery, and then cut into 0.2 m lengths. Pore water samples were extracted from each length using a device similar to that described by Patterson et al. (1978).

Cores of tailings solids from below the water table were taken at piezometer nests T1, T5, and T6 by augering to the water table with 8.9 in hollow-step augers, and then percussion-driving a continuous section of 7.62 cm diameter thin-walled aluminum tube. Cores were immediately sealed after recovery. Solid samples from these cores were analysed for carbonate-mineral content by the method described by Barker and Chatten (1982).

A stretch of Buckles Creek was instrumented to assess the impact of the discharge of tailings-derived groundwater to the stream. A preliminary survey was conducted to locate zones where high-Fe groundwater is seeping into the stream. These zones were tentatively identified by accumulations of Fe hydroxide precipitate on the stream bed. During this survey the pH and electrical conductance of the stream was measured at several stations, and one sample was analysed for Fe$^{2+}$ and Fe$^{3+}$ (Fig. 3).
Minipermeameters were installed in the bed of Buckles Creek to collect samples of the shallow groundwater and to measure the hydraulic gradient between the shallow groundwater and stream bed (Fig. 3). The minipermeameters were constructed from lengths of polyethylene tubing with one end slotted and screened with polyester mesh. The design and installation method is described by Lee and Cherry (1978).

Seepage meters were installed in Buckles Creek at three locations in order to determine the ratio of groundwater discharge to the stream (Fig. 3). The seepage meters were constructed from the ends of plastic barrels 0.3 m in diameter with approximately 0.15 m of wall attached. A hole approximately 0.11 m in diameter was drilled in the centre of the end of the barrel and a one-hole stopper attached. The seepage meter was installed by pushing the barrel wall firmly into the sediments of the stream bed so that the groundwater discharging across an area equal to the barrel cross section was intercepted. The groundwater discharge was measured by attaching a plastic bag to the stopper and collecting the inflow to the barrel over a timed period. This technique is described in detail by Lee and Cherry (1978).

RESULTS AND DISCUSSION

Chemical analyses of the pore water in the Nordic Main tailings at the time of deposition between 1960 and 1969 apparently do not exist; however, the general chemical characteristics of the waters are believed to have been similar to the effluent from one of the two existing large acid-leach mills (the Quirke mill) in the Elliot Lake area that is currently operated by the same company that operated Nordic mill (Table I). An analysis of the effluent discharged from this mill shows that the major anions present are SO₄²⁻ and NO₃⁻ introduced during the ore processing. The dominant cation is Ca⁺⁺ derived from the lime and limestone added during tailings neutralization. The Quirke effluent contains low concentrations of Fe, Al, and most heavy metals, and has a pH between 10 and 11. Personnel that worked at the Nordic mill indicate that effluent from this mill had a pH in the 7 to 9 range. After the discharge of tailings to the impoundment ceased, unsaturated conditions develop at shallow depths in the tailings allowing oxygen and precipitation to enter the tailings and initiate pyrite oxidation.

ACID GENERATION

A zone of active pyrite oxidation was identified at shallow depths in the vadose zone of the Nordic Main tailings by Smyth (1981). Results of analyses on pore waters extracted from cores obtained from the vadose zone at sites T1, T3, and T5 in the Nordic Main tailings show that extremely high concentrations of iron occur as distinct bulges in the chemical profile (Fig. 5). The trends in Fe are paralleled by the SO₄ concentrations. The pH ranges from 1.4 to 3.6. In addition to the high concentrations of Fe and SO₄, rapid pyrite oxidation is indicated by the depletion of oxygen from the gas-filled porosity with increased depth below the surface (Fig. 5). The cumulative effect of pyrite oxidation since surface water was drained from the tailings in 1970 has resulted in a reduction in the pyrite content of the tailings solids at shallow depths (Fig. 5).

Pyritic in the tailings is oxidized by oxygen or Fe(III) as described by the two reactions:

\[ \text{FeS}_2 + 7/2 \text{O}_2 + \text{H}_2\text{O} + \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \]  
(1)

\[ \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} + 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \]  
(2)

The reaction shown in equation 2 requires bacteria to catalyze the oxidation of Fe(II) to Fe(III), and is the primary mechanism by which pyrite is oxidized under low pH (less than 4) conditions (Singer and Stumm, 1970). The presence of iron oxidizing bacteria in low-pH zones of the Elliot Lake tailings has been established by McCreary (1976) and Silver and Taylor (1981).

Both equations show that Fe(II) and SO₄²⁻ are released in a 1:2 molar ratio. Additional H⁺ is generated when the released Fe(II) is subsequently oxidized and precipitated as ferric hydroxide or as basic iron sulfate.
**TABLE 1.** Chemical analyses of water samples from the Quirke tailings area (neutralized tailings), the Nordic Main tailings (piezometer nest T6), and the inner and outer zones of the plume in seepage area A (all analyses mg/L except pH and pe, or as noted)

<table>
<thead>
<tr>
<th>Lab</th>
<th>Quirke Tailings*</th>
<th>T6 8.3 m</th>
<th>Inner Core M1-6 (1981)</th>
<th>Outer Zone M12-8 (1981)</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td>field</td>
<td>10.9</td>
<td>5.66</td>
<td>4.24</td>
</tr>
<tr>
<td>pe</td>
<td>field</td>
<td>-</td>
<td>5.52</td>
<td>6.13</td>
</tr>
<tr>
<td>Fe total</td>
<td>2</td>
<td>1.4</td>
<td>6030</td>
<td>5116</td>
</tr>
<tr>
<td>Al</td>
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<td>&lt;3.0</td>
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<td>215</td>
</tr>
<tr>
<td>SiO₂</td>
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<td>-</td>
<td>51.5</td>
<td>27</td>
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<tr>
<td>Ca</td>
<td>2</td>
<td>612</td>
<td>388</td>
<td>433</td>
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<tr>
<td>Mg</td>
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<td>375</td>
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<tr>
<td>Na</td>
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<td>36</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>K</td>
<td>2</td>
<td>142</td>
<td>206</td>
<td>103</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1</td>
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<td>14100</td>
<td>12332</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>1</td>
<td>-</td>
<td>&lt;2.0</td>
<td>&lt;0.04</td>
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<tr>
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<td>14</td>
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<td>31</td>
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<td>Zn</td>
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<td>Co</td>
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<tr>
<td>Pb</td>
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<td>0.44</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>0.04</td>
<td>8.0</td>
<td>33</td>
</tr>
<tr>
<td>Alk (as field)</td>
<td>-</td>
<td>95</td>
<td>24</td>
<td>77</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Ra TOTAL pCi/L</td>
<td>1679²</td>
<td>412³</td>
<td>-</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-</td>
<td>575</td>
<td>-</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* Analyses done by Rio Algom Laboratory, March 1977, A.J. Vivyurka, written communication.

1. University of Waterloo laboratory
2. Rio Algom Environmental Control Laboratory
3. $^{226}$Ra, Monenco Analytical laboratory
Both equations show that Fe(II) and SO$_4^{2-}$ are released in a 1:2 molar ratio. Additional H$^+$ is generated when the released Fe(II) is subsequently oxidized and precipitated as ferric hydroxide or as basic iron sulfide:

$$\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{7}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$$ (3)

$$\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{5}{2}\text{H}_2\text{O} + \frac{1}{3}\text{K}^+ + \frac{1}{3}\text{KFe}_{3}\left(\text{SO}_4\right)_{2}(\text{OH})_6 + 4\text{KSO}_4^{2-} + 3\text{H}^+$$ (4)

Minimal H$^+$ production occurs if the Fe(II) is oxidized but does not precipitate:

$$\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} + \text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{H}^+$$ (5)

The oxidation of pyrite, as represented in equations 1 through 5, produces from 1 to 16 moles of H$^+$ for each mole of pyrite oxidized, depending on the fate of the Fe.

The model of pyrite oxidation depicted by equation 2 predicts that Fe(III) will be abundant in solution where oxygen is present and bacterial action rapid; but once all available oxygen is utilized, Fe(III) will be reduced to Fe(II). Analytical data on iron speciation in the vadose zone at site T5 were obtained to test this hypothesis. Samples were found to contain up to 62% Fe(III) near the surface, while the iron in solution directly below the water table was almost entirely Fe(II) (Fig. 5). Although it is likely that some Fe(III) is lost from solution by precipitation, we conclude that the model of pyrite oxidation by Fe(III) mediated by bacterial oxidation of Fe(II) is supported by the available data.
Pyrite oxidation may continue below the vadose zone if Fe(III) persists in solution sufficiently long for it to move downward below the water table. The Nordic West Arm tailings area has been inactive for about 10 years longer than the Nordic Main tailings, and areas within it have reached a more advanced stage of acidification. At site UNIA, the groundwater pH was found to range from 0.9% in the shallower piezometer, to 1.46 at 6.3 meters depth below the surface. Concentrations of Fe(III) calculated from the Fe(total) and measured redox potential were found to range from 40% of the Fe(total) to less than 2%. At this site the zone of pyrite oxidation extends much deeper than the penetration of gaseous oxygen because of the transport of Fe(III) below the water table. The extreme acidification observed at this site is likely due to the coarse-grained nature of the tailings, which allows relatively deep penetration of O₂ gas.

Data on the gas-phase composition of the vadose zone at three sites on the Nordic Main tailings show that the depth of penetration of oxygen is strongly influenced by the grain-size and moisture content of the tailings. Depth of penetration of oxygen was found to be shallower in areas with fine-grained tailings and a high moisture content than in the area with coarser grained tailings and lower moisture content. As a result of these limits on the depth of oxygen penetration and the rapid uptake of oxygen during pyrite oxidation, the zone of pyrite oxidation remains at a shallow depth in the Nordic Main tailings. However, the data from the West Arm tailings suggests that pyrite oxidation may occur below the water table due to the transport of Fe<sup>3+</sup> in solution under very low pH conditions. If this occurs then a much greater thickness of tailings becomes available to oxidation and the potential for long-term acid production in the tailings is increased.

THE GROUNDWATER ZONE

Profiles of the chemistry of the groundwater in the Nordic Main tailings show a two-zone system consisting of an upper zone in which recharging precipitation has displaced the original process water and a deeper zone consisting of the original process water. This stratification is clearly displayed in the profile for piezometer nest T6, which is representative of sites with a shallow to moderately deep water table (Fig. 6, Table 1). The concentrations of Fe and SO₄<sup>2-</sup>, products of pyrite oxidation, are seen to be much greater at shallower depths in the tailings. The sharp increase in these constituents along with decreasing Cl concentration at less than 10 m depth approximately marks the boundary between downward-moving recharge water and the process water. The gradual decrease in Fe and SO₄ from 10 to 5 m depth indicates that the flux of these solutes to the water table, and thus pyrite oxidation, has been decreasing in recent years; the same trend is observed over most of the Nordic Main tailings.

The pH of the recharge water decreases at shallower depths in the tailings; however, the pH values are much higher than what would be predicted from the Fe concentrations and the stoichiometry of pyrite oxidation. This indicates that a significant amount of pH buffering has taken place. Decrease in pH is accompanied by increasing pe, indicating more oxidizing conditions in the recharge waters.

Elevated concentrations of aluminum and silica are found in the recharge waters, as a result of the dissolution of primary aluminosilicates and secondary solid phases due to the low pH conditions (Fig. 6). Cobalt concentrations in the recharge waters are much higher than in the process waters and show a pattern of distribution typical for Ni and Zn as well (Fig. 6). These metals are released at approximately the same time as Fe; however, elevated concentrations of Pb are found at shallower depths, which suggests that transport of this metal is retarded with respect to Fe. The heavy metals are derived from the oxidation of pyrite and accessory sulfide minerals, as well as the dissolution or desorption of metals previously mobilized during the milling of the ore and reprecipitated during tailings neutralization.

Similar data for piezometer nests T2, T3, T4, T5, and T6 produced races
Samples of groundwater at T6 show that $^{226}$Ra activity ranges from 67 pCi/L at 6.3 m below ground surface to <12 pCi/L at 8.3 m depth (Fig. 6). Most of the groundwaters in the Nordic Main tailings area contain $^{226}$Ra activities in the 67 to 150 pCi/L range, and although $^{226}$Ra activity is generally higher in the high-Fe recharge water, it does not appear to be strongly dependent on pH (Cherry et al., 1980). The distribution of $^{224}$Th, $^{230}$Th, and $^{232}$Th activities show no discernible trends with depth and from the data available no correlation can be made between high thorium activities and high acidity or low pH (Table 2).
TABLE 2 Results of radionuclide analyses for water samples from piezometer nest T6, Nordic Main tailings area (all results are in pCi/L except uranium which is expressed in µg/L; precision represented as ±1 standard deviation). (Analyses by MONENCO Analytical Laboratories, Calgary, Alberta)

<table>
<thead>
<tr>
<th>Piezometer Depth, m</th>
<th>Pb $^{210}$ (±10%)</th>
<th>Th $^{228}$</th>
<th>Th $^{230}$</th>
<th>Th $^{232}$</th>
<th>Ra $^{226}$</th>
<th>µg/L Uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>1708 ±2</td>
<td>19 ±5</td>
<td>4 ±2</td>
<td>95 ±7</td>
<td>1360</td>
<td></td>
</tr>
<tr>
<td>6.3</td>
<td>1265 ±1</td>
<td>6 ±2</td>
<td>&lt;0.5</td>
<td>67 ±4</td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>2746 ±2</td>
<td>3 ±1</td>
<td>&lt;0.5</td>
<td>135 ±3</td>
<td>5200</td>
<td></td>
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<tr>
<td>8.3</td>
<td>203 ±5</td>
<td>6 ±2</td>
<td>1.0 ±0.5</td>
<td>412 ±4</td>
<td>440</td>
<td></td>
</tr>
<tr>
<td>9.3</td>
<td>37 ±3</td>
<td>1.0 ±0.5</td>
<td>&lt;0.5</td>
<td>111 ±7</td>
<td>78</td>
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</tr>
<tr>
<td>10.6</td>
<td>63 ±2</td>
<td>13 ±4</td>
<td>4 ±2</td>
<td>129 ±5</td>
<td>36</td>
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<tr>
<td>12.0</td>
<td>55 ±2</td>
<td>4 ±2</td>
<td>1.0 ±0.5</td>
<td>117 ±5</td>
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<td></td>
</tr>
<tr>
<td>13.3</td>
<td>51 ±2</td>
<td>1.0 ±0.5</td>
<td>&lt;0.5</td>
<td>100 ±5</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

Concentration profiles of uranium and $^{210}$Pb in tailings water at this site show that elevated concentrations of these radionuclides occur in the low-pH, acidic shallow groundwater (Fig. 6, Table 2). This distribution is similar to that of the other heavy metals (Zn, Co, Ni) except that the peak concentrations of U and $^{210}$Pb occur at shallower depths. A positive correlation between high acidity and high concentrations of U and $^{210}$Pb has previously been noted in shallow groundwaters in the Nordic West Arm tailings area by Moffett and Tellier (1978). These radionuclides are probably mobilized by a combination of dissolution and desorption reactions due to decreased pH and increased Fe$^{2+}$ concentrations.

The geochemical profile described above is typical for much of the Nordic Main tailings; however, there are sites, such as T3 and T7, where low-pH, high-Fe waters have penetrated the entire tailings thickness. Even more severe acidification is found in tailings that have been inactive for longer than the Nordic Main tailings. The Nordic West Arm and Lacnor tailings have been inactive for about 10 years longer than the Nordic Main tailings (Fig. 7). At site UW4 in the West Arm tailings, the groundwater pH is below 1.5 through the entire tailings thickness and concentrations of Fe and SO$_4$ range between 3500-9000 and 4500-14000 mg/L, respectively (Fig. 7a). Analyses of groundwater collected at the Lacnor tailings in 1980 showed moderate Fe concentrations throughout the profile with a peak concentration of 1890 mg/L at 7.3 m depth (Fig. 7b). The pH ranged from 6.05 at 7.3 m depth to 1.98 at 1.5 m depth. Data obtained for the same profile in 1983 showed that groundwater quality is still deteriorating with the pH now ranging from 1.51 to 3.97.

The current rate of downward migration of recharge water in the Nordic Main tailings was studied by annual sampling of piezometer nests during the period 1979 to 1983. Changes in the concentration of Fe or Cl were used as criteria for determining the rate of movement: for example, at T1 the movement of the leading edge of the 3,000 mg/L concentration of Fe indicates a downward velocity of approximately 0.3 m/year for the period of record (Fig. 8). Similar data for piezometer nests T2, T3, T4, T5, and T6 produced rates
Figure 7 Profiles of the groundwater geochemistry for piezometer nest UW14 in the Nordic West Arm tailings, and the piezometer nest in the Lacnor tailings showing pH and concentrations of iron, sulphate, and cobalt (from Dubrovsky et al., 1985).

Figure 8 Profiles of the groundwater geochemistry for piezometer nest T1 in the Nordic Main tailings showing Fe, pH, and Cl for the period 1979 to 1983 (adapted from Dubrovsky et al., 1985).
ranging from 0.24 to 2.5 m/year (Dubrovsky et al., 1985). This range of values compares well with rates of downward migration estimated from: 1) the total depth of penetration of the high Fe front; 2) calculations using the Darcy equation and hydraulic parameters measured in the field; and 3) estimates of the annual flux of infiltration into the tailings surface (Dubrovsky et al., 1985).

The relative constancy of the pH values measured at the above sites during the same period is noteworthy (Fig. 8), and is attributed to pH buffering reactions in the tailings. As a result of the buffering, downward movement of low pH conditions is retarded relative to the downward movement of Fe and $SO_4^{2-}$.

APPLICATION OF CHEMICAL EQUILIBRIUM CONCEPTS

An understanding of the geochemistry of Fe and Al is particularly important because hydrolysis and precipitation/dissolution reactions involving these metals act as strong pH buffers. In addition, as much as 80,000 pCi/L of $^{226}$Ra has been found associated with jarosite, a basic iron sulfate which has been identified in both fresh and weathered tailings (Kaiman, 1977 and 1978). Understanding of the behaviour of these metals can be furthered by applying equilibrium concepts to calculate the aqueous speciation of ions, and to identify relationships between solution chemistry and solid phases present in the tailings. Most useful, such calculations can indicate particular solid phases that may limit the concentration levels of important aqueous constituents. Equilibrium calculations in this study were performed using the WATEQ2 speciation model (Ball et al., 1979).

Iron speciation is a function of the pH and redox potential (pe) of the water. Because of the interrelations of Fe activity, pH and pe, Fe speciation and solid phase stabilities are often illustrated by means of pe-pH diagrams. The progressive change in the pH and pe of groundwater at site T6 in the Nordic Main tailings is shown in Fig. 9. The data show that with increasing depth in the tailings, the increase in pH is coupled with a decrease in pe which results in a distribution of data points along the $Fe^{2+}/(am)Fe(OH)_3$ boundary line. A similar trend has been noted for groundwaters in sulfide tailings in New Brunswick (Boorman and Watson, 1976). This trend suggests that the groundwaters are near equilibrium with $(am)Fe(OH)_3$.

Near equilibrium is indicated by the data; however, the calculation does not indicate whether equilibrium is being maintained by dissolution or precipitation of the solid phase. Equilibrium in the tailings groundwaters could be maintained by either process; $(am)Fe(OH)_3$ may be precipitating as the pH of high-Fe water increases due to $H^+$-consuming reactions during downward flow; or $(am)Fe(OH)_3$ precipitated during tailings neutralization prior to deposition may be dissolving due to removal of Fe(III) from solution by pyrite oxidation.

Equilibrium calculations also show that tailings groundwaters in the neutral pH range are supersaturated with respect to siderite ($FeCO_3$) with saturation indices (SI) ranging from 0.34 to 1.7. On the basis of this evidence it is believed that siderite precipitation is occurring in the neutral-$pH$ tailings zone.

The stability fields of jarosite ($KFe_3(SO_4)_2(OH)_6$) for two water chemistries (high Fe and $SO_4^{2-}$, and low Fe and $SO_4^{2-}$) were plotted using the pH for jarosite dissolution of 94.6 calculated by van Breemen (1976) from the experimental data of Brown (1970) at 25°C (Fig. 9). The calculations show that jarosite has a large stability field for typical K, $SO_4^{2-}$, and Fe activities found in the low-pH tailings waters, and all samples with a pH below approximately 5 are highly supersaturated.

$\{AlSO_4(OH)*OH_2OH\}$ is the Al-limiting phase in acid mine waters with pH < 3.3.

In the Nordic Main tailings, groundwaters with a pH between 3.3 and 5.5 are undersaturated with respect to $(am)Al(OH)_3$ and allophane. In these waters basaluminate is close to saturation and may limit Al concentration in the groundwaters.
Figure 9 pe-pH plot for iron species and solid phases for groundwaters from the Nordic Main, Nordic West Arm, and Lacnor tailings. The data for piezometer nest T6 are represented by 'x'. The heavy line is drawn for: $[\text{Fe}]=10^{-4.35}$, $[\text{K}]=10^{-3}$, $[\text{SO}_4^{2-}]=10^{-2}$, and $\log K_{\text{Fe(OH)}_3}^{38}$. The thin boundaries are for: $[\text{Fe}]=10^{-1}$, $[\text{K}]=10^{-2.5}$, $[\text{SO}_4^{2-}]=10^{-1.8}$, and $\log K_{\text{Fe(OH)}_3}^{38}$. (adapted from Dubrovsky et al., 1985).

High degrees of jarosite supersaturation in acid mine drainage have been reported by other researchers (Nordstrom et al., 1979; Miller, 1979; Peterson and Krupka, 1981) and it is suggested that jarosite may precipitate only in favourable microenvironments (Nordstrom et al., 1979). The 5 data points from site UW14 in the Nordic West Arm tailings fall close to the line of jarosite equilibrium and it is possible that at this location jarosite solubility is effective at controlling solution composition (Fig. 9). However, although jarosite has been identified by XRD in old tailings (Kaiman, 1977) and could be precipitating, equilibrium with jarosite is not realized in most groundwater in the Nordic Main and West Arm Tailings.
The aqueous chemistry of Al in the tailings is similar to that of Fe$^{3+}$. The concentration of Al in natural waters with a near neutral pH is often limited by the solubility of amorphous or crystalline aluminum hydroxide or clay minerals. Stoichiometric values calculated for the amorphous aluminosilicate allophane, $(\text{Al(OH)}_3)_{(1-x)}(\text{SiO}_2)_{(x)}$, show that most of the tailings groundwater with a pH greater than 5.5 is supersaturated with respect to this mineral. Precipitation of a SiO$_2$-containing solid phase, possibly allophane, is suggested by the fact that SiO$_2$ concentrations are depressed below the solubility product of amorphous silica in waters in which allophane is supersaturated, a phenomenon that has been observed in other waters actively precipitating allophane (Wells et al., 1977). In this pH range most samples are close to saturation with respect to amorphous aluminum hydroxide, (am)Al(OH)$_3$.

It has been proposed that Al concentrations in acidic high-sulfate waters are controlled by the precipitation of basic aluminum sulfates (Nordstrom, 1982; van Breemen, 1973 and 1976). Based on a review of the literature on acid sulfate waters, Nordstrom (1982) has proposed that for acid mine waters with a pH between 3.3 and 5.7 and containing $10^{-2}$ molar sulfate, amorphous basaluminate is likely to be the first precipitate from solution and control Al concentrations. These authors also suggest that amorphous jarvanite ($\text{Al}_2\text{O}_3\cdot\text{OH}\cdot\text{SH}_2\text{O}$) is the Al-limiting phase in acid mine waters with pH < 3.3.

In the Nordic Main tailings, groundwaters with a pH between 3.3 and 5.5 are undersaturated with respect to (am)Al(OH)$_3$ and allophane. In these waters basaluminate is close to saturation and may limit Al concentration in solution. In the groundwater with a pH < 3.3, both basaluminate and jarvanite are undersaturated in almost all of the samples. These relationships can be illustrated by plotting data for the tailings groundwater and the lines describing solution equilibria with (am)Al(OH)$_3$, basaluminate, and jarvanite on a graph of log Al$^{3+}$ activity versus pH (Fig. 10). The graph was drawn for a constant SO$_4^{2-}$ activity of $10^{-1.8}$. At high pH the data follows the trend of the (am)Al(OH)$_3$ line. At a pH of 4.0 ± 0.3 the data indicates that (am)Al(OH)$_3$ is undersaturated and suggests equilibrium with respect to basaluminate. At pH < 3.5 the Al$^{3+}$ activity appears to be independent of pH.

Due to the great difficulty of isolating and making positive identification of solids present in small quantities in the tailings, along with the amorphous nature of many of the precipitates, there is little direct evidence for the presence of specific Fe and Al solid phases. More work is needed in this area.

ACID NEUTRALIZATION PROCESSES

Surface water in the Elliot Lake area has a very low buffer capacity, and therefore the migration of low pH waters from the tailings into surface water can have a major effect on surface water quality. As essentially all of the Fe in solution below the water table is in the 2+ oxidation state, we can assume that a molar ratio of 1:2 for Fe and H$^+$ production results from pyrite oxidation (equation 1). The relative rate of downward movement of the low pH (high H$^+$ activity) condition can therefore be appraised by comparison with the depth to which the other pyrite oxidation products, Fe and SO$_4^{2-}$, have penetrated the tailings.

Figure 6 shows that the peak concentrations of Fe and SO$_4^{2-}$ are located at greater depths in the tailings than the low-pH condition, indicating that H$^+$-consuming reactions are effective. Mechanisms involved in the pH neutralization include dissolution of calcium carbonate, dissolution of aluminosilicate minerals, dissolution of iron and aluminum hydroxides, and surption of H$^+$. Profiles of pH at shallow depths in the tailings show that much of the H$^+$ consumption occurs above the water table (Fig. 5). The high concentrations of Al and SiO$_2$ in solution indicate that this neutralization in the vadose zone is likely the result of the dissolution of primary aluminosilicates. Although the pH of the solution is increased by this dissolution, substantial acidity persists in the form of dissolved aluminum.
Neutralization below the water cable in the tailings by dissolution of calcium carbonate was first suggested by Blair (1981). The calcium carbonate probably originated as an impurity in the lime added to the tailings during tailings neutralization before discharge or was precipitated by absorption of CO₂ from the atmosphere during the lime neutralization of tailings. The consumption of H⁺ by calcium carbonate dissolution is described by the reaction:

\[ 2H^+ + CaCO_3(s) → Ca^{2+} + H_2CO_3^- \]  \tag{6} 

The above reaction, which describes calcite dissolution below a pH of 6, shows that 1 mole of calcium carbonate will neutralize 2 moles of hydrogen ions.

Analyses of tailings solids sampled at T1, T5, and T6 in the Nordic Main tailings revealed a maximum carbonate mineral content of from 0.025 to 0.06 weight percent (Fig. 11). These values are similar to the average of 0.06 wt. % determined on samples from another inactive tailings, the Williams Lake tailings, in the Elliot Lake district (Feenstra et al., 1981) and 0.048 wt. % for recent tailings from the Qirke mill (R. Nicholson, personal communication). Although there is a strong correlation between fine grain-size and high carbonate content in the Qirke and Williams Lake samples, no such relationship was found in the Nordic Main tailings. This lack of correlation with grain-size is probably due to a dominant control of depth on carbonate-mineral content.
Figure 11 Profiles of the carbonate mineral content of the tailings solids at piezometer nests T1, T5, and T6 in the Nordic Main tailings. (from Dubrovsky et al., 1985).
The sharply-reduced carbonate-mineral contents of the tailings at shallow depths in the profiles are attributed to the removal of calcium carbonate from the tailings solids by low-pH infiltration. The very low amount of solid-phase carbonate that remains at shallow depths may be due to precipitation from acid dissolution by precipitated coatings of gypsum, ferric hydroxides, or aluminum hydroxides, or to the presence of secondary siderite. Siderite may persist in the tailings at lower pHs than calcite due to the high concentrations of Fe(II) in solution. Even the slight amount of carbonate mineral present is sufficient to reduce the rate of downward transport of low-pH conditions to 75% of the average linear groundwater velocity or less.

HYDROGEOCHEMISTRY OF THE SAND AQUIFER

SEEPAE OF WATER FROM THE TAILINGS

As the recharge waters move downward through the Nordic Main tailings, the original pH-neutral process water passes from the base of the tailings into the underlying sand aquifer, in which it flows laterally towards the south. Around the south and east perimeter of the dam, where the water table is near the tailings-aquifer contact, process water has already drained from the tailings and acidic recharge water is now entering the aquifer. There are four sites at which this acidic seepage has moved outward from the vicinity of the dam. Seeage Areas A, B and C are distinct seepage sites while Area D represents a diffuse seepage location (Fig. 3).

In Area A, the sand aquifer is several metres thick and there exists a well-defined contaminant plume near the water table. This plume, which has pH values between 4 and 6, extends laterally several hundred metres downstream towards the south. There is no surface indication of the existence of the plume such as iron staining. Area B is of minor extent and thickness, and the entire area is acidic with pH values of 2 to 4. Heavy iron staining of the surface occurs in Area B. Area C has not been instrumented, but surface iron staining is apparent. Groundwater in the aquifer at Seeage Area D has pH values of 4 to 6; however, concentrations of most ions are lower than in other areas. A distinct plume has not developed in Area D, probably because groundwater flow in the aquifer is parallel to the dam in much of this area. Only the plume in Area A is examined further, because of the high density of bundle piezometers and the abundance of geochemical data for this plume. This plume has been monitored in detail because it exhibits a well-developed range of geochemical zones.

THE GROUNDWATER ZONE

Geochemical trends in the plume are illustrated by profiles for their vertical "centerplane" and for the one-dimensional "centerline" along the direction of flow (C-C' in detail A, Fig. 3). The average linear groundwater velocities along line C-C' vary from about 440 m/yr at the dam to about 210 m/yr at 300 m from the dam to about 50 m/yr at 100 m. Cross sections through the plume perpendicular to flow indicate that lateral and vertical dispersion are minor (Morin, 1983).

The plume in Area A can be divided into three regions based on the centerplane profiles of the aqueous concentrations for pH, iron, which is the major cation, and sulfate, which is the major anion (Fig. 12). Following the terminology of Morin et al. (1982), the inner core has a pH < 4.8, iron > 5000 ppm, and sulfate < 11000 ppm (Table 1). The outer core lies near the water table and extends to about 10 m from the base of the dam. The outer zone has a pH > 5.5, iron < 2500 ppm, and sulfate < 7000 ppm (Table 1). The outer zone lies under the inner core near the dam and it extends southerly beyond the inner core, where it occupies the full saturated thickness of the aquifer from about 49 outwards (Fig. 16). The outer zone is composed of both pH-neutral
Figure 12: Centerplane profiles of the plume in area A showing pH (A), and concentrations of iron (B) and sulphate (C). The inner core of the plume can be clearly seen extending beyond the road at the left of the profile.
Figure 13 Centerplane profile of the plume showing concentrations of aluminum (A) and nickel (B), and activity of $^{226}$Ra (C).
process water at depth and altered ex-inner-core water near the water table. The transition region between these two zones is the neutralization zone in which pH increases and concentrations of iron, sulfate, aluminum, nickel, \(^{228}\text{Ra}\) and many other species decrease as water flows through this zone (Fig. 13).

Because no major chemical reactions occur in the inner core, it can be considered a passive feature; except for minor carbonate reactions, the outer zone is also passive. Thus the neutralization zone is the active zone in which aqueous species are removed from solution by liquid-solid interactions, especially precipitation-dissolution of minerals.

Yearly profiles of pH and iron along the centerline demonstrate that the rate of movement of the neutralization zone is dependent on the value of pH or concentration of iron chosen for comparison (Fig. 14); the higher pH values or lower iron concentrations on the downdgradient side of the neutralization zone show a higher rate of movement than the upgradient side. The reason for this difference in rates is that distinct sub-regions, which are discussed below, comprise the neutralization zone (Fig. 16); each sub-region has a unique migration rate. Nevertheless, an average rate of movement is about 1 m/yr. Because the groundwater velocity is approximately 400 m/yr, the retardation factor for the neutralization zone is 1/400 or 0.2% of the groundwater velocity. The precipitation-dissolution reactions that cause this significant retardation of tailings-derived constituents will now be examined.

**APPLICATION OF EQUILIBRIUM CONCEPTS**

As with the tailings geochemistry, iron minerals, aluminum minerals and a few other compounds are important as controls of aqueous concentrations of iron, aluminum, and sulfate. When these minerals precipitate upon pH neutralization, the co-precipitation and adsorption of heavy metals and radionuclides also occurs. Thus precipitation directly or indirectly accounts for the decreasing concentrations of most ions through the neutralization zone.

The suite of minerals that precipitate in the aquifer is different from the tailings suite. Direct identification of these minerals on the sand matrix has not been accomplished because they usually comprise less than 1 weight-percent of the sand, and thus are below the mineralogical detection limit of standard methods. The exception is calcite, which has been detected in thin-section analysis. The presence of carbonate mineral content at levels of 0.85 wt% in the sand has been confirmed by the analytical method of Barker and Chatten (1982).

As the acidic, high-iron seepage from the tailings, which forms the inner core, advances southward in the aquifer, it comes into contact with calcite in the neutralization zone. Calcite dissolution then neutralizes pH while increasing Ca and dissolved inorganic carbon (DIC) concentrations, as indicated by Equation 6. Because inner-core water contains high concentrations of \(\text{SO}_4^{2-}\) (Fig. 12) and is at saturation with respect to gypsum, the release of Ca into solution causes the precipitation of gypsum, thereby accounting for the observed decrease in \(\text{SO}_4^{2-}\) and only minor changes in observed aqueous Ca through the neutralization zone.

For Fe (Fig. 12), most of which is Fe\(^{2+}\) in Area A, the increase in DIC by Equation 6 can cause the precipitation of siderite:

\[
\text{Fe}^{2+} + \text{H}_2\text{CO}_3 \leftrightarrow \text{FeCO}_3(s) + 2\text{H}^+ 
\]

If oxidation can occur the increase in pH would cause precipitation of Fe(\(\text{OH}\))\(_3\):

\[
\text{Fe}^{2+} + 3\text{H}_2\text{O} + X \leftrightarrow \text{Fe(\text{OH})}_3(s) + 3\text{H}^+ + Y
\]
where $X$ and $Y$ are a redox couple that allow the change in valence of iron from $2^+$ to $3^+$. The contribution of each of these mineral-precipitation reactions to Fe removal in the plume has been evaluated through many methods (Morin, 1983; Morin and Cherry, submitted). For example, the grouping of data points along the upper boundary of the stability field for FeCO$_3$ in Figure 15 suggests that precipitation of siderite controls the concentration of Fe$^{2+}$ at neutral pH values. This observation, along with other lines of evidence, indicates that nearly all Fe precipitates as siderite.

An additional complexity is that siderite apparently does not precipitate directly when calcite is present, but instead replaces calcite:

$$\text{Fe}^{2+} + \text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+} + \text{FeCO}_3(s)$$

Figure 13 Centerplane profile of the plume showing concentrations of aluminum (A) and nickel (B), and activity of $^{220}$Ra (C).
Relative to Equation 7, this reaction does not significantly affect acidity or DIC levels, but contributes to the concentration of Ca, thereby causing further gypsum precipitation.

Most of the aqueous aluminum (Fig. 13) is probably removed from solution from pH neutralization by the precipitation of amorphous gibbsite:

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(	ext{OH})_3 \text{ (s)} + 3\text{H}^+ \]  \tag{10}  

Saturation-index calculations indicate that a dehydrated form of gibbsite (e.g., boehmite) and allophane probably also precipitate in certain areas. The aluminum mineral and its representative solubility are different for each sub-region of the neutralization zone, and aluminum solubility, expressed as the ion activity product \( [\text{Al}^{3+}] [\text{OH}^-]^3 \), varies over 2 orders of magnitude through the neutralization zone.
When all of the above precipitation-dissolution reactions are considered, the following conceptual model for solute behaviour and migration is formed. When inner-core water first moves into a portion of the aquifer containing calcite, calcite dissolves which causes pH neutralization, siderite replaces calcite, and gypsum and aluminum minerals precipitate. When calcite is depleted, siderite and aluminum minerals dissolve in sequence (reverse of Equations 7 and 10), neutralizing pH, but to a lesser extent than calcite. A step function for pH and other ions can be used to represent these processes conceptually along the centerline, with plateaus representing the aforementioned sub-regions of the neutralization zone (Fig. 16). The length
of each sub-region increases with time and each sub-region migrates faster than the adjacent upgradient sub-region (Morin, 1983).

In order to predict the equilibrium chemistry in each sub-region and to simulate the migration of these zones, a family of computer programs named ADNEUT (Acid-Drainage Neutralization) was created (Morin, 1983; Cherry et al., 1984). The ADNEUT programs simulate groundwater movement by discretizing a streamtube into a series of cells and passing the aqueous content from one cell to the adjacent downgradient cell at each time step. Solid- and liquid-phase equilibrium is computed for each cell before transport to the next cell occurs. These programs have assisted in clarifying the details of acidic contaminant behaviour and migration in subsurface flow systems through sensitivity studies, simulation of observed data, simulation of plume development in Area A, and simulation of possible future migration in Area A.

An evaluation of the effects of sorption and co-precipitation on the heavy metals and radionuclides indicate that co-precipitation with major minerals is probably more important than adsorption (Morin, 1983). Results from a radionuclide speciation-saturation index model (Morin, 1983), indicate direct precipitation of radioactive compounds such as Th(5O₄)₂ and USiO₄ may also be occurring in the neutralization zone. Because of the operation of this mixture of processes, the migration of heavy metals and radionuclides in the aquifer is more difficult to simulate than major ions.

The above conceptual model and ADNEUT have also been successfully applied to several uranium-tailings seepage sites in Wyoming (USA) and to a uranium waste-rock site near Bancroft, Ontario (Morin, 1983).

PLUME IMPACT ON BUCKLES CREEK

Results from two piezometer bundles, NP-1 and NP-2, installed adjacent to Buckles Creek show the presence of groundwater with elevated Fe concentrations and high electrical conductance (Fig. 17). At NP-1 an Fe concentration of 110 mg/L was found just below the water table, while at NP-2 the Fe concentration in the shallowest piezometer was 180 mg/L. At both locations there is a peak in the Fe profile at 8 to 10 m depth. Measured water levels indicate that at NP-2 there is a strong upward gradient at less than 4 m that will cause transport of high-Fe groundwater to the stream. However, the hydraulic gradient is downward from 4 to 8 m depth and it is likely that the deeper portion of the plume extends laterally southeastward beneath the stream. Water level measurements at NP-1 show no discernable vertical gradients, and flow here is dominantly horizontal.

Analyses of surface waters in beaver ponds upstream of the concrete weir shown in Figure 3 are indicative of the background water quality. Electrical conductance was found to be less than 50 µS/cm and the pH ranged between 6.9 and 7.2. Brown staining of the stream bed in these areas is believed to have been caused by organic compounds. The sample of groundwater from minipiezometer MP-3 is representative of the ambient groundwater (Table 3). The sample has a high pH and low concentrations of Fe and SO₄²⁻.

The zone where groundwater from the tailings plume discharges to Buckles Creek is identified by high values in the electrical conductance in the groundwaters sampled from the minipiezometers downstream of the weir (Fig. 18). The electrical conductance of the groundwater increases from less than 1000 µS/cm at MP-6 to greater than 2000 µS/cm at MP-7. The electrical conductance ranges from 1600 to 3500 µS/cm between MP-7 and MP-20, then decreases to 760 µS/cm at MP-23. Therefore the zone of discharge of contaminated groundwater extends approximately from MP-7 to MP-20, a distance of about 120 m.
Figure 17 Profiles of hydraulic head and iron concentrations for piezometer bundles NP-1 and NP-2 adjacent to Buckles Creek.

<table>
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<th>Electrical Conductance (μS/cm)</th>
<th>Fe$^{2+}$ mg/L</th>
<th>Fe mg/L</th>
<th>SO$_4^{2-}$ mg/L</th>
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<td>7.1</td>
<td>110</td>
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<td>2</td>
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<td>0.033</td>
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<tr>
<td>MP-21</td>
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<td>1000</td>
<td>23</td>
<td>24</td>
<td>350</td>
<td>0.096</td>
</tr>
</tbody>
</table>
The pH of the shallow groundwater sampled in the minipiezometer ranges from a high of 7 in the groundwaters that are not affected by tailings drainage to 5.7 at MP-14 (Fig. 18). The pH of the groundwater decreases gradually from MP-6 to MP-14, and the minimum pH coincides with the highest electrical conductance observed. Groundwater pH then increases to almost background values before decreasing again to 5.8 at MP-20.

Analysis of six samples of groundwater for Fe show that the trend of Fe concentration correlates with the electrical conductance (Table 3, Fig. 18). Fe increases from 12 mg/L at MP-5 to a maximum of 359 mg/L at MP-14, then decreases to 24 mg/L at MP-21. The results of redox titrations showed that essentially all of the Fe is ferrous (Fe²⁺).

**SURFACE WATER - BUCKLES CREEK**

![Surface Water Graph]

**GROUNDWATER - MINIPIEZOMETER SAMPLES**

![Groundwater Graph]

Figure 18 Geochemical data for the Buckles Creek area: A) pH and electrical conductance of surface waters in Buckles Creek; B) pH, electrical conductance and iron concentration of shallow groundwater beneath Buckles Creek sampled using minipiezometers.

The impact of the discharge of plume groundwater to Buckles Creek is indicated by an increase in the electrical conductance of the stream from 240 μS/cm at GBC-1 to a maximum of 1300 μS/cm at GBC-4 (Fig. 18). The increase in electrical conductance is accompanied by a decrease in pH from 6.5 to 6.15; however, the pH of the stream increases to 6.4 by sampling station GBC-5, a distance of about 100 m.

When high-Fe groundwaters discharge to the stream, the mixing of the oxygenated surface water and groundwater will result in the oxidation of the Fe²⁺ to Fe³⁺ and the subsequent precipitation as (am)Fe(OH)_3, as represented by the following equations:
\[
\begin{align*}
\text{Fe}^{2+} + 1/4 \text{O}_2(\text{aq}) + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+
\end{align*}
\] (11) (12)

While the oxidation of one mole of Fe\(^{2+}\) consumes one mole of H\(^+\), the precipitation of Fe\(^{3+}\) generates three moles of H\(^+\), resulting in a net production of two moles of H\(^+\). The combined reaction causes the pH of the solution to decrease. For example, the oxidation and precipitation of 100 mg/L of Fe\(^{2+}\) will result in a pH of 2.4 in an unbuffered solution.

Prediction of the impact of Fe\(^{2+}\) oxidation and precipitation on the stream requires an assessment of both the stream flow and the total flux of contaminated groundwater into the stream in order to calculate a dilution factor. The stream flow has been estimated to range from 7.5x10\(^{-3}\) to 2.7x10\(^{-1}\) m\(^3\)/s (Blair, 1981). The groundwater component can be calculated using measurements of groundwater seepage flux into the stream made at three locations (Fig. 3). At MP-9 the rate of seepage was too low to be measured. At MP-14 and MP-18 average seepage fluxes of 0.45 and 0.49 L/min x m\(^2\) were measured.

By assuming that seepage of contaminated groundwater occurs along a 150 m length of stream bed with an average width of 1 m, and applying a representative seepage flux of 0.5 L/min x m\(^2\), the total discharge of contaminated groundwater to the stream is calculated to be 1.25x10\(^{-3}\) m\(^3\)/s. This discharge constitutes between 0.5 to 17% of the total streamflow.

A 'worst case' assessment of the impact of contaminated groundwater on Buckles Creek can be made by assuming the minimum observed streamflow of 7.5x10\(^{-3}\) m\(^3\)/s, the groundwater discharge calculated above, and assuming an average Fe concentration of 100 mg/L. The assumption of low streamflow is appropriate in that the sampling was done in mid-July. At this flow rate the groundwater inflow would be diluted by a factor of 6, and a pH of 3.22 would result in an unbuffered solution. Even at maximum streamflow, a pH of 4.74 would be produced in an unbuffered solution. It is clear from the high pH values observed in the stream that either oxidation and precipitation of Fe\(^{2+}\) is not occurring, or a significant amount of buffer capacity exists in the surface and groundwater.

One source of neutralization is the carbonate alkalinity of the solutions. At a pH of 7 and atmospheric pCO\(_2\), the carbonate alkalinity of the surface waters will be approximately 10\(^{-6.35}\) mole/L HCO\(_3^-\). At maximum streamflow the alkalinity in the surface water is more than adequate to neutralize the H\(^+\) produced by 100 mg/L Fe; in fact this alkalinity would be sufficient to neutralize the specified groundwater flux if it contained 250 mg/L Fe. At low flow the alkalinity of the surface water will be sufficient to neutralize only about 8% of the H\(^+\) produced by the precipitation of 100 mg/L Fe; the resulting pH will be near 2.5. This predicted pH is much lower than that observed in the stream in July, and other sources of H\(^+\) neutralization may be involved.

An additional component of alkalinity is introduced by the groundwater seepage itself: analyses of groundwaters from piezometer bundle M-14 showed that in groundwater with between 84 and 102 mg/L (1.5 to 1.8 mM) of Fe\(^{2+}\), the alkalinity ranged from 1.8x10\(^{-3}\) to 3.9x10\(^{-3}\) mole/L HCO\(_3^-\) (Morin, 1983). Thus, the groundwater discharge itself contains enough alkalinity to neutralize at least one-half of the potential H\(^+\) production.

In view of the large amounts of alkalinity present in the ground and surface waters, it is likely that the pH of the stream will not be depressed due to Fe precipitation during periods of moderate to high flow. At low flow the alkalinity is not sufficient to maintain a high pH, and other explanations for the pH observed in the stream in June must be considered. Alternative hypotheses include:
oxidation of Fe$^{2+}$ is inhibited.
oxidation of Fe$^{2+}$ to Fe$^{3+}$ is occurring, but precipitation of Fe(OH)$_3$ is inhibited.
precipitation of Fe(OH)$_3$ is occurring and there are other sources of H$^+$ neutralization.

High dissolved organics in the stream could provide validity to either of the first two hypotheses by chelating the Fe and preventing it from entering into reactions. The one sample of surface water analyzed for Fe was found to contain 23 mg/L of Fe$^{2+}$, suggesting that the oxidation of Fe in the stream may be inhibited. However, the formation of Fe(OH)$_3$ on the stream bed has been observed, and it is likely that additional pH buffering occurs due to the presence of dissolved organics, suspended solids, or interactions between the surface water and the stream bed.

CONCLUSIONS

The Nordic Main tailings, which have similarities to most of the other old uranium tailings in the Elliot Lake district, have become a source of acidic water that emanates from the tailings via surface and subsurface pathways. The subsurface pathways begin in the vadose zone of the tailings where invasion of oxygen and water causes pyrite oxidation that results in low pH and high concentrations of iron and some heavy metals and radionuclides. From the vadose zone the water gradually moves downward through the tailings. During movement through the tailings, the transport of H$^+$, Al, heavy metals, uranium, and $^{210}$Pb is retarded by geochemical processes, while Fe and SO$_4^{2-}$ travel at about the average linear groundwater velocity.

After penetrating the entire tailings thickness and underlying peat layer, the high-Fe groundwater enters the glaciofluvial aquifer, where the essentially horizontal flow system moves the tailings-derived water laterally from beneath the tailings. In the aquifer the transport of the above-mentioned solutes are highly retarded due to reactions related to the high calcite content of the sand, except for Fe$^{2+}$ and SO$_4^{2-}$ which are less strongly retarded by the replacement of calcite with siderite and precipitation of gypsum.

Near the southern limit of the dam for the Nordic Main tailings impoundment, the input of acidic, low-pH water from the tailings has resulted in the depletion of the calcite in the aquifer, and a plume containing elevated concentrations of several heavy metals and radionuclides has developed. The metal-rich inner core of the plume extends only about 10 m from the base of the dam and is moving at about 0.2% of the groundwater velocity. However, the transport of moderate-to-high concentrations of Fe$^{2+}$ and SO$_4^{2-}$ is only slightly retarded, and groundwater containing concentrations of Fe$^{2+}$ and SO$_4^{2-}$ above background levels extend over 100 m from the tailings, where they discharge to a small stream. At present the discharge of Fe-rich groundwater to the stream has little impact on the surface-water quality. The concentrations of Fe in the groundwater discharge will continue to increase in the future, eventually causing degradation of the surface waters.
PROGNOSIS

Analyses of the solid tailings at three sites in the Nordic Main tailings have shown that the pyrite at shallow depths is gradually being depleted by oxidation. In areas of fine-grained tailings (T1 and T3) the pyrite has been completely removed from the upper metre of tailings, while at an area with coarse tailings (T5) a large fraction of the pyrite originally present is still found near the tailings surface. At present, the thickness of the zone of oxidation, as indicated by the depth of penetration of $O_2$ gas, varies from 0.7 m to 1.5 m; thus, considerable mass of pyrite still exists in the vadose zone. Oxygen will move deeper into the tailings as pyrite depletion continues, and therefore it is expected that the pyrite that remains now will eventually be oxidized. Mass-balance calculations show that the observed pyrite contents of 5 to 15% are sufficient to continue to produce acidic groundwater with Fe concentrations of 1000 mg/L for several decades to several hundred years, depending on the depth of penetration of the zone of oxidation.

When pyrite is totally removed from the vadose zone, the rate of acid production will decrease but not cease entirely. Pyrite oxidation below the water table will occur, but will be limited by the availability of oxygen transported either as dissolved oxygen in infiltrating precipitation, or by diffusion through the vadose zone. Much of the water below the water table at W14 on the Nordic West Arm tailings area has a pH of less than 1.5, and analyses show that much of the Fe in solution is Fe$^{3+}$. If the oxidation of pyrite by Fe$^{3+}$ is occurring below the water table, then the amount of acid production may not be severely limited by oxygen availability. Even after all pyrite oxidation has ceased, low-pH conditions will be maintained by the alteration of jarosite or other basic Fe or Al sulfates as shown by the following reaction:

$$KFe_3(SO_4)_2(OH)_6 + 3H_2O + 3Fe(OH)_3 = K^+ + 2SO_4^{2-} + 3H^+$$ (13)

Regardless of future production of acid in the vadose zone, there already exists a large reservoir of acidic water below the water table in the Nordic tailings that is migrating downward at a rate of between 0.25 and 2.5 m/y. At present the high-Fe, low-pH groundwater has reached the bottom of the Nordic Main tailings in only a small percentage of the impoundment area. However, at the observed migration rates the high-Fe water will occupy the entire tailings thickness over most of the tailings area within the next three decades. Low-pH conditions migrate downward at a rate that is 75% or less of the average downward groundwater velocity, and will not reach the base of most of the tailings mass for 40 years or more. The arrival of low-pH conditions will be accompanied by higher concentrations of heavy metals, $^{210}$Pb, and uranium.

After the high-Fe, low-pH groundwater penetrates the entire tailings thickness, the total flux of contaminated groundwater into the aquifer underlying the tailings, and into fractured bedrock beneath the aquifer, will increase. At present, the inner core of the plume in the aquifer at area A has a cross-sectional area of only 3 m$^2$ where it exits the tailings; however, due to the high groundwater velocity at this location, a significant flux of tailings-derived water results. This flux is equivalent to the total amount of precipitation that is intercepted annually by 0.13 hectares, or less than 0.5% of the tailings impoundment surface. An increase in the area contributing acidic water to the aquifer may result in an increase in the thickness and lateral extent of the plume, as well as the development of additional areas where acidic groundwater discharges from the tailings.

The inner core of the plume is migrating at a rate of approximately 0.2% of the average linear groundwater velocity, or 1.0 m/yr, and at present extends only 10 m from the base of the dam. The groundwater velocity decreases by a factor of 10 between piezometer bundles M-1 and M-10. It will take on the order of 1000 years for the inner core to migrate the 160 m distance to Buckles Creek. When that occurs, groundwater containing high concentrations of heavy metals and some radionuclides will discharge directly to the surface-water system. This arrival time prediction is based on the assumption that low-pH water will continue to emanate from the tailings for this period of time.
Groundwater with concentrations of Fe greater than 1000 mg/L extended beyond piezometer bundle M-12 in 1982, and is migrating toward Buckles Creek at a rate of about 30 m/yr. At this rate, groundwater with Fe concentrations greater than 1000 mg/L will reach Buckles Creek within a year. Data on the water quality of the stream in 1982 indicated that the stream was impacted by contaminated groundwater seepage; however, the pH remained near neutral. As the Fe concentrations in the groundwater discharging to Buckles Creek increase, the pH buffer capacity of the stream may be exceeded and lower pH conditions may result.

At the present time acceptable water-quality conditions in the streams and lakes downstream from the Nordic tailings area are maintained by lime and barium chloride treatment of surface drainage waters from the tailings. The prognosis presented above is that the need for such treatment facilities will increase rather than decrease in future decades, and that it is very unlikely that major interventions using engineering means, other than complete removal, would provide a basis for avoiding the need for long-term water-quality treatment of surface waters. These conclusions do not necessarily apply to the tailings impoundments in use in the Elliot Lake district because these impoundments offer possibilities for preventing pyrite oxidation from reaching the relatively advanced stage that now exists at the Nordic tailings.

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REFERENCES


CONTAMINANT MIGRATION FROM URANIUM TAILINGS


