

SOCIETY OF MINING ENGINEERS OF AIME

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Morin
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82-114



CHEMICAL COMPOSITION AND GEOCHEMICAL BEHAVIOR OF CONTAMINATED GROUNDWATER AT URANIUM TAILINGS IMPOUNDMENTS

John A. Cherry

University of Waterloo
Waterloo, Ontario, Canada

Thomas A. Shepherd

Water, Waste & Land, Inc.
Fort Collins, Colorado

Kevin A. Morin

University of Waterloo
Waterloo, Ontario, Canada

For presentation at the SME-AIME Annual Meeting
Dallas, Texas - February 14-18, 1982

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Abstract. Groundwater monitoring conducted at an acidic uranium-tailings impoundment in Wyoming and at one in Ontario indicate that at these unlined impoundments situated on unconfined sand aquifers, there exist well-developed plumes of contaminated groundwater. In the literature similar results are reported for three other unconfined aquifers at mill sites in Wyoming. The plumes extend for distances of several hundred to a few thousand metres from the impoundments. They have a zone of low pH beneath and adjacent to the impoundments and a larger zone of near-neutral pH that extends to the outer limits of the plume. The low-pH zones are generally small compared to the neutral-pH zones because the advance rate of the fronts of acidic tailings-derived water is slower than the average velocity of groundwater which controls the advance of the high pH zone. The retardation of the acid fronts is a result of geochemical reactions that cause hydrogen-ion consumption in a slowly-advancing neutralization zone.

Within each of the plumes, the low-pH zone has high concentrations of transition metals, heavy metals and radionuclides. In the neutral-pH zones all of the metals and radionuclides occur at significantly lower concentrations and are generally at levels much below those specified in national drinking water standards. An exception at two of the Wyoming sites is uranium, which exists at levels close to the drinking water limit. A second exception is ferrous iron at the Ontario site, which occurs at high concentrations throughout most of the plume. The carbonate alkalinity at this site is much lower than at the Wyoming sites.

The field data indicate that even in very permeable aquifers with a low content of silt and clay, there is normally a considerable capacity for acid-front retardation. To take advantage of this capacity to control contaminant movement in the design, operation and decommissioning of tailings impoundments, it is necessary to be able to predict the rate of acid-front movement. This predictive task has two primary components. The first is to identify the important flow paths from the tailings through the groundwater system and the second is to determine the degree of acid-front retardation that will occur as the tailings-derived water moves along these flow paths. Relative to these two tasks determination of the effects of hydrodynamic dispersion is generally of lesser importance and simple approximations that do not involve field or laboratory tests are probably adequate.

In order to effectively apply the acid neutralization concept to the prediction of subsurface contaminant migration at uranium-mill tailings, improved representations of hydrogeochemical behavior of iron and aluminum in the neutralization zone and of the consumption of hydrogen ions through reactions with carbonate and aluminum-silicate minerals are required. Along with the hydrogen ions contained in the tailings water the ferrous iron represents a large potential source of acid but the extent to which ferrous iron converts to ferric iron to produce acid is problematic. Detailed hydrogeochemical evaluation of existing contaminant plumes and the performance of laboratory experiments under appropriate redox conditions are prerequisites for the improvement of

predictive models. However, the existing field and laboratory data provide a basis for preliminary predictions of contaminant migration from acidic uranium tailings impoundments.

Introduction

In the past few years subsurface migration of contaminants from uranium-mill tailings impoundments has become an issue of specific concern to nuclear and environmental regulatory agencies in the United States and Canada. To meet the needs of licensing procedures for new tailings impoundments or for the continued use of existing tailings impoundments, field and laboratory investigations of the movement and attenuation of tailings-derived contaminants in groundwater at various impoundments have been completed or are now in progress. Studies are also being conducted at inactive tailings impoundments to determine the impact on groundwater that has already occurred and to aid in the preparation of remedial-action plans. It has only been during the past few years that much of the hydrologic and geochemical information from these studies has become available.

The purpose of this paper is to provide a brief description of the hydrogeochemical characteristics of zones of contaminated groundwater at tailings impoundments located on permeable deposits and to outline the main geochemical processes that are known to be or suspected to be major influences on the behavior of contaminants in these zones. Only impoundments that have received tailings from acid-leach mills are considered. The ultimate goal of our investigations is the development of improved models for prediction of the migration of tailings-derived contaminants in permeable zones. The data that are available at present, while preliminary, provide insight into the nature of the hydrogeochemical systems that cause subsurface attenuation of the various radioactive and non-radioactive constituents.

Although the subsurface behavior of contaminants from uranium-tailings impoundments has some similarities to the behavior of contaminants from other types of waste disposal systems, the degree of importance of several of the hydrogeochemical processes are sufficiently different to warrant the development of conceptual models that are specific to the system. The most distinctive characteristics of seepage from acid-leach, uranium-tailings impoundments are the extremely low pH and the high ferrous iron concentrations of the water. The subsurface behavior of these two parameters is the focus of the discussions presented herein.

This paper is based primarily on studies of a tailings impoundment in south central Wyoming, which we conducted in cooperation with other investigators in 1979-1980 and on investigations that are being conducted at an inactive tailings impoundment in the Elliot Lake area of north-eastern Ontario. Preliminary results of the Elliot Lake investigations have been described by Blair et al. (1980) and Morin et al. (1982). Information from these studies has been supplemented by field and laboratory data obtained from published and unpublished reports and papers pertaining to other tailings disposal areas in Wyoming.

Hydrochemistry of Tailings Water

Analyses of water discharged with tailings solids from acid-leach mills in the western United States are shown in Table 1. Also shown in this table is a representative analysis for pore water in Elliot Lake tailings that have become acidified as a result of the oxidation of pyrite (FeS_2). The tailings in the mills in the Elliot Lake uranium district are neutralized with lime and limestone prior to discharge to the impoundments. However, over a period of years or decades pyrite oxidation in the near-surface tailings zone causes acidification to the extent that in most of the old tailings impoundments, much of the pore water has a pH below 3 or 4 and high concentrations of iron, aluminum, heavy metals and radionuclides. The nature of the subsurface contaminant-migration problem in the Elliot Lake district therefore has similarities with problems in the southwestern United States. The hydrogeochemical processes in inactive tailings impoundments in the Elliot Lake district are described by Blair et al. (1980), Cherry et al. (1980) and Feenstra et al. (1981).

The data for Wyoming tailings listed in Table 1 show a consistency in pH (1.8-2) and variability of most elemental concentrations. Without exception, however, the tailings waters have high concentrations of SO_4 , Fe, Al and moderate concentrations of Ca, Mg and Si. Concentrations of many heavy metals, transition metals, As and Se and radionuclides are generally above the drinking water limits but vary considerably from site to site, presumably because of variability of ore chemistry. Chloride is also variable and depends on the milling procedure, however, it is generally less than 500 mg/L. It is apparent from Table 1 that numerous elements in acidic tailings water are much above drinking water standards and therefore there are numerous elements of interest with regard to the potential for contaminant migration in groundwater flow systems.

It should be noted that, for convenience, drinking water limits are used throughout for comparative purposes. In most tailings disposal environments drinking water limits are not an appropriate standard by which to judge the impact of the tailings-derived contaminants on the local groundwater and surface water.

Field Observations

Of interest in this paper are the results of groundwater monitoring at acid-leach uranium mills with tailings impoundments on unconfined aquifers. These sites are conducive to the development of zones of contaminated groundwater. They therefore represent the most likely situations for adverse impact on groundwater and surface-water resources. From sites for which groundwater data are available, we have selected those that have been monitored in sufficient detail to provide adequate information on the spatial distributions of contaminant plumes and in particular on the distribution of the zones of acidic and neutral water within the plumes.

Four of the tailings disposal sites are located in south central or central Wyoming (sites 1, 2, 3 and 4). Site 5 is located in the

Elliot Lake uranium district in northeastern Ontario.

South Central Wyoming

Groundwater investigations were conducted at site 1 in south central Wyoming in 1979-1980. Site 2 was monitored in 1980 and 1981 by Hoffman and Playton (1981). The general hydrogeochemical characteristics of these two sites are represented in Figures 1 and 2. Neither of the impoundments has outlets for surface flow and therefore the only losses of water originating as mill effluent and rain and snowmelt are by way of evaporation or seepage into the groundwater zone. Other information on the tailings impoundments is summarized in Table 2. Each of the tailings impoundments rests on a thin unconfined aquifer of alluvial origin. Seepage from the bottom of the impoundments has entered the aquifers and travelled laterally in the direction of the water-table slope. At each of the sites the areal extent of the zone of contamination in the aquifer was determined by the sulfate concentrations or the electrical conductance of the groundwater.

The areal extent of the plume of contaminated groundwater at site 1 is displayed in Figure 3. In the most permeable part of the sand aquifer, the contaminated zone extends a distance of approximately 1000 m from the tailings dam. This zone has high concentrations of SO_4 , Cl, HCO_3 , Na, Ca and Mg.

The pH of the groundwater at the site is generally between 6.5 and 7.5 (Figure 3) except for a small area close to the central segment of the tailings dam where the pH drops to 6. The pH of the water in the tailings impoundment is in the range of 1.7 to 1.9. The near-neutral pH zone within the contaminant plume is devoid of hazardous concentrations of all toxic metals, toxic non-metals and radionuclides. This indicates that geochemical processes within the aquifers beneath the tailings impoundments and close to the tailings dam have caused removal of nearly all of the hazardous elements that occur in the low-pH tailings water. The neutral part of the plume is not more noxious with respect to inorganic contaminants considered in a drinking water context than the common variety of plume that emanates from municipal landfills (Cherry et al. 1981, Nicholson et al. 1982). It should be noted that the shallow aquifers at each of the sites described in this paper are not used as sources of drinking water.

At site 1 the only groundwater zone with pH levels that are significantly below background (<6.5) extends about 100 m from the base of the tailings dam. The pH in this area is in the range of 5.5 to 6.5. No pH values below 5.5 were detected in any of the monitoring wells even in the wells beneath the tailings dam. We expect that very low-pH water exists in the upper part of the aquifer immediately beneath the tailings pond, however this cannot be confirmed because no monitoring wells exist in this zone. The zone of slightly depressed pH that protrudes from beneath the dam is referred to as the core of the contaminant plume. The core and the neutral-pH zone beyond the core has very high total-dissolved solids and high concentrations of SO_4 , Cl and Na. The concentrations of K, Ca, Mg

and HCO_3 are also well above background in the plume. Of the non-radioactive elements that have maximum permissible limits in drinking water standards, only F and Se occur at levels above the limits in the core of the plume near the dam. High Se concentrations were detected in only one monitoring well. Of the radioactive elements, only ^{226}Ra was reported at levels above the drinking water limit. The reliability of the radium and selenium analyses is in question and the possible occurrence of high radium in the plume remains to be evaluated by additional analyses. The concentrations of Fe and Mn in the core are above background levels but are very low relative to the acidic tailings water.

At site 2 a plume of contaminated groundwater extends at least 300 m from the tailings dam. The outer limit of the plume has not yet been delineated because difficulties caused by complexities in the topography and stratigraphy. A more extensive area in the upper aquifer than that shown in Figure 2 contains tailings-derived seepage. In most of this area, characterised by high SO_4 concentrations (Figure 2), the pH of the groundwater is below 4 or 5. The most extensive occurrence of low pH-high SO_4 water occurs to the northwest of the tailings impoundment. In this area the concentrations of Fe, NH and Ca are very high. In the low-pH core of the plume several transition metals and heavy metals also occur at very high concentrations. In the neutral-pH part of the plume, however, they are below the drinking water limits. The relationships between pH and concentrations for Al, Fe, Mn, Cd, Cr, Pb, Ni and Zn are shown in Figure 4. The radionuclides ^{226}Ra , ^{230}Th , and to a lesser extent ^{210}Pb were also found to be high in the low-pH zone. Mercury, CN, Ag and phenol occurred at extremely low or non-detectable concentrations in all parts of the plume.

The main identified differences between the conditions at sites 1 and 2 are the lengths of time during which tailings seepage has entered the aquifers and the apparent average groundwater velocity in the aquifers. Seepage of tailings water into the aquifer began in 1976 at site 1 and in 1962 at site 2. At site 1 the estimated average groundwater velocity is approximately 50 to 200 m/yr whereas at site 2 it is about 1100 to 1800 m/yr in the northwestern plume segment (Hoffman and Playton, 1981).

Central Wyoming

The distributions of contaminants and the related hydrogeochemical interpretations for site 3 in central Wyoming are described by D'Appolonia Consulting Engineers Incorporated (1977). Summaries of this investigation are presented by Taylor and Antommaria (1978) and Taylor (1980), in which emphasis is placed on the spatial distributions of pH, ^{226}Ra , U and As and on the results of laboratory tests for aquifer parameters and distribution coefficients. The results of a detailed investigation of site 4 are described briefly by Highland et al. (1981). The tailings impoundments at sites 3 and 4 have been in operation since 1958 and 1960, respectively. The impoundments have no surface outflow and therefore the tailings effluent and water input from rain and snow are lost from the impoundments by seepage and evaporation. The movement

of groundwater and contaminants at sites 3 and 4 have been simulated using numerical models by Haji-Djafari et al. (1979) and Highland et al. (1981), respectively.

The tailings impoundment at site 3 is situated on a thin deposit of aeolian sand and alluvial gravel that lies on a much thicker unit of slightly indurated sandstone (Figure 5). Beneath the sandstone there is an extensive layer of silty sandstone that appears to cause contaminants to occur primarily in the overlying part of the groundwater system even though the entire sequence of sedimentary deposits is a saturated continuum from the water table downward. The seepage of sedimentary deposits is situated in a granite bowl that opens towards the northwest and southwest. The seepage from the tailings impoundment has caused a water-table mound to form on the regional groundwater system within the sedimentary deposits. Groundwater flow radiates outward from the impoundment towards the northwest and southwest (Figure 5). Taylor and Antommario indicate that most of the lateral groundwater flow is through the sandstone, which has an average hydraulic conductivity of 1.5×10^{-2} cm/s. With an effective porosity of 35 per cent and water-table gradients presented by Haji-Djafari et al. (1979), the Darcy equation yields values of average linear groundwater velocity in the range of about 250 to 1000 m/yr. The highest values probably occur close to the tailings impoundment because the water-table slope is steepest in this area. The gradient gradually declines away from the impoundment as indicated by the water-table contours in Figure 5.

The zone of tailings-impacted groundwater extends about 1300 m to the northwest of the impoundment and about 2000 to 3000 m to the southwest. The zone of acidic groundwater, designated by the pH=4.5 contour line, extends only 300 m to the northwest and about 450 m to the southwest. The low-pH front has advanced at a rate that is about one-fifth to one-tenth of the average groundwater velocity in these directions. These reduced rates of acid front migration have been estimated from the information presented by Taylor and Antommario (1978) and Haji-Djafari et al. (1979). Figure 6 shows the distribution of pH, U, As, and ^{226}Ra at site 3.

At site 4, the seepage from the tailings pond enters a thin aquifer composed of alluvial sand and gravel and weathered sandstone. This aquifer has a perched water table. The aquifer is bounded on the bottom by a relatively impervious claystone (Figure 7). The aquifer becomes thinner towards the north and terminates at a distance of about 800 m from the tailings impoundment. In this area, groundwater discharges from the aquifer.

Highland et al. (1981) indicate that elevated SO_4 and Cl extends 650 m from the impoundment. In the most permeable zones in the aquifer the pH=5 contour occurs at a maximum distance of 250 m from the impoundment (Figure 7). Highland et al. state that a zone with a chemical composition essentially equivalent to the tailings liquor has progressed 65 m from the tailings pond. They indicate that although the zone of contamination occupies most of the perched aquifer

no contamination has been detected in the aquifer beneath the claystone.

Elliot Lake

Three active and five major inactive tailings impoundments exist in the Elliot Lake uranium mining district. Although the tailings were discharged from the mills in a neutralized condition, the oxidation of pyrite has caused much of the pore water in four of the inactive impoundments to become acidic. Pyrite oxidation occurs primarily within a metre of the surface of the tailings and the acidic water gradually moves downward through the tailings (Cherry et al. 1980; Feenstra et al. 1981). After a period of years or decades, acidic water in some areas reaches the bottom of the tailings. In some areas acidic water is now seeping into the underlying geological materials. One of the inactive tailings areas where this has occurred, designated as the Nordic Main tailings, is the focus of a detailed investigation of the movement of tailings-derived constituents in the groundwater zone. The results of early phases of this on-going investigation are described by Blair et al. (1980) and Morin et al. (1982).

The Nordic Main tailings impoundment is situated in a valley underlain by sand and gravel (Figure 8) of moderate to high permeability. In the southeastern part of the tailings area, an extensive zone of contaminated water protrudes laterally in the sand and gravel from beneath the dam (Figure 8). The extent of this zone is readily identified on the basis of high concentrations of iron and sulfate in the groundwater. At its maximum, the plume of tailings-impacted water extends to a distance of approximately 400 m from the dam. The core of the plume, defined as the zone in which the pH is less than 5, extends only about 15 to 20 m from the dam (Figure 9). Beyond the core most of the plume has pH values in the range of 6.0 to 7.0.

The chemical composition of the zone of contaminated groundwater at the Elliot Lake site was monitored in the fall of 1979 (Blair et al. 1980) and in the summers of 1980 (Morin et al. 1982) and 1981. The average groundwater velocity in the contaminated zone has been determined using the modified form of the Darcy equation and by borehole dilution tests. In the core of the plume the groundwater velocity is approximately 500 to 1000 m year. The front of the low pH core, however, is advancing at a rate of only a few metres per year (Figure 10). Therefore at this site there is both spatial and temporal evidence that the zone of low pH is strongly retarded relative to the rate of groundwater flow. The amount of retardation is on the order of 0.1 to 0.3 per cent of the groundwater flow rate.

The low pH-core is similar to the low pH zones at sites 2, 3 and 4 in Wyoming in that it contains high concentrations of metals and radionuclides. Beyond the low pH zone where the pH is >6, all radionuclides occur at much lower concentrations, as do all of the metals except iron. In the pH >6 zone the water chemistry has high sulfate concentrations and in this regard is similar to the Wyoming sites. It also has extremely high concentrations of iron, whereas the Wyoming sites have low iron values and much

higher levels of sodium and magnesium. The concentrations of ^{226}Ra in the pH >6 zone are generally in the range of 1-10 pCi/L compared to the Wyoming sites where the ^{226}Ra values are less than 5 pCi/L. Uranium in the pH >6 zone is less than 0.1 mg/L while at sites 1 and 3 in Wyoming uranium in the neutral-pH zones is generally between 0.5 and 5 mg/L. No uranium data has been reported for site 4.

Another difference between the neutral-pH zone at the Elliot Lake site and the neutral zones at the Wyoming sites is the acidity (hydrogen-ion producing potential) of the water. At the Wyoming sites, the acidity of the neutralized groundwater is represented primarily by the concentration of hydrogen ion in solution (i.e. the pH) and therefore is insignificant in the neutral pH zone. At the Elliot Lake site, however, the acidity is extremely high and is represented almost entirely by ferrous iron in solution. The ferrous-iron acidity is converted to acid only if Fe^{2+} is oxidized to Fe^{3+} , liberating H^+ in the process. Such a reaction can present an environmental hazard if seepage of the contaminated groundwater enters the oxidizing environments of streams or marshes. This oxidation process can cause a large decline in pH if the water has a low buffering capacity, which is the case in the Elliot Lake district where effects of the acid release from tailings drainage are under constant surveillance and mitigative action is common. In the Wyoming environment the seepage of neutral tailings-derived water into surface streams can have only very minor impact because no Fe^{2+} is present and the SO_4^{2-} , Cl^- and the other major cations that do occur in the water are not elements to which the stream ecology is normally very sensitive.

Geochemical Processes

In this section the hydrogeochemical processes that are considered to be an influence on the behavior of contaminants in groundwater at the five field areas are described. The processes have in general been deduced from evaluations of the contaminant distributions at the field sites in conjunction with mass-balance and equilibrium-geochemical considerations. The description of the hydrogeochemical processes represents the preliminary stage in the development of a thoroughly documented model for the behavior of acidic tailings seepage in permeable sandy deposits.

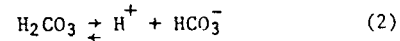
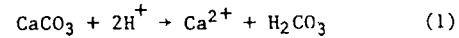
Without exception the hydrochemical data from the field sites indicates that in the low-pH cores of the plumes, the groundwater is severely contaminated with metals and radionuclides and that in the neutral-pH zones all metals and radionuclides occur at much lower concentrations, which are nearly always below the limits for drinking water. There is little doubt that pH is the primary factor in the hydrogeochemical behavior of the plumes and therefore the emphasis in the following discussion is on the sources and mechanisms for release of hydrogen ions and on the mechanisms for hydrogen ion consumption within the plumes.

The hydrogeochemical processes that are considered in the following discussions are listed in Table 3. Nearly all of the processes release

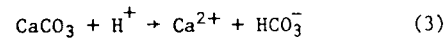
hydrogen ions from the tailings-derived acidity or consume hydrogen ions through the congruent dissolution of mineral or amorphous phases.

Calcite Dissolution

Numerous investigators have attributed the retardation of acid fronts at tailings impoundments primarily to the neutralization effect caused by the dissolution of calcite (Taylor and Antommario, 1978; Taylor, 1980; Blair et al. 1980; Shepherd and Cherry, 1980; Morin et al. 1982). This neutralization process can be represented as,



In the neutralization zones of the plumes, the pH rises from levels generally below 3 or 4 to levels that are above 5.5 or 6. As the pH rises an increasing percentage of the dissolved inorganic carbon in solution occurs as HCO_3^- rather than H_2CO_3 . If the pH rises above about 6.5, the overall neutralization process can be represented as



If the aquifer contains dolomite in addition to or instead of calcite, the neutralization process can be described by similar equations, with the addition of Mg^{2+} in a 1:1 stoichiometric ratio with Ca^{2+} .

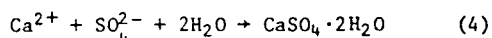
In the most simple representation of acid-front retardation in the groundwater zone, hydrogen ions are consumed by calcite dissolution as represented in Eq. 3. The retardation of the advance of the acid front is then defined as the number of pore volumes of water with a specified hydrogen-ion concentration that must pass through a representative volume of the porous medium in order to completely remove the total mass of calcite in the volume. In this conceptualization it is assumed that the rate of groundwater flow is slow relative to the rate of calcite dissolution and that the acid front advances by plug displacement. Spreading of the acid front by hydrodynamic dispersion is therefore neglected.

If the assumptions inherent in this conceptualization are valid, it follows that only a small weight percent of calcite is necessary to provide significant retardation of an advancing low-pH zone. For example a sand with a porosity of 33 per cent, an average solid-phase specific gravity of 2.6, and a calcite content of 1 per cent would neutralize 52 pore volumes of acid seepage with a pH of 2. If the calcite content is 0.1 per cent, 5.2 pore volumes will be neutralized and so on in direct proportion to the calcite content. In these calculations it is assumed that the initial pH is an exact measure of the total H^+ available for neutralization. Other important sources of H^+ are described below. Because at least a very small content of calcite and/or dolomite occurs in nearly all geologic units in the uranium mining districts in the western United States and in the glacial deposits in the Elliot Lake area, carbonate-mineral dissolution is a reasonable starting point in the development of concepts to account

for acid-front retardation.

Gypsum Precipitation

The dissolution of calcite releases Ca^{2+} to the groundwater (Eq. 3). Because tailings seepage is normally saturated with respect to gypsum, the Ca^{2+} addition causes precipitation of gypsum by the common-ion effect,



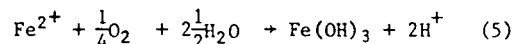
Gypsum is a mineral that precipitates readily from slightly supersaturated waters in porous media. The Ca^{2+} content of tailings liquor (Table 1), the Ca^{2+} content of the acidic pore water in Elliot Lake tailings (Cherry et al. 1980; Feenstra et al. 1981) and the Ca^{2+} content of the interior segments of the plumes at the field sites are almost invariably in the range of 400 to 600 mg/L. All of these waters have high SO_4^{2-} contents. This relative invariability of Ca^{2+} is considered to be caused by the solubility control of gypsum. Further, it is likely that gypsum precipitation is the only significant geochemical attenuation mechanism for SO_4^{2-} in the contaminant plumes.

Sulfate is not toxic in drinking water, however its presence in the plumes may be viewed with concern because it commonly exists throughout the plumes at concentration levels that are considerably above background levels. In some situations seepage of SO_4^{2-} -rich water into streams may cause deterioration in the ecological status of the stream. At high concentrations it could render the water unfit for consumption by livestock. The attenuation of SO_4^{2-} is therefore of some practical interest. In addition to the geochemical attenuation of SO_4^{2-} , hydrodynamic dispersion causes concentration decline by mixing. The effects of dispersion are described later in this paper.

In addition to the common-ion effect caused by calcite dissolution, gypsum precipitation is caused by the dissociation of aqueous complexes of ferrous iron and sulfate that occur when ferrous iron is removed from solution. In solutions that have high ferrous iron concentrations, much of the dissolved iron is present as $\text{FeSO}_4^0(\text{aq})$ and therefore the solubility of gypsum is much higher than in water with low ferrous-iron concentrations. This is evidenced by the fact that when gypsum is dissolved in pure water at 25°C, the equilibrium concentrations of total Ca^{2+} and SO_4^{2-} are only 440 and 1470 mg/L, respectively (Cherry, 1969). When it is dissolved in water with high concentrations of ferrous iron, the equilibrium SO_4^{2-} and Ca^{2+} concentrations are in the range of 10,000 to 15,000 mg/L. We attribute these extremely high levels to the greatly increased solubility of gypsum caused by the complexing of ferrous iron with sulfate. This interpretation is supported by the results of solubility calculations using an equilibrium geochemical program known as WATEQ 2 described by Ball et al. (1979). The geochemical attenuation of SO_4^{2-} is intimately associated with the attenuation of ferrous iron, which is discussed below. In the neutral portion of a plume which contains low concentrations of Fe^{2+} , SO_4^{2-} concentration would be expected to be in the range of 1500 to 4000 mg/L depending on the concentration of other major cations present.

Behavior of Iron

Although it is well established from the field investigations that much of the iron in the tailings seepage is removed from solution as neutralization occurs, the mechanism of removal is problematic. Taylor and Antommaria (1978) and Taylor (1980) invoke the precipitation of iron hydroxide as a major removal mechanism. They consider the occurrence of iron hydroxide to be important because of its considerable capability to scavenge metals and radionuclides from solution. The extent to which iron is removed by precipitation of ferric hydroxide is crucial in the developments of conceptualizations for the behavior of the hydrogeochemical system. This is the case because the precipitation reaction for iron hydroxide releases hydrogen ions,



which would be available for dissolution of carbonate or other mineral phases. If this occurs, the prediction of the acid neutralization must include the H^+ contributed from the formation of iron hydroxide as well as the initial H^+ indicated by the pH of the solution prior to oxidation.

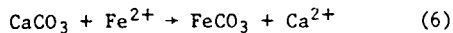
The iron concentrations in the tailings liquors represented in Table 1 can be used to obtain an indication of the relative magnitude of this potential source of H^+ . At the very low pH of the tailings water (i.e. pH=1.8-3), essentially all of the dissolved iron is ferrous iron. The concentrations in Table 1 range from 500 to 10,000 mg/L. For purposes of the following illustrative calculations, a representative value of 2000 mg/L (0.0358 mol/L) is used. If this iron is oxidized and precipitated as $\text{Fe}(\text{OH})_3$, and if the effects of H^+ buffering at low pH are neglected, 0.0716 mol/L of the H^+ will be released. If the pH of the water prior to oxidation is considerably above 2, the pH during oxidation will decline to the vicinity of 2 where buffering effects will moderate the tendency for further pH decline. In the absence of appreciable carbonate-mineral content even the precipitation of a minor portion of the total iron in tailings seepage with high iron concentrations can cause the pH to decline to the pH range between 2 and 3. The predictions of acid-front retardation are therefore dependent on predictions of iron behavior.

Although precipitation of iron hydroxide likely occurs in contaminant plumes at uranium tailings impoundments, mass-balance considerations impose a severe limitation on the total quantity of iron (II) that can be removed by this mechanism. The mass of iron (II) that can be removed depends on the availability of an oxidizing agent. Because of the geochemical nature of the tailings sites, the only significant oxidizing agent expected to occur in the plumes is oxygen. In situations where the groundwater zone (i.e. porous media saturated under positive pressure) is continuous from the tailings into the aquifer as is the case at the sites described in this paper, the only source of oxygen to the tailings seepage is from mixing with oxygenated uncontaminated water in the aquifer. Such mixing occurs by hydrodynamic dispersion. The availability of oxygen through dispersion is limited because of the low solubil-

ity of oxygen in water (≈ 10 mg/L). Water with 10 mg/L O_2 would only be capable of oxidizing 70 mg/L of Fe (II). This is a minor fraction of the total Fe (II) that occurs in the low-pH tailings water. Morin et al. (1982) used this line of reasoning to dismiss Fe (II) oxidation and ferric hydroxide precipitation as a major process in the contaminant plume at the Elliot Lake site.

In the first few weeks or months after the tailings impoundments began operation, a partially-saturated zone probably existed beneath most of the tailings impoundments. The gas phase in this partially-saturated zone may have initially contained considerable oxygen. However this gas phase would have been expelled as the front of tailings seepage moved downward or as the seepage through the partially-saturated zone raised the water table into the tailings. It is possible that the oxidation of ferrous iron occurred during this very early period of seepage. However, once the expulsion of the gas was complete or the gas-phase oxygen consumed, anoxic conditions would be established.

Morin et al. have suggested that in the neutralization zone, ferrous iron is removed from solution by the incongruent dissolution of calcite and formation of siderite ($FeCO_3$),



with most of the released Ca^{2+} being removed by precipitation of gypsum as described previously (Eq. 4). The precipitation of jarosite ($KFe_3(SO_4)_2 \cdot (OH)_6$) has also been invoked by some investigators as a mechanism for iron removal but this requires the conversion of Fe (II) to Fe (III) and therefore is limited in importance because of the mass-balance limitations described above.

Another mechanism that can cause removal of iron is cation exchange. As a divalent cation, ferrous iron may in some cases compete favorably in neutral solutions with major cations such as Na^+ , Ca^{2+} and Mg^{2+} for occupation of the exchange sites.

Ferrous iron could also be removed by the precipitation of iron sulfide (FeS_2). It is unlikely, however, that this is an important mechanism. There is no evidence indicating that the contaminant plumes are sufficiently reducing to cause the production of significant quantities of sulfide. Groundwater zones in which the reduction of sulfate to reduced sulfur species occur are normally those that contain organic matter as a reducing agent within microbiologically active zones (Freeze and Cherry, 1979).

Regardless of the mechanism of iron removal, the removal is only temporary. It occurs in the neutralization zone, which has neutral-pH water in front and low-pH water behind. The neutralization zone advances in the direction of groundwater flow at a rate that is retarded relative to the average groundwater velocity. Because the concentrations of nearly all of the toxic metals and radionuclides are directly related to the pH of the water, the rate of advance of the neutralization zone is the rate of advance of the front of very poor quality groundwater. As the neutralization zone advances, iron compounds such as siderite that formed in the neutralization zone are dissolved in the acidic water that follows

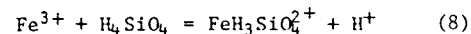
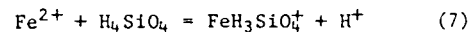
the neutralization zone. The dissolution of the siderite causes consumption of hydrogen ions in the same manner as calcite dissolution so that

it is still the total carbonate mineral content that provides for retardation of the acid front. If siderite rather than iron hydroxide forms, the acidity represented by the ferrous iron is not converted to acid. Only the H^+ concentration of tailings liquor or the H^+ from the hydrolysis of Al need to be consumed. If iron hydroxide forms, the total distance of acid front advance will be greater in a given time period.

A major hydrochemical difference between the Wyoming plumes and the Elliot Lake plume is the large differences in iron concentrations in the neutral-pH zones. In the pH >6 parts of the Wyoming plumes the iron concentrations are low, almost without exception less than 1 mg/L. In the Elliot Lake plume, the iron concentrations throughout most of the pH >6 part of the plume are in the hundreds to thousands of milligrams per litre range. At the Wyoming sites the pH throughout much of the neutral segments is slightly higher than in the Elliot Lake plume. The concentrations of dissolved inorganic carbon are also higher at the Wyoming sites. These two factors would tend to limit Fe (II) to lower concentrations because of lower solubility of siderite, however this explanation cannot be evaluated because of the lack of comparable field-determined redox and pH data for the various sites. At the Elliot Lake site where detailed field measurements of pH, redox potential and alkalinity were made, the high Fe (II) concentrations are consistent with siderite stability and solubility relations computed using equilibrium thermodynamic relations.

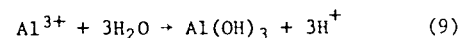
Behavior of Al and Si

Nearly all of the Al and Si contained in the acidic tailings water is removed in the neutralization zone by the precipitation of amorphous silica and gibbsite ($Al(OH)_3$), or aluminosilicate compounds. At pH levels below 10 the solubility of amorphous silica ($SiO_2(am)$) is not directly dependent on pH (Stumm and Morgan, 1970; Iler, 1979) and therefore the rise in pH alone would not cause precipitation of $SiO_4(am)$. The solubility is, however, dependent on the iron concentration because of the formation of ferric iron-silicic acid complexes,



The decline in concentrations of uncomplexed iron that occurs in the neutralization zone will cause an increase in the concentrations of uncomplexed silica, which would tend to cause the precipitation of amorphous silica in the neutralization zone.

The solubility of gibbsite declines by more than ten orders of magnitude from pH=2 to pH=6 (Lindsay, 1979) and therefore it is reasonable to expect that much of the Al is removed as a result of gibbsite precipitation in the neutralization zone,



Because this reaction is an acid producer, the aluminum acidity must be taken into account in considerations of the degree of retardation provided by the carbonate minerals. If large concentrations of Al are present in solution, this source of H^+ may be important. The concentrations of Al in solution at pH below 4 are probably controlled by the solubility of alunite ($KAl_3(SO_4)_2(OH)_6$), jurbanite ($Al(SO_4)(OH) \cdot 5H_2O$) or basealuminite ($Al_4(SO_4)(OH)_{10} \cdot 5H_2O$) which in the presence of sulfate are, generally less soluble than gibbsite (Nordstrom 1982). At some locations, the concentrations of Al and Si may be controlled by the precipitation of aluminosilicates, rather than the precipitation of amorphous silica and gibbsite. The first aluminosilicate to precipitate from most natural groundwaters is the x-ray-amorphous mineral, allophane (Paces, 1973). At the Elliot Lake site, the plume waters are consistently undersaturated with respect to amorphous silica and gibbsite, but are usually at saturation with respect to allophane.

Laboratory Investigations

To our knowledge the geochemical processes associated with the neutralization of acidic water passing through slightly calcareous porous geological media have yet to be elucidated in detail by means of laboratory experiments. However, the acid-front retardation effect has been demonstrated in the laboratory by Crim, Shepherd and Nelson (1979), Gee et al. (1980) and Shepherd and Martin (1980). In all reported laboratory investigations actual or prepared acid tailings solution were passed through soil columns under saturated flow conditions. In the experiments by Gee et al. and Crim, Shepherd and Nelson, the soils were natural clays representing proposed liner material. The soil samples tested by Shepherd and Martin were taken from potential tailings disposal sites to determine their contaminant retardation properties. The measured calcite concentrations of all samples were in the range of 0.02 to 0.4 weight percent. The pH of the tailings solutions used in the different experiments varied from 2.0 (Gee et al.) to 0.5 (Shepherd and Martin, and Crim, Shepherd and Nelson). As would be expected acid breakthrough for the column experiments varied depending upon the calcite content of the soil, pH of the influent tailings solution and other factors. From a pH 2 tailings solution passed through a clayey silt with calcite content of 0.04, weight percent, Gee reported acid breakthrough in 3 to 5 pore volumes and for an overburden soil with calcite content of 0.02 weight percent, 2 to 4 pore volumes. Shepherd and Martin tested three site soils with average calcite contents of 0.2, 0.3 and 0.4 weight percent respectively. Acid breakthrough using 0.5 pH influent tailings solution in columns packed with these soils came after the passage of 1.5, 3.7 and 17 pore volumes respectively.

Effluent chemistry was monitored in all experiments and showed the same effect of pH on contaminant concentrations. Transition and heavy metals and radionuclide concentrations remained low until the effluent pH began to fall below neutral levels. These results are consistent with the field observations described previously in this

paper for the Wyoming sites. Gee et al. indicate that upon contact with the clayey silt the ferrous iron was oxidized, thereby causing precipitation of amorphous ferric hydroxide, which was indicated by rust coloring. The low iron concentrations in the effluent prior to pH decline also supports this conclusion. Iron precipitation would not be expected to occur in liners or in water-saturated geological deposits beneath tailings impoundments because of the lack of availability of oxygen or any other suitable oxidizing agent. Precipitation of iron hydroxide is much more likely in laboratory experiments because it is very difficult to prevent entry of some oxygen into the system.

In order to compare the acidic front retardation observed in the column experiments with the retardation calculated from the per cent carbonate-mineral content in the geological materials in the columns, the test data reported by Shepherd and Martin (1980) is used. The total acidity of the influent solution is calculated by adding the moles of H^+ provided by the H_2SO_4 initially contained and by the release of H^+ as a result of the precipitation reactions for $Fe(OH)_3$ (Eq. 5) and $Al(OH)_3$ (Eq. 9). On this basis the total acidity is 0.45 moles H^+/L [0.27 moles/L from H_2SO_4 (13.44 g/L), 0.08 moles/L from Fe^{2+} (2220 mg/L), and 0.095 moles/L from Al^{3+} (857 mg/L)]. Using this value, the reported effluent volumes to the point of acid breakthrough, the weight of soil in the columns, and the $CaCO_3$ content of the soils the theoretical acid neutralization capacity can be compared to the actual amount of acid consumed in each column. The acid neutralization capacity of the soils in three columns account for consumption of 43, 26 and 29 per cent of the total acidity passed each. It is obvious from this data that additional sources of acid consumption must be present in the soils of the columns.

The additional acid consumption capacity necessary to account for neutralization is likely available as cation exchange. The tendency for H^+ exchange to cause retardation depends on the capability of H^+ to compete with other cations for occupancy on the exchange sites. Wiklander (1964) states that the "relative replacing power" of cations including H^+ is determined by the mineralogy of the material, the exchange capacity and the nature of the ions. He indicates that H^+ normally competes favorably with Na^+ and in some cases with the other major cations.

Cation exchange capacity (CEC) was reported for two of the three soils tested. These soils, identified as Residual and Transported, had measured CECs of 7.4 meq/100 g and 11.5 meq/100 g respectively. These were also the two soils which provided the lowest acid consumption capacity based on $CaCO_3$ content (29% for Residual and 26% for Transported). By including cation exchange capacity in calculating the acid consumption capacity for these soils a total acid consumption capacity of 83 per cent for the Residual soil and 127 per cent for the Transported soil results.

Although cation exchange was apparently an important influence on the retardation observed in the laboratory experiments by Shepherd and Martin, we do not expect that it is a major mechanism in zones in sandy aquifers with high permeability. High-permeability zones are

normally very low in clay mineral content and have correspondingly low cation-exchange capacities. However, as these column test results demonstrate, useful acid retardation and consumption information for site soils can be obtained from laboratory evaluations.

As part of the investigation of the Elliot Lake plume, three column experiments were conducted. One of these was done in the field where low-pH, ferrous-iron rich water from the core of the plume was pumped for several hours directly from a piezometer through a column of sand. The sand was obtained from a borehole sample of the aquifer. The sample was acid washed and had sand-sized crushed calcite added to it. The experiment was conducted in the field in order to minimize oxidation of the plume water during the experiment. The purpose of the experiment was not to monitor the low-pH breakthrough but rather to determine the length of time needed for calcite dissolution with accompanying precipitation of gypsum and siderite. Identification of these precipitates in the column by x-ray diffraction indicated that these reactions occur within a few hours.

In the other two experiments, which were conducted in the laboratory, waters with a pH of 2 and 4 and no iron or aluminum were passed through saturated columns of acid-washed, calcite-enriched sand. Acid breakthrough in the pH=2 experiment occurred at a time close to that predicted from mass-balance calculations based on the input pH and the known weight of CaCO_3 in the column. The shape of the breakthrough curve was closer to being linear than S-shaped. This curve shape was not represented closely by simulations based on the advection-dispersion equation using a simple retardation factor. In the pH=4 experiment poor agreement between the calculated and observed breakthroughs was obtained. It is believed that kinetic factors had a much greater influence in this experiment. Additional laboratory experiments are being performed in order to further evaluate the factors that control the behavior of flowing acidic water in sand with low CaCO_3 contents.

Prediction of Contaminant Migration

The prediction of the migration of tailings-derived contaminants in groundwater is a task that is commonly undertaken by hydrogeologists and geotechnical or environmental engineers as part of the licensing procedures for new tailings impoundments or for continued use of existing impoundments. The approaches that are being used in this endeavor are continually evolving. A detailed review of existing methods would probably be obsolete by the time of publication. Our purpose here is to consider in a rather general context the main components of the most-commonly used predictive approach and to draw attention to the main implications of the hydrogeochemical concepts that we have drawn from the field and laboratory investigations described above.

Mathematical models for contaminant migration in groundwater from uranium tailings disposal areas generally include computational routines to accomplish three main tasks. The first task is the simulation of groundwater flow from the impoundment in the domain in which contaminants will migrate. The second and third tasks involve

the simulation of the dispersion and geochemical processes which will control the concentration of contaminants along the groundwater flow path.

Groundwater Flow

Powerful mathematical methods for simulation of groundwater-flow patterns have been available for more than a decade. The most useful models are based on numerical solutions (finite difference or finite element methods) to the groundwater flow equations. Examples are described by Freeze and Witherspoon (1967), Pinder and Gray (1977), and Nelson et al. (1980). If the investigation of contaminant migration pertains to an existing tailings area under stable flow conditions, adequate representation of the flow system can in some cases be obtainable directly from the field data by the preparation of maps and cross sections without the use of formal mathematical simulations. If the predictions of contaminant migration pertain to different conditions, such would occur at a site where the impoundment has yet to be put into operation or at sites where the flow conditions will change due to changes in operation or initiation of decommissioning procedures, application of sophisticated mathematical models may be necessary.

The essential task in the evaluation of the groundwater flow system is the representation of the critical flow paths and velocities that will control movement of contaminants away from the impoundment. Uncertainties that exist in predictions of these paths at field sites are normally related primarily to inadequacies in the field data rather than inadequacies of the mathematical models that are used in simulations of the flow systems.

Dispersion

Hydrodynamic dispersion is the process that causes mixing between the tailings-derived water and the natural groundwater in the aquifer through which the tailings-derived water moves. Dispersion causes the interface between the two types of waters to spread so that the contaminant concentrations exhibit a gradual decline in the direction of movement of contaminant plumes (i.e. in the longitudinal direction). If the plume moves in a primarily horizontal direction through an aquifer, such as at the five field sites described in this paper, dispersion causes mixing with the water above and below the plume (vertical dispersion), along the lateral periphery of the plume (lateral dispersion), and at the front of the plume (longitudinal dispersion).

Most mathematical models for contaminant migration in groundwater that include the effects of flow, referred to as advection, and the effects of hydrodynamic dispersion are known as advection-dispersion models. The theory upon which these models are based is described by Bear (1972) and Fried (1975). A recent review of the capabilities and limitations of these models is provided by Anderson (1979). Since the late 1960's advection-dispersion models in analytical and numerical form have been applied to problems of contaminant migration at various types of waste-disposal and waste-leakage sites (Baetsle, 1967; Pinder, 1972; Robertson, 1974; Konikow and Bredehoeft, 1974).

In recent years advection-dispersion models have been used to simulate contaminant migration in aquifers at uranium tailings impoundments. Haji-Djafari et al. (1979) used a finite-element, advection-dispersion model for two dimensional simulations of contaminant distribution patterns at site 3 in Wyoming. In our investigation of site 1, simulations of contaminant distributions were performed by means of an analytical solution to the advection-dispersion equation. Highland et al. (1981) presented simulated contaminant distributions for site 4 but they did not describe the numerical method used to represent the advective-dispersive transport.

The use of advection-dispersion models for simulation or prediction of contaminant migration at large-scale field sites is currently the subject of much controversy. The controversy is primarily due to the uncertainty in the nature and magnitude of the model parameter used to represent the dispersion process. This parameter is known as dispersivity. The difficulties associated with conceptual representation and measurement of this parameter are described by Anderson (1979), Gillham and Cherry (1981), Gillham et al. (1982) and Anderson (1982). Field and laboratory studies of sandy aquifers have led to the conclusion that dispersivity values obtained from laboratory measurements do not provide realistic results when used in mathematical simulations of contaminant plumes in field situations. There is also considerable evidence in support of the conclusion that the values commonly obtained from the various types of standard small-scale field tests for dispersivity do not provide realistic representation of the dispersion that occurs in large-scale contaminant plumes. These scale differences are attributed to the effects of heterogeneities in the aquifers. Several explanations of the manner in which heterogeneities affect dispersion have been provided (Gillham and Cherry, 1981, Schwartz, 1977, and Gelher et al., 1979) but at present it is not possible to claim reliable representations of dispersion in models for predictions of contaminant migration of large spatial and temporal scales.

An indication of the variability in the values of dispersivity used in advection-dispersion models is provided by the simulations of sites 1, 3 and 4 in Wyoming. For site 3, Haji-Dafari et al. (1979) used a value of 0.3 m for longitudinal dispersivity. Highland et al. (1981) used a value of 6.5 m for site 4. At site 1 a good calibration with the concentration distribution for Cl^- was obtained using a value of 80 m for longitudinal dispersivity. Direct measurement of dispersivity by means of field tracer tests were not done at any of these sites.

Although this situation is unsatisfactory when advection-dispersion models are used for some types of subsurface contaminant migration problems we do not consider the dispersion problem to be a major liability in the evaluation of contaminant migration in sandy aquifers at uranium tailings impoundments of the type considered in this paper. This is the case because we perceive the main components of contaminant-migration analyses at tailings impoundments to be those that involve the identification of the critical groundwater flow paths and the representation of the attenuation of contaminants by geochemical processes. The effects of dispersion can probably be ade-

quately represented as a gross approximation using simple mathematical models to obtain estimates of the possible dispersive influence. The use of two or three dimensional numerical advection-dispersion models of the type that currently exist is generally unwarranted considering the limitations of the field data and the overriding importance of the flow and the specific geochemical components of the system.

Chemical Mass Transfer

The representation of geochemical processes in models for contaminant migration at uranium tailings impoundments is normally accomplished using distribution coefficients and a parameter representing the acid-neutralization capacity of the medium (Haji-Djafari et al., 1979; Nelson et al., 1980; Shepherd and Cherry, 1980; Highland et al., 1981). The use of distribution coefficients determined from laboratory batch tests is a direct adaptation of methods developed for predictions of the subsurface movement of radionuclides from nuclear-reactor wastes (Baetsle 1967, Grisak and Jackson, 1978 and others).

In investigations of contaminant migration at uranium tailings impoundments distribution coefficients for numerous elements are normally determined over a wide range of pH, from strongly acidic to neutral (Taylor and Antommaria 1978; and Gee et al., 1980). In these tests it is observed that at low pH the distribution coefficients for heavy metals and radionuclides are very small or zero at low pH and that they are large at neutral pH. For example, based on the results of batch determinations of distribution coefficients for metals and radionuclides in samples of geological materials from site 4 in Wyoming, Highland et al. (1981) concluded: "Regardless of the means by which the tailings liquor was neutralized (whether it has been contacted with claystone, silty sandstone, sandstone or neutralization with calcium hydroxide) concentrations of most elements were virtually identical at a specific pH value". These results are therefore consistent with the field and laboratory observations described previously in this paper and they support the conclusion that pH is the dominant factor controlling the chemical quality of water in contaminant plumes.

There is little to be gained from any additional batch-type investigations of distribution coefficients for contaminants in uranium-tailings liquors. The distribution coefficient as a parameter in predictive models is based on the assumption of a linear isotherm. As change from low to high pH occurs, nearly all of the metals and radionuclides of interest in tailings seepage undergo large decreases in liquid-phase concentration as a result of precipitation of amorphous or mineral phases. For a linear isotherm to occur, the isotherm must be established under a condition of non-variable pH and the mechanism of chemical mass transfer must be adsorption or ion exchange. Therefore, acid neutralization can not be included in the determination of distribution-coefficient values.

In the neutralization zone of an advancing contaminant plume where the metals and radionuclides are transferred to the solid phase by precipitation, co-precipitation and adsorption, the geological medium has undergone major geo-

chemical changes. It is reasonable to expect that calcite dissolution and the formation of siderite, gypsum, gibbsite, aluminosilicates and minor amounts of iron and manganese hydroxide have considerably altered the adsorptive capabilities of the porous medium. There is no reason to believe that batch tests on samples of geological materials that have not undergone these changes bear much geochemical resemblance to those in the field in the neutralization zone where the important mass transfers of major elements, toxic metals, non-metals and radionuclides occur. This deficiency in the distribution coefficient approach has been described by Reardon (1981) for non-pH varying systems and the conclusions reached are applicable to an even greater degree where neutralization is the controlling process of geochemical retardation. Although the usefulness of distribution coefficients is questionable, this however, does not prevent the development of meaningful predictions of contaminant movement from uranium tailings impoundments. The important step in the formulation of a predictive model is not the distribution-coefficient step but rather the choice of methods for prediction of the advance of the acid front. Taylor (1980), Nelson et al. (1980) and Shepherd and Cherry (1980) have suggested that the per cent solid-phase carbonate content of ($\text{CaCO}_3\%$) can be used as a measure of the ability of porous geological materials to raise the pH of tailings seepage to neutral levels. This is undoubtedly a useful first step but there are two main problems with regard to the implementation of this approach within the context of predictive models. The first problem involves the prediction of the concentration of H^+ that will be neutralized by reaction with calcite and other solid phases. The second is the determination of the effective acid-neutralization capability of the porous medium.

Prediction of the H^+ available for neutralization requires prediction of the behavior of iron and aluminum in the groundwater system. Because ferrous iron occurs at levels of thousands of milligrams per litre in tailings seepage, it is a significant potential source of acid in the water. For the acid from the iron acidity to be released for neutralization, ferrous iron must be oxidized to ferric iron. The prediction problem becomes primarily a task of predicting the redox behavior of iron during migration along the subsurface flow paths. At present the literature presents almost no information on the geochemical behavior of iron or aluminum in groundwater at tailings impoundments or on the redox conditions in the zones of contamination. However, based on field observations it is expected that most iron in the system will remain reduced and therefore not contribute to the total H^+ content.

The effective capacity of the porous medium to consume H^+ is undoubtedly related to the percent calcite in the porous medium and possibly to reactions involving aluminosilicate minerals. It is possible that not all of the carbonate-mineral content of the porous medium is available for reaction in the neutralization zone. This may be the case because of the formation of precipitate coatings on the carbonate-mineral grains, which could occur as a result of the precipitation of non-carbonate minerals such as gypsum, gibbsite aluminosilicates and possibly oxides or iron and

manganese. The development of protective precipitate coatings on calcite particles and an associated decline in neutralization capacity has been observed in studies of acidic drainage from coal mines. This information may not be directly relevant to the behavior of tailings seepage in groundwater because in the coal mine environment aerobic conditions prevail whereas in the groundwater zone beneath tailings impoundments anaerobic conditions are expected.

Summary and Conclusions

The evaluation of data from groundwater monitoring networks at four tailings impoundments in Wyoming and one in the Elliot Lake district of Ontario, each of which is located on permeable deposits of sand and gravel, has indicated that tailings-derived constituents such as SO_4^{2-} , Na^+ , Ca^{2+} and Mg^{2+} move as rapidly or nearly as rapidly as the groundwater. At these sites plumes containing these major constituents have travelled hundreds or thousands of metres from the impoundments. In contrast the distance of advance of low pH water is significantly regarded. At one site the acid front has not moved beyond the toe of the dam. At another site the acid front has advanced only a few tens of metres from the dam. And at the other three sites the acid front has advanced hundreds of metres, but nevertheless the distance of advance is much less than the advance of the mobile contaminants such as SO_4^{2-} . The field data provide conclusive evidence of the neutralization of acidic water in the permeable sandy aquifers.

At the four sites for which detailed chemical data is available, the acidic zones within the plumes contain high concentrations of transition metals, heavy metals and radionuclides. The neutral-pH zones in front of the acidic zones contain low concentrations of nearly all toxic metals and radionuclides. The significant exception is the Elliot Lake site where iron occurs at high concentrations throughout the plume and can cause acidification of unbuffered surface waters.

From mass balance and other geochemical considerations it is apparent that the neutralization zone between the low pH and neutral pH segments of each of the plumes is a zone in which precipitation of several important minerals or amorphous compounds occurs. These include siderite, gypsum, amorphous silica, aluminosilicates and possibly hydrous oxides of iron and manganese. Within this zone calcite and dolomite and possibly some aluminosilicate minerals dissolve. Within this geochemically active neutralization zone, the various toxic metals and radionuclides are effectively removed by precipitation, co-precipitation and adsorption. These constituents therefore move at the rate of advance of the neutralization zone.

The task of predicting the subsurface migration of hazardous metals and radionuclides in sandy aquifers is primarily dependent on the prediction of the advance rate of the acid front. This prediction depends on the amount of H^+ initially present in the tailings solution and on the conversion of acidity (Fe^{+2} and Al^{+3}) to acid and on the efficiency of the consumption of hydrogen ions through reactions with solid phase in the porous media. The degree to which ferrous iron

is oxidized to ferric iron is of critical importance because the acidic tailings seepage contains large concentrations of ferrous iron. At present the capability of models for prediction of acid front migration cannot be evaluated in detail because of the lack of adequate field and laboratory data on the hydrogeochemical processes that occur within the neutralization zone. However, it can be concluded that the use of distribution-coefficient based concepts of contaminant movement in acid tailings seepage is not supportable. Field and laboratory column data, while lacking in some instances, still provides the basis for predictive modeling of contaminant migration potential. Refinement in laboratory and field testing to determine acid-neutralization indices are needed. However, application of the information already at hand about the neutralization processes that occur as acid seepage moves through calcareous geologic media is sufficient to provide useful evaluations of contaminant movement.

Acknowledgements

In the investigation of site 1 in Wyoming, William Robertson conducted much of the field work and participated in all aspects of the data interpretation. Andrew Robertson of Steffen, Robertson and Kirsten Limited, Vancouver, assisted with the project administration and Paul Davis with the field investigations.

Administrative and technical assistance in the investigations of the Elliot Lake site were provided by Al Vivyurka, Tjoe Lim and Nand Dave. We extend our thanks to Rob Blair who introduced us to the problem of tailings acidification and seepage in the Elliot Lake area and who initiated the field investigations at the Elliot Lake site in 1978.

Funding for this project was provided by a research agreement from the Canadian Department of Energy, Mines and Resources.

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Table 1. Chemical Analysis of Water in Acidic Uranium Tailings Impoundments
(in mg/L except where noted otherwise).

Parameter	(a) West Gas Hills, Wyo.	(b) Highland Mill, Wyo.	(c) NRC GEISS	Site 1, Wyo.	(d) Nordic Main, Ont.	(1) Drinking Water Limits
pH	1.9	1.8	2.0	1.8	2.7	*6.5 - 8.5
TDS or EC	15000	18200 μ mho	35000	14600	12200	*500
SO ₄	11650	12850	30000	9200	21700	*250
Cl	317	97	300	1700	7	*250
Fe	942	2200	1000	500	6030	*0.3
Mn	30	64	500	170	1.2	*0.05
Al	273	578	2000	205	933	-
K	-	-	-	90	174	-
Na	288	330	200	1400	12	-
Ca	661	484	500	500	380	-
Mg	326	650	-	370	98	-
Si	196	233	-	-	51	-
NH ₄	782	-	500	0.5	-	-
NO ₃ as N	-	16	-	2.9	<10	10
As	1.5	3.5	0.2	53	-	0.05
B	-	-	-	0.2	-	-
Ba	0.01	-	-	0.08	-	-
Cd	0.8	<0.1	0.2	0.13	-	1.0
Cr (total)	-	3.0	-	0.81	-	.05
Cu	-	3.0	50	0.8	49	*1.0
F	-	-	5	21	11	1.4 - 2.4
Hg	-	-	0.07	0.03	-	0.002
Mo	1.0	<5.0	100	0.14	-	-
Ni	4.1	2.6	-	1.6	5.0	-
Pb	-	<1.0	7	-	4.0	0.05
Se	1.9	<1.0	20	95	-	0.01
Zn	12.1	7.8	80	1.6	5.0	*5.0
Ra-226 (pCi/L)	1,170	13,200	250	350	140	3 (1)
Pb-210 (pCi/L)	16,700	2,250	250	200	1,700	100 (2)
Th-230 (pCi/L)	100,000	227,250	90,000	-	19	2,000 (2)
U-Nat (pCi/L)	8,140	9,685	3,400	-	-	30,000 (2)
U-Nat (mg/L)	-	84.8	-	38.2	5.1	0.02 (3)

(a) data from Highland, et al. (1981).

(b) data from Gee, et al. (1980).

(c) data from U. S. Nuclear Regulatory Commission, Final Generic Environmental Impact Statement on Uranium Milling, NUREG-0706, 1980.

(d) data from Neil Dubrovsky, personal communication, 1981.

(e) U. S. EPA National Interim Primary (1976) and Secondary (1979) Drinking Water Standards.

Asterisk (*) identifies non-enforceable, aesthetic drinking water quality standards.

(1) U. S. EPA Interim National Drinking Water Standards set for the ²²⁶Ra limit at 3 pCi/L, the ²²⁶Ra + ²²⁸Ra limit is 5 pCi/L, and the gross alpha limit is 15 pCi/L excluding U and Rn. No U limit has been adopted. Note that the Canadian mandatory limit for ²²⁶Ra is 27 pCi/L but 3 pCi/L is recommended as an objective.

(2) The limits for Pb-210, Th-230 and U-nat shown are the NRC maximum permissible concentration in water released to unrestricted areas as reported in 10CFR, Part 20 (Revised Jan. 1980). The Pb-210 and Th-230 limits are 10% of the recommended maximum concentrations for continuous exposure for workers, published by the ICRP (1959). The 10% ICRP (1959) recommended maximum concentration for U-nat is 20,000 pCi/L vs. NRC's 30,000 pCi/L limit. Ten percent of the ICRP recommended maximum concentration for workers is a generally accepted exposure limit for the general public.

(3) U-nat limit of 0.02 mg/L is the Canadian drinking water standard lowered from 5 mg/L in 1978.

Table 2. Summary of Operational and Monitoring History and Hydrogeological Features of the Five Study Sites.

Site	Location	Company	Impoundment Use Period	Aquifer Type and Base	Aquifer Thickness	Main Monitoring Period	Average Groundwater Velocity (m/yr)	Maximum Extent of Plume	Maximum Extent of Acid Front
1	South central Wyo.	-	1970, original impoundment 1976; extension	alluvial sand on clay layer	5-10 m	1979	100-250	1200 m	not beyond dam
2	Shirley Basin Wyo.	Petrotonics	1962 to present	alluvial sand on clay layer	5-10 m	1979-80	1100-1800	300 m	300 m
3	Jeffrey City Wyo.	Western Nuclear	1958 to present	aeolian sand and alluvial gravel on slightly indurated sandstone and silty sandstone on granite	100 m	1976-77	250-1000	1500 m	-
4	Gas Hills Wyo.	Federal American Partners	1960 to present	alluvial sand, gravel, weathered sandstone on claystone	20 m at dam, thins away from dam	1980-81	-	650 m	250 m
5	Nordic Mine Elliot Lake Ont.	Rio Algom	1960-1968, surface water drained off in 1970, grass cover, >1976	glacio-fluvial sand on fractured rock	10-15 m	1979-81	500-1000 near the dam, large decreases away from dam	400 m	15 m

Sources of information: site 1, site investigation report by J. A. Cherry, T. A. Shepherd, Wm. Robertson and A. M. Robertson, 1980, unpublished data.
 site 2, Hoffman and Playton (1980).
 site 3, Taylor and Antommaria (1978), Taylor (1980).
 site 4, Highland, Murdock and Kemp (1981).
 site 5, Blair et al. (1980), Morin et al. (1982) and unpublished data.

Table 3. Summary of Plausible Geochemical Processes Pertaining to the Major Dissolved Constituents and the Interaction Between the Liquid and Solid Phase in the Neutralization Zone.

Process	Reaction	Comments
Calcite dissolution (incongruent)	$\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	Dolomite dissolution may also occur
Calcite dissolution (congruent)	$\text{CaCO}_3 + \text{Fe}^{2+} \rightarrow \text{FeCO}_3 + \text{Ca}^{2+}$	Siderite does not occur in aerobic zones
Siderite dissolution	$\text{FeCO}_3 + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{HCO}_3^-$	Causes acid neutralization after the disappearance of calcite
Gypsum precipitation	$\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Ca provided from calcite dissolution and cation exchange
Iron hydroxide precipitation	$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 2\frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 2\text{H}^+$	Limited due to availability of oxygen below the water table
Aluminum hydroxide precipitation	$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{H}^+$	Gibbsite or amorphous aluminum hydroxide
Alumino-silicate precipitation	$2\text{Al}^{3+} + \text{H}_2\text{O} + 2\text{H}_4\text{SiO}_4 \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+$	Formation of halloysite or similar mineral
Alunite precipitation	$\text{K}^+ + 3\text{Al}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+$	Solubility constraint at lower pH
Amorphous silica precipitation	$\text{H}_4\text{SiO}_4^0 \rightarrow \text{SiO}_2(\text{am}) + 2\text{H}_2\text{O}$	Solubility depends on iron content
Cation exchange	$\text{H}^+ + \text{M} [\text{solid}] \rightarrow \text{M}^+ + \text{H} [\text{solid}]$	H^+ competes for exchange sites with major cations such as K, Na, Ca, Mg

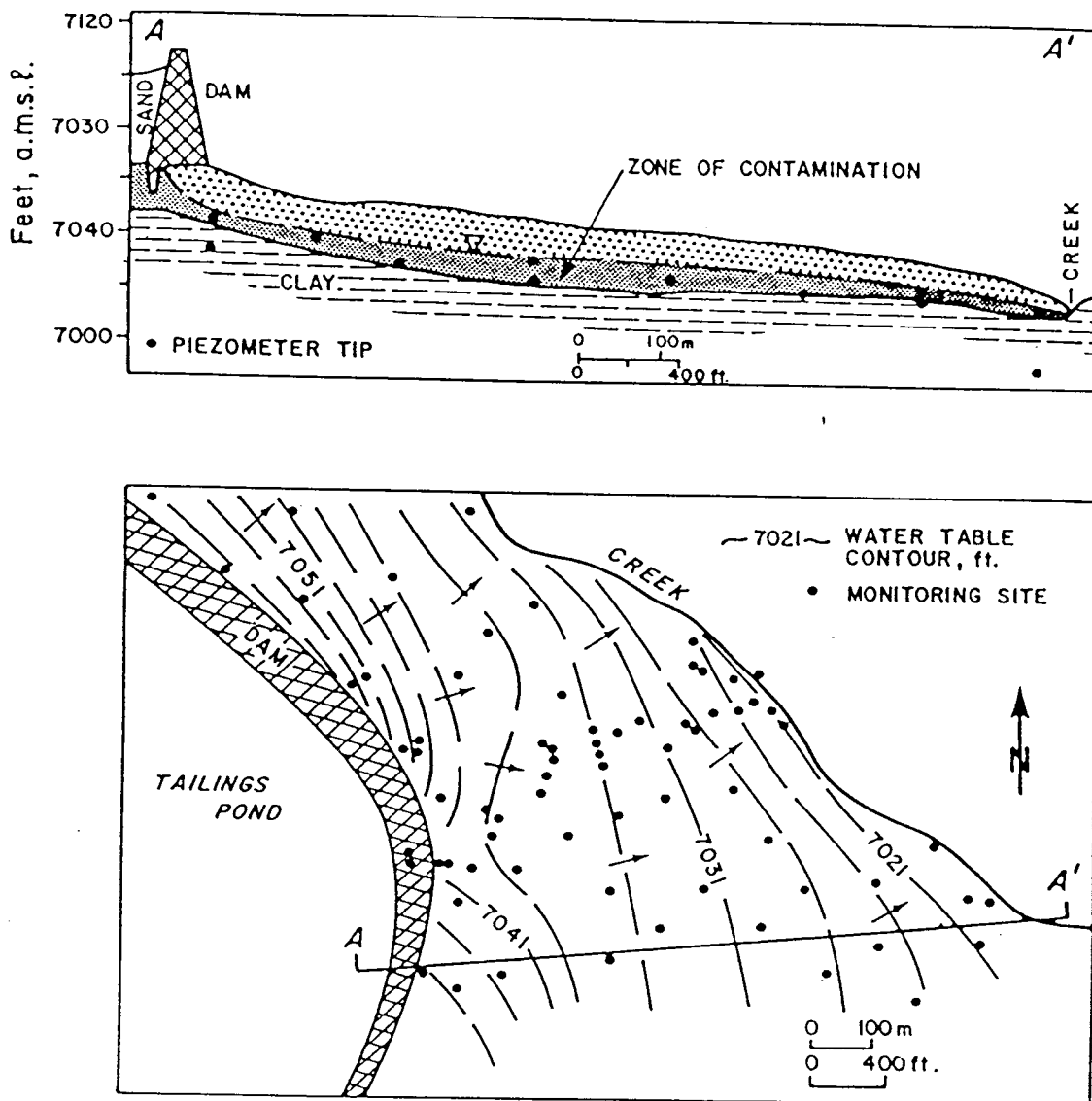


Figure 1. Hydrogeological cross section and water table map for Site 1.

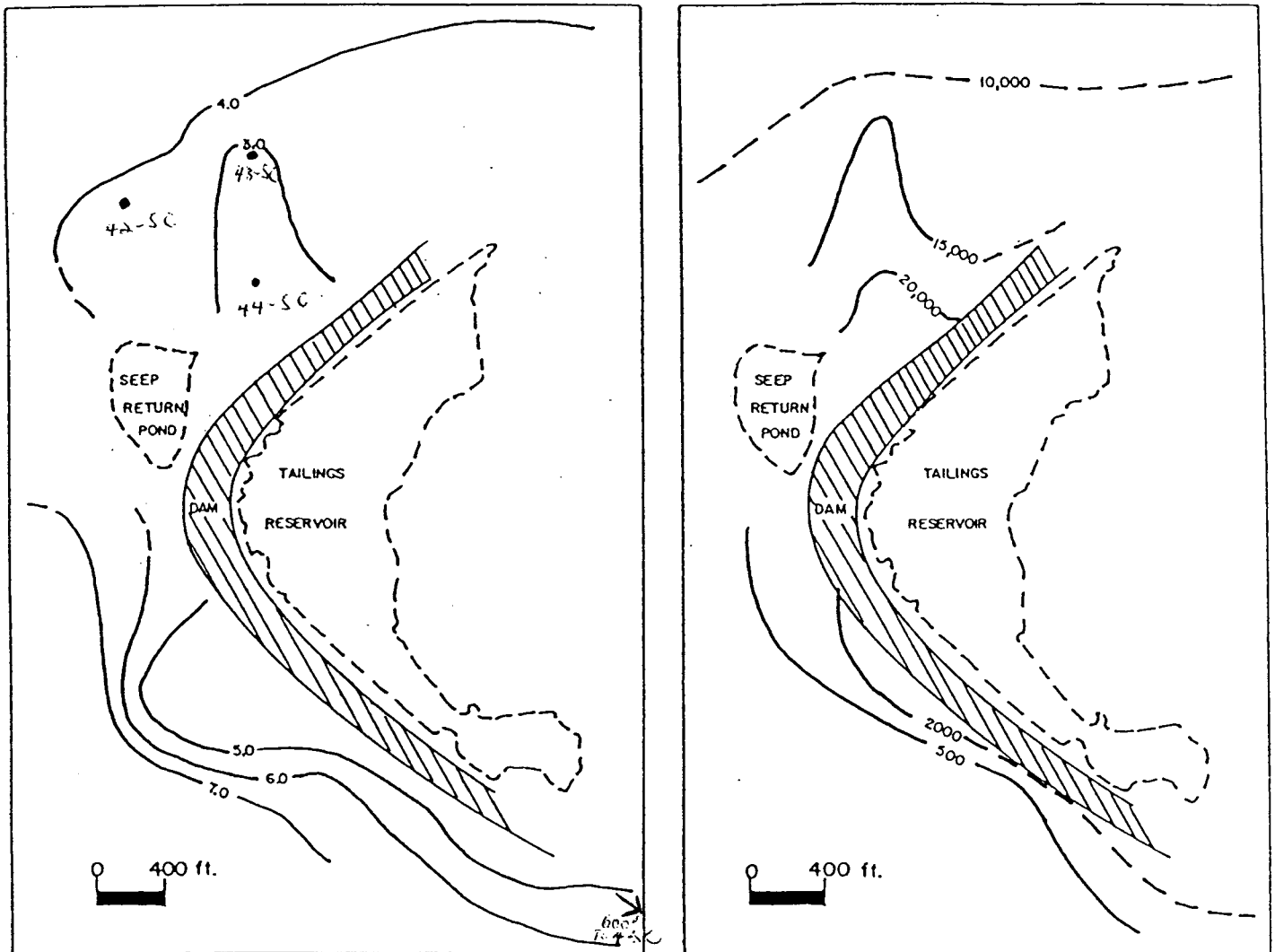


Figure 2. Hydrogeological cross section and areal distribution of pH and SO_4 in the upper sand aquifer (adapted from Hoffman and Playton 1981).

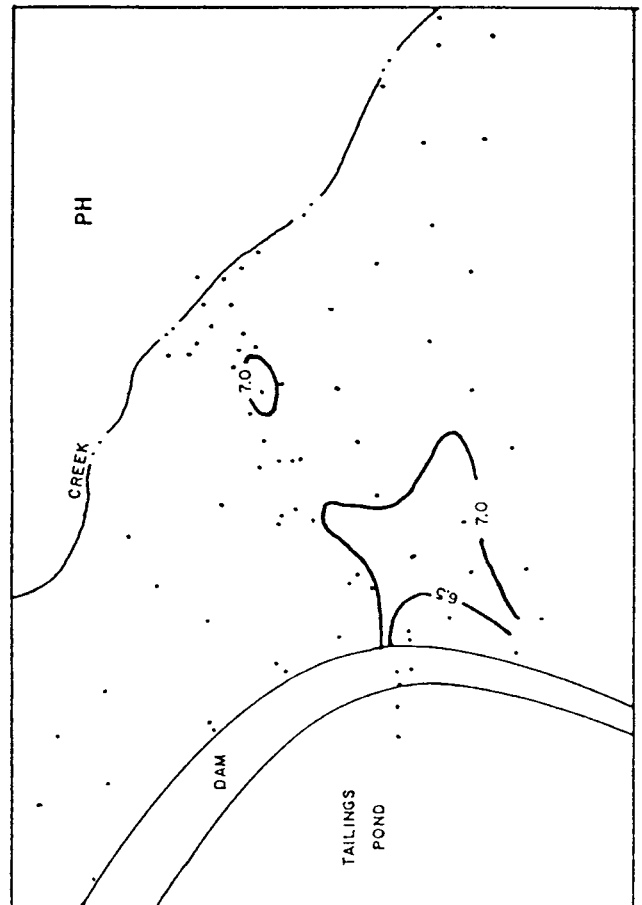
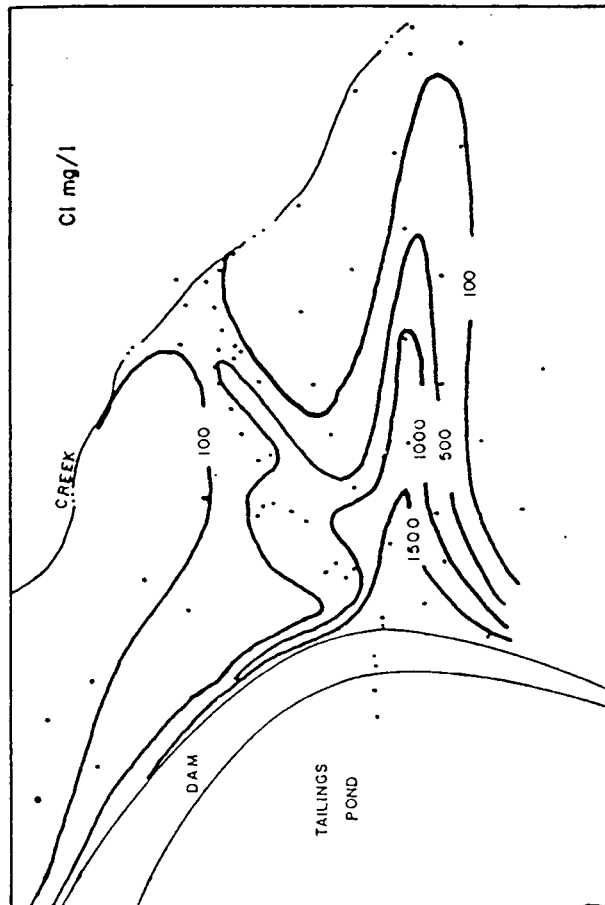
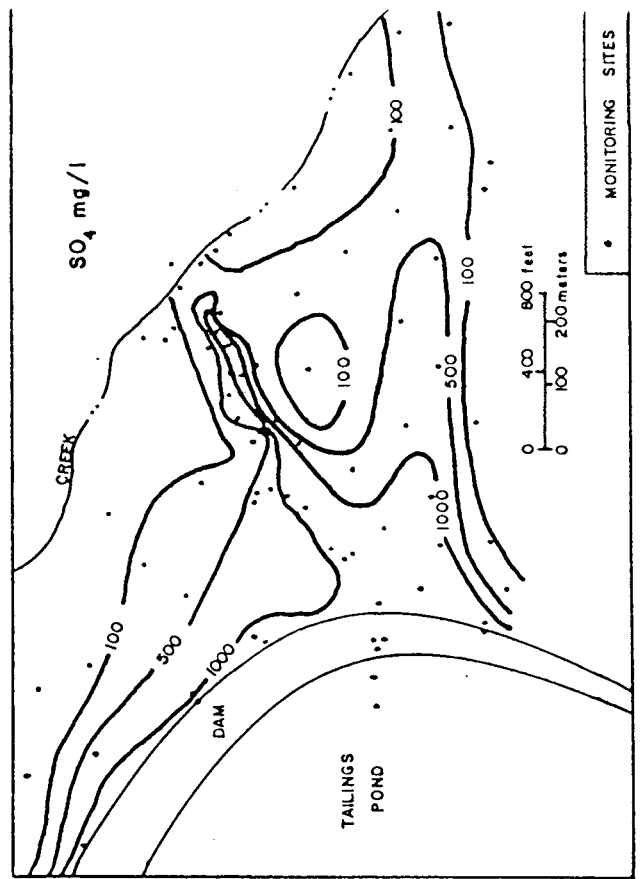
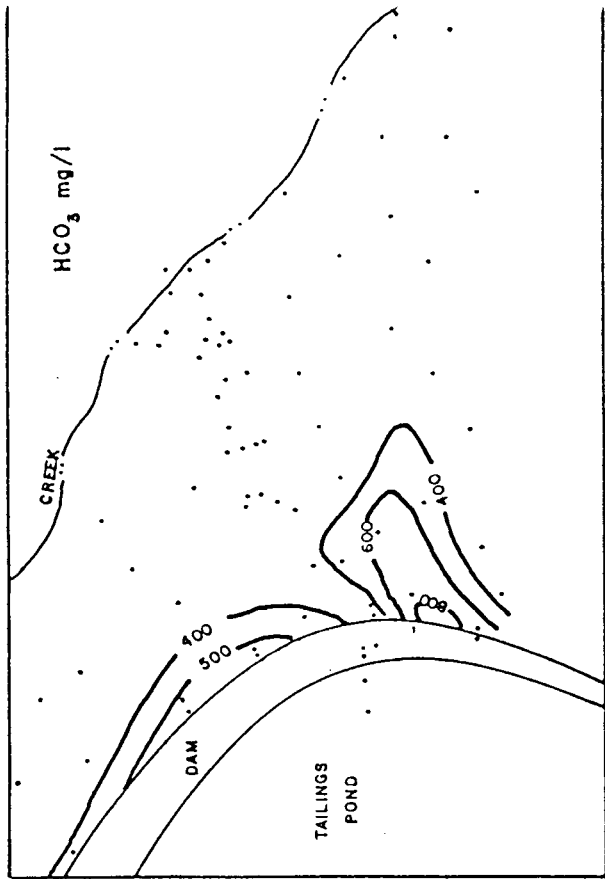


Figure 3. Areal distributions of pH, HCO_3^- , Cl and SO_4 in the shallow sand aquifer at site 1.

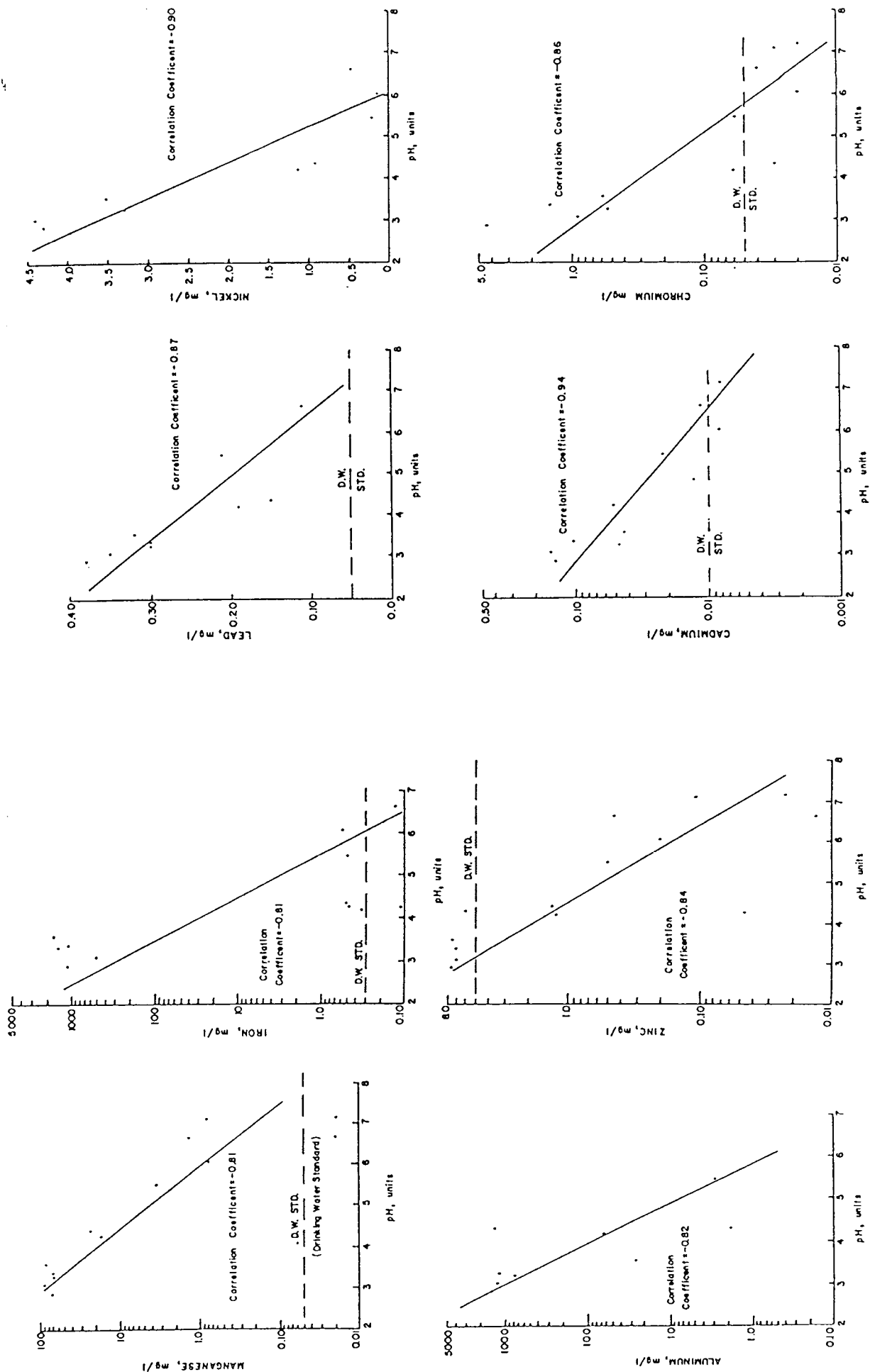


Figure 4. Graphs of pH versus concentrations of metals in the zone of contamination in the upper sand aquifer, site 2 (adapted from Hoffman and Playton, 1981).

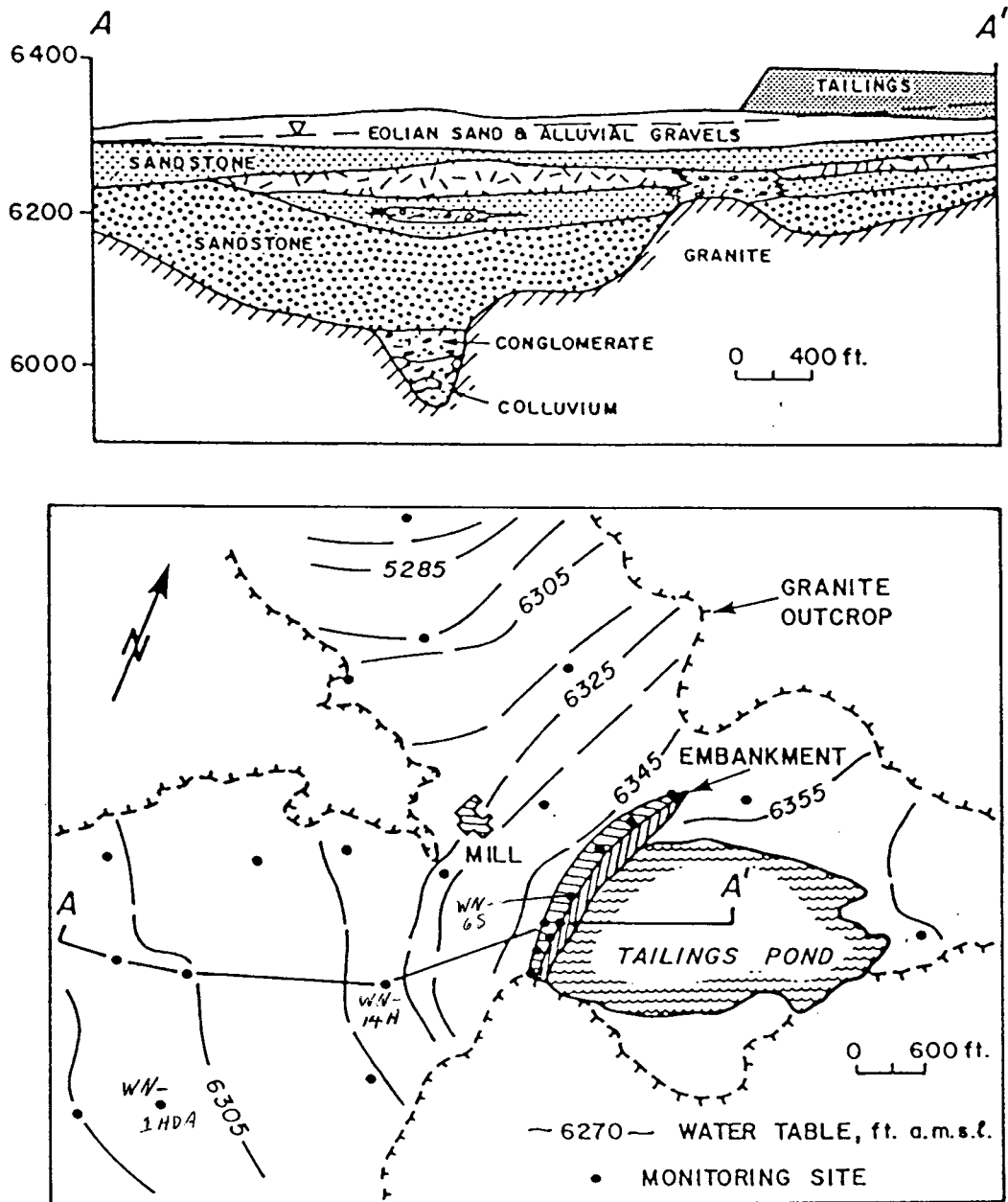


Figure 5. Hydrogeological cross section and water table map for site 3 (adapted from Taylor and Antommaria, 1978, and Taylor, 1980).

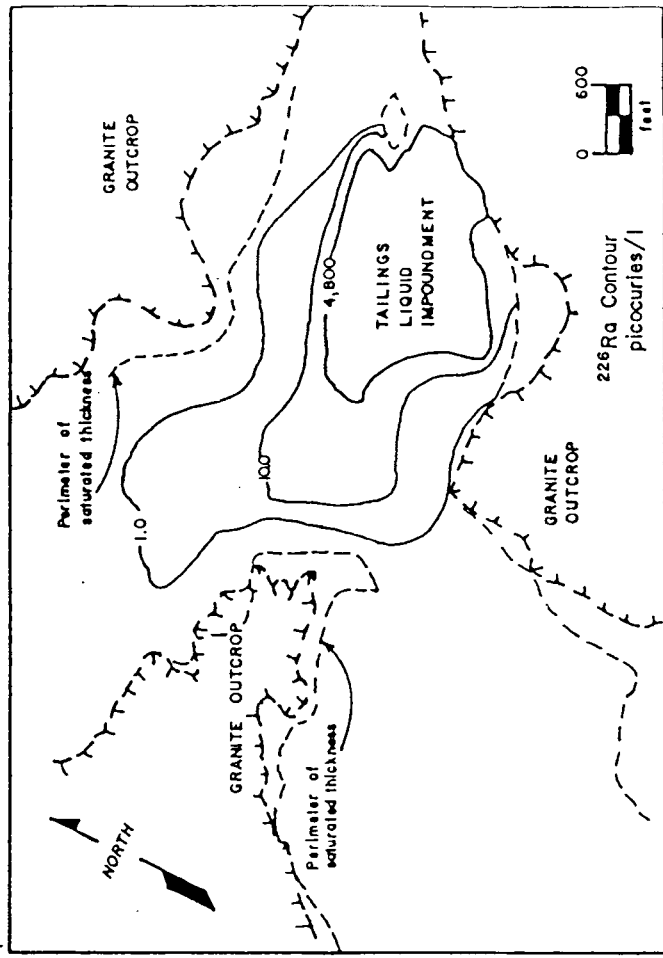
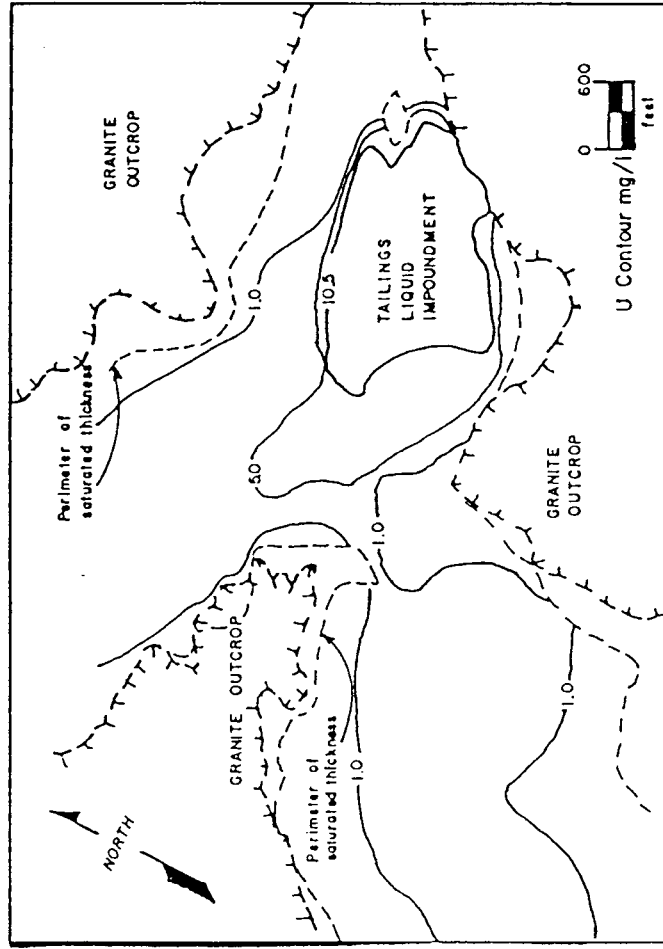
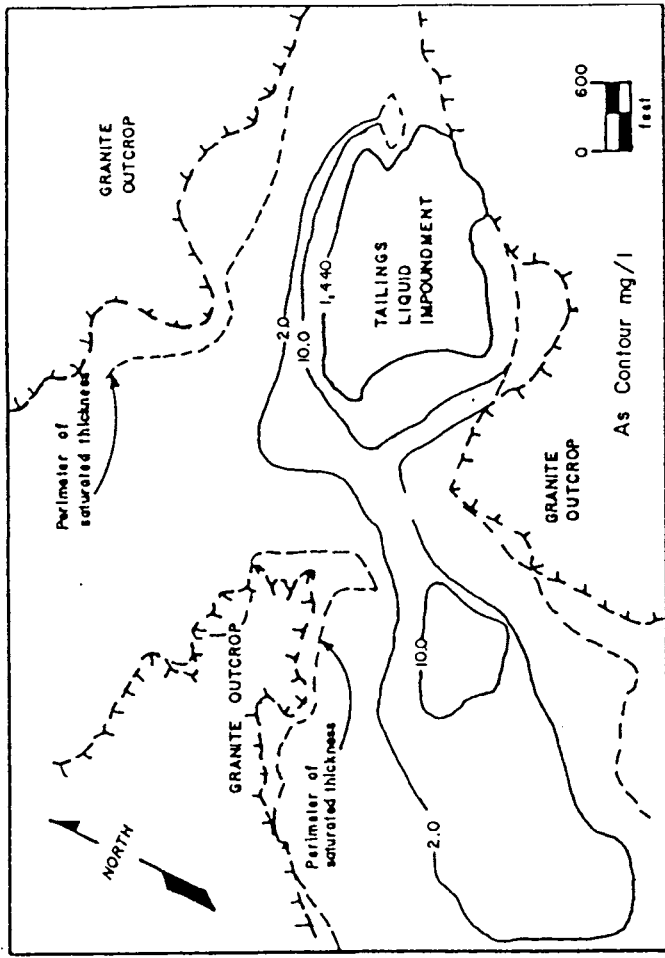
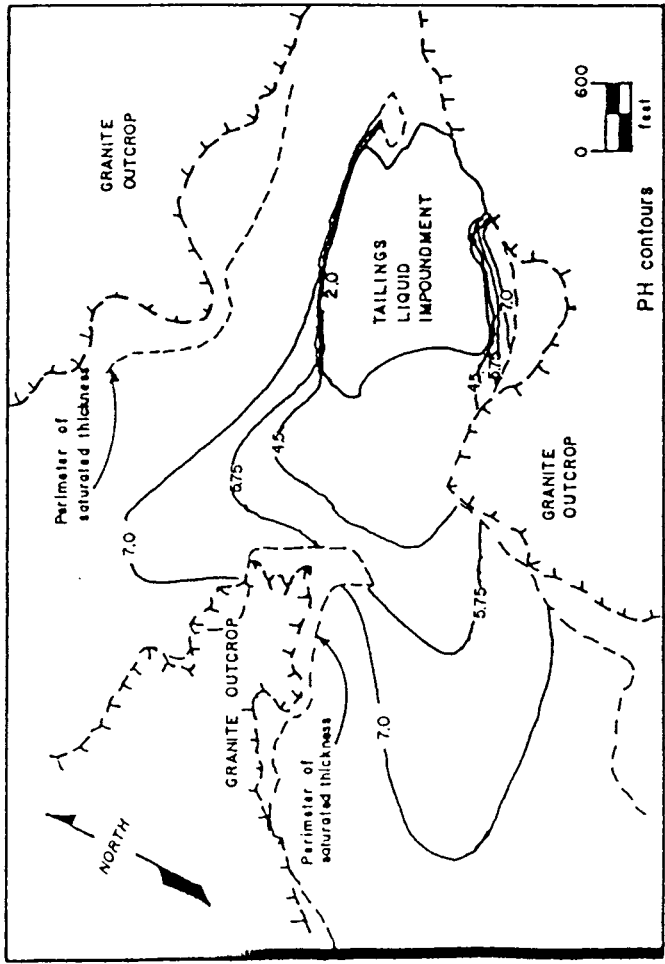


Figure 6. Areal distributions of pH, U, As and ^{226}Ra in the aquifer at site 3 (adapted from Taylor, 1980).

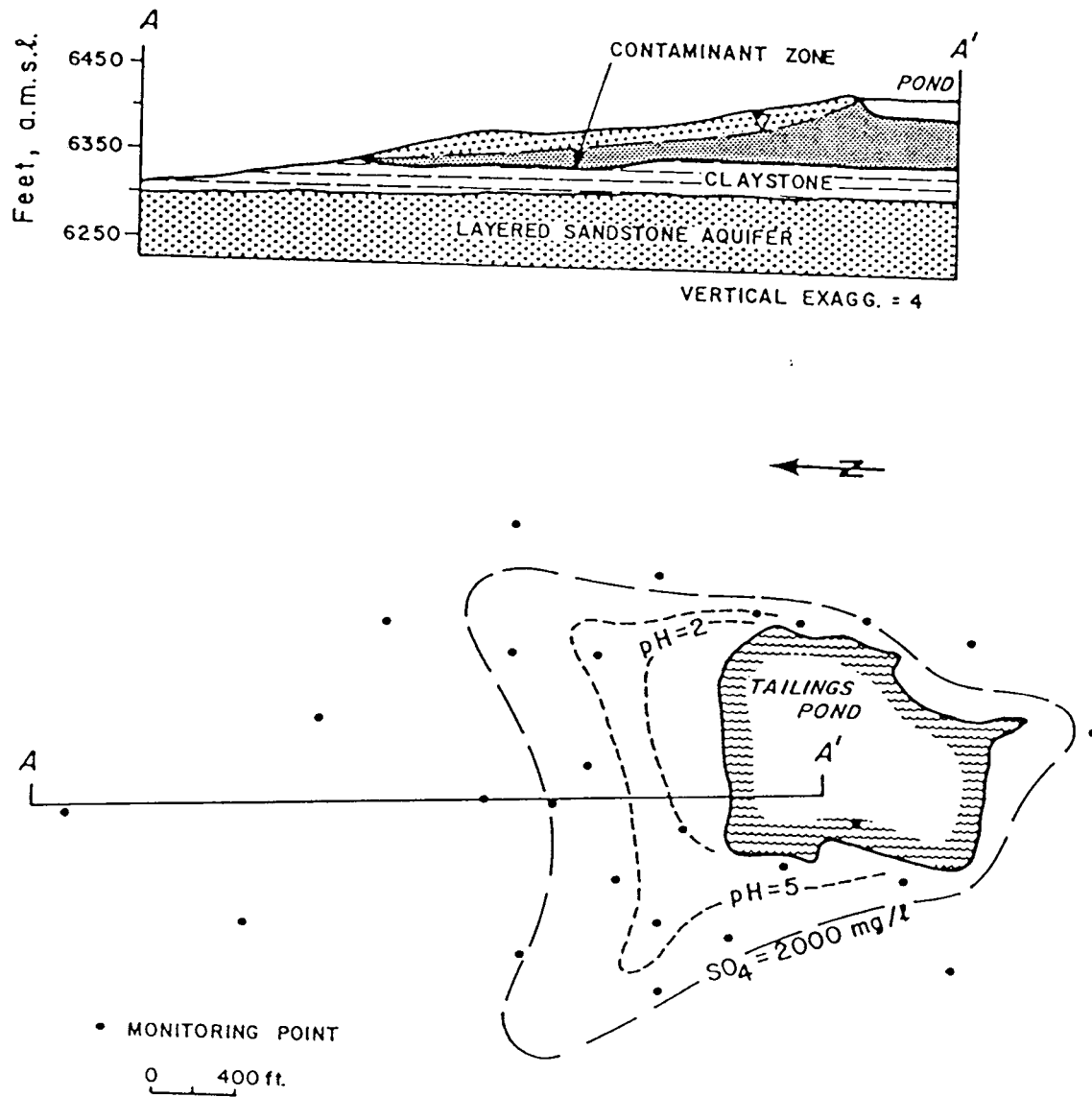


Figure 7. Hydrogeological cross section and map showing pH and SO_4^{2-} zones at site 4 (adapted from Highland et al., 1981).

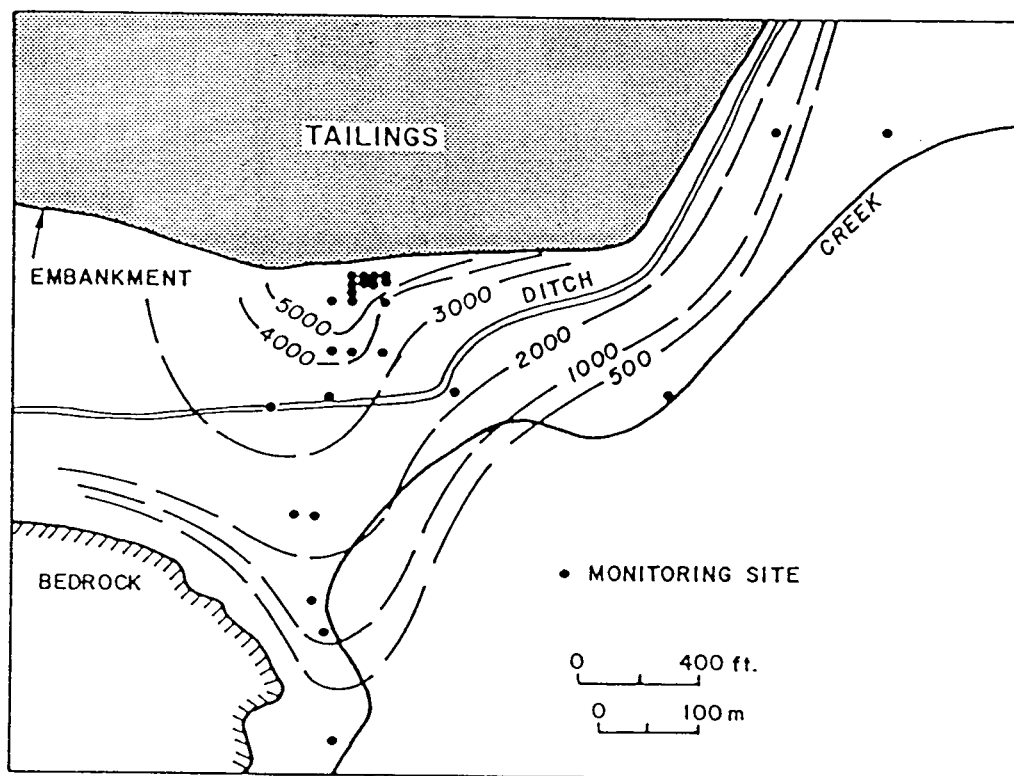
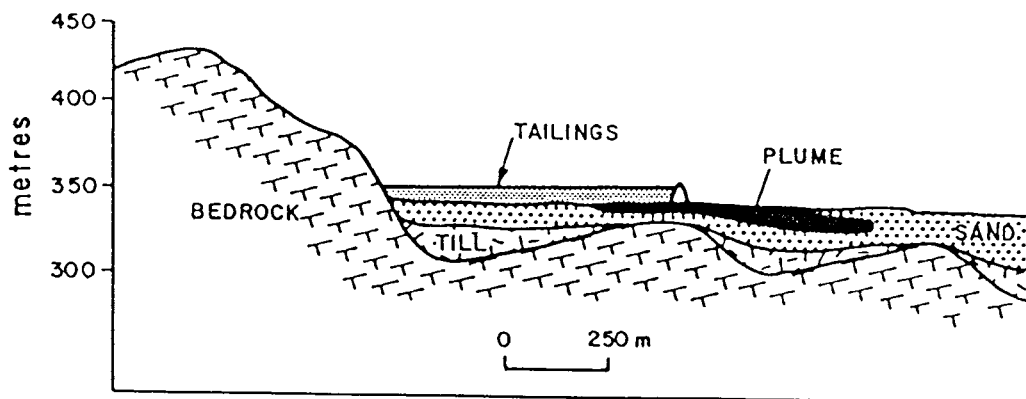


Figure 8. Hydrogeological cross section and map of SO_4 contamination in the sand aquifer at the Nordic Main tailings impoundment (adapted from Blair et al., 1980, and Morin et al., 1982).

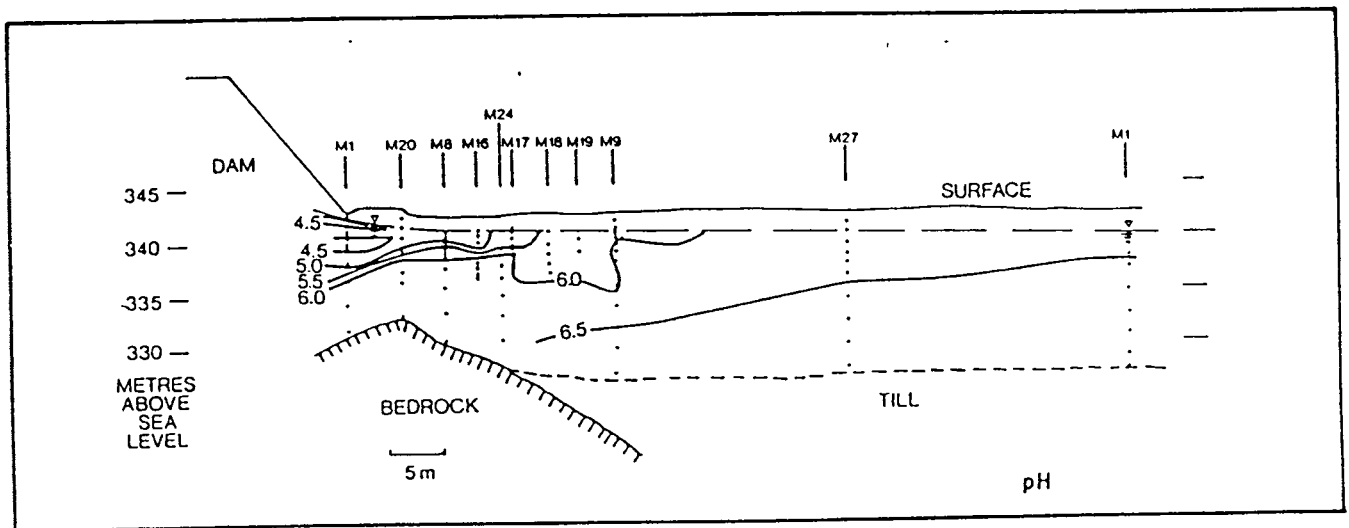
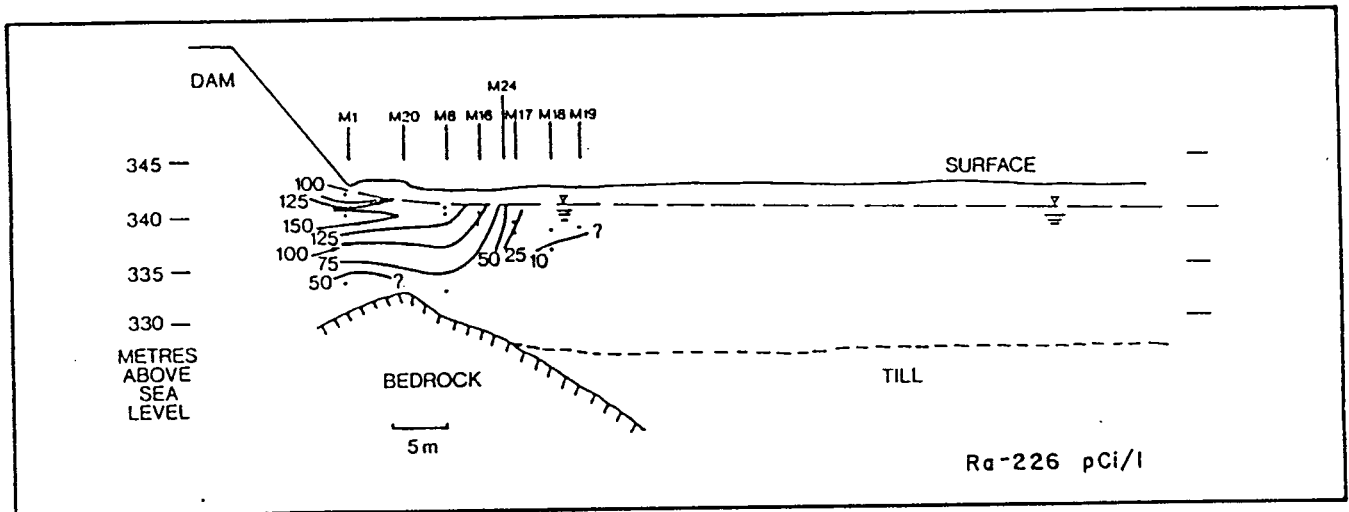
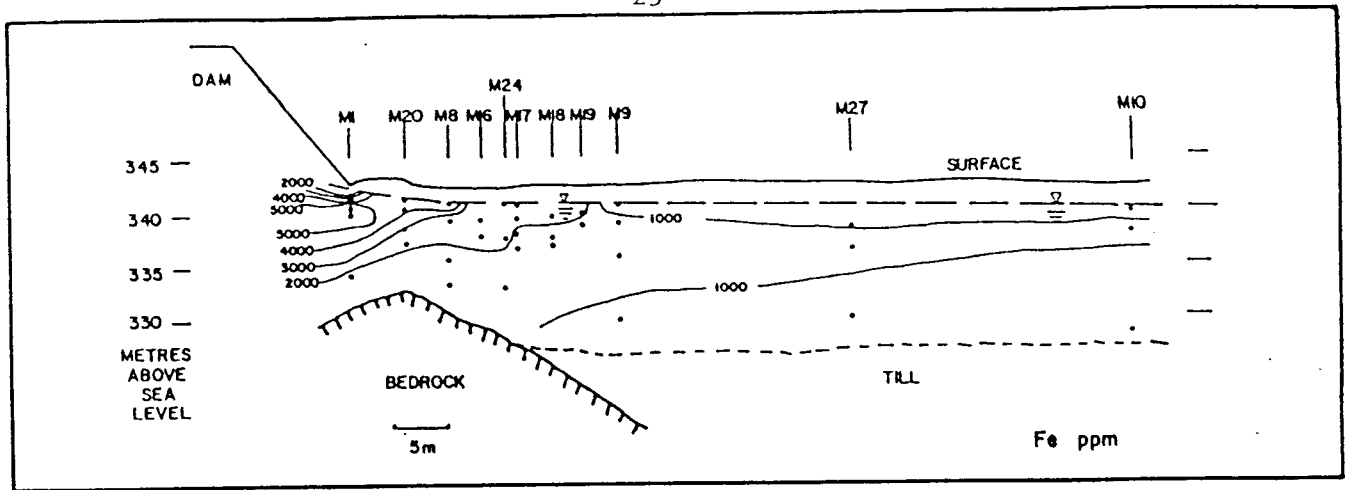


Figure 9. Cross sections through the acidic core of the plume showing distributions of pH, Fe, and Ra-226 in the Nordic plume.

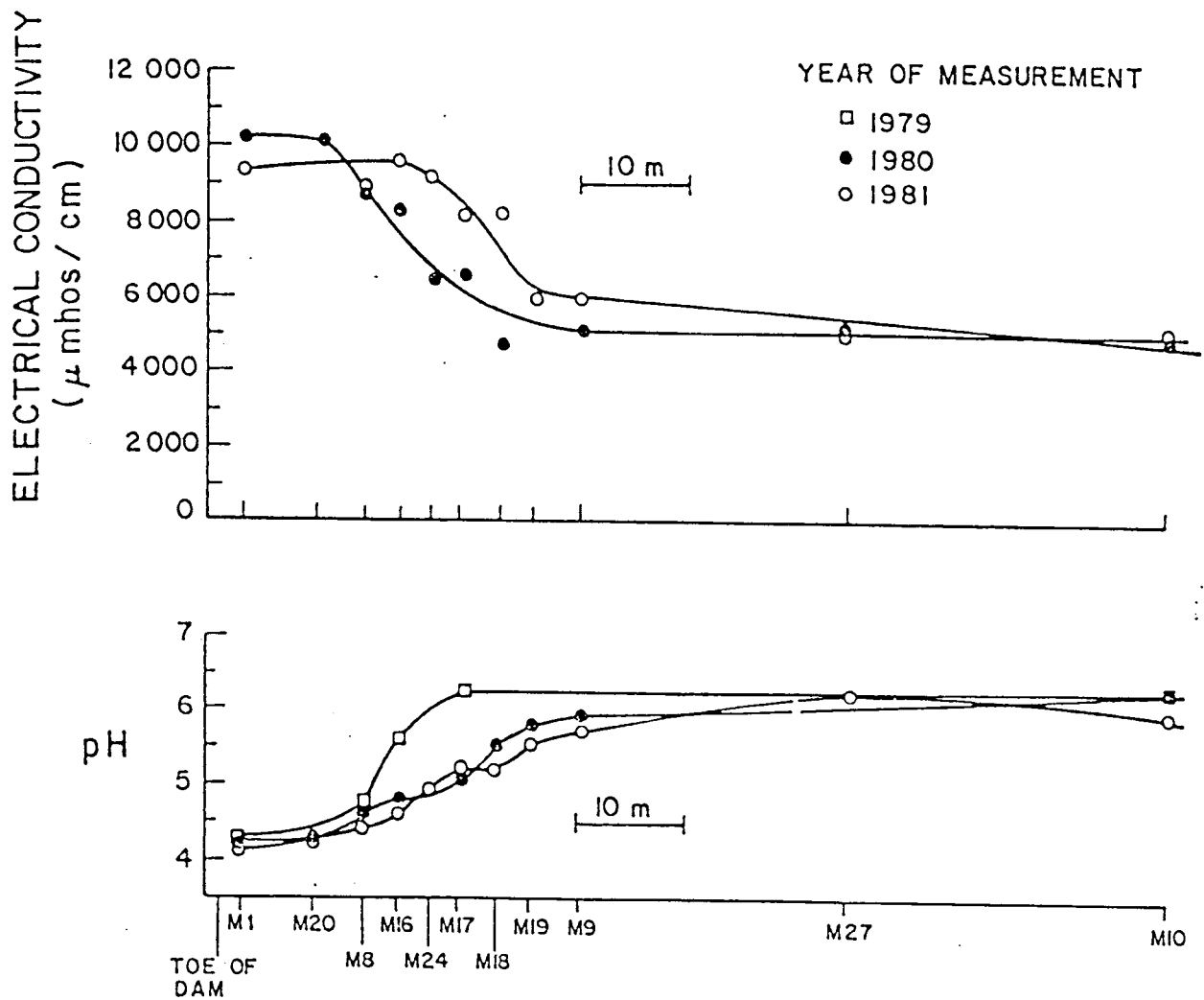


Figure 10. pH and electrical conductivity versus distance from the dam at the Nordic site.