

TRACE AMOUNTS OF SIDERITE NEAR A URANIUM-TAILINGS IMPOUNDMENT, ELLIOT LAKE, ONTARIO, CANADA, AND ITS IMPLICATION IN CONTROLLING CONTAMINANT MIGRATION IN A SAND AQUIFER

KEVIN A. MORIN* and JOHN A. CHERRY

*Institute of Groundwater Research, Department of Earth Sciences, University of Waterloo, Waterloo,
Ont. N2L 3G1 (Canada)*

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Abstract

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Some aspects of the low-temperature geochemistry of siderite are reviewed, especially the siderite–calcite solid solution. The understanding of this solid solution is limited by metastability, reaction kinetics and lack of experimental work. Also, loss of siderite by oxidation and acidification upon sampling and analysis limit the practical understanding of siderite behavior. Because of the lack of reliable direct evidence of siderite presence, results of the field study demonstrate the probable presence and mechanisms of formation of siderite through indirect aqueous-based methods: pH–pe diagram, saturation indices of minerals calculated through a speciation model, availability of reactants for precipitation reactions and stoichiometry of precipitation reactions. The mechanism of formation in the aquifer at the field site is the replacement of calcite, and both calcite and siderite occur at levels of less than 1 wt.%. Calculations show this minor amount of carbonate has a major effect on contaminant migration through pH neutralization. The replacement of calcite by siderite at the field site removes a substantial portion of the aquifer's neutralization capacity.

1. Introduction

Much published work on siderite (FeCO_3) pertains to its occurrence in iron-bearing formations, and relatively few detailed field and experimental studies (e.g., Singer and Stumm, 1970) have been made on siderite at temperatures typical of shallow groundwater systems.

This lack of information is understandable in light of the fact that the Fe forming siderite is in the 2+ state; this ferrous iron quickly oxidizes when exposed to the atmosphere, such as upon sampling, and when exposed to oxidizing water. Upon exposure, the siderite is converted to a ferric (3+) oxide compound. The lack of information on siderite is unfortunate, because it may lead to the unjustified assumption that siderite is not an important iron mineral in active groundwater systems. Yet the presence of siderite, even in trace quanti-

*Present address: Mines Pollution Control Branch, Saskatchewan Environment, P.O. Box 3003, Prince Albert, Sask. S6V 6G1, Canada.

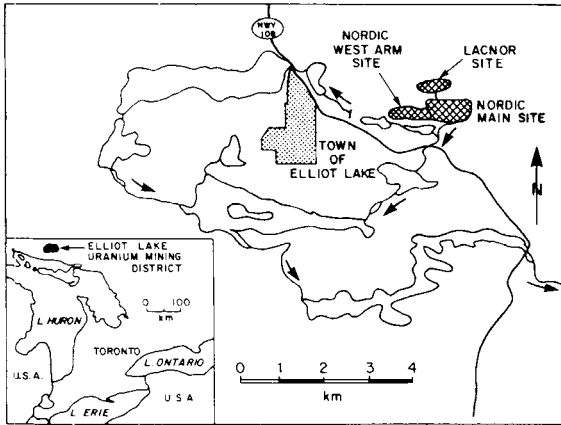


Fig. 1. Elliot Lake and surrounding area.

ties, as opposed to the presence of other iron minerals carries important implications on the type of groundwater in contact with the compound and on the evolution of this groundwater along its flowpath.

This paper describes a recent occurrence of siderite and demonstrates its impact in controlling contaminant migration from a uranium-tailings impoundment. The field study site

is the Nordic Main uranium-tailings impoundment, Elliot Lake, Ontario.

The Nordic Main uranium-tailings impoundment and surrounding area (Figs. 1–3) were chosen by the Institute for Groundwater Research of the University of Waterloo, Ontario, for detailed studies of geochemical processes occurring in and around uranium tailings. The Nordic Main tailings impoundment is located in a valley which contains a local sand aquifer and an essentially impermeable bedrock base (Fig. 3). The Nordic Main tailings were initially drained of ponded surface water in the late 1960's and the 3–7 wt.% pyrite in the tailings then came into contact with atmospheric oxygen and acid production began. The acid production created low-pH, high-iron, high-sulfate pore water containing significant concentrations of many other contaminant ions. This water then began seeping from the tailings into the underlying sand aquifer and began moving southward through the aquifer (Fig. 3).

The geochemical processes operating in the area were first discussed by Blair et al.

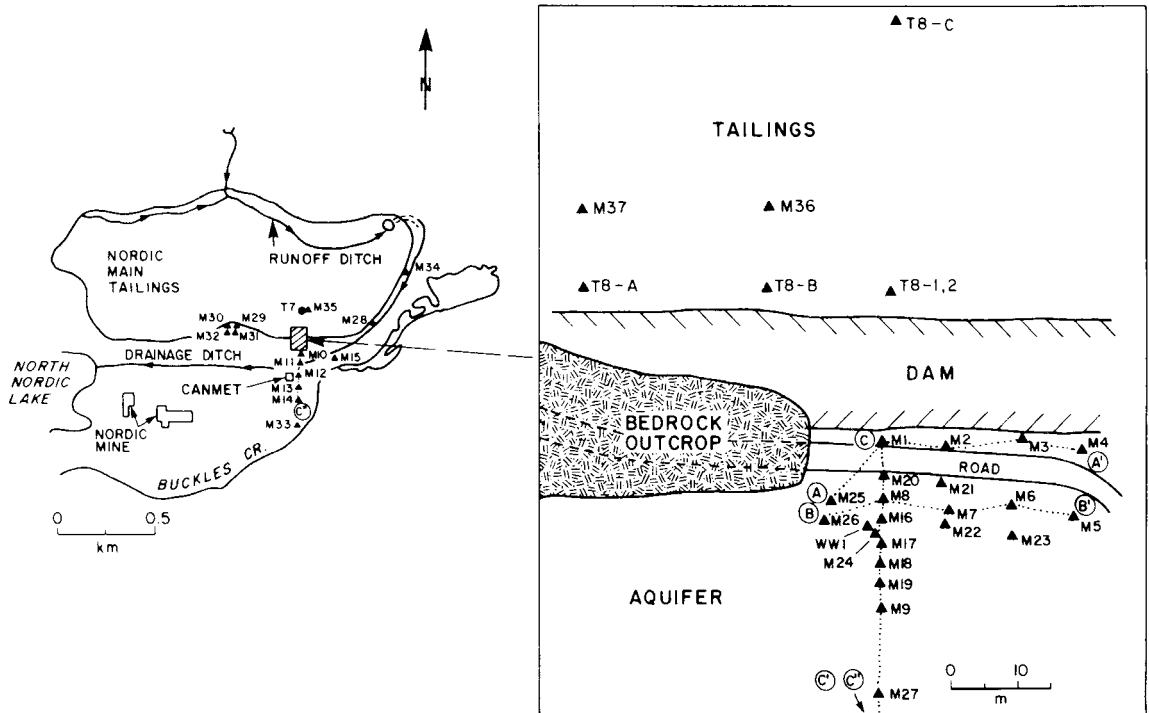


Fig. 2. Piezometer locations and general map of the Nordic Main area.

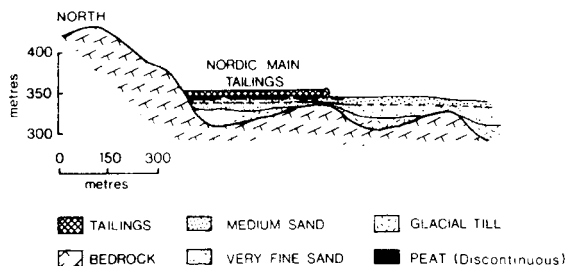


Fig. 3. Generalized north-south cross-section through the Nordic Main area.

(1980) and Blair (1981). Later detailed studies described surface water-groundwater interactions on the tailings (Blowes, 1983), water and gases in the unsaturated zone of the tailings (Smyth, 1981), the saturated zone of the tailings (Dubrovsky et al., 1985a, b; Dubrovsky, 1986), and pH neutralization of tailings seepage in the surrounding aquifer (Morin et al., 1982; Morin, 1983; Dubrovsky et al., 1984, 1985).

Because pH neutralization of the acidic seepage was occurring in the surrounding aquifer, the presence of a carbonate compound, particularly calcite, was suspected. Because a great deal of aqueous ferrous iron was lost from solution upon neutralization, the formation of siderite by the replacement of calcite was also suspected.

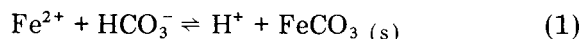
2. Theory

A compilation of information on the mineralogy, thermodynamics, kinetics, associations, sampling problems and analytical problems for siderite and associated minerals (Fe-sulfides and Fe-phosphate) is located in appendix A of Morin (1983). This section is based on that compilation.

The formation of siderite can occur in one of three ways: chemical reduction of a ferric iron compound, direct precipitation from solution, or substitution of Fe^{2+} into another carbonate with which siderite forms a solid solution. As examples of the first method of formation, Tancredi et al. (1975) believe that siderite in the Amazon delta is formed by alteration of limonite in reducing

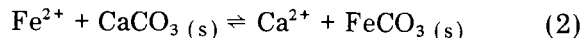
waters and Postma (1982) observed siderite formation by reduction of goethite by organic matter. However, the remaining two methods of formation are important here, because they involve significant liquid-solid interactions with aqueous Fe in order to form siderite.

The dominant direct-precipitation reaction in neutral-pH water is:



This reaction indicates many characteristics of a siderite-precipitating environment: (1) the groundwater must be relatively high in dissolved carbonate (neutral to alkaline pH) in order for substantial quantities of siderite to form; (2) the environment is under reducing conditions so that Fe will occur in the 2+ state rather than the 3+ state; and (3) the pH and dissolved carbonate of the groundwater will vary as eq. 1 operates. Siderite precipitation from 2000 to 40 ppm aqueous Fe requires ~4 hr. (Thornber and Nickel, 1976).

Siderite may also originate through the replacement of calcite or aragonite:



This reaction indicates many characteristics of a siderite-forming environment: (1) solid-phase carbonate is already present; (2) the environment is under reducing conditions so that Fe will occur in the 2+ state rather than the 3+ state; and (3) the amount of dissolved carbonate in the groundwater is not affected by eq. 2. Detectable replacement of calcite by siderite requires tens to hundreds of hours (Babcan, 1970).

The one characteristic which greatly complicates the geochemistry of siderite is that siderite is one end-member of a solid-solution series with common carbonates: calcite (CaCO_3), magnesite (MgCO_3) and rhodochrosite (MnCO_3) (e.g., Goldsmith, 1959). For calcite, significant end-member substitution of Mg is well documented (e.g., Plummer and Mackenzie, 1974). Substitution in siderite is not as well documented. Morin (1983) located nine references containing analyses of

natural siderite; the data of Pearson (1979) showed the maximum average of 18% substitution of other end-members: 7% CaCO_3 and 11% MgCO_3 . The other analyses ranges from 0.15% to 3.5% CaCO_3 , from 0% to 5.2% MnCO_3 , and from 0.2% to 10.2% MgCO_3 .

In cases where siderite forms by the replacement of calcite or aragonite, a significant amount of Ca could be expected to be present in siderite. As is typical in solid-solution series (Winchell, 1951), this remaining Ca affects the physical and chemical properties of siderite. Likewise, when the replacement of calcite begins, the initial Fe affects the physical and chemical properties of the calcite.

In order to explain basic concepts, calcite—siderite will initially be treated as a complete solid solution, i.e. a full range of compositions exists from pure calcite to pure siderite. The inaccuracies in this initial assumption will then be addressed. The mathematically-correct form of the solubility product of a solid solution is shown by Lippmann (1977, 1980) and Gresens (1981a, b) to include the sum of the activities of the cations. For the calcite—siderite solid solution:

$$K = (u[\text{Ca}^{2+}] + v[\text{Fe}^{2+}]) [\text{CO}_3^{2-}] \quad (3)$$

where u and v are weighting factors for the preference of one ion over another in the crystal structure.

Assuming $u = v = 1$ (see following paragraph for further details on this assumption), the equations in Gresens (1981b) can be used to predict the solubility-product value from X_{FeCO_3} , which is the mole-percentage of FeCO_3 in the solid carbonate, and from $N_{\text{Fe}^{2+}}$, which represents the ratio $\{[\text{Fe}^{2+}]/([\text{Fe}^{2+}] + [\text{Ca}^{2+}])\}$ in the solution. Fig. 4 shows these relationships, based on the approximate solubility products of CaCO_3 ($\sim 4 \cdot 10^{-9}$) and FeCO_3 ($\sim 4 \cdot 10^{-11}$) at 10°C and based on the assumption that the complete solid solution exists at 10°C . Curve 1 is the solidus and curve 2 is the solvus; tie lines are horizontal.

For example, if $N_{\text{Fe}^{2+}} = 0.1$, K would equal $4 \cdot 10^{-10}$ (Fig. 4) and $([\text{Fe}^{2+}] + [\text{Ca}^{2+}])[\text{CO}_3^{2-}]$ could be approximated by $(1.11[\text{Ca}^{2+}]) \times [\text{CO}_3^{2-}]$, which is essentially the form of the

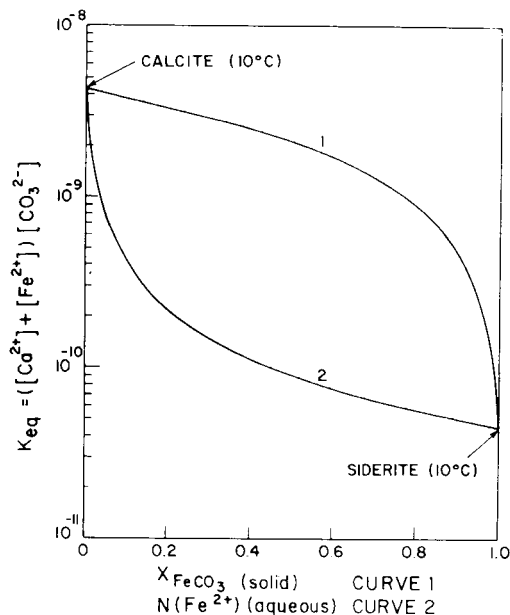


Fig. 4. Solubility of the siderite—calcite solid solution. Calculated from equations in Gresens (1981b).

solubility product of pure calcite. Therefore, any computer program which speciates the water in equilibrium with this carbonate would predict that the water is about one order-of-magnitude undersaturated $\{4 \cdot 10^{-10}/(1.11 \times 4 \cdot 10^{-9})\}$ with respect to calcite. Again, if $N_{\text{Fe}^{2+}} = 0.1$, then $([\text{Fe}^{2+}] + [\text{Ca}^{2+}]) \times [\text{CO}_3^{2-}]$ can be approximated by $(10.0 \times [\text{Fe}^{2+}])[\text{CO}_3^{2-}]$. Therefore, the predicted saturation state of the water with respect to pure siderite is $\{4 \cdot 10^{-10}/(10.0 \times 4 \cdot 10^{-11})\} = 1.0$ or, in other words, the water is at saturation with respect to pure siderite. As a result, identification of the particular composition of $(\text{Ca,Fe})\text{CO}_3$ in equilibrium with a solution is not easily made on the basis of aqueous data, although saturation and supersaturation with respect to siderite will usually indicate the presence of some form of the solid solution. The effect of the weighting factors, u and v in eq. 3, on this example and on the solubility of the solid solution in general (when $u \neq v \neq 1$) is significant, but little information on weighting factors for calcite—siderite exists. Also, the weighting factors could be complex, based on the work of Lahann and Siebert (1982). As the assumption $u = v = 1$ is

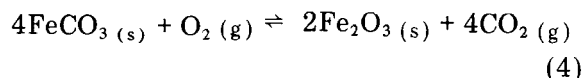
generally unrealistic and no detailed information on u and v could be found, it is not possible at the present time to reliably predict the solubility of the solid solution.

The above discussion has assumed that calcite and siderite form a complete solid solution; the inaccuracies in this assumption and their effect on solubility will now be addressed. The foremost inaccuracy is that calcite and siderite do not form a complete solid solution. In fact, Lippmann (1980) shows that the maximum theoretical amount of substitution of Fe in calcite and Ca in siderite is less than 0.2% at 25°C. As a result, Lippmann demonstrates the relationship of solubility values (K in eq. 3) to $N_{\text{Fe}^{2+}}$ through a eutectic diagram in which either essentially pure calcite or pure siderite may form. This eutectic diagram also indicates that, when the aqueous ratio $[\text{Fe}^{2+}]/[\text{Ca}^{2+}]$ is greater than 0.01, pure siderite forms, otherwise pure calcite forms. However, as pointed out above, up to 7% CaCO_3 has been found in siderite, which indicates that there is a large metastable range in the calcite—siderite solid solution; the presence of this metastable range is also shown mathematically by Lippmann (1980). Solubility within this metastable range could be difficult to define and may be dependent on solution composition.

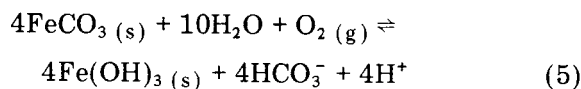
Another inaccuracy in the calcite—siderite solid solution, which also renders solubility predictions even more difficult, is the assumption of chemical equilibrium. In low- p_e , high-Fe waters, supersaturation with respect to pure siderite is commonly observed. For example, supersaturation of up to 1.5 orders-of-magnitude has been observed in landfill leachate (Buszka, 1982), acid drainage (Nordstrom, 1977), bog-deposit pore waters (Postma, 1977, 1981), swamp sediments (Postma, 1982), and uranium-tailings seepage (Morin, 1983). The probable stabilities of undocumented ferrous-iron complexes (Singer and Stumm, 1970; Mattigod and Sposito, 1977; Langmuir, 1979) are not great enough to account for this supersaturation. Postma (1981) attributes the supersaturation to slow kinetics

of siderite formation and Postma (1982) attributes supersaturation to very small crystal size. As direct precipitation of siderite is 98% complete from 2000 ppm Fe in solution in 4 hr. (Thorner and Nickel, 1976), kinetics of direct precipitation would not account for significant, persistent supersaturation. As the replacement of calcite by siderite requires up to hundreds of hours to approach completion (Babcan, 1970), kinetics of replacement could account for some cases of observed supersaturation. However, Morin (1983) found that siderite supersaturation ($\log SI > +0.5$) persisted for many years and that the degree of supersaturation was dependent on the aqueous ratio of $[\text{Fe}^{2+}]/[\text{Ca}^{2+}]$. This suggests solution-dependent metastability. In summary, because of possibly complex weighting factors, an incomplete solid solution, and the existence of kinetic or metastable controls, the precise characterization and solubility of the calcite—siderite solid solution cannot be defined at the present time.

Another difficulty with the calcite—siderite solid solution is the problem of detecting its presence because, when exposed to an oxidizing environment, FeCO_3 converts to a dark ferric oxide. The oxidation reaction in air can be generally expressed as:



The probable oxidation reaction in aerated water is:



Also, if pore water in contact with a siderite sample contains high levels of ferrous iron, then oxidation of the sample will initiate ferric hydroxide precipitation and the resulting acidity may dissolve the siderite.

In addition to the problem of oxidation of siderite and high-Fe pore water, which requires that a sample be obtained and transported in an air-tight sampling device, another

problem is the low detection limit required to identify important levels of siderite (down to ~0.01 wt.%). At first 0.01 wt.% siderite seems insignificant, but, as Berner (1980) points out, even 0.02 wt.% calcite can cause a 20% increase in dissolved Ca^{2+} in marine-sediment pore water. This important point for trace amounts of calcite also holds for siderite.

Morin (1983) found that a rapid, easy method for detecting siderite was to rapidly place the solid sample on a glass slide and use a scanning X-ray diffractometer with a high-sensitivity setting. The material cannot be ground because this would greatly increase the rate of siderite oxidation (Jamieson and Goldsmith, 1960). However, because of the faint peaks produced by the small amounts of siderite, because the coarse-grained material must be used without grinding resulting in weak and missing peaks, and because the solid solution causes shifts in the locations of peaks, this method does not yield conclusive results unless extensive preparation and testing of standards are undertaken and detailed statistical measurements of peaks are made. These requirements were not met as part of this study.

Detecting trace amounts of siderite by scanning electron microscopy was found by Postma (1977) to be unsatisfactory, because the siderite oxidized during polishing and mount preparation. However, Postma (1981) mounted unpolished samples and was thus able to identify siderite crystals of up to 25- μm diameter.

In summary, no reliable method for detecting trace amounts of siderite could be located. As a result, direct evidence of the presence of trace amounts cannot always be obtained. However, McIntyre (1984) describes crystal-surface techniques which may allow detection of trace amounts of siderite if oxidation is prevented.

3. Field and experimental methods

Piezometers installed in the glacio-fluvial sand aquifer (Fig. 2) are multi-level bundle-

type piezometers (Cherry et al., 1983). They consist of varying lengths of 0.9-cm I.D. polyethylene tubing, each with a 10-cm long, 0.9-cm I.D. polyethylene piezometer screen at the bottom. The screens with accompanying tubing were taped to a length of 1.5-cm I.D. PVC pipe for support. This design allowed the rapid installation of up to twelve small individual piezometers at various depths in one borehole.

The pH and Eh of the groundwater in each piezometer were obtained by continuously pumping water via a peristaltic pump through a 100-ml air-tight flow-through cell containing electrode probes. The flow-through cell prevented fluctuations and errors caused by the mixing of air with the groundwater. The pH of the groundwater was measured with a pH meter and combination pH electrode after calibration in pH 7 and pH 4 buffers. Following standardization in Zobell's solution, the Eh of the water was taken with a specific-ion meter and a combination Pt electrode with a button-type Pt disk of ~1.3-cm² area. Electrical conductance was measured with a conductance meter and probe following standardization in KCl solutions. Water samples were filtered through 0.45- μm membrane filters in a 142-mm-diameter disk filter. As the water was filtered, it was directed into polyethylene bottles, acidified with concentrated HCl, and sent to laboratories for analysis.

The results of water analyses and field measurements were entered as input into the chemical-equilibrium computer program, WATEQ2 (Ball et al., 1979). WATEQ2 results provided concentrations of free ions, ion pairs and complexes, and provided saturation states of the water with respect to many solid compounds.

Solid samples of aquifer material for calcite analysis were taken from auger flites during exploratory drilling and piezometer installation. A 1-m continuous core for siderite analysis was obtained by driving an air-tight 5-cm-diameter aluminum tube into the aquifer. Upon recovery, the tube was quickly sealed and returned for analysis. When the tube was opened, aquifer material was quickly placed

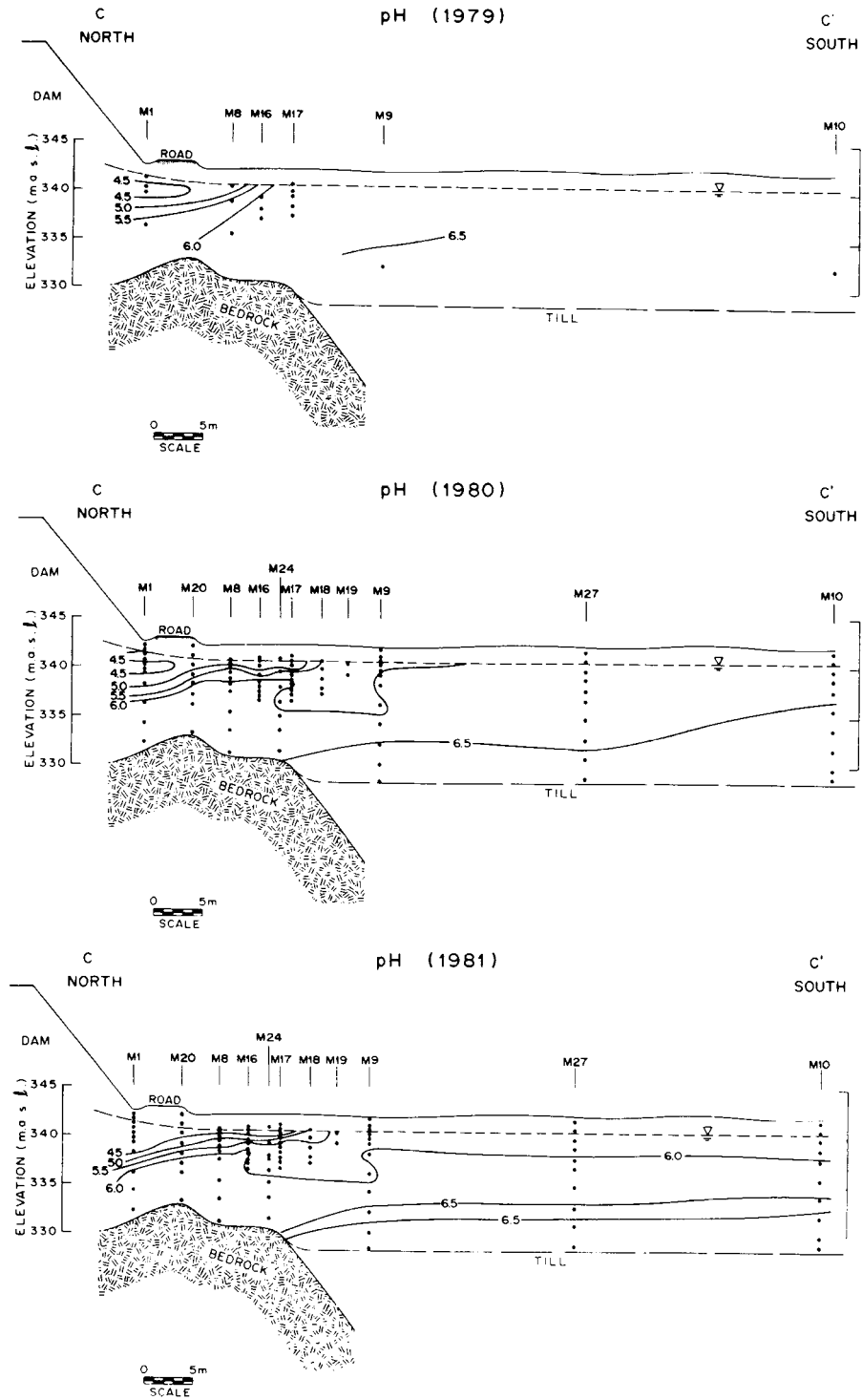


Fig. 5. For caption, see next page.

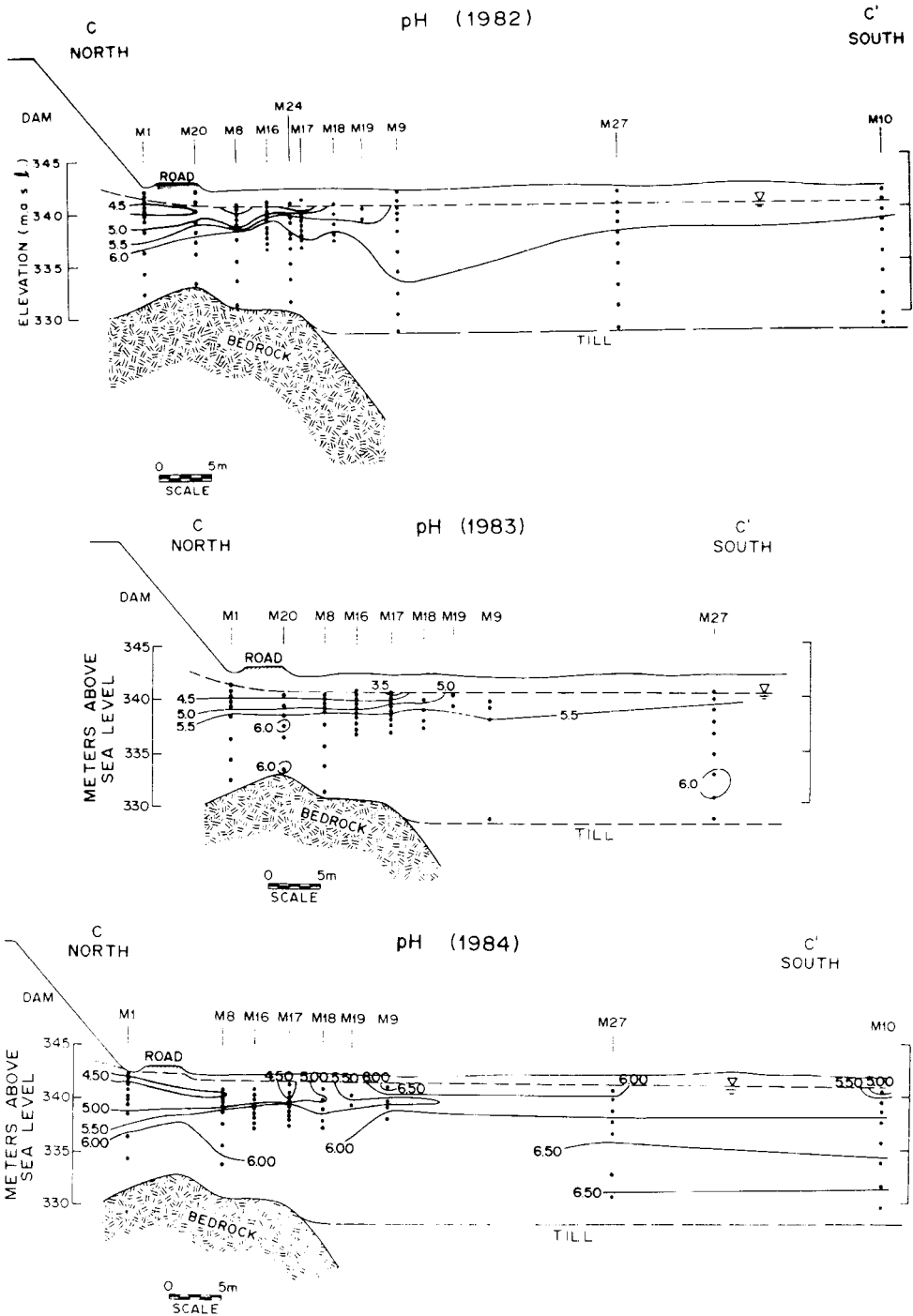


Fig. 5. pH profiles for the centerplane.

on glass slides and inserted into a scanning X-ray diffractometer. A high-sensitivity setting was used in order to detect faint peaks from the trace-concentration carbonate. Results,

which were inconclusive, are discussed in detail in Morin (1983).

A "field column" experiment was devised as a simple test of the rate at which siderite

replaces calcite in the high-Fe seepage from the Nordic Main tailings. About 25 wt.% of high-grade medium-grained crushed calcite was added to HCl-washed medium-grained sand. The combined material was placed in a Plexiglas® column of 16-cm length and 10-cm diameter. The column was transported to the Nordic Main site, flushed with CO₂ gas, and then flushed every few hours with low-pH, high-Fe water pumped directly from bundle

piezometer M1 (Fig. 2). After 24 hr., the column was sealed. The column was opened in the laboratory and the sand was quickly placed on glass slides and inserted into a scanning X-ray diffractometer.

4. Water chemistry

Seepage area A (Fig. 2) contains the contaminant plume described by Blair et al.

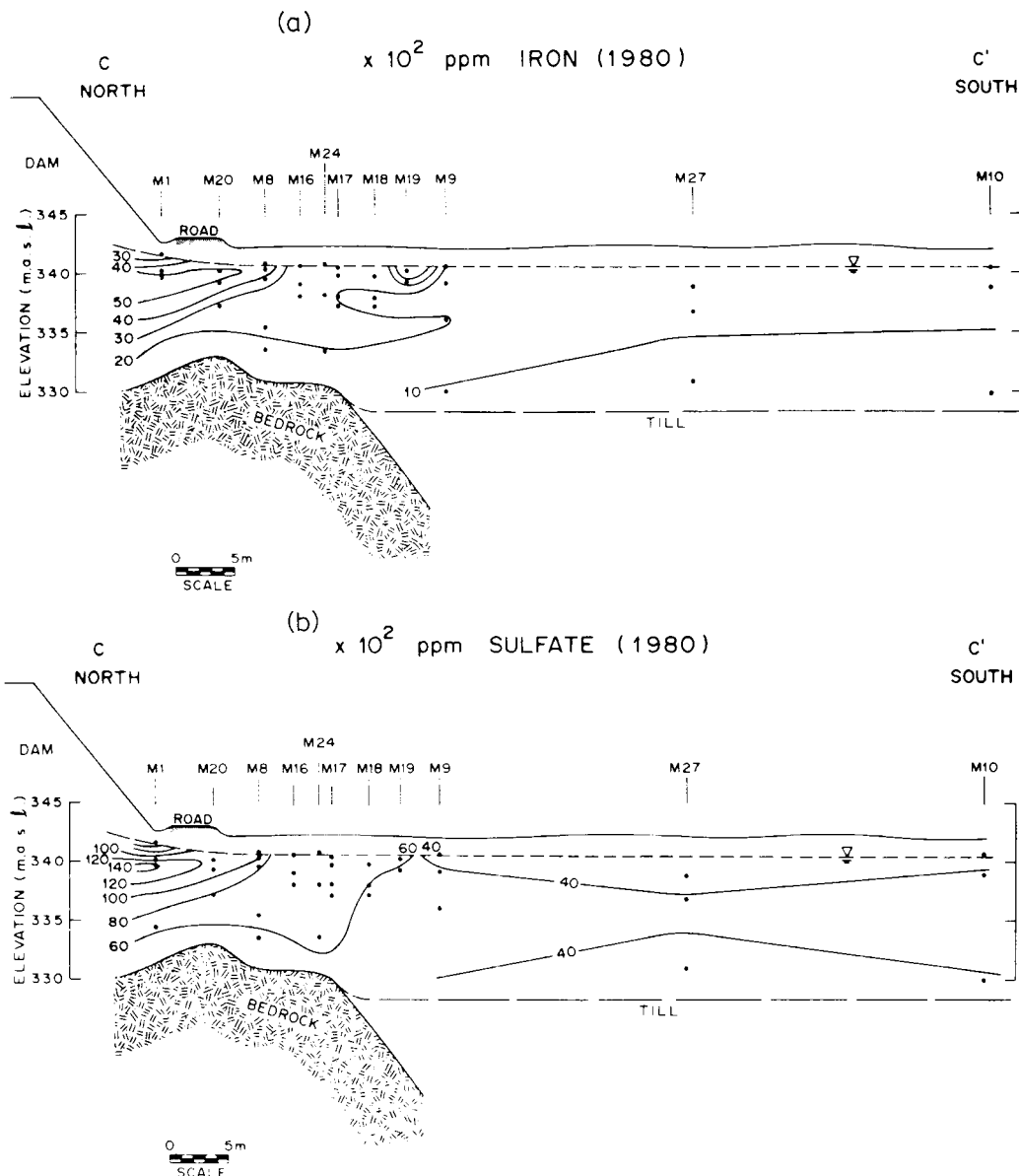


Fig. 6. a. Iron profile for the centerplane.
b. Sulfate profile for the centerplane.

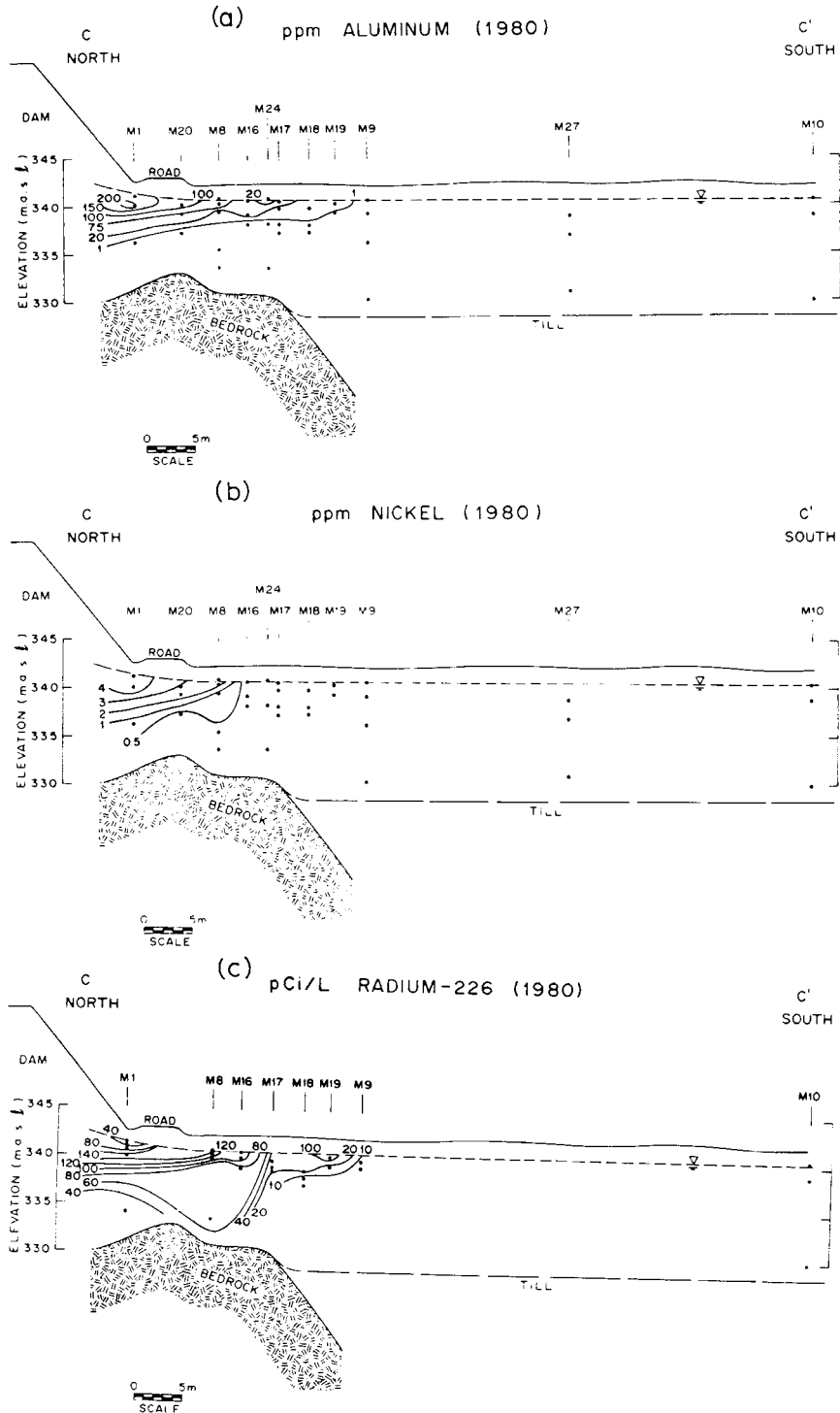


Fig. 7. a. Aluminum profile for the centerplane.
 b. Nickel profile for the centerplane.
 c. Radium profile for the centerplane.

(1980) and Morin et al. (1982). Through physical and chemical hydrogeologic information, Morin (1983) defined a vertical two-dimensional centerplane representing the center axis of the contaminant plume; the bundle piezometers representing the centerplane are M1, M20, M8, M16, M24, M17, M18, M19, M9, M27 and M10 (Fig. 2).

Figs. 5–7 contain aqueous-concentration profiles through the centerplane and centerline. Iron (Fig. 6a) is the major cation in solution and sulfate (Fig. 6b) is the major anion. Morin et al. (1982) and Morin (1983) divided the centerplane into three regions based on aqueous concentrations. The “inner core” has a pH < 4.8, iron > 5000 ppm and sulfate > 11,000 ppm. The inner core lies near the water table, extends only ~10 m from the base of the impoundment dam, and represents acidic tailings water which has seeped from the base of the tailings near the dam. The “outer zone” has pH > 5.4, iron < 2500 ppm and sulfate < 7000 ppm. The outer zone surrounds the inner core near the dam and, from M19 outwards, encompasses the entire saturated thickness of the sand aquifer. The transition zone between the inner core and the outer zone is the “neutralization zone”, in which pH is neutralized and concentrations of most ions decrease sharply (Figs. 5–7). Fig. 5 shows that the neutralization zone is generally migrating downgradient $\sim 1 \text{ m yr.}^{-1}$ which is 1/440 of the groundwater velocity near the dam (Morin, 1983). Thus, the downgradient movement of the inner core and neutralization zone is highly retarded with respect to water movement. The variability of the migration rate, which depends on the pH contour line chosen for the calculation, is a consequence of the sub-regions within the neutralization zone (discussed in Section 6).

5. Evidence of the presence of siderite

Aqueous data provide indirect evidence for the existence of siderite in the neutralization zone. As direct evidence is not conclusive, this evidence is important. The speciation data

and saturation states provided by the computer program, WATEQ2 (Ball et al., 1979), assisted greatly in data evaluation.

Several thousand ppm of iron (Fig. 6a) and sulfate (Fig. 6b) are lost (in the proportion of 1 Fe : 1 SO₄ on a molal basis) from solution in the neutralization zone. Morin (1983) found that adsorption and ion exchange could not account for this loss, thereby leaving chemical precipitation as the likely cause. The first obvious precipitate is a ferrous iron sulfate compound, but this compound can be ruled out for many reasons (Morin, 1983). For example, the loss of sulfate is easily explained by the precipitation of gypsum (CaSO₄·2H₂O), which is at saturation throughout the Nordic Main area. Thus the loss of aqueous Fe is through the precipitation of another Fe compound, of which the two most likely are Fe(OH)₃ and siderite.

The formation of siderite by replacement of calcite (eq. 2) and by direct precipitation (eq. 1) has already been discussed. Because over 99.9% of aqueous Fe in area A is in the 2+ state according to WATEQ2, the appropriate precipitation reaction for Fe(OH)₃ is:

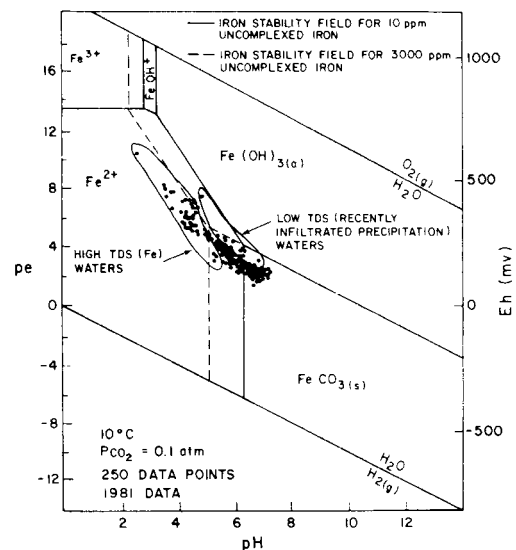
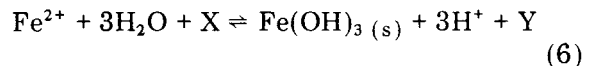


Fig. 8. pH-pe-Fe stability diagram with seepage area A data.

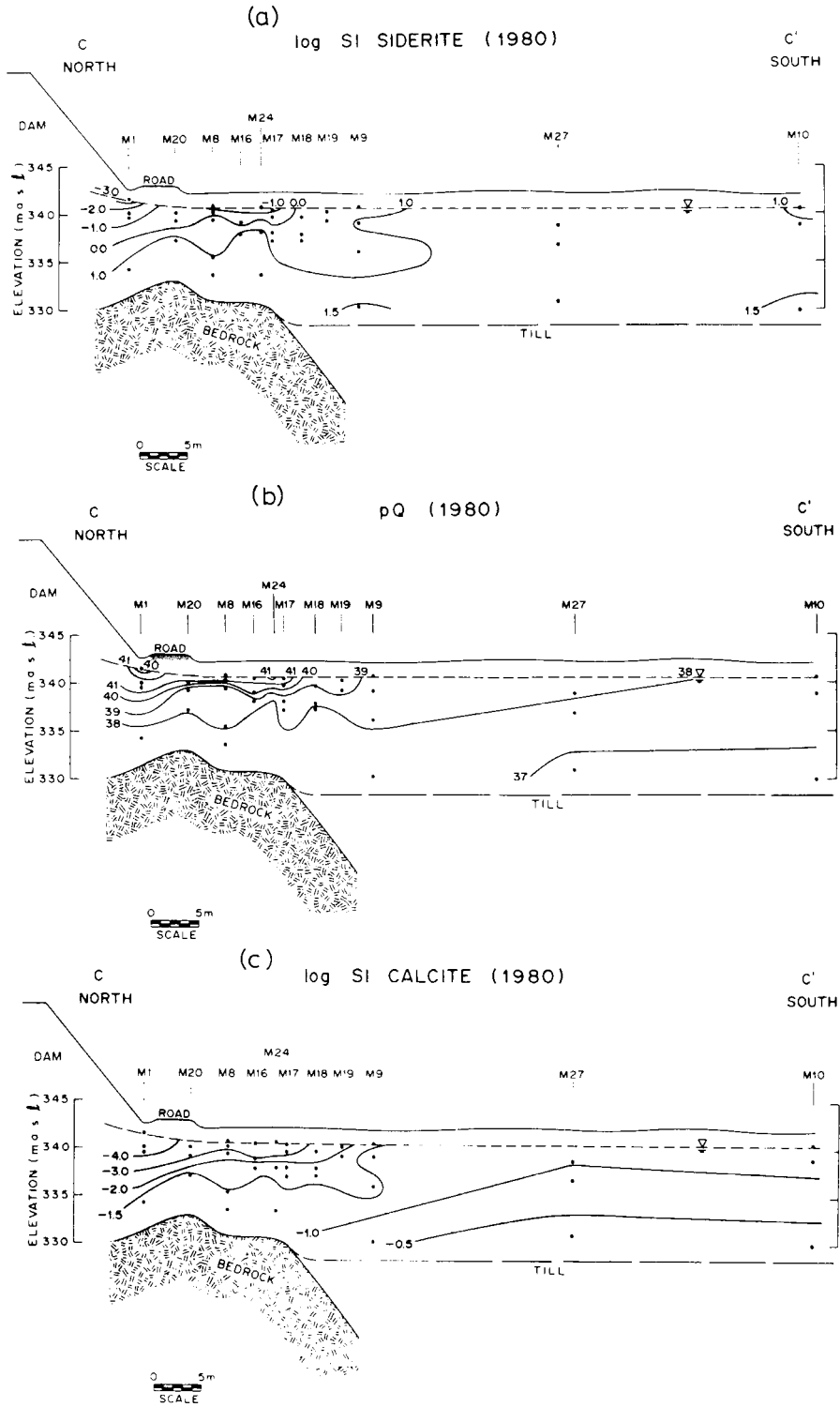


Fig. 9. a. $\log SI_{\text{siderite}}$ profile for the centerplane.
 b. pQ profile for the centerplane.
 c. $\log SI_{\text{calcite}}$ profile for the centerplane.

where X and Y are a redox couple that provide the electron transfer for the change of ferrous iron to ferric iron. Eq. 6 has a much greater effect on acidity levels per mole of Fe precipitated than eqs. 1 and 2.

There are several geochemical techniques that can be used to evaluate which Fe compound is forming in the aquifer. First is the pH-pe-Fe stability diagram (Fig. 8). This diagram indicates that siderite might be forming. However, such pH-pe diagrams are of limited value, because of assumptions made in their preparation such as the concentration of the free ion (e.g., Fe^{3+}) is equal to the total concentration of the element in the free ion's stability field. This leads to the more rigorous approach of complete speciation of water analyses and calculation of saturation indices.

Fig. 9a contains the $\log SI_{\text{siderite}}$ profile for the centerplane. The saturation index, SI, is equal to the ratio: (ion activity product)/(equilibrium constant) at solution temperature. Fig. 9a, which was drawn assuming linearity of $\log(SI)$ -values between data points, indicates that pure siderite is at saturation in the neutralization zone and supersaturated in the outer zone. As previously discussed in Section 2, the amount of Ca in the siderite and the solubility of the Ca-siderite cannot be evaluated.

The solubility of $\text{Fe}(\text{OH})_3$ is examined through pQ-values (Langmuir and Whittemore, 1971; Whittemore and Langmuir, 1975):

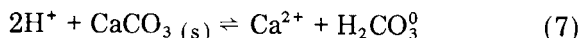
$$pQ = -\log[\text{Fe}^{3+}][\text{OH}^-]^3$$

These researchers and Nordstrom et al. (1979) believe that at 25°C $\text{Fe}(\text{OH})_3$ precipitation can only occur in the pQ range of 37 to ~ 39 ; in the range of ~ 40 to 44, dissolution of relatively crystalline precipitates occurs. Fig. 9b contains the pQ profile for the centerplane corrected to 25°C . The neutralization zone contains pQ-values of ~ 40 and, thus, $\text{Fe}(\text{OH})_3$ is unlikely to precipitate.

The third technique for selecting the precipitate is redox reactions. For siderite to precipitate in the neutralization zone, little redox change is required because most of the aque-

ous Fe is already in the 2+ state. However, for $\text{Fe}(\text{OH})_3$ to precipitate, eq. 6 indicates that another major redox couple must be present and that the maximum amount of $\text{Fe}(\text{OH})_3$ which can precipitate is represented by the concentration of X. Morin (1983) examined four redox couples ($\text{NO}_3^- - \text{NH}_4^+$, $\text{SO}_4^{2-} - \text{H}_2\text{S}$, $\text{O}_2 - \text{H}_2\text{O}$ and $\text{Mn}^{3+} - \text{Mn}^{2+}$) present in the groundwater and determined that, by assuming the redox changes in the couples are rapid, a maximum of ~ 20 ppm Fe could precipitate as $\text{Fe}(\text{OH})_3$.

The final technique for evaluating $\text{Fe}(\text{OH})_3$ precipitation is the stoichiometry of eq. 6. Assuming that there is sufficient X to allow the observed precipitation of ~ 3000 ppm (0.055 *m*) Fe, then 0.16 *m* H^+ is produced. Because pH is neutralized in the neutralization zone by calcite (discussed in Section 6), then the amount of dissolved inorganic carbon (DIC) produced by this additional 0.16 *m* H^+ is ~ 0.08 *m* by:



when pH remains below 6.4. Yet DIC remains at ~ 0.005 to ~ 0.010 *m* through the neutralization zone. Therefore, based on aqueous data the loss of Fe in the neutralization zone is most likely by the formation of siderite.

Fig. 9c contains $\log SI_{\text{calcite}}$ profiles for the centerplane. Because calcite is suspected of causing most of the pH neutralization, this diagram is initially surprising because it suggests that no calcite is present. Yet when the principles of siderite-calcite solid solution are recalled (Section 2), this undersaturation is in fact anticipated.

In order to check for the existence of calcite and to obtain a quantitative indication of the calcite content of the aquifer, solid samples were taken from deep in the aquifer near the sand-bedrock and sand-till contacts (Fig. 3) where Fe concentrations are lowest and pH is high. X-ray diffraction results were inconclusive because of the problems mentioned in Section 2. Thin-section analysis indicated the presence of $\sim 1\%$ calcite as both grains and grain coatings. For a more quanti-

tative measurement of the trace calcite, samples were analyzed by the method of Barker and Chatten (1982). The concentration varied from ~0.31 to > 1.44 wt.% calcite in four samples from near the sand-bedrock contact, with an average of 0.85 wt.% (Morin, 1983). Based on this, the entire aquifer is assumed to have originally contained ~ 0.85 wt.% calcite. Near the water table where Fe concentrations are relatively high and siderite is stable, the calcite is probably being replaced by siderite.

Solid samples were also taken from near the water table for quantitative carbonate analysis. However, these samples yielded low results, possibly because when exposed to the atmosphere the high-Fe concentrations in the pore water then precipitated as $\text{Fe}(\text{OH})_3$ and much of the carbonate (up to 0.2 wt.%) was therefore lost by neutralization of the resulting acidity (eq. 6). Also, because some of the calcite had been converted to siderite, some siderite may have oxidized.

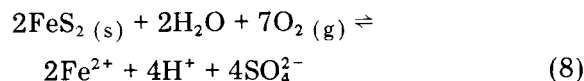
A brief test of the replacement of calcite by siderite in the aquifer is provided by the field column experiment. In this experiment, inner-core water from M1 was periodically pumped into a column containing sand and 25 wt.% crushed calcite. After 24 hr., the column was returned for analysis. As with the aquifer material, the matrix was not ground, thus producing the problems pointed out in Section 2. Some very minor peaks possibly representing siderite were located on the X-ray scans, suggesting that the replacement of 25 wt.% calcite requires much more than 24 hr., in agreement with the results of Babcan (1970). This does not give a reliable indication of the length of time required to replace less than 1 wt.% calcite as found in the aquifer.

In summary, various types of evidence support the hypothesis that the loss of 3000 ppm of aqueous Fe is probably the result of siderite formation and that the replacement of calcite by siderite is apparently occurring in the aquifer.

6. Effects of trace amounts of siderite on contaminant migration

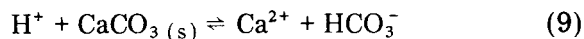
Siderite is one facet of a conceptual model which describes the migration of contaminants from uranium-tailings impoundments. The details for and evidence of this conceptual model are covered in detail in Morin (1983) and are abbreviated in Morin et al. (1982), Dubrovsky et al. (1984) and Morin and Cherry (in prep.). The model is summarized here with little discussion of its operation.

In the Nordic Main tailings, pyrite comes into contact with infiltrating precipitation and atmospheric oxygen and is oxidized. The overall reaction is:

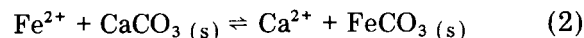


This reaction creates low-pH, high-iron, high-sulfate pore water in the tailings. Because the solubilities of some compounds increase and the sorptive capacity of solids decrease as the pH decreases to acidic values, heavy metals and radionuclides are released into the acidic pore water. Thus pH is a major control on the aqueous concentrations of many ions. Evidence for this scenario operating in the Nordic Main tailings is presented in Dubrovsky (1986).

As the acidic water seeps from the tailings into the aquifer, it eventually comes in contact with calcite and is neutralized as described by eq. 7. If pH rises above 6.45 (10°C), the dominant reaction is:

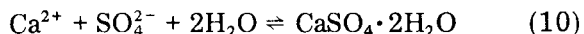


Because of high Fe concentrations, calcite is also lost by replacement:



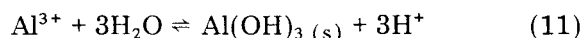
Eq. 2 produces 1 mole of aqueous calcium for every mole of aqueous iron lost. This increase in calcium causes the precipitation of

gypsum, which is at saturation throughout the aquifer, by the reaction:



Thus, for every mole of aqueous iron lost by calcite replacement, one mole of aqueous sulfate is lost by gypsum precipitation and aqueous calcium concentrations remain relatively constant.

As pH neutralization occurs, solubility of aluminum is exceeded and aluminum compounds such as $\text{Al}(\text{OH})_3$ precipitate:



The decrease in aluminum concentrations can be seen in Fig. 7a. Also, Morin (1983) and Morin and Cherry (in prep.) conclude that upon neutralization adsorption, chemical precipitation, and coprecipitation remove heavy-metal ions (Fig. 7b) and radionuclides (Fig. 7c) from solution.

Quantitative calculations can be made in order to show the importance of trace amounts of carbonate if the groundwater is envisioned as travelling along the plume centerline through a streamtube of cross-sectional dimensions $1 \text{ m} \times 1 \text{ m}$. This streamtube is divided into sections of 1-m length, thereby forming a series of 1-m^3 cells in which the various geochemical reactions occur as the groundwater advances. Because the porosity of the sand near the water table is 0.36, a cell contains a pore volume of 0.36 m^3 (360 l) of groundwater and 0.64 m^3 of sand; because the specific gravity of the sand is 2.98, there is $\sim 1.91 \cdot 10^6 \text{ g}$ of sand in a cell (Morin, 1983). The aquifer is assumed to have originally contained $\sim 0.85 \text{ wt.}\%$ calcite and therefore each cell originally contained $1.62 \cdot 10^4 \text{ g}$ (162 mol) of calcite. By eq. 7, 162 mol calcite can neutralize 324 mol H^+ . Because the pH of the inner-core water is ~ 4.5 , one cell (360 l) would contain $\sim 0.011 \text{ mol H}^+$. Therefore, $0.85 \text{ wt.}\%$ calcite can neutralize $324/0.011 = 28640$ cells' worth of H^+ or, in other words, the calcite would retard the acid-front movement by $\sim 0.011/324 = 3.5 \cdot 10^{-5}$ of the groundwater velocity. The observed retarda-

tion is only $1/440 = 0.002$, so there is another process also "consuming" calcite and this is siderite formation. Assuming that siderite is insoluble, i.e. it does not re-dissolve after forming, the amount of calcite consumed is easily calculated. Because there is 3000 ppm Fe (0.055 mol) lost over the 5-m length of the neutralization zone, there is a conversion of 19.5 mol calcite to "insoluble" siderite in the five cells representing that zone. Thus, the total loss of calcite in the neutralization zone is 19.5 mol (to siderite) and 0.011 (to pH neutralization), or essentially 19.5 mol. The new retardation factor is thus $(19.5/162 \times 5) = 0.02$, as compared to the observed factor of ~ 0.002 . A very close match (~ 0.003) is obtained when all precipitating and re-dissolving compounds, such as siderite, are considered and the significant pH-buffering capacity of the solution is taken into account. A computer program, ADNEUT (Morin, 1983), was written to perform these complex calculations.

In the foregoing discussion, the neutralization zone was treated as a single entity.

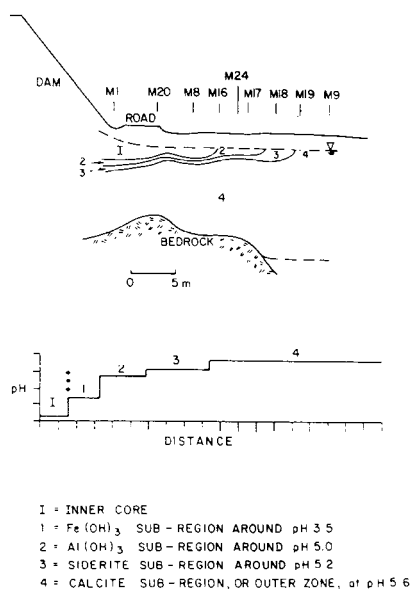


Fig. 10. Schematic of sub-regions with application to seepage area A.

However, simulation of the conceptual model by the chemical equilibrium-transport model, ADNEUT (Morin, 1983), has shown that the neutralization zone is composed of sub-regions (Fig. 10). Each sub-region is controlled by one of the solids of the conceptual model. For example, in seepage area A at the Nordic Main impoundment, one sub-region is the calcite sub-region, in which calcite is being actively replaced by siderite, and $\text{Al}(\text{OH})_3$ is precipitating. Calcite neutralizes the pH in this sub-region to 5.7. After the calcite is completely replaced, siderite begins dissolving, neutralizing the pH to 5.2, while $\text{Al}(\text{OH})_3$ continues to precipitate. After siderite is removed, $\text{Al}(\text{OH})_3$ begins dissolving, neutralizing the pH in its sub-region to 5.0. In this way, the migration of the inner core with its high levels of contaminants is significantly retarded with respect to groundwater velocity by the trace amounts of compounds.

The application of the conceptual model to uranium-tailings seepage at some Wyoming, U.S.A., impoundments is briefly discussed in Cherry et al. (1982) and application of ADNEUT to these Wyoming sites and another site in Ontario is discussed in Morin (1983) and Morin and Cherry (in prep.). Details of the internal workings of ADNEUT can be found in Morin (1983, 1985).

7. Summary

This paper has reviewed some aspects of the low-temperature geochemistry of siderite. Siderite forms by three basic mechanisms: (1) chemical reduction of a ferric compound; (2) direct precipitation from solution; and (3) substitution of Fe^{2+} into another carbonate mineral. The last mechanism is important in this study and, thus, the solid-solution series between calcite and siderite was examined in detail. This solid solution does not display a complete range of substitution and the solubilities of calcite and siderite are affected by substitution, metastability and reaction kinetics. Lack of theory and experimental work prevent a practical understanding of the calcite-siderite solid solution.

Additional problems lie in sampling for and analysis of siderite. Oxidation of siderite and of associated Fe-rich pore water upon sampling may remove siderite from a sample. Common analytical methods may allow siderite to oxidize before analysis. Also, common methods are not capable of detecting siderite at levels representative of some active groundwater systems (<1 wt.%).

Because of the lack of direct evidence, results of the field study demonstrated the probable presence of siderite through indirect aqueous-based means: pH-pe diagram, saturation indices of minerals calculated through a speciation model, availability of reactants for precipitation reactions, and stoichiometry of precipitation reactions. These indirect lines of evidence indicate that siderite has apparently formed in the aquifer at the field site by the replacement of calcite, and siderite and calcite are present at levels less than 1 wt.%. Observed supersaturation with respect to siderite did not appear to be a kinetic effect.

The relatively low levels of carbonate are unimportant from a general viewpoint, but are substantial from a geochemical viewpoint. In the absence of other reactions, calcite at 0.85 wt.% in the aquifer is capable of retarding migration of the acidic seepage to $\sim 1/28000$ of the groundwater velocity. Where siderite "consumes" calcite by replacement, thereby lowering neutralization capacity, retardation is reduced to 1/50 of groundwater velocity. When all aqueous buffering reactions and redissolution of siderite and other precipitated minerals are considered, a good agreement is obtained between calculated and observed retardation which is 1/440 of groundwater velocity.

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