Field Investigation of a Small-Diameter, Cylindrical, Contaminated Ground-Water Plume Emanating from a Pyritic Uranium-Tailings Impoundment


ABSTRACT: As part of a larger study on the geochemical behavior and computer simulation of subsurface seepage from pyritic tailings impoundments, a detailed field study of such seepage has been conducted. At the field site, the tailings lie over a glaciofluvial sand aquifer. Near the southeastern corner of the tailings, acidic contaminated water (pH 4) seeps through the base of the tailings into the sand aquifer and flows laterally to the south as a distinct, roughly cylindrical plume. This plume contains up to 6000 ppm iron, up to 14,000 ppm sulfate (SO₄), and elevated levels of other contaminants. The acidic seepage eventually encounters carbonate minerals in the aquifer, pH is then neutralized, and contaminants are attenuated through chemical precipitation, co-precipitation, and adsorption over a distance of several meters. At the edge of the impoundment, the ground-water plume has a cross-sectional area of about 3 m². Although the cross-sectional area suggests the plume is rather unimportant, the ground-water velocity is about 440 m/year, resulting in a laterally flux of more than 10⁷ L of contaminant laden water each year. The multiple level bundle piezometers installed to define this small diameter plume are described and the installation techniques used to minimize disturbance of the plume are also addressed. Each bundle contains up to twelve individual piezometers with a vertical screen spacing of as small as 0.5 m. Horizontal distance between bundles is as small as 2.5 m.

The high total dissolved solids (TDS) water in the plume presents many problems for field and laboratory geochemical measurements. High partial pressures of carbon dioxide (CO₂) in the water result in acidification and subsequent pH fluctuation upon sampling. Because of the high degree of temperature-sensitive aqueous complexing in the water, temperature variations can affect pH measurements. Mixing of air with the water initiates iron oxidation. To acidify and stabilize a water sample, 30 mL of concentrated hydrochloric acid (HCl) must be added to each litre of sample, lowering the pH to about 1.5. Laboratory analysis of these samples often requires significant dilution, and the addition of neutral pH and alkaline reagents to the sample causes ferrous hydroxide precipitation and subsequent instrument clogging. Techniques are described to circumvent many of these problems and collect reliable physical and chemical hydrogeologic data on this site.

KEY WORDS: ground water, water contamination, piezometers, water sampling, uranium tailings

In order to define the physical and chemical hydrogeology in and around uranium-tailings impoundments, the Institute for Groundwater Research at the University of Waterloo initiated field studies in the Elliot Lake uranium district of Ontario. The main field site was the pyritic Nordic Main impoundment (Figs. 1 and 2), which lies on a glaciofluvial sand aquifer (Fig. 1). An initial ground-water survey in 1978 indicated acidic, contaminated seepage was entering the aquifer and flowing southward in the region labeled "Seepage Area A" on Fig. 2 (1). Beginning in 1979, Area A was instrumented with piezometers and a roughly cylindrical, acidic plume of small diameter was defined near the impoundment dam. Through an iterative approach, the seepage area was further instrumented and monitored until late 1984. This temporal and spatial monitoring, in addition to information from other tailings sites, allowed the definition of contaminant migration, the delineation of processes controlling contaminant concentrations, the formation of a general conceptual model of behavior, and the computer simulation of past, present, and future migration (1-7).

Because of the unusual nature of the seepage—for example there are several thousands of ppm iron at neutral pH—installation and monitoring were carefully defined and implemented while emphasis was placed on relatively low-cost materials. Through an iterative approach, the techniques were modified until good-quality data were obtained.

This paper presents the requirements identified at the site for installation and monitoring, the techniques employed to fulfill the requirements, and the rationale for the techniques. Also briefly presented are techniques used for monitoring the tailings.

Piezometer Design and Installation

Because the plume has a cross-sectional area of about 3 m² near the impoundment dam in Seepage Area A, a closely spaced three-dimensional network of piezometers was required.
Fig. 2—Nordic Main tailings impoundment area. Contours in the tailings indicate depth to water table in meters.

Additionally, short screens and small diameters were desired in order to obtain depth-specific samples and minimize standing water in the pipe. Consequently, multilevel bundle piezometers were chosen (Fig. 4) [8]. The bundle piezometers at the field site, marked "M" on Fig. 5, consist of up to twelve individual minipiezometers, terminating at different depths, attached to a polyvinyl chloride (PVC) centerpipe for support. The limit of twelve is the consequence of the inside diameter (approximately 8 cm) of the hollow-stem augers discussed below. Each individual minipiezometer in a bundle consists of flexible 0.9-cm-inside-diameter polyethylene tubing with a 10-cm-long, 0.9-cm-inside-diameter polyethylene screen at the base. The screen was made by plugging the end of the tube and drilling holes through the polyethylene tube. The perforated tube was then wrapped in synthetic screen material; initial screen wrap was probably nylon while later wrap was polyethylene. The base of the PVC centerpipe was similarly plugged, drilled, and wrapped. The screens, tubing, and PVC pipe were brought to the field site unassembled.

The glacial-fluvial sand in Seepage Area A is cohesionless below the water table, at a depth of about 1 to 3 m. As a result, retrieval of a relatively undisturbed sample was extremely difficult (See later section on solid sampling). In order to provide a stable opening for the installation of piezometers, either casing or hollow-stem augers were required. Because the sand was capable of flowing upward into either of these alternatives and nearly filling them within several seconds, a bottom plug was required. The faster method of hollow-stem augers was chosen and a laboratory-grade rubber stopper plugged the bottom of the augers. A long narrow metal plate was attached across the face of the stopper and held in place with a stainless-steel bolt through the center of
the stopper (Fig. 4) in order to prevent it from moving up into the augers during drilling. Rotation of the augers was minimized so that minimal disturbance of the sand occurred. During augering, the depth of each minipiezometer was decided with vertical spacings ranging from 0.5 to 3 m, the materials assembled, and the tubing attached to the PVC centerpipe with nylon-reinforced tape. When the desired total depth of the centerpipe was reached, the bundle was inserted into the center of the auger string. As the string was pulled upwards by a cable and winch, the bundle was repeatedly slammed down onto the stopper until the stopper popped out. The augers were then pulled up around the bundle and the sand quickly and tightly collapsed around the piezometers. No sand-crack packs and seals were required. Because no foreign fluids were used for augering, typical well development was not necessary.

A PVC well of about 4 cm diameter and 6 m length was installed at WW1 (Fig. 5). The lower 3 m of well was screened with a slot size of about dₚ of the sand. Installation techniques were those used for the bundle piezometers.

Collection of Physical Hydrogeologic Data

Bundle piezometer installations were allowed to stabilize for at least one week prior to data collection. Because the sand collapsed tightly around the bundles, no open hydraulic connections were likely created along piezometer pipes between various levels in the aquifer. This conclusion is supported by water chemistry (below) which shows differences in certain locations over a vertical distance of 0.5 m. Physical, as well as chemical, data are compiled in Refs 2 and 5.

Water levels were measured with a narrow coaxial cable attached to a meter, buzzer, or light. Water levels indicated that flow in the sand was essentially horizontal toward the south with a westward component of flow as water flowed around the bedrock outcrop (Fig. 5). This information was essential for determining the position of flow lines (line C-C' on Fig. 5) along which chemical changes and contaminant migration could be followed. Finite-element simulation and sensitivity study of flow along the vertical cross section of C-C' were performed [5].

Hydraulic conductivity of the sand was measured by several techniques. A pump test was performed 1.5 km to the west of Seepage Area A, yielding $K = 1.4 \times 10^{-4}$ m/s; recovery of an observation well yielded $1.2 \times 10^{-4}$ m/s, and permeameter tests on disturbed samples from Area A yielded $2.1 \times 10^{-4}$ m/s for the upper portion of the sand where the plume is located [1]. In order to obtain an undisturbed conductivity, a borehole dilution test was performed to obtain an undisturbed velocity from which conductivity was calculated using measured gradients and porosities.

The borehole dilution apparatus (Fig. 6) employed a double packer assembly which was used to isolate a 0.3-m section of piezometer WW1. The circulation tubing was of small diameter and short length to minimize the volume in the circuit. The intended injection solution was distilled water, but it was believed this would not provide a sufficient electrical conductivity contrast. As a result, a concentrated sodium chloride (NaCl) solution was injected. The resulting flow of the test [5] indicated a velocity of $1.4 \times 10^{-3}$ m/s (440 m/yr) which led to a hydraulic conductivity of $1.0 \times 10^{-4}$ m/s in excellent agreement with other values. The velocity measurement indicated that, although the plume cross section is only about 3 m², the plume represents a volume flow of more than $10^4$ L of water each year.

Grain-size analyses of the sand were also used to calculate hydraulic conductivities by the method of Musch and Denny [91], which includes $d_{50}$, $d_{10}$, $d_{30}$, and $d_{90}$ in the calculation. The mean of four analyses was $1.2 \times 10^{-4}$ m/s.

Collection of Chemical Hydrogeologic Data

There appears to be no artificial vertical hydraulic connection created in the aquifer by piezometer installation based on observed sand collapse and sharp changes in chemical concentrations between
vertically adjacent screens. Measured chemical parameters and observed ranges of concentrations in Seepage Area A are listed in Table 1. Detailed data are compiled in Refs. 2 and 5.

The general approach for collecting data followed the recommendations of Environment Canada (19). Environment Canada recommendations are partially based on those of the U.S. Environmental Protection Agency.

Because the water levels in piezometers located in Seepage Area A are within 3 m of the surface, water was pumped directly from the piezometers by simply attaching a pump to the top of the pipe. In this way, the piezometers also represented dedicated sampling tubing, thereby minimizing cross-contamination of samples.

Contamination of water samples by the pump mechanism and atmosphere was minimized by the use of a peristaltic pump. The pump was connected to the piezometer top through silicone tubing and polyethylene connectors. In most cases, an airtight seal was obtained at the piezometer top and the ground water thus remained isolated from the atmosphere as it passed through the piezometer screen, tubing, and pump.

Duration of pumping and pumping rate from any one piezometer in a bundle was minimized so that (1) degassing by vacuum of the high CO2 levels was minimized and (2) water was not drawn from a higher or lower level in the aquifer; otherwise the sample would not be representative of conditions at the pumped piezometer. In past years, this effect was noted during pH measurements after 10 to 15 min at a pumping rate of about 0.5 L/min. The lowering of the water table around a bundle has also been noted when shallow piezometers are pumped (David and Lim, personal communication). As a general rule, no piezometer in Area A was pumped for more than 10 min at 0.5 L/min, resulting in the removal of 5 to 40 piezometer volumes, depending on the depth of the screen. Because pH values occasionally required more than 5 min to stabilize during pumping, the field study was broken into two independent tasks: collection of pH and other data, and collection of water samples.

Field pH was measured by continuously directing pumped water into a covered 150-mL container ("flow cell") containing a combination pH electrode which was inserted through a hole in the cover (Fig. 4). Water passed from the flow cell by flowing through an opening or exit tube in the cover. In this way, water in the flow cell was constantly being replaced and refreshed, and CO2 degassing and atmospheric disturbances of pH measurements were minimized. The flow cell was kept in a water bath, consisting of the water that continuously flowed from the cell, to minimize effects of temperature fluctuation on pH measurement. Temperature fluctuations were usually less than 3°C.

The pH probe and meter were calibrated in nominal pH 7 and pH 4 buffers, which were replaced at least once every 24 h and were kept in the water bath. Buffers at ground-water temperatures minimize temperature-equilibration time of electrodes. At ground-water temperatures, the pH 7 buffer was about 7.06 and that of the pH 4 buffer about 4.00. For the first day of measurements in each field season, the pH meter was calibrated with buffers about once an hour. After the stability of the equipment was established, calibration checks were made about once every 2 to 5 h. Calibration checks often did not deviate by more than 0.04 pH units from the buffer value. In one extreme case, the pH 7.06 buffer read 7.18 after five pH measurements and 30 min time; the meter was readjusted to 7.06 and the pH 4.00 buffer then read 4.00. This indicated the preceding
five ground-water pH values could probably be adjusted by a constant value (~0.12 pH units in this case) rather than a pH-dependent value (see Ref 11 for further discussion of pH meter behavior) although it was not clear when the shift of 0.12 units occurred over the 30 min. For all pH measurements, water was pumped at a rate of about 0.5 L/min through the flow cell until a drift of less than 0.02 pH units/min was noted and the value was then recorded as field pH. Approximately 5 min of pumping was often required before the pH stabilized. The pH probe and cell were rinsed with distilled water between each measurement.

Eh was measured with a combination platinum electrode having a 1.3-cm² platinum button. The electrode was standardized with Zobell's solution and inserted into the flow cell with the pH electrode. The reliability of the resulting Eh measurements was evaluated following the suggestions in Ref 12.

Electrical conductivity of the water was measured by taking a sample of about 100 mL in a small container after pH and Eh had been recorded. Because the cell constant of the conductivity cell varied through the field study, the cell constant was measured at each bundle with potassium chloride (KCl) standards. Conductivity was later corrected to 25°C and recorded in $\mu$S/cm. However, because conductivity measurements are insensitive to neutral-charge aqueous complexes and because up to half of the aqueous ions in the plume water exist as neutral complexes, electrical conductivity was not considered a reliable quantitative parameter in this study.

The second phase of the field study, which began after all pH, Eh, and conductivity measurements had been taken, involved water sampling and field alkalinity titrations. Fifty to 100 piezometers were selected each year for water sampling and subsequent laboratory analysis. Water was pumped via a peristaltic pump through a 142-mm disk filter assembly, similar to that described in Ref 13, containing 0.45-μm nitrocellulose filter paper. New filter paper was used for each sample, and adsorption of metals onto the filter following initial flushing was considered negligible when compared with concentrations (Table 1). After pumping the piezometer for a few minutes and after flushing the system with about 1 L of ground water to wet and stabilize the filter and to rinse the sample container, the filtered water was directed into a 4-L polyethylene container. After collection the sample was acidified with 30 mL concentrated HCl/L of sample, lowering the pH of the sample to about 1.5. This relatively large volume of acid was required to stabilize the high concentrations and to overcome SO₄, HSO₄, pH buffering around pH 2. This volume also highlights the weakness of procedures which specify a volume of acid/L sample (for example, 2 mL (10)). HCl was chosen over the other acids because (1) its strength minimized acid addition, (2) other acids would cause supersaturation and mineral precipitation by anion addition, and (3) HCl minimized artificial redox reactions in the sample. A separate, acidified 100 mL sample was collected for chloride analysis only, because chloride is not significantly adsorbed by many precipitated minerals above pH 2. The filter assembly was rinsed with distilled water and a new filter was installed before the next sample was taken.

While the water was filling a sample container, a smaller container was rinsed with distilled water, rinsed with filtered ground water, and then filled with about 50 mL of ground water. This water was titrated for alkalinity using standardized HCl. Hydrochloric acid was again used for the same aforementioned reasons. Although alkalinity is not wholly attributed to HCO₃⁻, measured dissolved inorganic carbon (DIC) in Area A waters compared well with calculated DIC by assuming the concentration of HCO₃⁻ was equal to alkalinity [5]. Samples for DIC analysis were collected directly from pump tubing in glass syringes. The tips of the syringes were sealed immediately and returned to the laboratory for analysis. Reagents were added directly to the syringes and the resulting gas was directly injected into gas-chromatography equipment. In this way, atmospheric contamination was minimized.

In 1984, five of the 50 sampled piezometers were selected for replicate sampling. Because over 10 L of ground water had to be pumped from each of these five piezometers, water quality was expected to change during sampling as water moved from a higher to lower elevation in the aquifer into the screen. This problem had two major implications. First, because representative water may not be obtained and the plume could be disturbed, only nonstratigraphic piezometers were chosen. Second, because water quality could change during pumping, once large sample had to be taken and homogenized before splitting into replicates; otherwise comparison of "replicate" analysis could be invalid. Therefore, the following technique was used for each of the five piezometers. A 15-L plastic bucket was rinsed with distilled water, rinsed with diluted HCl (pH 1), rinsed with distilled water, shaken dry, and covered with a sheet of thick styrofoam. Tygon tubing carried water from the filter assembly into the bucket through a hole in the styrofoam. As the water was filling the bucket, the bucket was occasionally agitated to assist in mixing of water, and concentrated HCl was added (30 mL HCl/L water). When the bucket was filled, it was gently agitated, then the water was poured into seven 4-L polyethylene collapsible containers approximately 1 L at a time. The containers were marked with various piezometer numbers so that all appeared as an integral part of the sampling program from different locations. Sample distribution for the seven containers was three to the main analytical laboratory and two each to two other laboratories. Table 2 contains the letter requesting analysis to each of the laboratories, following the recommendations in Ref 14.

As a general indicator of variation in water quality during pumping of the large 15-L sample, two alkalinity titrations were made during pumping—at the beginning and the end. For the three samples with pH > 5 (alkalinity > 30 ppm HCO₃⁻), variation in alkalinity was less than 10% within analytical accuracy; for the two samples with pH < 5 (alkalinity < 30 ppm HCO₃⁻), variation was between 20 and 25%, which is considered the general limit of accuracy at low concentrations. This indicates that there was probably no major variation in water quality during pumping. Nevertheless, the 15-L sample was homogenized before partitioning. Results of this data quality study are given in Ref 2.

Most samples were delivered to the laboratory within 48 h of sampling and were stored at ambient temperature in the laboratory.

TABLE 2—Letter requesting analyses.

| Sample | Ca, Mg, K, Na | Fe, Mn, Co, Zn, Ni, Pb | SiO₂ | SO₄ | CI | NH₄ | NO₂ | Total uranium | Total thorium | Radium-226 | Please enclose with the results of analyses a brief description of the method used to analyze each species (one or two sentences only), the frequency of calibration for each method, and the precision for each method. | Send results and details on methods to: | Kevin Morin | Morijk Enterprises |
|--------|--------------|------------------------|------|-----|----|-----|-----|---------------|--------------|------------|------------------------------------------------------------------------------------------------|-----------------------------|-------------------|
Laboratory Analysis, Data Quality, and Speciation

Chemical analysis of Seepage Area A waters was found to be difficult. High concentrations of iron and sulfate and elevated levels of other metals produced interferences. Analysis of anions by column-exchange methods was problematic, because dissolution through the addition of pH-neutral reagents initiated iron precipitation, which subsequently coated the resin. Thus, iron had to be removed before analysis. Because of the high levels of sulfate, sulfate was often analyzed by gravimetric methods, probably accounting for the relatively high observed analytical error.

The reliability of overall analysis was evaluated through cation-anion balances:

\[
\text{Error} = \frac{|(\text{CAT} - \text{AN}) - 0.5(\text{CAT} + \text{AN})|}{\text{AN}} \times 100\%
\]

where CAT is the sum of cations in equivalents per litre and AN the sum of anions in equivalents per litre.

Mean errors for 1980, 1982, and 1984 were +7.98%, +1.10%, and +6.18%, respectively. However, because iron and sulfate are dominant in concentrations, the error is sensitive only to the reliability of their analysis. In order to assess the accuracy and precision of all aqueous constituents, the 1984 study included replicate sampling described in the previous section [2].

Water analyses indicated that significant geochemical processes were operating as the plume water flowed southward from the tailings impoundment. Most contaminant concentrations decreased and pH increased along the flowpath defined by water level data (see earlier section on collection of hydrogeologic data). Because chemical precipitation-dissolution, including pH-neutralizing carbonate-mineral dissolution, was the likely cause of change, water analyses were speculated [15]. The speculation program, WATEQ2 [16], was used for this study and saturation indices calculated by WATEQ2 indicated which minerals were likely involved in precipitation-dissolution.

Solid Sampling

Because saturation indices indicated that mineral precipitation-dissolution was probably occurring, undisturbed-unoxidized solid samples were required for analysis. Because mass balance calculations indicated that most reactive minerals would be at concentrations of less than 1 weight %, detection limits of most current methods did not allow identification of reactive minerals [17].

Initial disturbed sand samples for grain-size analysis and thin-section examination were obtained from auger flights. Iron-staining on these samples indicated aqueous iron had oxidized and precipitated, thereby creating acidity which could dissolve up to 0.2 weight % of the calcite identified in thin-section examination and through the method of Barker and Chaten [18]. Also, iron oxidation suggested that the minor amount of siderite expected to occur probably oxidized to ferric hydroxide [17]. Therefore, attempts were made to obtain an undisturbed sample and maintain its isolation from the atmosphere.

Standard split-spoon sampling failed because the cohesionless sand would flow upward into the hollow-stem augers whenever the centerpole was pulled. A split-spoon sample could not be taken from inside the augers because the sampler could jam within the augers. A variation on the standard method, employing the rubber stopper described earlier, failed because sand flowed into the augers upon popping the stopper and, on the first and only attempt, nearly jammed the sampler below the base of the augers.

Other methods were tried. A steel plug with a swing gate was placed on the base of the augers. According to theory, as augering proceeded, the gate remained closed and no sand entered the augers. When desired depth was reached, a sampler was lowered from the surface which completely covered the gate aperture. The auger string was then turned slightly in the reverse direction, causing the gate to open, and sand theoretically flowed into the sampler. This method failed because the coarse matrix sheared the gate off during augering. Driving of long (6 m) thin-walled aluminum pipe with various sample catchers at the base failed because the cohesionless sand would flow past the sample catchers.

In despair, this driving of long pipe was continued without sample catchers until some of the cored sand jammed inside the pipe on one occasion. This core was sealed tightly, returned for analysis, and opened in a nitrogen-filled glove box. Because most relevant analytical methods required long periods of time for preparation or special preparation techniques, thereby allowing sample oxidation, rapid X-ray diffraction scans of the sand were made [3,17]. Results were inconclusive because of low concentrations.

Tailings Installations

Installation and monitoring techniques employed in the tailings were similar to those for the sand aquifer [4,19]. However, because of the low hydraulic conductivity, small grain size, and deep water table at some locations, the piezometers were standard open-standpipe PVC rather than multi-level bundles. Screens were of a nonstandard design: perforated PVC wrapped with Vyon (registered trademark of Povair Ltd., United Kingdom, also known as Sinterpore), which is made of polyethylene, has a 50-μm pore size to prevent tailings from entering the piezometer, and has a relatively high conductivity to allow rapid water influx and single-well response tests. The base of the screen was tapered (Fig. 7) to allow percussion driving of the piezometers into the tailings.

Water sampling from the piezometers involved small-diameter polyethylene tubing and a peristaltic pump [19]. Where the water table was less than 7 m deep, a steady low volume of water was pumped into the flow cell (see earlier section on collection of hydrogeologic data) and

---

**Figure 7**—Vyon piezometer point.
sample container. Where the water table was deeper, the polyethylene tubing was used as a bailer by turning the pump on high speed, lowering the tubing to the base of the piezometer, allowing the water to rise as high as possible in the tubing, then pulling the tubing to the surface. This method minimized contact with the atmosphere. Downhole syringe sampling was also used, but offered no significant advantage [19]. As with solid sampling in Seepage Area A, tailings were sampled with long, thin-walled aluminum pipe which was driven into the peat layer beneath the tailings, thereby plugging the pipe and allowing sample recovery.

Summary

The presence of a cylindrical ground-water plume of small diameter in acidic tailings seepage required a detailed monitoring network consisting of multilevel bundles composed of up to twelve minipiezometers in each bundle. Vertical spacing between adjacent screens in a bundle was as small as 0.5 m and horizontal spacing between bundles was as small as 2.5 m. Installation techniques were designed to minimize the physical and chemical disturbance of sand and plume.

The plume water is sensitive to many conditions, such as temperature variation, mixing with the atmosphere, and degassing of CO₂. Techniques to minimize these problems during data collection were discussed. Because of the large amount of pH buffering in the water, an unusually large amount of acid was added to samples for proper stabilization. Laboratory analysis of water was difficult because of the addition of pH-neutral reagents, which initiated chemical precipitation, which in turn plugged equipment. Also, less-accurate analytical methods were sometimes substituted to avoid machine problems.

Collection of undisturbed sand samples was difficult. The driving of long, thin-walled aluminum pipe eventually provided a sample.

Techniques for and problems with the tailings were similar. Piezometer screens included a Vyon cover to prevent tailings from entering the piezometer.

Acknowledgments

Funds for this study were provided by the Natural Science and Engineering Research Council (Canada) Strategic Grant G0679, The Department of Energy, Mines, and Resources (Canada), Rio Algom Ltd., the Institute for Groundwater Research, and Morwijk Enterprises.

References


