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Contaminant migration in a sand aquifer near an inactive uranium tailings impoundment, Elliot Lake, Ontario

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An investigation of the movement of contaminated groundwater from inactive uranium tailings through a sand aquifer is being conducted at the Nordic Main tailings impoundment near Elliot Lake, Ontario. During 1979 and 1980, multilevel bundle-type piezometers were installed at several locations around the edge of the tailings impoundment. Chemical analysis of water samples from the bundle piezometers indicate that a major contaminant plume extends outward through a sand aquifer from the southeastern part of the Nordic Main impoundment dam.

In the vicinity of the contaminant plume, the sand aquifer varies in thickness from about 9 to 15 m. The plume has two distinct segments, referred to as the inner core and the outer zone. The inner core, which has a pH of 4.3–5.0 and extends about 15 m from the foot of the tailings dam, contains several grams per litre of iron and sulfate, and tens of pCi/L of ^{226}Ra and ^{210}Pb . Water levels in piezometers within the inner core show that groundwater is moving horizontally, away from the tailings impoundment, with a velocity of up to several hundred metres per year. The outer zone, which extends a few hundred metres downgradient from the dam, is characterized by hundreds to thousands of milligrams per litre of iron and sulfate, less than 15 pCi/L of ^{226}Ra , and a pH greater than 5.7. Comparison of 1979 and 1980 data shows that the front of the inner core is advancing a few metres per year, which is less than a few percent of the groundwater velocity. This retardation of movement of the inner core is caused by neutralization of the acidic water as a result of dissolution of calcium carbonate in the sand. With the rise in pH, precipitation of iron carbonate and possibly some iron hydroxide occurs and the contaminants of main concern such as ^{226}Ra , ^{210}Pb , and uranium are removed from solution by adsorption or coprecipitation.

Une étude du mouvement à travers un aquifère sableux de l'eau souterraine contaminée par un dépôt abandonné de stériles d'uranium est en cours au "Nordic Main tailings impoundment" près d'Elliot Lake, Ontario. En 1979 et 1980 des piézomètres multiples en chapelet ont été installés à différents emplacements à la périphérie de l'aire de dépôt de stériles. L'analyse chimique des échantillons d'eau prélevés dans les chapelets de piézomètres indique qu'une importante traînée de contaminant se développe vers l'extérieur à travers l'aquifère sableux à partir de la zone sud-est de l'aire de dépôt.

Dans la zone de cette traînée de contaminant, l'aquifère a une épaisseur variant de 9 à 15 m. La traînée présente deux éléments distincts, identifiés comme noyau intérieur et zone extérieure. Le noyau intérieur, qui a un pH de 4.3–5.0 et s'étend jusqu'à environ 15 m du pied du barrage de retenue des stériles, contient plusieurs grammes par litre de fer et de sulfates et des dizaines de pCi/L de ^{226}Ra et de ^{210}Pb . Les niveaux d'eau dans les piézomètres à l'intérieur du noyau interne indiquent que la nappe se déplace horizontalement en s'éloignant de l'aire de dépôt de stériles à une vitesse atteignant plusieurs centaines de mètres par an. La zone extérieure, qui s'étend jusqu'à quelques centaines de mètres à l'aval du barrage, est caractérisée par des centaines à des milliers de milligrammes par litre de fer et de sulfates, par moins de 15 pCi/L de ^{226}Ra et par un pH supérieur à 5.7. La comparaison des observations de 1979 et 1980 montre que le front du noyau interne avance de quelques mètres par an, ce qui représente moins que quelques pourcent de la vitesse de la nappe. Ce retard du mouvement du noyau interne est dû à la neutralisation de l'eau acide par suite de la dissolution du carbonate de calcium dans le sable. Avec l'augmentation du pH, la précipitation de carbonate de fer et peut-être d'hydroxide de fer se produit et les contaminants les plus problématiques, tels que le ^{226}Ra , le ^{210}Pb et l'uranium sont éliminés de la solution par absorption ou co-précipitation.

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Introduction

Large-scale mining and milling of uranium from a quartz-pebble conglomerate occurs in the Elliot Lake district of Ontario. In the mills, uranium is dissolved

from the crushed ore by the sulfuric-acid-leach process. The residual solids have an average grain size of less than 0.074 mm and contain between 3 and 7 wt% pyrite (FeS_2). After removal of the dissolved uranium from the

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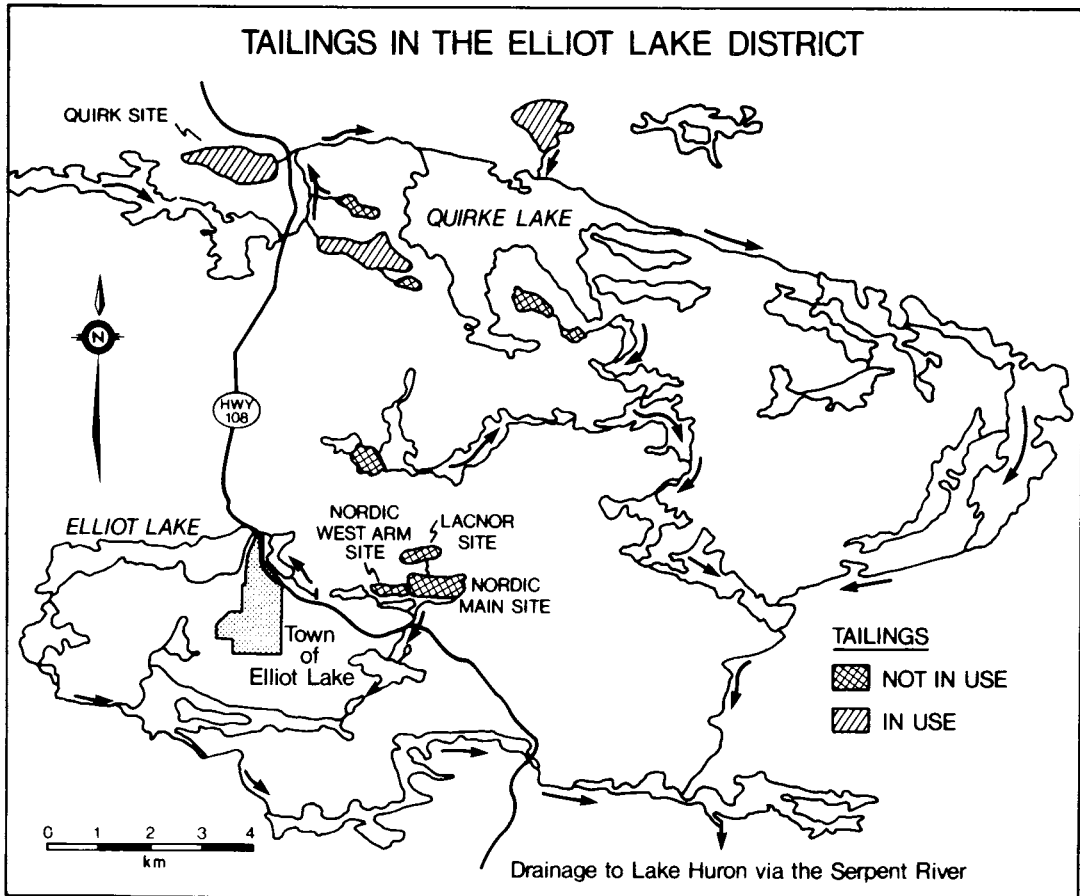


FIG. 1. Location of the Nordic Main tailings impoundment and other impoundments in the Elliot Lake district.

acidic process water, the latter is neutralized to a pH of 8–10 by the addition of lime and limestone, and then the water and solids are discharged as a slurry to tailings impoundments.

When several mills ceased operation in the Elliot Lake district in the 1960s, the neutralized process water began to drain from the tailings, oxygen and infiltrating precipitation reacted with pyrite to produce high-iron, high-sulfate, and low-pH water, and the low-pH water caused the release of some radionuclides and heavy metals from the tailings solids (Blair *et al.* 1980; Cherry *et al.* 1980a).

Degradation of water quality may occur if the released radionuclides and heavy metals pass from the tailings into subsurface flow systems and into nearby surface watercourses. In surface watercourses the resulting degradation of water quality is easily observed and remedial measures are quickly initiated before a major environmental problem develops. However, in subsurface flow systems degradation of water quality is not readily detected and remedial measures are not easily accomplished. In order to assess whether remedial

measures are necessary before final tailings abandonment, and which measures may be suitable, information is needed on the behavior of tailings seepage in groundwater flow systems.

The Nordic Main tailings impoundment, about 4 km east of the town of Elliot Lake (Fig. 1), was chosen for detailed investigations of tailings seepage. During the period of 1960–1968, the Nordic Main tailings were deposited in an impoundment situated on a glaciofluvial sand aquifer (Fig. 2). Poned surface water was drained from the tailings area in 1970 and a grass cover was established through the period 1971–1978.

The study of the migration of groundwater-borne contaminants from the Nordic Main tailings began in 1979 and the results of the 1979 investigations are presented by Blair *et al.* (1980). Blair and his co-workers defined the shape and chemistry of a zone of contaminated groundwater emanating from the tailings and suggested some geochemical processes to account for the chemistry. Our paper presents data obtained in 1980 and shows the first direct evidence of plume movement by comparing 1979 and 1980 contaminant

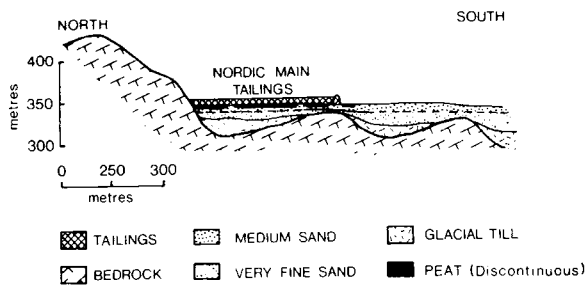


FIG. 2. Generalized geologic cross-section through the Nordic Main area.

distributions. A hypothesis to account for the chemical characteristics and retardation of the zone of most severe contamination in the sand aquifer is assessed using geochemical information on the solid and liquid phases in the aquifer.

Previous work

Blair *et al.* (1980) established a network of piezometers in the aquifer near the Nordic Main tailings in 1979. Chemical analyses of groundwater from these piezometers indicated that there is a contaminant plume extending several hundred metres southward from the tailings dam (Fig. 3). The core of this plume is acidic. Although Blair *et al.* installed three nests of piezometers in the tailings north of the plume, they did not locate the area of the tailings from which the acidic water originates.

The results of the 1979 water analyses for pH and radium are contoured in Figs. 4a and 5a (see Fig. 7 for piezometer locations). Blair and co-workers found that the most contaminated water, which contained high concentrations of iron, sulfate, and radium and had a low pH, extended only several metres from the base of the dam. Beyond this zone, the groundwater had relatively moderate concentrations of iron and sulfate with background radium concentrations and a near-neutral pH.

The network of piezometers in the Nordic Main tailings was expanded in 1980 (Cherry *et al.* 1980a). The probable source area of the low-pH plume water was located approximately 100 m inward (northward) from the dam in the general vicinity of piezometer nest T7 (Figs. 6 and 7). The lateral extent and nature of this source area will be defined during the 1981 field season. In the source area, low-pH water apparently flows downward through the tailings into the underlying sand aquifer, and then flows horizontally towards the south.

Groundwater monitoring

Piezometers installed in the glacio-fluvial aquifer during the 1979 and 1980 field seasons were multilevel bundle-type piezometers (Cherry *et al.* 1980b). These

piezometers consist of varying lengths of 0.9 cm id polyethylene tubing, each with a 10 cm long, 0.9 cm id polyethylene piezometer screen at the bottom. The screens, with accompanying tubing, were taped to a length of 1.5 cm id PVC center pipe for support. This design allowed the rapid installation of up to 12 small, individual piezometers at various depths in one bore-hole.

Hollow-stem continuous-flight augers were used to drill a hole for each bundle piezometer. Before drilling, the center of the auger was plugged at the bottom with a rubber stopper. When the desired depth was reached the bundle was lowered down the center of the augers, the rubber stopper was knocked out, and the augers were raised with the bundle remaining in place in the hole. The glaciofluvial sand, which is cohesionless, collapsed immediately around the bundle.

The locations of bundle piezometers in the Nordic Main area are shown in Fig. 7. Piezometers M1–19 were installed in 1979; M20–34 and WW1 in 1980. Piezometers M20–27 were installed to expand the piezometer network in the plume. Piezometer M33 was installed to locate the southern edge of the plume, M28 and M34 to monitor migration of possible contaminants from the east side of the dam, and M29–32 to monitor contaminant migration in an area between two bedrock outcrops designated as a seepage area in Fig. 6.

Water levels in the bundle piezometers were measured using a coaxial-cable electric probe. Water samples were taken from piezometers by means of a peristaltic pump. In the field the pH and Eh of the water samples were measured inside a 100 mL flow-through cell to prevent errors and fluctuations caused by the mixing of air with the water. After calibration in pH 7 and pH 4 buffers, the pH of the water was measured with a pH meter and combination probe. The Eh of the water samples was taken with a specific-ion meter and combination platinum electrode, after standardization in Zobell's solution. Specific conductance was measured with a conductance meter and probe, following standardization in stock KCl solutions. Water samples were filtered through 0.45- μ m membrane filters in a 142-mm-dia. disc filter of the type described by Kennedy *et al.* (1976). As the water was filtered, it was directed into plastic bottles, acidified with concentrated HCl, and sent to laboratories (see Table 1) in which the analyses were conducted.

Stratigraphy

The stratigraphy of the plume area is relatively simple (Fig. 2). There are four to six distinct layers, depending on the exact location in the area. These layers are described below in order of increasing depth.

The surficial layer covering the plume area south of the dam is a 1-m-thick deposit of fill, which was placed

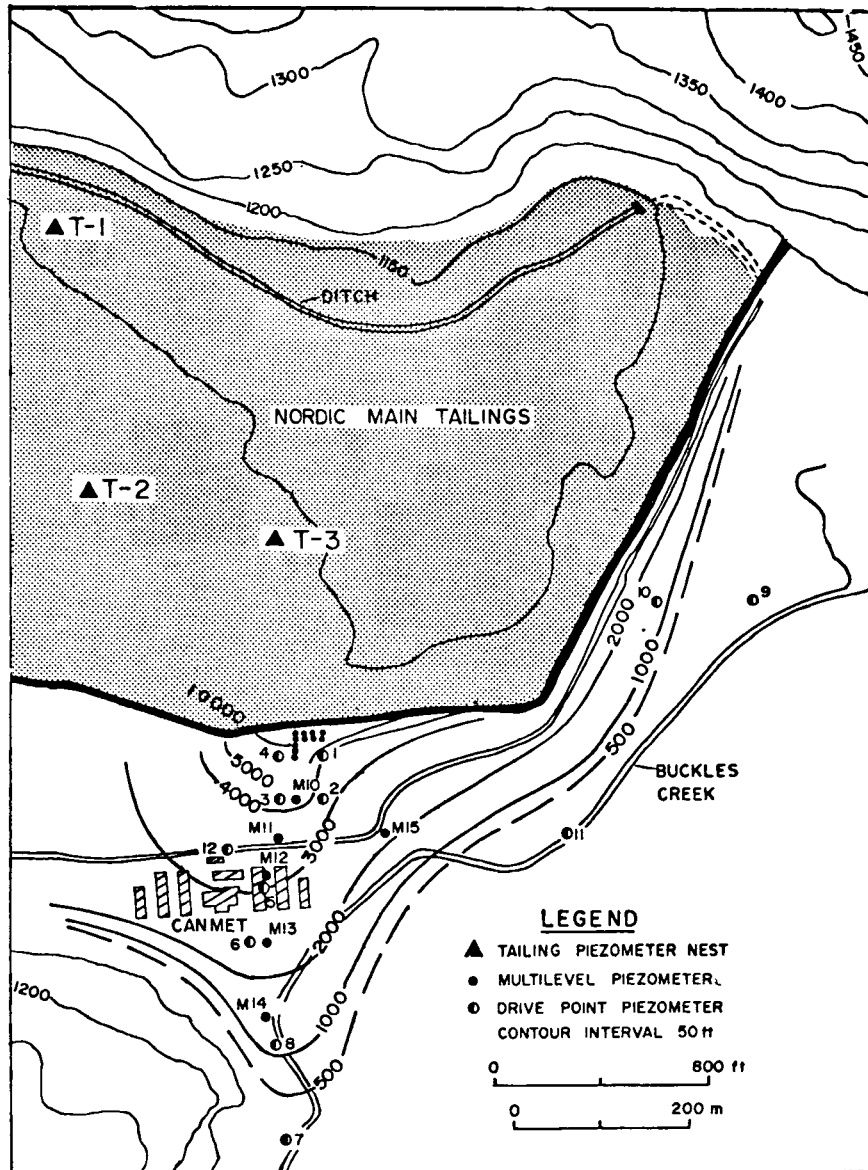


FIG. 3. Topography of the study area and areal distribution of sulfate (mg/L) in the aquifer in 1979 (from Blair 1980).

and levelled during dam construction in the 1960s. The fill is comprised of cobbles, gravel, and sand.

In some areas, such as within several metres of the dam, there is a 1-m-thick layer of peat underlying the surficial fill. This discontinuous layer of peat contains logs in some places.

The next two layers comprise the glaciofluvial sand aquifer. Most of the low-pH contaminated water lies in the upper layer of the aquifer. This upper layer consists of dark tan, medium-grained sand, has a porosity of about 36%, and varies in thickness from 4 to 8 m. A typical grain-size distribution is shown in Fig. 8. This sand has a relatively high specific gravity of about 2.98

that is caused by the large percentage of magnetite and other heavy minerals in the sand.

The lower layer in the sand aquifer is a light gray, very fine-grained sand. The thickness of this layer varies from about 3 m to greater than 8 m (bedrock not reached at T7). A typical grain-size distribution is shown in Fig. 8. The lower sand has a specific gravity of about 2.87. Grain-size analyses indicate that there are probably a few coarse silt beds in this layer. A thin, fine-grained layer may separate the upper and lower sands in the plume area.

Underlying the sand aquifer is sandy till or Precambrian bedrock (Fig. 2), which is mainly a basic meta-

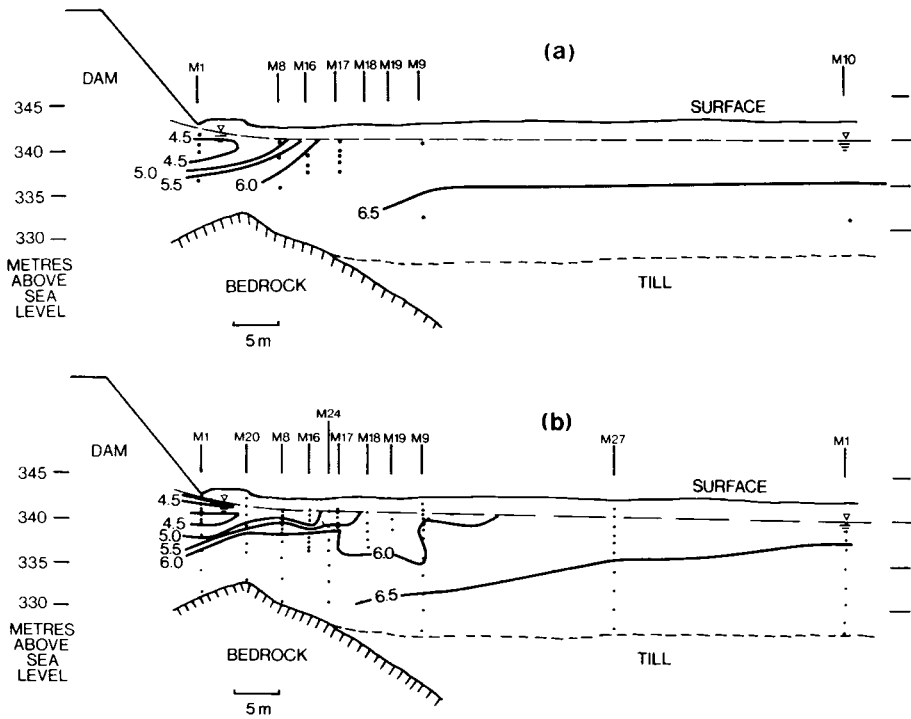


FIG. 4. The pH of groundwater in the plume in: (a) November, 1979 (data from Blair 1980); (b) August, 1980.

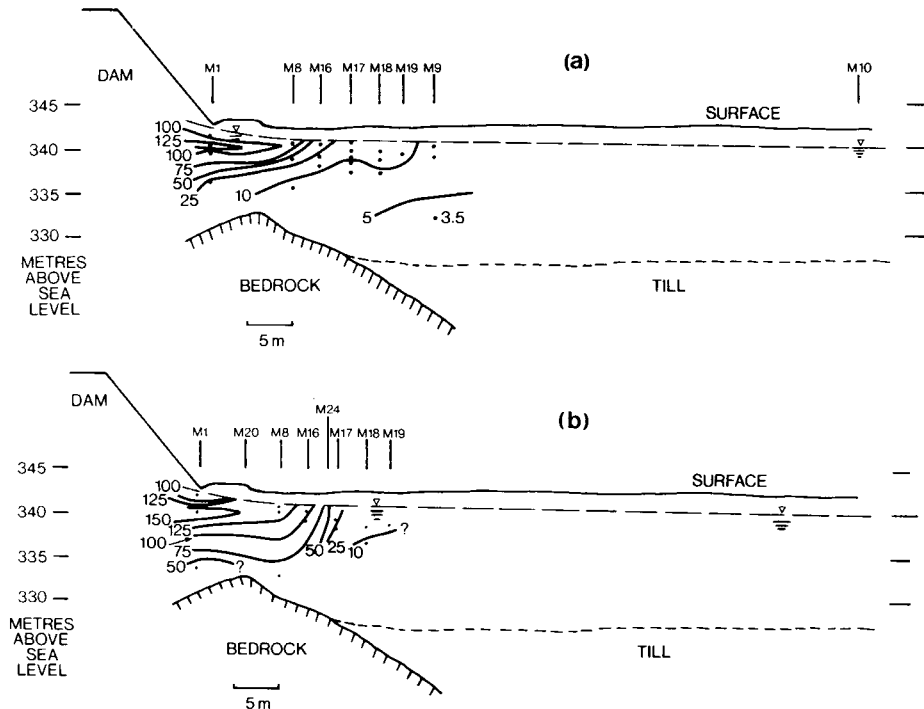


FIG. 5. Radium-226 (pCi/L) in the plume in: (a) November, 1979 (data from Blair 1980); (b) August, 1980.

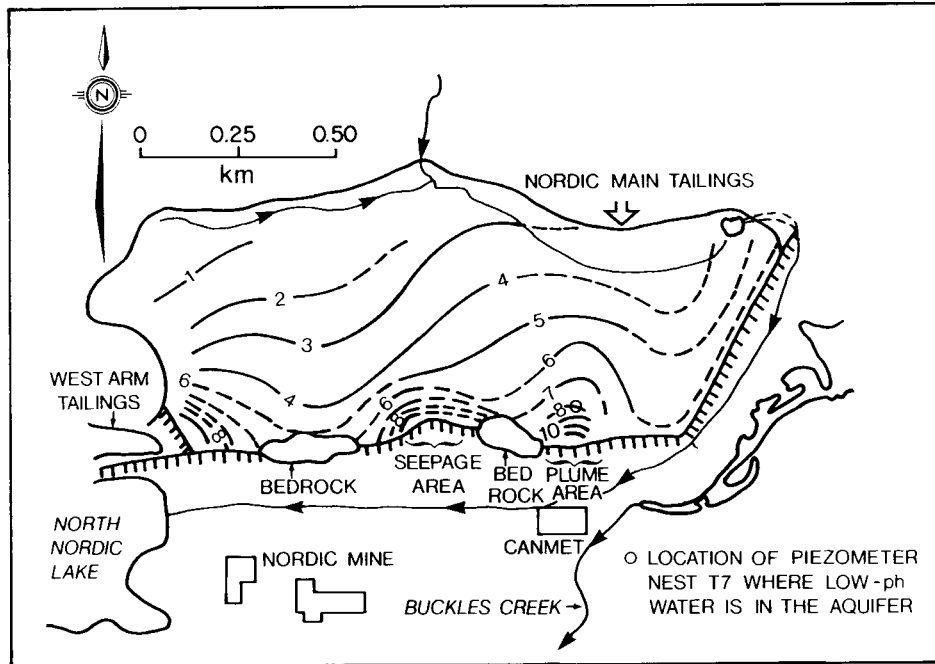


FIG. 6. Map of hydrogeologic features in the study area (adapted from Cherry *et al.* 1980). Water-table contour interval is 1 m.

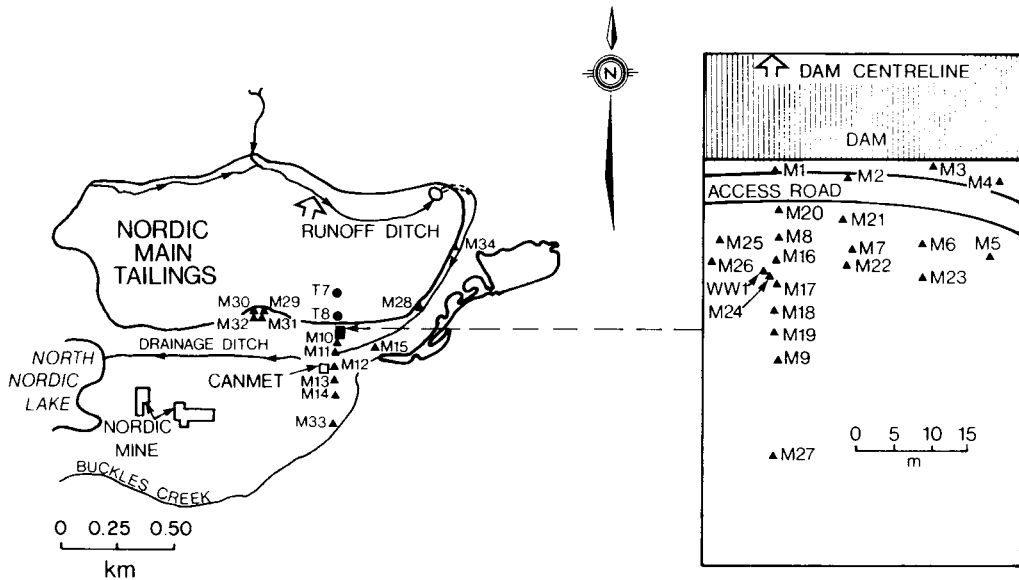


FIG. 7. Locations of bundle piezometers in the aquifer and piezometer nests in the tailings near the dam.

sedimentary deposit. A thin pebble lag lies on top of the bedrock surface and the till lies in depressions of the bedrock surface. Neither the till nor the bedrock were penetrated with the hollow-stem augers.

Physical hydrogeology

Blair *et al.* (1980) indicate that the hydraulic conductivities of the upper and lower sands are approximately

10^{-4} and 10^{-5} m/s, respectively. These values are based on permeameter tests of disturbed samples and on a pumping test made in the aquifer beneath the West Arm tailings about 1.5 km west of the plume area.

Grain-size distributions can be used to calculate hydraulic conductivities. Four empirical methods for this calculation are summarized by Freeze and Cherry (1979, pp. 350–351). We used the results of Masch and

TABLE 1. Summary of results of chemical analyses of groundwater from the plume

Parameter	Laboratory*	Range in the plume (ppm unless marked)
Fe	1	80–5390
Ca	1	47–500
Mg	1	13–519
Na	1	2.6–51
K	1	1.6–127
Mn	1	1.0–49
Cu	1	<0.01–0.04
Co	1	<0.01–4.90
Zn	1	<0.01–1.00
Pb	1	< 0.1–4
Ni	1	< 0.1–4.1
Al	1	< 0.1–187
SO ₄	2	305–12 900
SiO ₂	2	9.1–74.1
PO ₄	2	<1.0
Alkalinity (as HCO ₃)	3	6–906
pH	3	4.3–6.8 pH units
Eh	3	+110 to +410 mV
Specific conductance	3	1000–10 000 μS
²²⁶ Ra	4 and 6	4–162 pCi/L
²¹⁰ Pb	5	<10–110 pCi/L
²²⁸ Th	6	<0.5–9.7 pCi/L
²³⁰ Th	6	<0.5–6.2 pCi/L
²³² Th	6	<0.5–1.7 pCi/L
U	6	<0.2–520 μg/L

*1—Chemistry Laboratory, Research and Development, Rio Algom Ltd., Elliot Lake, Ont.; 2—Geochemistry Laboratory, University of Waterloo, Waterloo, Ont.; 3—field measurement by Kevin Morin; 4—laboratory measurement by Tjoe Lim; 5—CANMET, Ottawa, Ont.; 6—MONENCO Analytical Laboratories, Calgary, Alta.

Denny (1966), because their method uses a range of grain sizes rather than one grain size. It is therefore more sensitive to characteristics of the entire grain-size distribution.

Six grain-size distributions were measured in samples from the plume area: four samples of the upper sand and two samples of the lower sand. Arithmetic-mean hydraulic conductivities for the upper and lower sands from the Masch and Denny methods were about 1.2×10^{-4} and 5.3×10^{-5} m/s, respectively. These values agree well with the values from Blair *et al.* (1980), especially for the upper sand.

The elevation of the water table (Fig. 9) at each bundle was considered to be the water level in the shallowest piezometer in the bundle. Because yearly fluctuations of the water table are less than 0.2 m, steady-state flow is a reasonable approximation of the flow conditions in the sand aquifer.

The southward gradient of the water table is about 0.050 near the dam, and decreases to about 0.005 approximately 20 m from the dam. The high gradient

near the dam is caused by the channeling of groundwater flow around the large bedrock outcrop in the dam (Fig. 6). Because the cross-sectional area of flow has decreased at the dam, flow continuity requires that the gradient increase. The gradient then decreases as the water passes the bedrock knob and the flowpaths diverge in a fan-shaped pattern.

Vertical components of the hydraulic gradients were calculated from measurements of head differences between each of the piezometers in a bundle. In the upper and lower sands, vertical gradients are less than 0.005 (the detection limit) and, thus, are probably not significant. However, there is a large head decrease of 0.1–0.2 m across the contact of the two sand layers, which causes local downward flux near the contact. The head decrease is probably caused by a thin, fine-grained bed between the sand layers.

The steady-state equation for calculating the average linear groundwater velocity is:

$$[1] \quad v = -Ki/n$$

where v = linear groundwater velocity, K = hydraulic conductivity, i = hydraulic gradient, and n = porosity.

Using the values presented above, the calculated groundwater velocities in the upper sand layer are about 1.7×10^{-5} m/s (about 525 m/year) near the dam and about 1.7×10^{-6} m/s (about 50 m/year) far from the dam. Because of the uncertainty in the hydraulic conductivity, the calculated velocity may be different

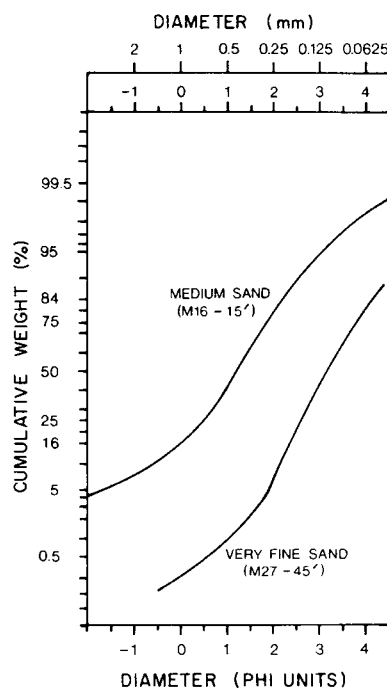


FIG. 8. Typical grain-size distributions for the sand aquifer.

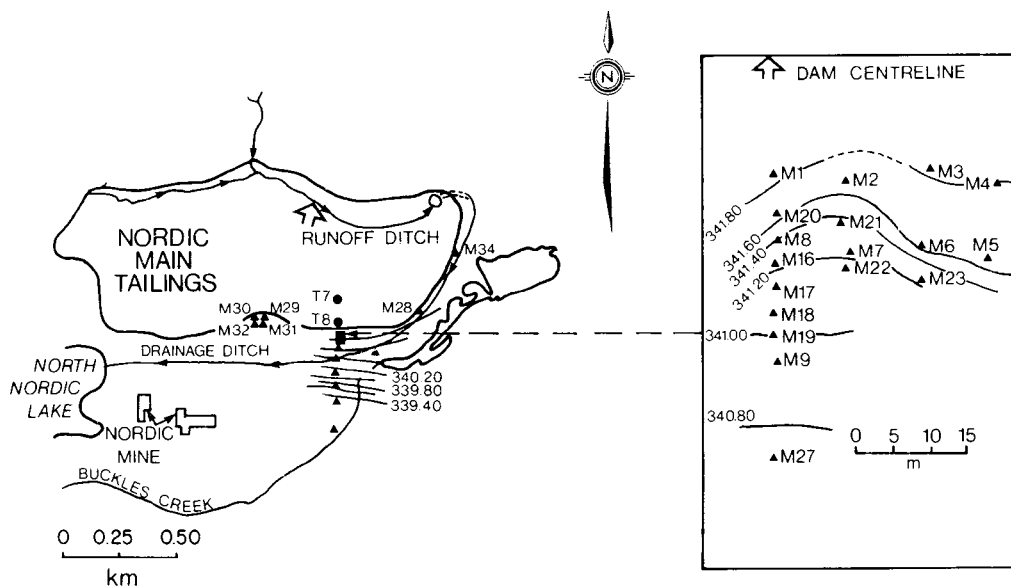


FIG. 9. Water table in the plume area (metres above sea level); contour interval is 0.2 m.

from the actual velocity by a factor of 2 or more. Therefore, the velocity near the dam is probably between 250 and 1000 m/year, with velocities in the middle part of the range being more probable. These calculated velocities agree well with the velocities given by Blair *et al.* (1980), whose calculations were based on 1979 gradients, an estimated porosity, and hydraulic conductivities from permeameter tests.

Chemical hydrogeology

Water chemistry and plume movement

Some results of the chemical analyses are presented in Figs. 4b, 5b, 10, 11 and Table 1. All piezometers were sampled for pH. Only three or four piezometers in each bundle were sampled for complete chemical analysis, with the sample points chosen from below, within, and above the plume. This sampling pattern was also used by Blair *et al.* (1980).

Figures 4, 10, and 11 show that there are two major zones to the plume, the inner core and the outer zone. The inner core and outer zone are arbitrarily defined by ion concentrations and are separated by a neutralization zone, in which concentrations decrease from inner-core levels to outer-zone levels. The neutralization zone will be discussed in a later section. The inner core extends about 15 m from the base of the dam and contains the highest contaminant concentrations. The pH of the water in the inner core is between 4.3 and 5.0; specific conductance between 10 000 and 6000 μS ; iron between 5390 and 3000 ppm; sulfate between 12 900 and 8000 ppm; radium-226 between 126 and 30 pCi/L; total thorium between 8.0 and 0.5 (detection level) pCi/L. Lead-210 varies from 110 pCi/L at the base of the dam to below detection (10 pCi/L) a few metres from the dam

and uranium varies from 520 $\mu\text{g/L}$ to about detection level (0.2 $\mu\text{g/L}$).

The outer zone surrounds the inner core near the dam and extends several hundred metres southward. The outer zone generally has a pH between 5.7 and 6.8. Specific conductance ranges from 5000 to 1000 μS ; iron from 3000 to 80 ppm; and sulfate from 8000 to 305 ppm. Radium-226 is less than 15 pCi/L; total thorium less than 0.5 pCi/L; lead-210 less than 10 pCi/L; and uranium less than 0.2 $\mu\text{g/L}$.

Several metres south of M14 (Fig. 7), the glaciofluvial sand terminates laterally against a cobbly, sandy till. Attempts to auger into and instrument the till were unsuccessful and therefore the southern extent of the outer zone is not well defined. However, M33 was installed about 120 m south of M14 and about 5 m east of a very large bedrock outcrop (Fig. 3). The piezometer is located in a small, 2-m-thick sand deposit, which is probably fill material underlain by bedrock. Water analyses from M33 indicate that only recently infiltrated precipitation is flowing through the sand. Therefore, if the plume exists as far south as M33, it is flowing through the till that is farther east of this site.

It was not possible for Blair *et al.* (1980) to determine the rate of advance of the inner core, because they had data from one field season only and did not know the source area in the tailings from which the low-pH water was emanating. A possible source area of the low-pH water was located in 1980, approximately 100 m north of the dam (site T7 in Figs. 6 and 7) or 130 m north of the present front of the inner core. The areal extent of the low-pH input area is not known. An average yearly velocity for the inner core can be obtained by dividing 130 m by the number of years since the low-pH water

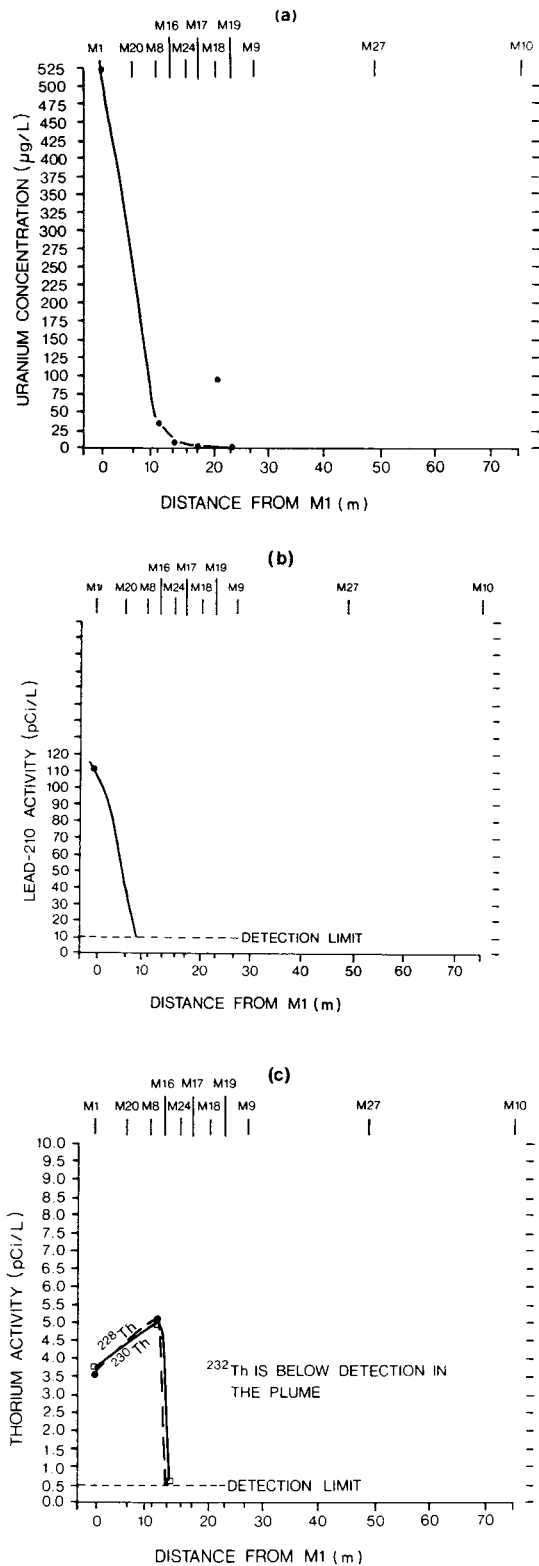
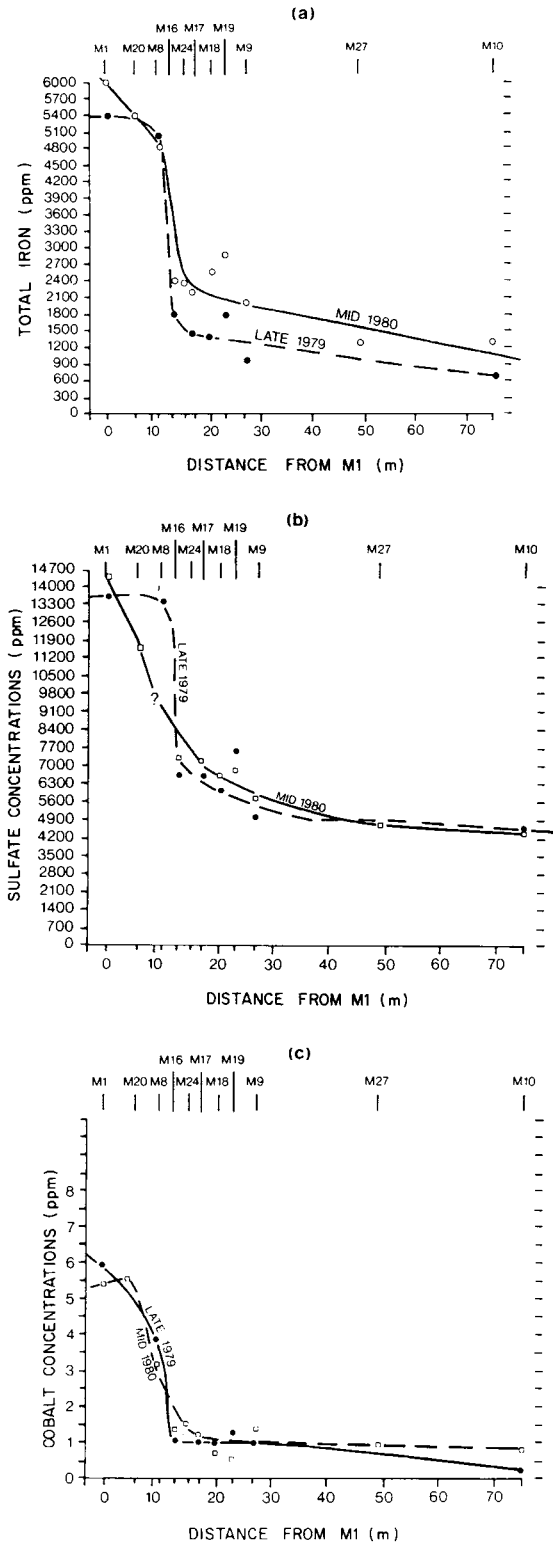


FIG. 10. Concentrations in 1979 and 1980 along a centreline extending southward through the plume: (a) iron; (b) sulfate; (c) cobalt. The centreline passes through the lowest pH sample point at each bundle.

FIG. 11. Concentrations in mid-1980 along a centreline extending southward through the plume: (a) uranium; (b) lead-210; (c) thorium.

first entered the aquifer. Because the tailings were drained in 1970, a time-span of 10 years will be assumed, although it may have taken a few years before the tailings produced acidic water. Thus, the minimum average velocity of the inner core over the 10-year span is about 13 m/year.

The rate of advance of the inner core for 1979–1980 can be found by examining Figs. 4, 5, and 10a. This observed velocity is about 2–5 m/year. Preliminary results for 1981 indicate that the velocity is about 2–3 m/year. The discrepancy between the calculated and the observed velocities can be accounted for by a higher velocity in the past as the inner core was moving beneath the tailings toward the dam. This higher velocity could have been caused by larger gradients within and beneath the impoundment as the tailings were initially draining.

The important observation is that the inner core is moving about 1% of the groundwater velocity. The reason for this retardation of the inner core relative to the groundwater velocity is discussed below.

Solid-phase geochemistry

The volumetric mineralogic composition of the upper sand is about 80% quartz, 10% magnetite, and 10% light mafics. The composition of the lower sand is about 85% quartz, 5% magnetite, and 10% light mafics. These minerals are relatively stable, so significant dissolution of the grains and accompanying changes in porosity and permeability are not a concern in this study.

Blair *et al.* (1980) attributed the retardation of the inner-core advance to chemical buffering by solid-phase carbonate such as calcite (CaCO_3) in the aquifer. Three sand samples analyzed by Blair *et al.* for percent-carbonate mineral content gave values from 0.008 to 0.14%. Thus it is reasonable to expect that the front of the low-pH inner core is neutralized as it advances and therefore the movement of the low-pH front is retarded with respect to the groundwater velocity.

In the 1980 field season, 25 auger-flight and split-spoon samples were taken from within or near the plume. Observation under a binocular microscope ($4\times$ magnification) of the carbonate dissolution in HCl revealed the presence of carbonate as a surface coating on the sand grains. The calcium carbonate was probably chemically precipitated onto the grains under past climatic conditions. However, carbonate mineral grains may also exist in the sand.

Carbonate analysis was performed in the Geochemistry Laboratory of the University of Waterloo, using the gas-chromatography method of trace-carbonate analysis. Detection level of the analysis was 0.002 wt% and, based on three duplicates, accuracy was within 3% of the given value. However, because the sand samples were exposed to the atmosphere during sampling and

preparation, it is expected that all of the iron in the pore water precipitated as $\text{Fe}(\text{OH})_3$, which, in turn, produced H^+ . The iron precipitate probably encapsulated and prevented dissolution of some carbonate as the acidity dissolved some or all of the unencapsulated calcite before analysis was performed. For example, precipitation of iron concentrations of about 2000 ppm (outer-zone concentrations near the dam) can consume up to 0.2 wt% carbonate. Thus, analyzed samples containing greater than a few tenths of 1 wt% carbonate indicate that H^+ from iron precipitation upon sampling has removed only a relatively minor amount of carbonate. However, samples found to contain a few tenths of 1 wt% or less indicated one or both of the following: either the original carbonate content equals the amount removed by iron precipitation plus the amount found through analysis, or the original carbonate content was actually low and was completely or partially encapsulated during iron precipitation. Because the method of carbonate analysis did not distinguish between excess carbonate and encapsulated carbonate, analyses yielding less than a few tenths of 1 wt% were not used for calculations of average values presented later.

Carbonate is below detection in the inner core and, because of the low pH, has probably been totally removed by dissolution. Measured carbonate in the upper sand, in contact with outer-zone waters, is below 0.2 wt%, which possibly indicates dissolution by pore-water oxidation upon sampling, by neutralization of slightly acidic water, or by acid rain (pH = 3.4–4.0 in this area). In the lower sand, there are four deep samples with values above 0.2%, averaging about 0.9 wt% carbonate. Because iron levels are relatively low and the pH is high at the depths from which the samples were taken, probably less than 0.1 wt% has been dissolved by iron precipitation upon sampling. The actual content of the upper sand is assumed to be close to this value, at least a few tenths of 1 wt%.

A split-spoon core of the sand aquifer was taken from a location about 5 m west of M8. The sand samples were analyzed for soil pH, total iron, total sulfur, sulfate/sulfide ratio, radium-226, uranium, lead-210, and loss-on-ignition. Some of the results are shown in Fig. 12 and will be discussed in the next section. However, soil pH is important here, because it supports the above observation that the lower sand has a noticeable carbonate content whereas the inner core has none, as shown by the higher soil pH at depth.

Interactions of solid and liquid phases

The key to understanding the behavior of the plume and, in particular, the relationship of the inner core to the outer zone lies in the chemical interactions of the groundwater with the solid matrix of the sand aquifer. Our purpose in this section is to present a geochemical

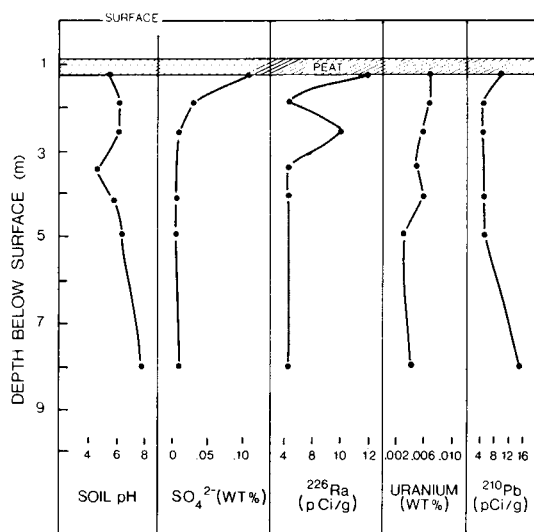
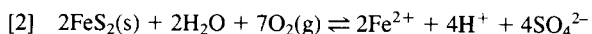


FIG. 12. Results of solid-phase chemical analyses of a core from borehole 5 m west of M8.

hypothesis to account for the observed hydrochemical patterns in the aquifer. The geochemical processes that occur in the tailings are described by Blair *et al.* (1980) and Cherry *et al.* (1980a).

When the neutralized process water drains from a tailings impoundment, oxygen and infiltrating precipitation begin to oxidize the pyrite at shallow depth in the tailings. The oxidation process involves several reaction steps, but the overall result can be expressed as:

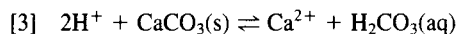


Pyrite oxidation continuously provides high concentrations of sulfate, iron, and hydrogen ions to the pore water. Because the solubility of some compounds increases and the adsorptive capacity of most solids for cations decreases as the pH drops from neutral to acidic values (Leckie and James 1974; Davis and Leckie 1978) and because H^+ displaces other cations as the pH decreases, a decline in pH causes the release of radionuclides and heavy metals from the tailings solids into the groundwater. As long as the pH remains low, these contaminant ions remain in solution; if the pH rises, they are again adsorbed onto the solids. Thus, it is expected that the chemical composition of the water that drains from the tailings into the aquifer is, for many chemical species, controlled by the pH of the groundwater. Because pyrite oxidation has probably occurred continuously in the tailings since the late 1960s and because the direction of groundwater flow is generally downward and through the tailings into the aquifer, acidic water from the tailings began many years ago to enter the aquifer in some parts of the tailings area.

For convenience, in the following description of

geochemical processes in the aquifer the contaminated groundwater from the tailings is considered to travel along streamtubes in the aquifer. The streamtubes consist of a line of connected cells or pore volumes, in which various chemical reactions occur as the water advances.

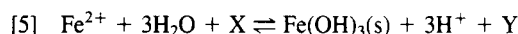
When the low-pH water first enters a cell, it is neutralized by dissolution of calcium carbonate.



As the pH rises iron is removed from solution by precipitation of iron compounds. Two iron compounds that are most likely precipitated are siderite (FeCO_3), which forms with Fe^{2+} , and iron hydroxide ($\text{Fe}(\text{OH})_3$), which forms with Fe^{3+} . These precipitation reactions can be expressed as,

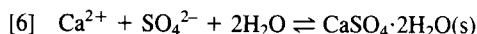


and



where X and Y are redox species that provide the necessary electron transfer for the change in valence state of iron. Equation [5] is an acid-releasing reaction. If it occurs in the presence of CaCO_3 , more CaCO_3 is dissolved. It is likely that the precipitation of iron hydroxide is a minor process in the aquifer. Because the pe of the water does not change significantly and because only minimal quantities of oxidizing species such as O_2 and NO_3^- exist in the plume, it appears that little Fe^{2+} is oxidized to Fe^{3+} . Thus, we conclude that most of the iron that is removed from solution as the pH rises does so by siderite precipitation. The pH and redox-potential measurements plotted on the stability-field diagram shown in Fig. 13 indicate that FeCO_3 is a thermodynamically stable mineral phase under the hydrogeochemical conditions that exist in the inner core and in the neutralization zone of the plume.

Because sulfate concentrations are high in the water as it enters the aquifer and because the water in the tailings is at or very near saturation with respect to gypsum, the calcium ions released from calcite (eq. [3]) probably cause the solubility of gypsum to be exceeded, thereby initiating gypsum precipitation,



As the low-pH water continuously enters the aquifer cell and is neutralized, all of the calcium carbonate in the cell is eventually dissolved and when this occurs the pH in the cell remains low. The low-pH water then advances to the next cell, where neutralization and the accompanying reactions described above begin again. In the cells where the calcite is consumed, thereby permitting a low-pH condition to exist, some of the previously

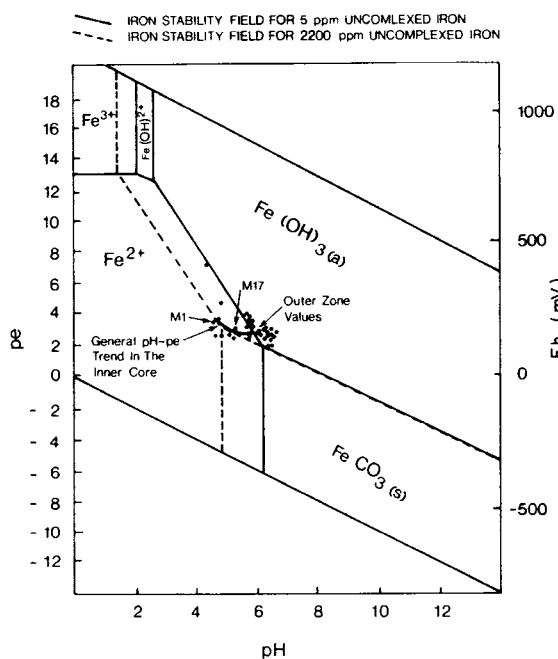


FIG. 13. Stability diagram for the iron system (CO_2 pressure = 0.1 atm (10 kPa) and 25°C) with results of field measurements of pH and pe in the plume.

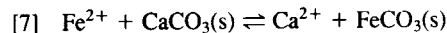
precipitated siderite or iron hydroxide probably redissolves in response to the low pH of the water.

To determine whether the hydrogeochemical model is consistent with the observed features of the plume and with the available information on the solid-phase composition of the aquifer, cell calculations with a mass-balance approach will be used. A 1-m^3 block of the upper sand is taken as the cell size. The porosity of the sand is 36% and so 0.36 m^3 (360 L) of the block contains groundwater and 0.64 m^3 contains sand. Because the specific gravity of the upper sand is 2.98, there is about $1.91 \times 10^6\text{ g}$ of sand in the 1-m^3 block. The original carbonate content of the upper sand is not known, but was probably a few tenths of 1 wt%. For the following calculations, the original carbonate content of the upper sand is assumed to be equal to the original content of the lower sand of about 0.9 wt%. Thus the cell contains $1.60 \times 10^4\text{ g}$ (160 mol) of calcium carbonate.

By [3], 160 mol of CaCO_3 will neutralize 320 mol of H^+ ions. Because the initial pH of the inner core is about 4.5, then 360 L (1 pore volume) contains about 0.011 mol of H^+ ions. Therefore, if there were no iron precipitation, 1 m^3 of sand would neutralize about 29 000 pore volumes of inner-core groundwater or, in other words, the inner-core velocity would be about 1/29 000 (about 0.003%) of the groundwater velocity.

However, as the calcium carbonate dissolves to neutralize the pH, the solubility product of siderite is exceeded and it precipitates. The only major source of

carbonate in the aquifer is the solid-phase carbonate and the effect of siderite precipitation is to consume 1 mol of calcite for every mole of iron precipitated.



As shown in Fig. 10a, there is a loss of about 2500 ppm of iron along the length of the neutralization zone (i.e., from M8 to M17, which is about 6 m) or, in other words, there is a loss of about 420 ppm of iron per metre of neutralization zone. When applied to the aquifer cell concept, this represents a loss of 2.6 mol of aqueous iron and, thus, of calcite per cubic metre of aquifer. Consumption of calcite by iron precipitation therefore exceeds consumption by pH neutralization by more than two orders of magnitude.

If the precipitated siderite dissolved, it would neutralize the groundwater in the same manner as does calcite dissolution. However, the inner core and neutralization zone are supersaturated with respect to siderite and are undersaturated with respect to calcite, according to preliminary results from the computer model for chemical equilibrium, WATEQF (Plummer *et al.* 1976). Thus only calcite can dissolve. The result is that, when the calcite is converted to siderite, little capacity remains for neutralization of the solution. Thus, the inner core moves faster than would be the case if siderite also contributed appreciably to the neutralization capacity.

Total consumption of calcite is 2.61 mol per cubic metre of aquifer. When this consumption is considered in all cells in the neutralization zone, an inner-core velocity of about 1/11 (about 9%) of the groundwater velocity is obtained. Although this result is based on the carbonate content of the lower sand, the carbonate content of the upper sand is probably close to the same value and, thus, would yield a similar velocity. This calculated retardation factor is close to the retardation factor obtained by comparison of the 1979 and 1980 data.

In addition to the general agreement of the calculated and actual retardation factors, the chemical model is consistent with other data obtained in 1980. For example, the evidence for iron precipitation, especially as siderite, is as follows. First, Fig. 10a indicates that iron is disappearing from solution along the flowpath, especially in the neutralization area. Second, the pH-pe-iron stability diagram (Fig. 13) shows that the trend of pH and pe (or Eh) in the inner core is controlled by decreasing iron concentrations, i.e., as uncomplexed iron decreases, the Fe^{2+} - $\text{FeCO}_3(\text{s})$ and the Fe^{2+} - $\text{Fe}(\text{OH})_3$ stability lines shift towards the right with the measured pH and redox values in the inner core following that shift. Third, as mentioned above, WATEQF calculations indicate that the water is supersaturated with respect to siderite and thus is capable of precipitating siderite.

The concentrations of radium-226, cobalt, uranium, lead-210, and thorium are shown in Figs. 5, 10c, and 11a,b, and c, respectively. The rapid decrease of concentrations near the neutralization zone is the result of adsorption and, possibly, coprecipitation. The relative importance of adsorption and coprecipitation to radium and uranium is discussed below in terms of a partitioning coefficient. This partitioning coefficient is the ratio of the concentration on or within the solid matrix to the concentration in solution. The coefficient is usually pH-dependent and soil-type-dependent. If coprecipitation is the more dominant process in the removal of ions from the water, partitioning coefficients for the plume will be much larger than experimental values for simple adsorption.

For calculation of partitioning coefficients, the solution concentrations were taken from M8, where the pH was about 4.5 in the inner core and about 6.2 below the inner core. Solid-phase concentrations were taken from sand-sample analyses (Fig. 12) from the site 5 m west of M8. The water chemistry at the site is similar to that at M8, but water analyses for radionuclides were not performed.

Concentrations of radium-226 (Fig. 5b) decrease rapidly as the pH (Fig. 4) rises above 6.0, between M16 and M17. The partitioning coefficient for radium-226 in the inner core, calculated from values in Figs. 5 and 12, is about 70 mL/g. This value agrees well with the value of about 80 mL/g calculated from an equilibrium constant by Lester *et al.* (1975). Unfortunately, these researchers did not give the pH and soil type used to determine this and other adsorption values, so the comparison with their values may not be very useful. The plume coefficient also agrees well with radium-226 coefficients of about 60 mL/g, measured at the University of Waterloo, in sand columns with a near-neutral pH (W. S. Clarke, personal communication, 1981). Therefore, radium appears to be controlled, at least in the inner core, primarily by adsorption and not coprecipitation.

Heavy metals, such as cobalt (Fig. 10c), decrease significantly in concentration between M20 and M16. In this region, iron (Fig. 10a), aluminum, and sulfate (Fig. 10b) concentrations also decrease sharply. Therefore, heavy metals are probably being adsorbed onto, or coprecipitating with, freshly precipitated iron compounds, aluminum hydroxide, and gypsum. No solid-phase data are available to calculate partitioning coefficients for these metals.

Uranium (Fig. 11a) is relatively high at M1 and very low at M8. Two uranium partitioning coefficients were calculated for the plume. The first, about 2000 mL/g, is for the inner core. The second, about 3600 mL/g, is for the zone below the inner core. These values agree well with the value of 2300 mL/g derived from Lester *et al.*

(1975). Thus uranium in the plume appears to be controlled primarily by adsorption.

Lead-210 (Fig 11b) shows the same trend as uranium. However, no partitioning coefficients could be calculated, because of the lack of data on the liquid-phase concentration and the total-lead concentrations in the solid phase.

Thorium (Fig. 11c) shows a trend similar to cobalt. No partitioning coefficients could be calculated, because of the lack of solid-phase data. As with the trace metals, adsorption or coprecipitation may be controlling thorium in the plume.

Although the geochemical hypothesis presented above is consistent with the main chemical features of the zone of contamination in the aquifer and with the results of mass balance calculations, many of the detailed aspects of the plume behavior have not yet been defined. More detailed investigations will be necessary in order to provide for a reliable methodology for prediction of subsurface contaminant migration from inactive tailings in the Elliot Lake region. Although many of the tailings areas in this region rest on fractured bedrock rather than unconsolidated deposits such as the Nordic tailings, an understanding of contaminant behavior in unconsolidated deposits should serve as a preliminary aid when considering the more complex and less monitorable conditions in the bedrock.

In the next phase of this investigation, additional field monitoring will be done so that more accurate rates of advance of the inner core will be obtained. Field tracer tests for groundwater velocity will be performed and cores will be collected for detailed solid-phase analyses and permeability tests. The ultimate objective of the investigation is to develop a model for simulation of the hydrogeochemical processes within the migrating zone of contaminated groundwater.

Summary of conclusions

The stratigraphy of the Nordic Main study area consists of a uranium tailings impoundment, which is underlain by a glaciofluvial sand deposit, which, in turn, is underlain by till and bedrock. The upper part of the sand deposit is a medium sand; the lower part, a very fine sand.

Pyrite oxidization in the Nordic Main tailings produces high-iron, high-sulfate, low-pH groundwater. The low-pH condition in the water causes the release of radionuclides and heavy metals from tailings solids. In part of the southeastern segment of the tailings, the acidic, contaminant-laden water is flowing downward through the tailings into the glaciofluvial sand.

This has resulted in a contaminant plume that extends southward beyond the dam near the southeast corner of the impoundment dam. The most contaminated water, the inner core, has a pH of less than 5.0 and has

relatively high concentrations of some major ions, heavy metals, and radionuclides. Comparison of 1979 and 1980 data indicates that the inner core is moving at a small fraction of the groundwater velocity. This retardation is the result of pH neutralization by dissolution of calcium carbonate. As the pH is raised towards neutral values by calcite dissolution, gypsum and an iron compound, probably siderite, precipitate. Thus, in the neutralization zone, iron and sulfate decrease significantly. Mass-balance calculations show that some of the neutralization capacity of the sand is removed by siderite precipitation, allowing the inner core to move significantly faster than would be predicted by simple pH neutralization.

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