

Metal Transport in Groundwater Contaminated by Acid Mine Drainage

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Acid mine drainage from a rock dump at an abandoned mine in Dalarna, Sweden, has contaminated the groundwater and created a leachate plume characterized by low pH and high concentrations of Fe, SO₄, and heavy metals. Groundwater samples have been collected in order to explain the observed spatial variations in groundwater chemistry. The mineralogy of soil samples collected at the water table has been identified by X-ray diffraction analysis. In order to determine which processes may be controlling the evolution of the leachate plume, the geochemical mass-transfer model PHREEQE is used to evaluate a possible reaction pathway controlling the reaction of the leachate plume with uncontaminated groundwater and the till aquifer. The results suggest that silicate weathering and goethite precipitation are the processes primarily controlling observed pH, pe, and Fe concentrations in groundwater direct down-gradient of the rock dump. Increases in K, Na, and Al concentrations along the flow path can be attributed to the feldspar weathering, while Al and SO₄ concentrations further down-gradient can be controlled by the precipitation of AlOH₂SO₄. The attenuation of heavy metal concentrations may be the result of adsorption and coprecipitation with goethite and other Fe oxides.

Introduction

Acid mine drainage is the result of the atmospheric oxidation of sulfidic mine wastes in contact with infiltrating water. This process releases sulfuric acid (H₂SO₄) and heavy metals into the drainage waters, which can lead to the acidification of

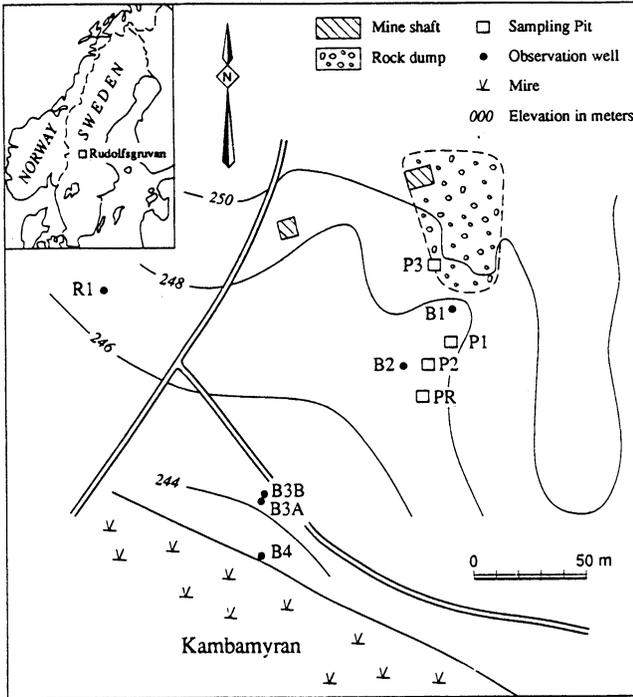


Fig. 1. Map of field site and its location in central Sweden.

recipient groundwater and surface water-bodies and ultimately to the deterioration of aquatic ecosystems. The site of the present study is an abandoned mine, Rudolfsgruvan, which is part of the Slättberg mines situated approximately 12 km south of Rättvik, in the province of Dalarna, Sweden (60°48'N, 15°15'E). Mining of copper, iron, and nickel ores commenced in 1805 (Löfstrand 1904) and ceased during the 1940s. The Slättberg mining field follows a two to six metre wide amphibolite dike in a WSW-ENE orientation, which has intruded into a reddish granitic gneiss host rock (Tegengren 1924). The ore occurs as impregnations in the dike, primarily as the sulfide minerals pyrite (FeS_2) and pyrrhotite (FeS) with lesser amounts of chalcopyrite (CuFeS_2). Waste rock derived from the excavation of the tunnels and shafts has been dumped direct adjacent to the mine, covering a surface area of about 1,300 m^2 with a thickness between one to two metres (Fig. 1). The waste rock material consists primarily of sand- to fist-sized rock fragments containing significant amounts of pyrite, pyrrhotite, and chalcopyrite.

The percolation of rain water and snow-melt through the unsaturated rock dump has created a leachate plume in the groundwater, characterized by low pH and high concentrations of Fe, heavy metals, and sulfate (SO_4). To predict the future evolution of the contaminant plume and to determine possible future impacts on environmental quality, it is necessary to understand the geochemical processes controlling the plume's evolution. The main objective of this investigation is to

explain the observed spatial variations in groundwater chemistry. Since it is believed that the major trends in the observed element concentrations are governed by acid neutralization processes and the precipitation of Fe oxides, these processes are primarily discussed in this paper. The analytic results of groundwater samples are interpreted in combination with mineralogical data from soil samples collected near the groundwater table and geochemical modeling.

Related Investigations

There have been a number of reports published in recent years regarding acid mine drainage related groundwater contamination. Of particular relevance to this study are those investigations which have discussed pH buffering mechanisms and the removal of metals by mineral precipitation. White *et al.* (1984) discussed the contamination of a shallow alluvial aquifer by an inactive uranium mill tailings pile, where a 1 km plume with elevated Na, Ca, SO₄, U, and Mo concentrations had developed in the course of 25 years. Although the tailings pore water was acidic (pH 1-2), the contaminated aquifer maintained a pH buffered at greater than 6.5, indicative of acid neutralization by the dissolution of carbonate minerals found in the soil and alluvium. In addition, the study determined that gypsum (CaSO₄·2H₂O) was precipitating, utilizing Ca derived from calcite (CaCO₃) dissolution and sulfate derived from the tailing leachate. Since oxidizing conditions persisted within the tailings, the precipitation of Fe and Al hydroxides was presumed to occur when the low pH tailing water mixed with the neutral pH groundwater. Similar findings were reported by Lind and Hem (1993), where copper mine runoff and leaching practices had created a groundwater contamination plume that had advanced down-gradient in a band of alluvium and contaminated groundwater along a 15 km flow-path. Aluminum, Fe, and Cu concentrations all exceeded 100 mg/l within the plume, at a pH of <5. Although the source water was initially acid (pH 2.7), the plume reacted with calcite during flow through alluvium, becoming less acid. Where oxygen was present and the water was partially neutralized, Fe oxides precipitated at the water table; Mn oxides formed at the water table at near neutral pH. It was believed that Cu, Zn, and probably other metals were being concentrated in the Mn oxide coatings on the aquifer material.

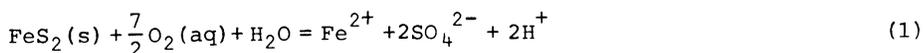
A geochemical study conducted by Dubrovsky *et al.* (1985) showed that pyrite oxidation in an inactive tailings deposit was creating a zone of low pH waters containing high concentrations of Fe, SO₄, and heavy metals. This contaminated zone was gradually displacing the underlying neutral-pH groundwater. The investigation indicated that Fe solubility was controlled by siderite (FeCO₃) at high pH, Fe(OH)₃ at moderate to slightly acid pH values, and possibly by jarosite (KFe₃(SO₄)₂(OH)₆) at low pH. Buffering reactions with small amounts of carbonate minerals in the tailings, along with the weathering of aluminosilicates and Al

hydroxides, have retarded the movement of the low-pH front relative to the rate of groundwater flow in the tailings.

A contaminant migration "flow-cell" model was used in a study by Morin and Cherry (1988) to simulate the neutralization of a groundwater contaminant plume created by drainage from an uranium tailings impoundment. The study indicated that major ions in the plume were controlled predominantly by precipitation-dissolution of the calcite-siderite solid solution, gypsum, and Al and Fe hydroxides, where acid neutralization was the result of the dissolution of one of these minerals. The investigation indicated that the neutralization zone could be divided into subregions, where the aqueous chemistry of each subregion was dominated by one of these minerals. The buffering sequence followed the order: calcite – siderite – $\text{Al}(\text{OH})_3$ – $\text{Fe}(\text{OH})_3$, buffering the solution within the pH ranges 5.5-6.8, 5.1-6.0, 4.3-5.0, and 3.0-3.7, respectively. These pH ranges are site dependent, varying according to the chemistry of the tailing drainage waters, the solubility of minerals, and site conditions.

Geochemistry Background

A thorough understanding of the chemistry of Fe in the studied groundwater system is necessary since Fe hydrolysis and precipitation/dissolution reactions act as strong pH buffers. In addition, by determining the behavior of Fe, it is also possible to understand the behavior of such heavy metals as Cu, Pb, and Zn, which will, to some degree, follow the fate of Fe. Iron in acid mine drainage-waters is primarily released through sulfide oxidation, which is well-documented (see Singer and Stumm 1970, Nordstrom 1982a, Sullivan *et al.* 1988). In general, the oxidation of pyrite (FeS_2), a common sulfide mineral, is initiated by its reaction with oxygen



In the presence of oxidizing agents, some of the Fe(II) will oxidize to Fe(III) and eventually precipitate as insoluble iron (III) oxides ("oxide" will be used as a collective term for oxides, hydroxides, and oxyhydroxides) or basic iron sulfates at a relatively short distance from the source. The equilibrium precipitation/dissolution of Fe oxides, such as goethite ($\alpha\text{-FeOOH}$), can effectively buffer pH according to the following reaction



The aqueous and mineral speciation of Fe is determined by pH, the redox potential (expressed as p_e , *i.e.* the negative log of the electron activity), and the availability of complexing ligands such as SO_4 . In natural aqueous environments, the redox system may or may not be in equilibrium. In a system with a number of reductants and oxidants, if the p_e of all the redox couples (*e.g.* $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{SO}_4^{2-}/\text{HS}^-$, $\text{CO}_2/$

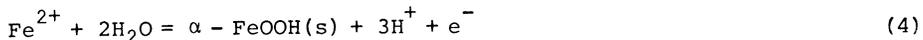
CH₂O) is the same, then the redox system can be considered in equilibrium and the measured pe would be the "system" pe. However, in natural systems the pe of each redox couple may be different and a "system" pe is therefore meaningless. Many groundwater systems are not well poised, and speciation calculations have shown that various redox couples are often in disequilibrium (Lindberg and Runnells 1984).

The redox reaction for determining the ratio of Fe²⁺ to Fe³⁺ in solution is determined from the reaction shown in Eq. (3), which has an equilibrium constant of logK = -13.02 (Nordstrom *et al.* 1990)



In acid mine drainage systems at low pH and with high total Fe²⁺ and Fe³⁺ activities, Eq. (3) provides a dominant and reversible couple that poises the redox conditions and is measurable with a platinum electrode. The measured redox potential for such systems has been shown to be an accurate representation of the system pe (van Breemen 1976, Nordstrom *et al.* 1979). Although it is possible for the Fe³⁺/Fe²⁺ couple to poise the redox conditions at higher pHs and lower Fe concentrations, such systems are extremely sensitive to contamination by dissolved oxygen (Grenthe *et al.* 1992).

If equilibrium exists with respect to goethite and the Fe redox couple, then Fe oxidation can be expressed as the combination of Eqs. (2) and (3)



Since "free" electrons do not exist in solution, the oxidation half-reaction (Eq. (4)) needs to be coupled with a reduction half-reaction such as the reduction of oxygen to water, the reductive dissolution of Mn oxides, or denitrification. In systems that are well-buffered with regard to decreases in pe and pH, the removal of Fe³⁺ through goethite precipitation at equilibrium will lead to a decrease in Fe²⁺ activity, as indicated in Eq. (4). When the pe is not well-buffered and the redox couples may be in disequilibrium, the precipitation of goethite would decrease Fe³⁺ activity and pe (*cf.* Eqs. (2) and (3), respectively).

Methods

The rock dump rests on sandy-silty glacial till, which varies in thickness from one to five metres across the site. Groundwater flows within the unconfined till aquifer and discharges into a fen, Kambamyran, which lies 145 m hydraulically and topographically down-gradient from the rock dump (Fig. 1). The entire site is covered by a cultivated pine and spruce forest (approximately 40 years old) with the exception of the rock dump and the fen, and is on podzolic soil. Six groundwater wells were installed on the site in September 1991. Each well was installed direct above bedrock, with slots along the lowest 40 cm of the pipe. Based on prior surface water

Table 1 – Data for groundwater wells on the study site. Water level data are from May 23, 1993. All data are in units of metres

Well	Distance from dump	Total Depth	Surface Elevation	Depth to Water Table
B1	10	2.9	247.54	1.22
B2	44	3.7	246.47	1.39
B3A	130	4.95	244.23	1.51
B3B	130	2.65	244.23	1.54
B4	144	1.14	242.47	0.26
R1	–	3.2	247.00	1.33

analyses from Kambamyran (see Herbert 1993) and topographical considerations, the wells are installed in locations which are judged to lie direct down-gradient of the rock dump (*i.e.* along a stream-line). Wells B3A and B3B were installed close together at different depths to determine if the chemical characteristics of the leachate plume vary with depth. Well R1 is a reference well which represents background groundwater quality.

Data regarding the total depth of the wells, surface elevation, and depth to water on May 23, 1993 are given in Table 1. The groundwater levels for this sampling episode were higher than the average values calculated from data from the past two years. Analytical results from the May 1993 sampling period are used in this study. Prior to sampling, all wells were purged of at least three casing-volumes of water, or were pumped until dry, and then allowed to recover. The temperature and redox potential of groundwater samples were measured in the field (Orion 96-78 combination platinum electrode), whereupon the samples were stored at 4°C and transported directly to the laboratory. Upon delivery, all groundwater samples were analyzed to determine pH, alkalinity (HCO_3^-), electrical conductivity (EC), SO_4 , nitrate (NO_3), and then preserved for cation analysis by acidifying with concentrated nitric acid to $\text{pH} < 2$. The pH was measured with a combination electrode (Radiometer), and alkalinity was determined by the methyl-red indicator method. Electrical conductivity was determined with a Phillips PW 9526 conductivity meter. Sulfate and NO_3 concentrations were determined using standard spectrophotometric methods. Cation analysis was performed with an atomic absorption spectrophotometer (AAS).

In May and June 1993, four pits were excavated (P1, P2, P3, and PR, see Fig. 1) so that soil samples could be collected for chemical and mineralogical analyses. The pits were excavated as deep as possible using a backhoe until the hardness of the till precluded further digging. Pits P1 and P3 are fairly shallow and will not be mentioned further in this study since the water table was not encountered. Pits P2 and PR were excavated to depths of 2.2 m and 2.3 m (C horizon), respectively, whereupon a reddish-brown horizon of oxide precipitation was observed at the water

table. This horizon is assumed to be derived from the precipitation of Fe oxide from the Fe-rich groundwater, and is clearly distinct and not associated with the reddish illuvial (B) horizon common in podzols. The Fe oxide precipitate occurs as mottles in P2 and as a coating on the sand grains and smaller pebbles in PR, welding them together. A groundwater sample was collected from pit P2.

Soil samples were collected from the bases of P2 and PR in order to identify the mineralogical composition of both the till material (C-horizon) and the oxide precipitates. Samples were treated by drying at 80°C and pulverizing in an agate mortar to a grain-size < 63 μm. The mineralogical composition of the samples was determined by powder X-ray diffraction (XRD) using CuKα radiation with a Phillips 1710 diffractometer. All samples were continuously scanned from 5° to 80°2θ at a scanning rate of 0.04°2θ per sec, with a sampling interval of 1.5 s. The scans were then visually compared to well-documented patterns published by the Joint Committee on Powder Diffraction Standards (1972) for identification.

Analytic Results

Groundwater Chemistry

The groundwater analytic results from the May 1993 sampling period are presented in Table 2, including the results for pit P2. As shown in Table 2, the trends in plume chemistry with increasing distance from the rock dump can be grouped as follows: 1) pe and Fe concentrations decrease; 2) pH increases; 3) Na, K, Mn, and Al concentrations reach maximums at P2 or B2; 4) NO₃ is removed to below its detection limit a short distance from the rock dump; and 5) SO₄ and the metals Cd, Cu, Ni, Pb, and Zn decrease in concentration. Although the results from P2 are not directly comparable to the other results, the results from previous investigations indicate that the groundwater quality does not change significantly from month to month. Thus, the P2 results can be assumed to be approximate values for the May sampling period. The last row in Table 2 shows the relative change in component concentration from well B1 to B4, where "Relative Change" (RC) is the common logarithm of the concentration in B1 divided by the concentration in B4. Alkalinity was below detection limits in all wells except the background well (R1) which contained 32 mg HCO₃⁻/L.

The redox potential measurements were stable only in B1 and B2 where it is assumed that the redox system is poised by the Fe³⁺/Fe²⁺ couple. Since the groundwater at B1 and B2 has high Fe concentrations, the measured pe should be quite accurate. However, the measurements were not stable in the other wells; the most stable reading for the remaining wells is shown as an approximate value. Down-gradient from the rock dump near B3A/B and B4, it is likely that the measured redox potential values actually represent mixed redox potentials because of the presence of dissolved oxygen and the decrease in Fe activity. At these wells,

Table 2 – Analytic results for groundwater samples collected May 1993. Water sample from pit P2 collected June 1993. All concentrations are in units of mg/L with the exception of the pH, pe, and EC

Well	pH ^a	pe	EC (μ S/cm)	NO ₃	SO ₄	Na	K	Ca	Mg	Fe	Al	Cu	Zn	Mn	Ni	Pb	Cd
B1	2.19	9.3	5770	114.4	3750	3.4	0.44	32	65	1110	59	40	18.5	4.4	32.1	0.29	0.155
(P2)	2.59	8.4 ^c	2700	<0.5	1520	8.4	2	31	46	205	123.6	19.7	11.6	7.7	14.2	0.19	0.080
B2	4.07	5.3	2010	<0.5	1190	8.2	2.5	226	63	29	34	8.4	9.9	8.3	8.6	0.05	0.057
B3A	4.03	7.0	646	<0.5	270	5.6	1.8	6.2	17	0.04	21	4	4.9	1.43	2.1	<0.05	0.021
B3B	4.08	6.8	542	<0.5	255	4.8	0.93	5.2	13	<0.01	20	3.5	3.4	1.15	1.5	<0.05	0.018
B4	3.96	6.8	923	<0.5	460	5.3	1.68	22.5	25	0.03	25	4.4	4.6	1.98	2.5	<0.05	0.025
R1	5.52	5.9	45	<0.5	12	2.2	0.5	3.9	0.6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.05	<0.05	<0.001
RC ^b	--	--	--	--	0.9	-0.2	-0.5	0.2	0.4	4.6	0.4	1.0	0.6	0.4	1.1	--	0.8

a) Average ground water temperature 5^o C.

b) Relative change (see text).

c) Estimated from goethite equilibrium.

the unstable redox potential measurements reflect the disequilibrium between the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{O}_2/\text{H}_2\text{O}$ couples; the redox potential poised by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple would be lower than the measured value. The redox potential was not measured in the groundwater sample from pit P2, where it was instead estimated from an assumed equilibrium with goethite at pH 2.59.

The small increase in metal concentrations and decrease in pH from B3A to B4 is most likely caused by the placement of well B3A off the center-line of the leachate plume, where leachate concentrations would be smaller. This decrease in concentration, however, may be also the product of increased dilution by infiltrating water or groundwater mixing, so it is not possible to confirm this assumption based on the chemical data alone.

Soil Mineralogy

The minerals identified in the oxide encrustations from pit PR are primarily goethite and quartz with trace amounts of lepidocrocite ($\gamma\text{-FeOOH}$). The soil sample from pit P2 consisted of the red Fe oxide mottles and the surrounding soil. During preparation of the sample for XRD analysis, much care was taken to separate the mottles from the unaffected soil. The XRD analysis of this sample identified primarily quartz, hornblende, K-feldspar (orthoclase) and plagioclase (oligoclase) plus small amounts of illite and mixed-layer chlorite-vermiculite. The mineralogy of this sample is typical of a till soil produced from a weathered amphibolite. There were no strong peaks for Fe oxide minerals identifiable on the XRD plot. The lack of identifiable Fe minerals may be caused by one or more of the following: 1) the reddish mottles are not the result of Fe oxide precipitation, but of other minerals such as Ti oxides; 2) the grain-size fraction used ($< 63\mu\text{m}$) is too coarse, so that there is too much interference with quartz and feldspars; and 3) the Fe oxide is in an amorphous or poorly crystalline form which is XRD transparent. Although the first option is possible, the author believes that the mottles do contain Fe oxides based on data from pit PR. The second and third options are, however, both likely explanations. The highest percentage of Fe oxides are usually found in the $< 2\mu\text{m}$ fraction, while most quartz occurs in coarser fractions (Schulze 1988). Additionally, poorly crystalline forms of Fe oxides, such as ferrihydrite, commonly form in Fe^{2+} -rich waters that are quickly oxidized and may contain much Si (Schwertmann 1988). In either case, further investigation is required to conclusively determine the mineral species present in the reddish mottles from P2.

Geochemical Modeling

The geochemical model PHREEQE (Parkhurst *et al.* 1980) has been used to determine the theoretical speciation of the investigated elements and to evaluate the possibility of mixing and mineral precipitation as a means of attenuating these elements in groundwater. During the reaction simulation PHREEQE can calculate pH, pe, the distribution of aqueous species, mineral saturation indices, the mixing

Table 3 – Solubility products of selected minerals common in acid mine drainage studies

Mineral	log K_{sp}
$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$	-4.008
<i>Hematite</i>	
$\alpha\text{-FeOOH} + 3H^+ = Fe^{3+} + 2H_2O$	-1.00
<i>Goethite</i>	
$KFe_3(SO_4)_2(OH)_6 + 6H^+ = K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O$	-14.80
<i>K-Jarosite</i>	
$FeSO_4 \cdot 7H_2O = Fe^{2+} + SO_4^{2-} + 7H_2O$	-2.209
<i>Melanterite</i>	
$\alpha\text{-Al(OH)}_3 + 3H^+ = Al^{3+} + 3H_2O$	8.11
<i>Gibbsite</i>	
$AlOHSO_4 + H^+ = Al^{3+} + SO_4^{2-} + H_2O$	-3.23
<i>Basic Aluminum Sulfate</i>	
$KAl_3(SO_4)_2(OH)_6 + 6H^+ = K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O$	-1.40
<i>Alunite</i>	
$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.58
<i>Gypsum</i>	

of two solutions, and the mass transfer of minerals into or out of the aqueous phase. The data required to predict the equilibrium composition of a solution consist of a chemical analysis of the sample to be modeled giving total dissolved concentrations for the components of interest, and any other relevant measurements, such as pH, pe, or the partial pressures of one or more gases. Although the processes of adsorption, coprecipitation, and solid-solution formation may also play an important role in the removal of metals from solution, these processes are not considered in the geochemical model. Species activities are calculated from activity coefficients according to the Davies equation. Groundwater in well B1 has the highest measured ionic strength (0.13 molal), which is within the applicable range for the Davies equation (about 0.5 molal).

At the low pH values and high SO_4 activities observed in the groundwater, the most common metal species calculated by PHREEQE are free metal ions and aqueous metal sulfate compounds. There is an increase in the per cent of free metal ions with distance from B1 as the SO_4 activity decreases. In order to determine which mineral phases may precipitate in groundwater, saturation indices have been calculated for a number of minerals commonly associated with acid mine drainage studies. The log of the solubility products ($\log K_{sp}$) of these minerals are tabulated in Table 3. For this study, the original PHREEQE database (Parkhurst *et al.* 1980) has been modified to include the critically reviewed and internally consistent thermodynamic database published by Nordstrom *et al.* (1990). The solubility product for $AlOHSO_4$ was obtained from van Breemen (1973).

Saturation indices of the minerals in Table 3 are presented in Figs. 2 and 3 as a

Metal Transport in Groundwater

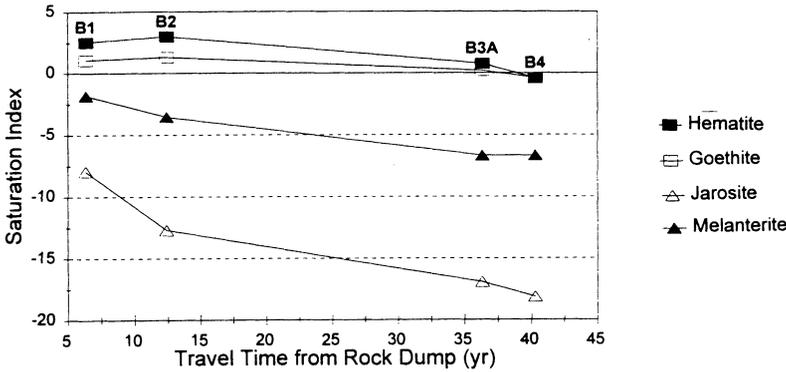


Fig. 2. Saturation of Fe minerals in groundwater as a function of estimated travel time from the rock dump.

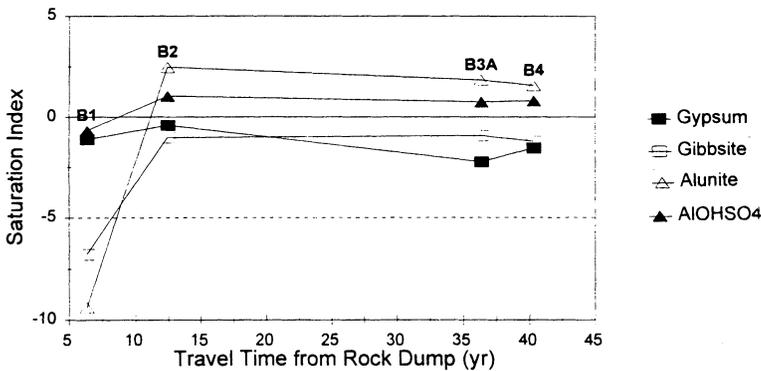


Fig. 3. Saturation of other minerals in groundwater as a function of estimated travel time from the rock dump.

function of the estimated travel time from the rock dump. The modeling results for Fe-containing minerals are shown in Fig. 2, and for the other minerals in Fig. 3. The figures show that the groundwater is saturated to oversaturated ($0.2 < SI < 1.3$) with respect to goethite and hematite for wells B1, B2, and B3A. All Al oxides and basic Al sulfates are undersaturated at B1. With increasing distance from the rock dump, the groundwater becomes oversaturated with respect to both $Al(OH)SO_4$ and alunite. All other relevant minerals in the PHREEQE database are undersaturated in the groundwater.

The travel time used for the x -axes in Figs. 2 and 3 was calculated from the Darcy equation for average linear velocity (v)

$$v = K \frac{i}{\phi} \quad (5)$$

where K , i , and ϕ are the saturated hydraulic conductivity (m/s), the hydraulic gradient, and the total porosity, respectively. The value for the hydraulic gradient was calculated from the difference in groundwater level from the well of interest to

the next, divided by their separation in metres (Table 1). The hydraulic gradient from the dump to B1 was estimated as 0.01. The hydraulic conductivity and porosity are assigned values of 10^{-6} m/s and 0.20, respectively, based on published values for Swedish tills from depths greater than 1 metre (e.g. Lundin 1982, Bishop 1991).

Discussion of Results

The data suggest that the major geochemical processes determining groundwater chemistry include Fe oxide precipitation, denitrification, primary mineral weathering, and basic Al sulfate precipitation. However, when determining which geochemical processes may be controlling the evolution of the leachate plume, it is important to consider what the sampled groundwater actually represents. The till aquifer is quite heterogeneous and the geochemical environment at the well screen may be significantly different from conditions at the water table. Since the wells are purged of at least three casing volumes prior to sampling, this minimizes the mixing of the sampled water with stagnant water present in the well and assures that the sampled water comes from the screened interval of the well casing. In fact, groundwater derived from small-scale heterogeneities within the screened interval, such as highly permeable sand lenses, may comprise a large percentage of the total sample volume, but the effect of these variations is beyond the scope of this investigation. At a larger scale, it is necessary to determine the effect of physical mixing on the solute concentrations. Although it is assumed that the dilution of groundwater contributes partially to the observed attenuation in element concentrations, this would account for only a small percentage of the total observed changes in such components as Fe, Al, and SO_4 .

Goethite Precipitation

As suggested by the chemical and mineralogical results, Fe is most likely removed from the groundwater by the precipitation of goethite. As mentioned previously, Eq. (4) must be coupled with a corresponding reduction reaction if the oxidation of Fe(II) to Fe(III) is to have any chemical significance. In addition to the reduction of dissolved oxygen to water, nitrate reduction (denitrification) to N_2 (g) is one possible couple. Nitrate has entered the groundwater through the use of N-containing explosives during the mining operations (Qvarfort 1993, personal communication) and is not detected in groundwater beyond well B1. Nitrate is likely removed by denitrification through the following irreversible reaction ($\log K = 207.08$, PHREEQE)



Coupling Fe(II) oxidation with denitrification results in the consumption of 1 mole of NO_3^- for every 5 moles of Fe^{2+} oxidized, or 46% of the total Fe in solution. According to the speciation calculations, NO_3^- is not stable at the pH/redox condi-

tions that dominate in well B1 and should completely reduce to gaseous N_2 , which escapes from the saturated zone. The oxidation of Fe(II) (Eq. (4)) may also be coupled to the reductive dissolution of Mn(III)/Mn(IV) oxides, which releases Mn(II). Evidence of this process may have been observed: elevated concentrations of Mn(II) have been measured in wells B2 and P2, relative to well B1.

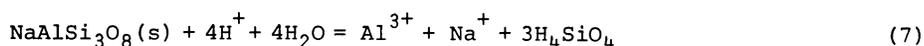
As presented in Table 2, the large differences in pH, pe, Ca and Fe concentrations between B2 and P2 appear rather unusual, considering their separation of 15 m. Previous sampling episodes have shown similar values for groundwater from B2. In 1988, an experiment was conducted on site to determine if the liming of the rock dump would lead to a decrease in groundwater acidity. Although the liming experiment had no apparent effect on the groundwater pH, there are appreciable amounts of crushed limestone still present on the rock dump. Based on this information, it is believed that well B2 was accidentally contaminated with a small nodule of this limestone during its installation. Additionally, a fine white particulate sediment was collected from the bottom of the sampling bottle from B2 and analyzed by XRD analysis. The results indicated that the substance was mostly gypsum, which is the expected product of calcite dissolution in a sulfate-rich groundwater. The limestone nodule and the precipitation of gypsum are not expected to have any significant influence on groundwater quality down-gradient from B2. The increase in pH and Ca concentration at B2 is therefore the result of calcite dissolution, while the decrease in pe and Fe concentration is probably controlled by the precipitation of goethite. The decrease in pe results from a decrease in the solubility of goethite at the higher pH, thereby reducing the Fe(III)/Fe(II) ratio.

All minerals containing the heavy metals Cu, Cd, Ni, Pb, and Zn are greatly undersaturated in the groundwater, so it is not expected that precipitation of these metals controls their solubility in groundwater. However, because of the well-documented ability of goethite and other Fe oxides to retain heavy metals by adsorption or coprecipitation (*e.g.* Benjamin and Leckie 1981, Kooner 1993), the fate of these heavy metals in acid mine drainage waters is probably determined to a large degree by the behavior of Fe. The attenuation of heavy metals in groundwater may therefore be related to the abundance of adsorbing surfaces and the probability of each respective metal to be adsorbed to such surfaces. In addition, SO_4 may also be retained by adsorption to goethite mineral surfaces (Parfitt and Smart 1978) or by inclusion as a structural component in Fe oxides resembling akaganéite (β -FeOOH; Bigham *et al.* 1990).

Acid Neutralization by Mineral Weathering

The response of a soil to acidic input depends on the buffer status of the soil, where typical soil buffers include calcite, silicate minerals, cation exchange reactions, and Al and Fe oxides. As suggested by the pH measurements from the site, it is possible that the leachate plume is buffered within two intervals: from about pH

2.1 to 2.6 (B1-P2) and further to about pH 4 (B3A-B4). The development of such zonations is common in acid mine drainage-contaminated groundwater (e.g. White *et al.* 1984, Morin and Cherry 1988, Walter and Norris 1991). The calcite content of the till aquifer is fairly low, as indicated by the low alkalinity in reference well R1, and would be insufficient to buffer the groundwater against the flux of sulfuric acid produced by sulfide oxidation. Silicate minerals, however, comprise a large percentage of the total mineral content of the soil, and could buffer the groundwater pH to the levels observed. The increase in K, Na, and Al concentrations from B 1 to P2 suggests that primary mineral weathering is releasing these components. Potassium feldspar (KAlSi_3O_8) and plagioclase [$(\text{Na,Ca})\text{AlSi}_3\text{O}_8$] have been identified by XRD analysis, and are likely sources of the released cations. For example, the acidic dissolution of a plagioclase feldspar (albite) releases Na, Al, and silicic acid



where Al may be subsequently removed from solution by substitution in the goethite mineral lattice or by precipitation as Al oxides, basic Al sulfates, or secondary aluminosilicates such as kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

The saturation indices for AlOHSO_4 and alunite suggest that these minerals may precipitate from the groundwater (see Fig. 3). These minerals have not been identified in the XRD analyses, but may be present instead as XRD-transparent phases. The mineral AlOHSO_4 is stable from pH 0 – 4 at high SO_4 concentrations (10^{-2} M), where its precipitation is believed to control the upper limit of Al solubility. Alunite is stable from pH 3.3 to 5.7, while gibbsite is the most stable phase at higher pH values (Nordstrom 1982b).

Chemical Evolution of the Groundwater

As discussed above, the major processes determining groundwater chemistry probably include the following: 1) groundwater dilution by mixing; 2) goethite precipitation; 3) denitrification; 4) primary mineral weathering; 5) basic Al sulfate precipitation; and 6) metal adsorption to the aquifer material. In order to determine if these processes may be determining the chemical evolution of the leachate plume, PHREEQE is used to evaluate a possible reaction pathway controlling the reaction of the leachate plume with uncontaminated groundwater and the till aquifer. Adsorption processes are not considered in this model. To ensure that the reaction path model does not become overly complicated, the model does not consider changes in Cd, Mn, Ni, and Pb concentrations.

Estimating Plume Dilution

In order to determine the amount of dilution a leachate plume undergoes during groundwater transport, it is common to use a non-reactive solute within the plume.

This solute is an indicator of the concentration change that can be expected from physical mixing and dispersion. Ideally, the tracer is a conservative component naturally occurring in the groundwater (*e.g.* Cl), or may be a substance that is injected into the flow system which is normally not present in significant concentrations (*e.g.* ^3H , ^{36}Cl). For this investigation, however, tracer tests have not been performed and conservative components such as Cl are not found in significant concentrations, so that an ideal tracer cannot be used.

Zinc has been chosen as a tracer since it is believed that this element is least retarded in the leachate plume. This assumption is based on the following observations: 1) all Zn-containing minerals are largely undersaturated in the leachate plume; 2) Zn is found at low concentrations (median: 50 $\mu\text{g/g}$) in typical Swedish tills (Andersson 1977); and 3) Zn^{2+} is not prone to adsorb to either amorphous or crystalline goethite surfaces at low pH. The PHREEQE speciation calculations indicate that Zn occurs as either Zn^{2+} or ZnSO_4 , with Zn^{2+} accounting for 54 – 62% of the total Zn species. Only 50% of Zn^{2+} is adsorbed at pH 6.75 – 7, and it is negligibly adsorbed to goethite below pH 5 (Benjamin and Leckie 1981, Kooner 1993). Although Zn cannot be expected to behave conservatively in the leachate plume since it can be coprecipitated with goethite, it is probably retained the least of the measured elements. If Zn is retained to some degree, then dilution estimates using Zn as a tracer will overestimate the contribution of mixing to plume dilution.

PHREEQE is used to calculate the approximate mixing required to dilute the Zn concentration measured in B1 to the level measured in B4. A solution with the same composition as reference well R1 is used to dilute B1 at a specified mixing ratio. The results of this simulation are shown in Fig. 4, which shows the decrease in Zn concentration and increase in pH as a function of the volume percentage of mixing fluid. As indicated by the figure, if the Zn concentrations at B1 and B4 are considered representative of the beginning and end products of the plume's evolution, then the volume of mixing solution required to produce such an attenuation is approximately 75% of the volume of the contaminated water. This gives a mixing ratio of 3:4 for the volume of uncontaminated to contaminated groundwater.

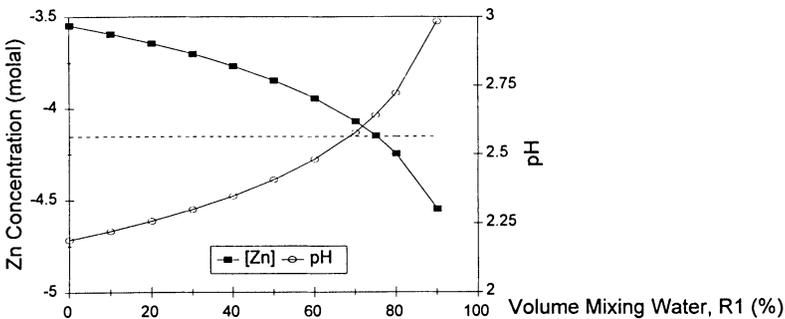


Fig. 4. PHREEQE simulation of the evolution of leachate plume (B1) by mixing with uncontaminated water (R1). Dashed line represents Zn concentration in well B4.

Modeling the Plume Evolution

The processes governing the evolution of the leachate plume are modeled in a series of three steps: 1) denitrification and goethite precipitation; 2) mixing; and 3) silicate weathering and goethite and AlOHSO_4 precipitation. For the first step, nitrate reduction (Eq. (6)) is coupled with goethite precipitation (Eq. (4)) at constant p_e . This mass transfer process is expected to occur rather early in the plume's evolution since NO_3 is removed quickly from the groundwater (*cf.* Table 2). The second step involves only the mixing of the contaminated water with the uncontaminated water, with no chemical reactions. The third step simulates the partial dissolution of feldspar minerals with goethite and AlOHSO_4 precipitation. The release of K and Na and the pH increase along the flow path have been attributed to silicate weathering, so plagioclase (albite, Eq. (7), $\log K_{sp} = 4.7$) and K-feldspar (microcline, $\log K_{sp} = 0.875$) are chosen to dissolve in the evolving fluid. Studies on Swedish tills have indicated that plagioclase can be expected to have a greater weathering rate and thus a greater impact on groundwater chemistry (Sverdrup and Warfvinge 1993). The PHREEQE simulations have shown, however, that the dissolution of albite and microcline at equilibrium produces unreasonable results with respect to pH, K, and Na. Albite dissolution at equilibrium releases more Na than observed, and overestimates acid neutralization. Microcline dissolution at equilibrium releases more K than observed, but neutralizes very little of the plume acidity because of its resistance to weathering. For this simulation, albite and microcline are therefore reacted with the solution at non equilibrium conditions ($\text{SI} < 0$) in order to best reproduce the observed pH and K and Na concentrations. Goethite precipitates at equilibrium and AlOHSO_4 is allowed to precipitate while oversaturated. The saturation index of AlOHSO_4 is held at 0.817, which is the measured value at B4 (see Fig. 3).

The results of this simulation are presented in Table 4, indicating that the effect of mixing plus the dissolution of about 4 mmoles albite/kg H_2O and 0.03 mmoles microcline/kg H_2O , followed by AlOHSO_4 precipitation, reproduce the observed pH and SO_4 , Al, K, and Zn concentrations at well B4 quite well. Although the simulated Fe concentrations are more than an order of magnitude greater than the observed values at B4, the difference is on the scale of 10 $\mu\text{moles/kg}$, which is considered insignificant relative to the total change in Fe concentration (about 20 mmoles/kg). The simulated p_e and Ca, Cu, and Mg concentrations are all relatively close to the observed values. The measured p_e was higher at B4 than simulated by the model, which may reflect contamination by dissolved oxygen. The deviation of the Cu concentration may be attributed to adsorption, which is not included in the PHREEQE simulations. The results in Table 4 suggest that Ca and Mg are released into the leachate plume, based on the discrepancy between the solution composition after mixing and the observed values at B4. Calcium and Mg may be released by the partial dissolution of a calcic plagioclase (*e.g.* anorthite) and hornblende, respectively. However, the large deviation of the simulated Na concentra-

Table 4 – PHREEQE simulation of leachate plume evolution in three steps: 1) denitrification and goethite precipitation; 2) mixing; and 3) silicate dissolution and goethite and Al(OH)₃ precipitation. Total nitrate, sulfate, and metal concentrations and mass transfer calculation presented in units of millimoles/kg H₂O. Nitrate was not detected (ND) is well B4; the simulated log concentration is -28.5. Well B1 is the starting state for the evolving water and well B4 is the modeling target

Reaction Step	Mass Transfer (+ dissolution/ - precipitation)	pH	pe	NO ₃	SO ₄	Fe	Al	K	Na	Ca	Mg	Zn	Cu
Well B1	--	2.19	9.30	1.85	39.24	19.98	2.20	0.011	0.15	0.80	2.69	0.28	0.63
1a	N ₂ (g) -0.927			-1.85									
1b	Goethite -9.27					-9.27							
Total 1	--	1.82	9.61	ND	39.24	10.71	2.20	0.011	0.15	0.80	2.69	0.28	0.63
Total 2	--	2.29	6.02	ND	9.90	2.68	0.58	0.012	0.11	0.27	0.69	0.071	0.16
3a	Microcline +0.03						+0.03	+0.03					
3b	Albite +4.01						+4.01		+4.01				
3c	Goethite -2.67					-2.67							
3d	Al(OH) ₃ -3.76				-3.76		-3.76						
Total 3	--	3.98	5.90	ND	6.15	0.009	0.84	0.043	4.12	0.27	0.69	0.071	0.16
Well B4	--	3.96	6.8	ND	4.79	0.0005	0.93	0.043	0.23	0.56	1.03	0.070	0.069

tion from the observed is most likely due to the simplicity of the model. The release of Na and acid neutralization are apparently not completely controlled by albite dissolution. In particular, it is probably the combined weathering of K-feldspar, plagioclase (both sodic and calcic), and hornblende that contributes to the neutralization of groundwater acidity. The observed releases of both Na and K and perhaps Ca and Mg suggest that a combined influence is indeed in effect.

Conclusions

The chemical data, mineralogy, and geochemical modeling discussed in this investigation suggest that silicate weathering and goethite precipitation are the processes primarily controlling observed pH, pe, and Fe concentrations in groundwater direct down-gradient of the rock dump. The increase in K, Na, and Al concentrations along the flow path can be attributed to feldspar weathering, while Al and SO₄ concentrations further down-gradient can be controlled by the precipitation of XRD-transparent AlOHSO₄. The attenuation of heavy metal concentrations may be the result of adsorption and coprecipitation with goethite and other Fe oxides.

The actual chemical evolution of the plume is obviously much more complicated than presented in the reaction path model, but the simulation may provide insight into whether the correct processes are under consideration. The model reproduced the observed element concentrations fairly well, and it is likely that silicate dissolution in the leachate plume does not proceed at thermodynamic equilibrium, but is a rate-controlled process. Compared to other reactions controlling groundwater pH, such as calcite dissolution, Mn oxide dissolution, or goethite precipitation, the dissolution of silicate minerals is very slow and probably cannot be modeled by assuming equilibrium mass transfer (Glynn, 1991). Mineral dissolution rates therefore need to be included in a model of contaminant transport involving silicate phases. In addition, the application of a multicomponent solute transport model could be used to determine the potential mixing that occurs in the groundwater relative to other geochemical processes. The use of such models will be reserved for future investigations.

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