IDENTIFICATION OF PROBABLE GROUNDWATER FLOW PATHS AT AN INACTIVE URANIUM MINE USING HYDROCHEMICAL MODELS[1]

by

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Abstract. The Midnite Mine is an open-pit uranium mine located in northeastern Washington State on the Spokane Indian Reservation. Mining operations ceased in 1981, leaving two large open pits, two waste rock piles, and several large low-grade ore piles. The oxidation of minerals containing reduced sulfur, such as pyrite, produces acidic water that leaches heavy metals from the ore and waste rock. An interception system was installed by the mining company, and approximately 500 million gal (1,900 million L) of contaminated water are now stored in these open pits.

The U.S. Bureau of Mines has initiated a study of the hydrochemistry of the mine to provide a portion of the information necessary to reclaim the site. A small number of monitoring wells were installed in 1989, and monthly samples have been collected from these and other selected surface locations. The computer programs WATEQ4F and BALANCE were used to assist in interpreting the groundwater chemistry and potential flow paths on the mine site.

Additional Key Words: hydrochemistry, uranium mine, computer modeling, acid mine drainage.

Introduction

The Midnite Mine is an inactive, hardrock uranium mine located on the Spokane Indian Reservation, Stevens County, WA, approximately 40 miles (64 km) northwest of Spokane and 8 miles (13 km) northwest of Wellpinit. The site was leased by Dawn Mining Co. in 1954 and included 811 acres (328 ha), of which 321 acres (130 ha) (an area about 0.5 mile [0.8 km] wide and 1 mile [1.6 km] long) were developed during mining operations. The mine ceased operations in 1981, leaving two open pits, several waste rock piles, and stockpiles of low-grade uranium ore (protore). An aerial view of the site taken in 1982 is shown in figure 1.

Since mining operations stopped, the Bureau of Indian Affairs (BIA) and the Bureau of Land Management (BLM) have been actively involved in planning remediation of the disturbed areas. Such remediation efforts are necessary because oxidation of pyrite and other sulfide minerals in the ore body forms acids that leach toxic metals, including radium and uranium, through the disturbed area.

As public concern about the quality of the environment has increased, the U.S. Bureau of

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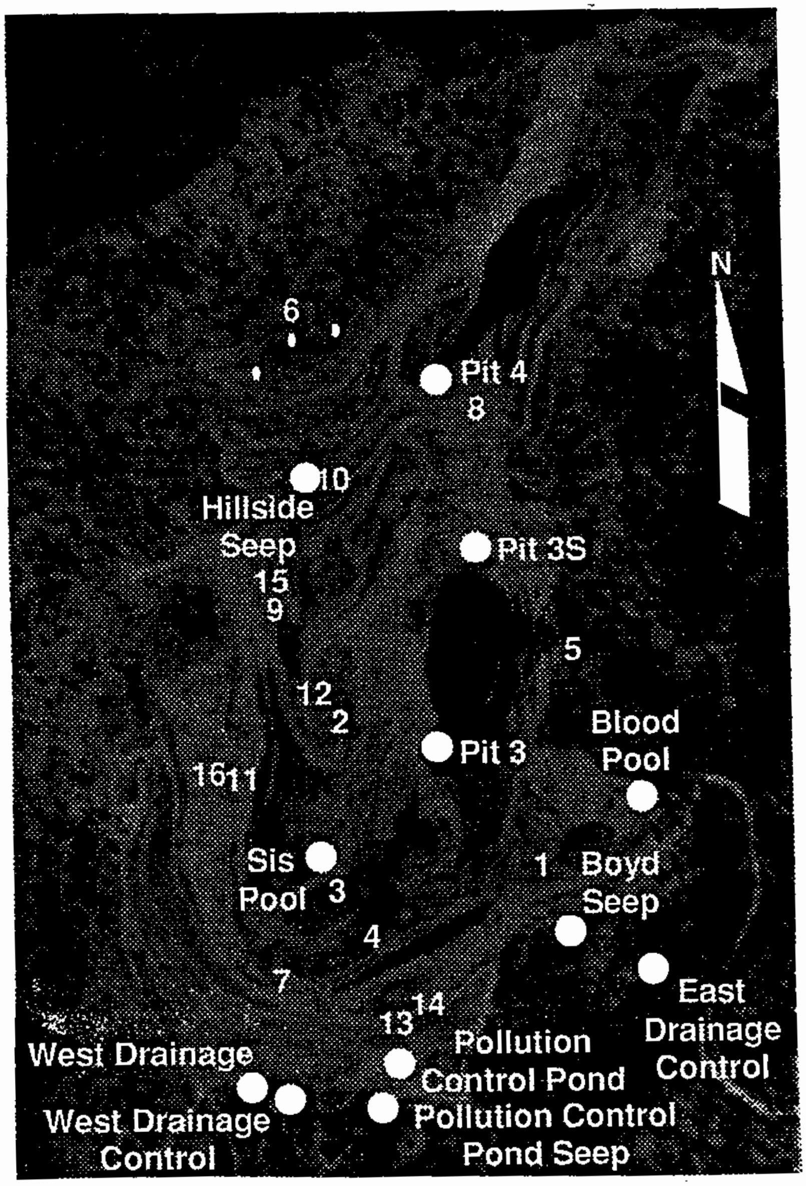

Figure 1.--Aerial photo showing sampling locations.

Mines has focused more of its research on methods to minimize the environmental impacts of mining activities. To assist the BIA and the BLM at the Midnite Mine, in 1988 the Bureau initiated an investigation of water-rock interactions at the mine. The groundwater flow system and the leaching characteristics of wastes have significant effects on the quantity and quality of water at the mine and impact the quality of water leaving the mine. Therefore, a thorough hydrogeological and hydrochemical characterization of the mine site is required to assist in designing appropriate remediation and reclamation activities. Researchers at the Bureau's Spokane Research Center (SRC) designed a monitoring network, supervised installation of sampling wells, and collected and analyzed samples.

The purpose of the present research is to determine water quality and define groundwater flow characteristics at the Midnite Mine as part of the effort to develop a reclamation plan. This paper describes a portion of the research that has been done to evaluate groundwater flow as it affects dewatering and reclamation of the two open pits. Also, the impact of the protore piles on ground water is described.

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Site Description

The Midnite Mine lies on the southwest slope of Spokane Mountain at the southern end of the Huckleberry Mountains, a minor range in the north-south-trending Selkirk system. It is located on the western edge of a 1-mile- (1.6-km-) wide roof pendant of the metasedimentary Togo Formation of the Belt Supergroup. This Precambrian sequence is about 600 ft (183 m) thick in the area and contains graphite-bearing argillite, schist, and phyllite with interbeds of marble, calc-silicate, and quartzite (Ludwig et al., 1981).

A porphyritic quartz monzonite intrusion of Late Cretaceous age crops out along the west side of the mine (Fleshman and Dodd, 1982) and forms the west highwall and ridge of pit 4 and part of the west highwall of pit 3. It is unclear whether the intrusive once cropped out between pits 3 and 4, because the area is now covered by waste rock.

The contact between the quartz monzonite and the metasediments appears to run north-south from the middle of pit 4 through pit 3 near the west wall. The contact is very irregular, and tabular mineralized zones are found in the troughs of the monzonite (Ludwig et al., 1981). Ore bodies are up to 60 ft (18 m) wide, 1,200 ft (366 m) long, 150 ft (46 m) thick, and 15 to 300 ft (4.6 to 91 m) below the surface. These ore bodies were emplaced in a series of depositional and enrichment stages (Milne, 1979; Fleshman and Dodd, 1982). Oxidized uranium minerals--autunite and metautunite--occur above the water table. Reduced primary uranium minerals--uraninite and coffinite--are found in the deep ore bodies below the water table. Pyrite and marcasite appear to be associated with the latter minerals. Several other sulfide minerals are also present in minor amounts: pyrrhotite, molybdenite, chalcopyrite, sphalerite, and galena.

Altitude of the mine ranges from 3,400 ft (1,036 m) above mean sea level at the northern end to 2,400 ft (730 m) at the southern end (figure 2). During the period the mine was active, six pits or subpits were opened. Four of these were subsequently backfilled with overburden and waste as mining progressed, while two pits (3 and 4) were left open (figure 1). The present bottom of pit 3 is about 430 ft (130 m) lower in elevation than the bottom of pit 4 (figure 2). Pit 3 contains approximately 430 million gal (1,628 million L) of water and is more contaminated than pit 4. Pit 4 contains approximately 70 million gal (265 million L) of water, much of which had been pumped from pit 3 during dewatering operations that began around 1979. As of June 1992, approximately 500 million gal (1,893 million L) of acidic waters had accumulated in the two pits at a rate of 25 to 50 million gal/yr (95 to 189 million L/yr). The water level in pit 4 remains fairly constant, responding only to seasonal variations. The water level in pit 3 is constantly rising because of precipitation and infiltration and because water is being pumped into it from the pollution control pond.

Many waste rock piles and eight low-grade ore (protore) piles remain on the mine site. The two largest waste rock piles are southwest of pit 4 and about 500 yd (457 m) south of pit 3. These have been designated Hillside Spoils and South Spoils, respectively. The pollution control pond was constructed in 1979 below South

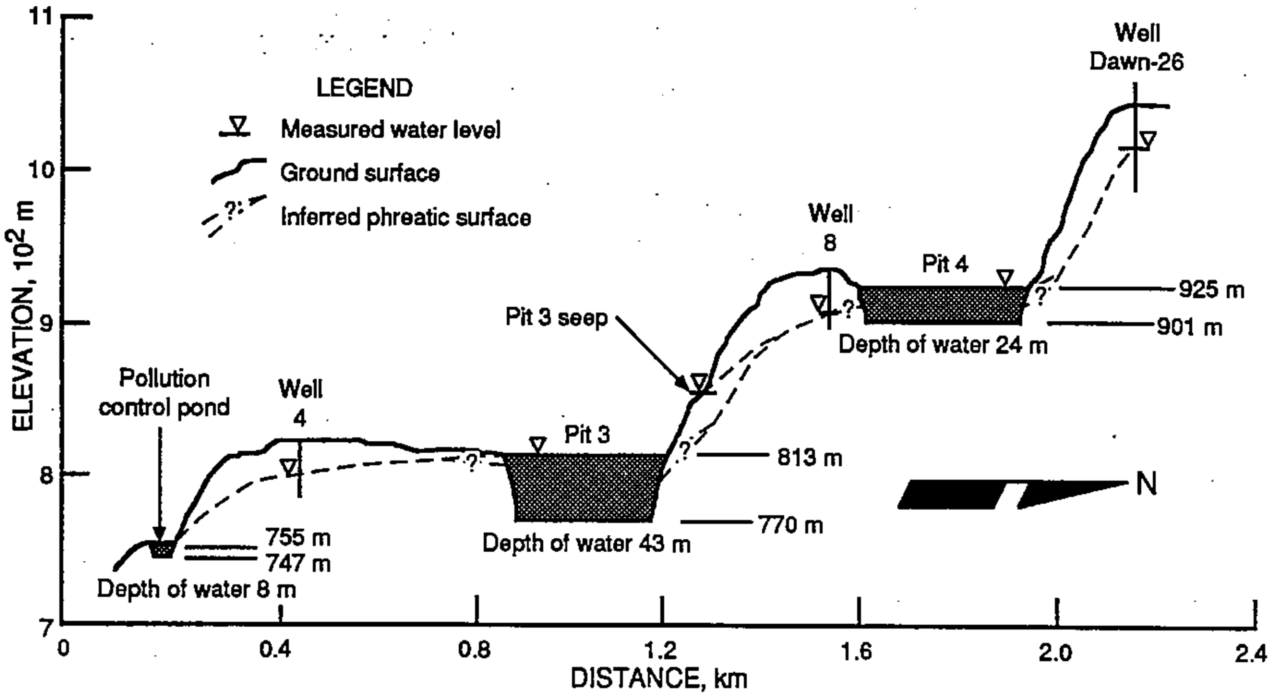

Figure 2.--North-south cross section across Midnite Mine. Vertical exaggeration 3 times.

Spoils to intercept seepage from the spoils (figure 2). Water from other seeps that have formed since that time are pumped to the pollution control pond and then to pit 3.

Precipitation at Wellpinit averaged 19 in/yr (48 cm/yr) from 1951 through 1980; from spring through fall, it comes as rain, while in winter, it is mostly in the form of snow. Recharge to the site consists of rainfall and snowmelt from the immediate vicinity. Discharge consists of evaporation, surface stream runoff, and a small amount of groundwater flow (Sumioka, 1991). Two tributaries to Blue Creek carry most of the water from the site; these streams were informally designated East Drainage and West Drainage.

Methods

Field Methods

Fifteen monitoring wells at seven locations and 14 surface locations were monitored monthly from December 1989 to April 1992 (figure 1). These sites were chosen to allow documentation of the full range of water elevation and quality at the mine. For example, well 6 was placed high on the ridge at the northern edge of the Hillside Spoils in order to sample uncontaminated water recharging the mine site, while several surface seeps on and below the South Spoils area are being sampled to collect water being contaminated within the mine.

During the selection of the field sampling locations, it was decided to concentrate data collection on the eastern side of the mine. This allowed more monitoring wells to be installed in that area and increased the probability of gathering sufficient data from a single area to understand the hydrogeology and geochemistry.

The 15 monitoring wells were drilled between August 8 and October 16, 1989, according to methods required for resource protection wells in Washington State (1990). A description of completion details are given in another paper (Williams, 1993).

Wells were pumped using air-driven submersible bladder pumps. Air pressure was used to inflate and deflate a bladder alternately and thereby pump water to the surface. In this way, the water sample did not contact atmospheric oxygen until after the field variables were measured. Changes in pH, oxidation-reduction potential (Eh), and alkalinity were minimized, and the chemical composition of the water sample was preserved.

Measurements of specific conductance, temperature, pH, Eh, and dissolved oxygen content were made in the field using a flow-through cell. The probes were calibrated according to the manufacturer's instructions and were replaced when their operation was sluggish or erratic.

Samples were obtained in accordance with standard Environmental Protection Agency sampling procedures (EPA, 1983) and transported to the analytical laboratory at SRC for chemical analyses of major cations, anions, and trace constituents.

The sampling procedure consisted of measuring the depth-to-standing-water level at each well. Then each well was pumped to remove at least three volumes of water standing in the casing while passing the water through a flow-through chamber containing probes for measuring temperature, pH, Eh, and specific conductance until these measurements stabilized. The alkalinity was measured within 5 min of sample collection using a digital titrator, then the dissolved oxygen readings were taken. The water was vacuum filtered through 0.45-μm filters and collected in two polyethylene 70-mL bottles after the bottles and caps were rinsed twice with the filtered water. One was left unacidified for anion analysis; the second was acidified with nitric acid for cation analysis.

As of April 1992, 28 months (November 30, 1989, through April 1, 1992) of readings and samples have been collected from the field; the samples have been analyzed, and the data have been entered into computer files.

Laboratory Methods

Cation analyses were performed on an ARL model 34000, inductively coupled plasma-atomic emission spectrometer (ICP-AES). This is a simultaneous instrument capable of analyzing up to 24 elements per sample. Samples from the first seven field collections were analyzed for all 24 elements. The analytical method was then shortened to remove elements that had measured values below the detection limit for the instrument. These elements and their detection limits (in mg/L) were arsenic (<1.5), selenium (<0.3), tin (<0.6), mercury (<0.4), and chromium (<0.02).

The ICP-AES was operated following EPA guidelines (EPA, 1983). Calibration solutions were prepared by serial dilution of stock standard solutions obtained from SPEX Industries, Inc., Edison, NJ. In addition to the check standard solutions specified by EPA, a large quantity of one of the mine water samples containing high concentrations of metal ions was collected and stabilized, and was used as an additional control sample during the analyses. The long-term precision of the analyses was ±5 pct for those elements whose concentrations were greater than 10 times the detection limit of the ICP-AES. Those elements whose concentrations were consistently less than 10 times the detection limit exhibited variations of up to ±20 pct.

Anion analyses were performed using a Dionex Series 4000i gradient ion chromatograph. The column used for this sample set, the AS4A, has the capability to detect 10 anions. The first few sample sets were analyzed for all possible anions, but the analytical procedure was shortened once the anions actually present had been identified. Routine analyses were performed for chloride, nitrate, and sulfate.

Quality control for anion analysis was similar to that for cation analysis and also followed EPA guidelines (EPA, 1983). The instrument was calibrated daily using a series of standards prepared from stock, single-ion standards obtained from Environmental Resource Associates, Arvada, CO. The eluant was prepared from Baker Analyzed, reagent-grade, sodium carbonate crystals and sodium bicarbonate powder to concentrations of 2.8 and 2.7 mM, respectively. An eluant flow rate of 2.0 mL/min was used.

Data Collection

Groundwater Elevations and Flow Paths

Water elevations in the monitoring wells varied from 3,171 ft (967 m) above sea level in well 6, located at the north end of the Hillside Spoils, to 2,600 ft (792 m) in well 7, located about 200 ft (60 m) north of the face of the South Spoils. Water elevations were different in those wells with multiple completions, indicating that the bentonite seals between completions successfully isolated the screened zones from each other. This isolation ensures that the samples collected for water quality monitoring are from one geologic formation and are not a mixture of water from several formations.

The direction of groundwater flow primarily follows the local topography, from north-northwest to south-southeast. Water flows from the ridges at the north end of the site toward the spoils piles and surface drainages at the south end of the site. The water elevation at well 5 was between 20 and 130 ft (6 and 40 m) higher than the water elevation in pit 3, depending on the depth of the completion zone and the season of the year. Therefore, water from pit 3 cannot migrate in the direction of the East Drainage, but must go in a southerly direction. The elevation of water in pit 3 was approximately 48 ft (15 m) higher than the elevation of Boyd Seep, suggesting that one of the sources for Boyd Seep might be pit 3. A more detailed discussion of this possibility is presented below.

Detailed information on the groundwater flow path is still lacking in some areas. Discussion of the groundwater flow will be given in another paper (Williams, 1993).

Computer Modeling Methods

Analytical data from field and laboratory measurements were entered into computer models to assist in determining the geochemical characteristics of the water samples. Modeling was also used to determine the changes in water chemistry that must occur along a proposed flow path in order for the water quality characteristics at one location to evolve into the characteristics at another location. The analysis of evolution of water chemistry along a proposed flow path can substantiate or refute the existence of a path between sampling locations. Typically, the models cannot prove the existence of a flow path. They can, however, provide convincing evidence against the existence of the proposed path.

The two programs used were WATEQ4F (Ball et al., 1987) and BALANCE (Parkhurst et al., 1982). WATEQ4F is a computational device that uses equilibrium equations and constants from a thermodynamic data base to identify and quantify the dissolved species in a water sample. It then uses that information to determine whether the water is saturated with respect to any of more than 500 mineral phases.

WATEQ4F expresses the degree of mineral saturation in a sample using a calculated value called the saturation index. The saturation index (SI) is defined as the log (base 10) of the ratio of the observed ion activity product (IAP) to the thermodynamic solubility product constant (K_{sp}). The sample is saturated if $IAP = K_{sp}$; it is undersaturated if $IAP < K_{sp}$; and it is supersaturated if $IAP > K_{sp}$. WATEQ4F calculates the $\log_{10}$ of this ratio to facilitate the evaluation of the saturation index in the printout. Thus, the sample is at equilibrium if $SI = 0$, undersaturated if $SI < 0$, and supersaturated if $SI > 0$.

BALANCE solves a set of linear equations based on the observed molality of two or three water samples, dissolution or precipitation of mineral phases, possible ion exchange reactions, and the gases known to be present. BALANCE does not utilize any thermodynamic data; it is strictly a means of setting up and solving a matrix of linear equations based on mass balance. The equations are derived from dissolution reactions of the mineral phases entered into the program. Table 1 presents mineral and gas phases that have been identified by previous investigators at the Midnite Mine. The calculation balances the mass in the chemical reactions necessary to produce water having one set of measured concentrations of constituents from one or two sources of water with measured concentrations from a different set, using mineral phases as needed.

Table 1.--Possible minerals and gases used as input BALANCE program

Phase	Formula
Albite	$NaAlSi_3O_8$
Anorthite	$CaAl_2Si_2O_8$
Calcite	$CaCO_3$
Diopside	$CaMgSi_2O_6$
Dolomite	$CaMg(CO_3)_2$
Ca-montmorillonite .	$Ca_{0.25}Si_4Al_{1.5}Mg_{0.5}O_{10}(OH)_2$
Carbon (organic) . . .	"CH_2O"
Carbon dioxide gas .	CO_2
Gibbsite	$Al(OH)_3$
Goethite	FeOOH
Gypsum	$CaSO_4 \cdot 2H_2O$
Jarosite K	$KFe_3(OH)_6(SO_4)_2$
Jurbanite	$Al(OH)SO_4 \cdot 5H_2O$
Kaolinite	$Al_2Si_2O_5(OH)_4$
K-feldspar	$KAlSi_3O_8$
K-mica	$KAl_3Si_3O_{10}(OH)_2$
Manganite	MnOOH
Oxygen gas	O_2
Pyrolusite	MnO_2
Silica	SiO_2
Sphalerite	ZnS

Sign conventions and solid phase generalizations are used in BALANCE. During input, an optional algebraic sign can be used in the mineral and gas input data table to constrain a solid phase to only dissolve (+) or only precipitate (-). A solid phase can do either if no sign is used. Algebraic signs are shown in the output to indicate if a mineral is constrained to be consumed (+) or precipitated (-). Only the stoichiometric ratios of elements in a solid phase, and not the mineralogy, are considered in BALANCE. Thus, ferrihydrite ($Fe(OH)_3$) and goethite (FeOOH) are equivalent minerals in BALANCE because they both contain one iron atom with a +3 oxidation number. Since acid water production involves oxidation-reduction reactions, it is necessary to conserve electrons when balancing the chemical equations. BALANCE uses a convention that defines a redox state for a solution as

$$RS = \Sigma^{I}_{i=1} m_i v_i \qquad (1)$$

where RS is the redox state of the solution, m_i is the molality of the ith aqueous species, v_i is the valence of the ith species, and I is the total number of species. The reader is referred to the USGS documentation of WATEQ4F and BALANCE for complete descriptions of the models and variables (Ball et al., 1987; Parkhurst et al., 1982; Ball and Nordstrom, 1991; Plummer et al., 1991).

The acceptance/rejection criteria for the possible flow paths produced from the computer programs were not based on statistical methods, such as reduction of residuals between actual chemistry and modeled results. Instead, a multistep process was used in determining the validity of a particular model.

All wells were drilled and completed in a manner that allowed water to be sampled from a specified zone. Each time sampling was done, the well was pumped until the water was representative of the water in the production zone. The water was then analyzed under controlled conditions as demonstrated by statistics on control samples. The data were entered into a spreadsheet and any errors were found through the use of scatter plots or trend analyses.

The data for a particular site at a particular time were then entered into the WATEQ4F program. This program evaluates whether the data entered are suitable for its computation techniques by evaluating charge imbalances. This, of course, provides only an indication of the self-consistency of the major anion and cation species. Accuracy and long-term precision of all data were determined using statistical evaluations comparing the data with control samples. If the charge imbalance criteria were satisfied, then WATEQ4F would proceed and would list saturation indices for a large number of mineral phases. The chemist, using chemical intuition and field experience, evaluated the output to determine its usefulness. Some inputs, such as pH or iron concentrations, were edited to assess their impacts on the output. When this phase was completed, determination of the thermodynamic equilibrium condition of the water sample was finished.

Based upon plausible flow paths as determined by field observations, two or three samples were compared to evaluate the changes that would be necessary for water at one location to evolve into water at a different location. Using the computer program BALANCE, the mass and charge balance between two samples were compared. BALANCE gives many solutions to a series of linear equations developed from dissolution equations for mineral phases and solution concentrations. The chemist provides the evaluation by varying the mineral phases selected or the ions included in the mass balance. Acceptance or rejection is based upon the selection of mineral phases and the plausibility of the computer-generated solution, not upon statistical criteria such as reduction of residuals.

Presentation and Interpretation of Data

The Midnite Mine is a dynamic system moving toward equilibrium. Large variations in water quality exist at the site and reflect differences in the types and extent of chemical reactions taking place. In the following discussion, the water quality data from specific sampling locations will be used to discuss the chemistry, after which differences in the chemistry will be used to evaluate possible flow paths on the site.

Most of the data in table 2 were produced from analyses of samples collected in May 1991 (sample collection 18). The use of data collected during a specific time period allowed water quality at different sampling locations to be compared at a particular moment in time. Observed changes in constituents over time at

Table 2.--Water quality characteristics

Location	Specific conductance, mS/m	pH	Eh, mV	SO_4, mg/L	Alkalinity, mg/L as HCO_3^-	DO, mg/L
Well 6	4.0	5.8	473	6.4	41	6.4
Pit 3	256.0	4.3	440	2,450	0	9.9
Boyd Seep . .	158.0	4.2	434	3,480	0	10.2
Well 1S	83.0	7.3	455	224	342	6.4
Pit 4	59.6	8.2	491	394	55	10.6
Pit 3 seep . . .	70.7	7.5	419	2,452	85	9.8
Well 4S	440.0	4.0	502	5,880	0	4.6

Location	Element, mg/L										
	Al	Ca	Fe	K	Mg	Mn	Na	Ni	Si	U	Zn
Well 6	<0.3	7.5	0.02	<1.5	2.6	0.007	4.1	<0.03	11.0	<1	<0.04
Pit 3	50.0	397.0	1.2	4.0	222.0	95.0	54.0	2.8	11.0	21	3.7
Boyd Seep . .	78.0	473.0	.24	12.0	358.0	82.0	65.0	3.2	15.0	18	5.3
Well 1S	<.3	12.0	.05	3.0	2.7	.07	232.0	<.03	8.8	<1	<.04
Pit 4	<.3	117.0	.03	3.0	29.0	.4	17.0	.05	9.2	3	<.04
Pit 3 seep . . .	<.3	200.0	.06	4.0	84.0	17.0	25.0	.06	.06	2	.09
Well 4S	191.0	477.0	33.0	7.0	642.0	377.0	46.0	11.0	11.0	48	11.0

selected sampling locations are also presented. Selected data from the computer models are given in tables 3 through 10.

There are two chemical processes that must be considered when evaluating the hydrochemistry of the Midnite Mine: acid water production caused by oxidation of minerals containing reduced sulfur (primarily pyrite) and reaction of the acid water with other minerals. A comprehensive review of the inorganic and microbial mechanisms of pyrite oxidation is presented by Steffen, Robertson, and Kirsten, Inc. (1988). Pyrite is oxidized when it comes into contact with air and water, leading to the formation of oxidized iron compounds and sulfuric acid.

Oxidation occurs in three major steps. The first step is the oxidation of pyrite by molecular oxygen. Pyrite has two oxidizable species, ferrous ion and sulfidic sulfur. During the initial solubilization, only the sulfur species is oxidized, and the iron is dissolved in the ferrous state (Fe^{2+}) (Lowson, 1982), as shown in equation 2.

$$\begin{aligned}&2FeS_2(s) + 7O_2(g) + 2H_2O \longrightarrow \\ &2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H^+(aq).\end{aligned} \qquad (2)$$

The second reaction is the oxidation of the Fe^{2+} to the ferric ion (Fe^{3+}) by molecular oxygen, which can be catalyzed by the bacteria *Thiobacillus ferrooxidans*.

$$\begin{aligned}&4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \longrightarrow \\ &4Fe^{3+}(aq) + 2H_2O(l).\end{aligned} \qquad (3)$$

Above a pH of 4, the reactions shown in equations 2 and 3 dominate the kinetics of pyrite oxidation with molecular oxygen as the oxidant (Nordstrom, 1982). Combining the equations shows that 15 moles of molecular oxygen are required for every 4 moles of pyrite oxidized, or a ratio of 3.75 moles O_2 to 1 mole FeS_2.

The third reaction involves the oxidation of pyrite by Fe^{3+}.

$$\begin{aligned}&FeS_2(s) + 14Fe^{3+}(aq) + 8H_2O \longrightarrow \\ &15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H+(aq)\end{aligned} \qquad (4)$$

As the pH falls below 4 and the solubility of Fe^{3+} increases, Fe^{3+} becomes the dominant oxidant (Nordstrom, 1982).

However, at many of the sampling locations at the Midnite Mine, the acid water reacts with other minerals, raising the pH and increasing the concentrations of sodium, calcium, and magnesium ions. For example, the reactions of anorthite or dolomite occur according to the equations:

Anorthite

$$2CaAl_2Si_2O_8(s) + 4H^+(aq) + nH_2O(l) \longrightarrow$$

Allophane

$$\begin{aligned}&Si_3Al_4O_{12}.nH_2O(s) + Si(OH)_4^0(aq) \\ &\quad + 2Ca^{2+}(aq).\end{aligned} \qquad (5)$$

Dolomite

$$\begin{aligned}&CaMg(CO_3)_2(s) + 2H^+(aq) \longrightarrow \\ &Ca^{2+}(aq) + Mg^{2+}(aq) + 2HCO_3^{1-}(aq)\end{aligned} \qquad (6)$$

(Sposito, 1989).

Therefore, elevated concentrations of calcium and magnesium ions become indicators of neutralization reactions.

At low pH levels, elevated concentrations of aluminum, manganese, zinc, and uranium ions are found in the water, but as pH increases as a result of neutralization reactions, concentrations of aluminum and manganese ions are controlled by precipitation of secondary minerals, as shown for aluminum ions in equation 6. Therefore, zinc and uranium are used to indicate the movement of toxic metals in water having a near-neutral pH.

Well 6

Well 6 is a source of uncontaminated water in the quartz monzonite intrusive. The well lies at the top of a ridge on the northwest flank of the mine site; water from this well represents recharge water shortly after it has entered the intrusive. Table 2 presents an average of values from water collected in August, September, and October of 1990. Any individual sample typically gave a charge balance greater than 10 pct, where the charge balance was calculated by dividing the difference between the sum of the cation species and the sum of the anion species by the average of the sums and then converting them to percent. The charge balance discrepancy appears to be caused by fluctuations in field alkalinity. Because no other temporal variations have been observed for other water quality measurements at well 6, an average was calculated that gave a better charge balance (<10 pct) and better represented water quality. The results show that water from this well is of magnesium-calcium bicarbonate type, highly oxygenated, nearly in equilibrium with atmospheric carbon dioxide, and contains low concentrations of total dissolved solids.

When the averages were entered into WATEQ4F, the output (table 3) indicated that the water was undersaturated for most of the primary minerals at the mine site, including the major feldspars and diopside. The only minerals with saturation indices near 1 or >1 were montmorillonite, which is a secondary mineral stable in neutral soils, some iron-bearing minerals, and quartz. The water contained low concentrations of iron as Fe^{3+}; these concentrations appear to be controlled by ferrihydrite solubility. Silica concentrations are usually controlled by amorphous silica, and in this sample, amorphous silica had a negative saturation index. The concentration values indicate kinetic control of silica instead of equilibrium control.

Boyd Seep

Temporal variations in water quality. A seep on the eastern side of the mine, known as the Boyd Seep, produces acidic water and elevated concentrations of toxic metals (table 2). Figure 3 presents seasonal fluctuations in amount of discharge and changes in pH, and calcium, magnesium, and sulfate concentrations. As flow in the system increased, concentrations of ions also increased and pH decreased. This coupling indicates that chemical reaction products were being flushed from reaction sites in the waste rock and brought to the surface. It was speculated that pyrite oxidation and acid water formation occur during the dry seasons, and soluble sulfate salts

Table 3.--Saturation indices for selected minerals from WATEQ4F using analytical data from well 6

Mineral	Formula	Saturation index
Albite	$NaAlSi_3O_8$	-1.904
$Al(OH)_3$		-.141
Allophane (amorphous)	$Si_3Al_4O_{12}\cdot nH_2O$	.680
Anorthite	$CaAl_2Si_2O_8$	-4.011
Calcite	$CaCO_3$	-3.214
Ca-montmorillonite	$Ca_{0.25}Si_4Al_{1.5}Mg_{0.5}O_{10}(OH)_2$	6.462
Diopside	$CaMgSi_2O_6$	-12.440
Ferrihydrite	$Fe(OH)_3$	.637
Gibbsite (crystalline)	$Al(OH)_3$	2.677
Goethite	FeOOH	6.528
Gypsum	$CaSO_4\cdot 2H_2O$	-3.471
Jarosite K	$KFe_3(OH)_6(SO_4)_2$	-6.905
Kaolinite	$Al_2Si_2O_5(OH)_4$	7.622
K-mica	$KAl_3Si_3O_{10}(OH)_2$	9.882
Manganite	MnOOH	-6.476
Pyrolusite	MnO_2	-10.561
Quartz	SiO_2	.577
Silica (amorphous)	SiO_2	-.609

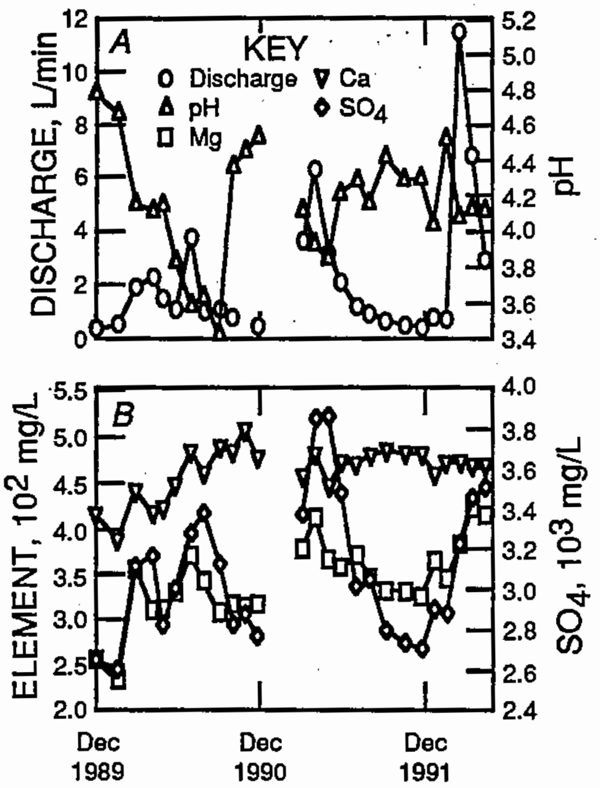

Figure 3.--Temporal variations in groundwater quality at Boyd Seep. *A*, Amount of flow and pH; *B*, calcium, magnesium, and SO_4. The intervals where no data exist were caused by no flow at the seep because of freezing temperatures.

Build up in the pore spaces in the sediments and the fractures in the rocks. The movement of water through the sediments during the wet period dissolves the salts and increases their concentrations in ground water in the spring.

Calcium concentrations were maintained at fairly constant levels after midsummer 1990. The saturation index for gypsum was near zero, showing saturation (table 4). After the system was flushed and concentrations of other ions decreased (note the time period July 1990 to December 1990 in figure 3, concentrations of calcium remained roughly constant. The gypsum that precipitated when sulfate concentrations were highest began to be dissolved, maintaining a saturated solution. The concentration of sulfate would have decreased even more if it had not been for the dissolution of gypsum. This mechanism is distorted by a continual increase in concentrations of reaction products, as seen in figure 3.

The quantities of several toxic contaminants moving out of the waste rock and to the surface, are calculated in grams per day as the product of flow rate (gallons per minute) and concentration (milligrams per liter). Plots of uranium and zinc are presented in figure 4. This figure again shows an increase in the mass of metal ions with increase in flow. It is also apparent that during several months of high flow, kilograms of toxic metals were brought to the surface in solution at this one location.

Possible flow path. Investigators have speculated that a flow path exists between pit 3 and

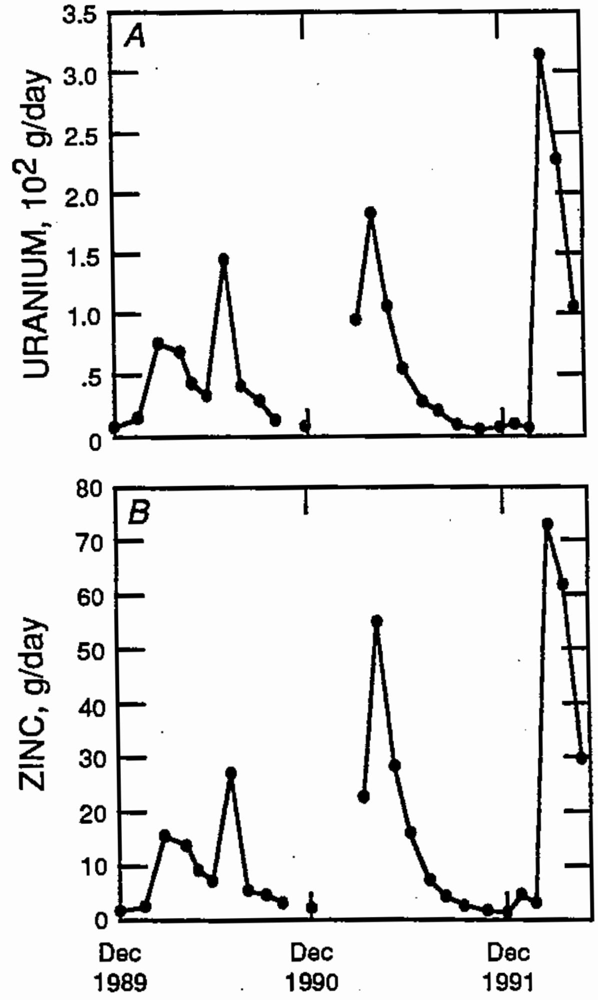

Figure 4.--Temporal variations in mass of released metals at Boyd Seep. *A*, Uranium; *B*, zinc.

Table 4.--Saturation indices for selected minerals from WATEQ4F using data from pit 3, Boyd Seep and well 1S

Mineral	Formula	Saturation index		
		Pit 3	Boyd Seep	Well 1S
Albite	$NaAlSi_3O_8$	-4.902	-4.855	-0.442
$Al(OH)_3$		-2.584	-3.066	-1.543
Allophane (amorphous)	$Si_3Al_4O_{12}\cdot nH_2O$	-.764	-.714	.852
Anorthite	$CaAl_2Si_2O_8$	-10.466	-11.562	-3.838
Calcite	$CaCO_3$	-7.167	-6.300	-.774
Ca-montmorillonite	$Ca_{0.25}Si_4Al_{1.5}Mg_{0.5}O_{10}(OH)_2$	.323	-.051	3.184
Diopside	$CaMgSi_2O_6$	-15.481	-15.774	-6.530
Ferrihydrite	$Fe(OH)_3$	-2.773	-3.839	2.034
Gibbsite (crystalline)	$Al(OH)_3$	.194	-.237	1.247
Goethite	FeOOH	3.118	2.052	7.925
Gypsum	$CaSO_4\cdot 2H_2O$	-.114	.023	-2.067
Jarosite K	$KFe_3(OH)_6(SO_4)_2$	-6.421	-9.198	-2.692
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.587	2.129	4.492
K-mica	$KAl_3Si_3O_{10}(OH)_2$	2.398	1.979	8.240
Manganite	MnOOH	-8.078	-8.363	-1.627
Pyrolusite	MnO_2	-13.702	-14.912	-4.111
Quartz	SiO_2	.707	.920	.610
Silica (amorphous)	SiO_2	-.625	-.447	-.730

Boyd Seep. The water elevation in pit 3 was approximately 15 ft (4.6 m) higher than the elevation of Boyd Seep (figure 2), and a fracture set is oriented along a line between pit 3 and Boyd Seep. Pit 3 is filling with water pumped back from collector wells, local infiltration, and direct precipitation. As the water elevation rises in the pit, the hydraulic gradient increases toward Boyd Seep, suggesting that water might be moving through a fracture in the calc-silicate formation and emerging at Boyd Seep.

The computer programs WATEQ4F and BALANCE were used to assist in evaluating such a flow path. Under equilibrium conditions, no model was found consistent with the hydrologic response of the system that could produce the water with concentrations found at the Boyd Seep when the model included water from pit 3.[2] On the basis of field observations and analytical data, the best model combines two types of waters that originate upslope from the seep.

One of the waters might originate in the zone sampled by well 1S. This zone would provide a year-round supply of water to the seep. To analyze a source of water that would respond to seasonal hydrologic events, infiltration water with properties similar to the type of water sampled at well 6 was included in the model. This scenario would provide water that has moved downslope and water that has a short flow path, so that part of the water flow would be continual and part would be responsive to short-term precipitation events.

Using the water quality data from wells 6 and 1S, 286 models were tested. Of these, two plausible models were found to satisfy the mass balance constraints (table 5).

The first model presented (model 5A) shows that no mixing of 1S water is necessary. This is a possible solution of mass balance constraints, since modeling has shown that the waste rock can produce acid water using input water similar to water from well 6.[3]

The second model (5B) gives a mixing ratio of approximately 27 pct 1S-type water to 73 pct

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[3] A complete description of the models attempted is described in a U.S. Bureau of Mines Report of Investigations to be published in 1993.

Table 5.--Input and output files from BALANCE evaluating mixing of water from well 1S with well 6-type water to obtain water similar to that found at Boyd Seep, millimoles per kilogram.

Element	Final, Boyd Seep	Initial 1, well 1S	Initial 2, well 6
Al	2.904	0.0003709	0.01112
C.	.001646	5.603	.6671
Ca	11.860	.2939	.1868
Fe	.004317	.0008190	.0004298
K	.3057	.08702	.002558
Mg	14.790	.1099	.1088
Mn	1.499	.001359	.0001238
Na	2.836	10.100	.179
S	36.350	2.332	.06621
Si	.5083	.2932	.3662
RS[1]	218.100	36.340	3.066

MINERAL AND GAS INPUT DATA

Albite	+Na	1.0	Al	1.0	Si	3.0
Calcite	+Ca	1.0	C	1.0	RS	4.0
CO_2 gas	- C	1.0	RS	4.0		
Diopside	+Ca	1.0	Mg	1.0	Si	2.0
Gibbsite	+Al	1.0				
Goethite	- Fe	1.0	RS	3.0		
Gypsum	- Ca	1.0	S	1.0	RS	6.0
Kaolinite	- Al	2.0	Si	2.0		
K-feldspar	+K	1.0	Al	1.0	Si	3.0
MnO_2	+Mn	1.0	RS	4.0		
O_2 gas	+RS	4.0				
Pyrite	+Fe	1.0	S	1.0	RS	0.0
SiO_2	Si	1.0				

OUTPUT DATA[2]

Mineral	Model 5A	Model 5B
Initial 1	0.0067	0.2678
Initial 2	.9933	.7322
Albite	+ 2.5904	
CO_2 gas	- -.6986	- -1.9874
Diopside	+ 14.6812	+ 14.6809
Gibbsite		2.6152
Goethite	- -19.6348	- -19.3529
Gypsum	- -3.0087	- -3.0364
K-feldspar	+ .3026	+ .2805
MnO_2	+ 1.4989	+ 1.4985
O_2 gas	+ 71.1415	+ 71.0888
Pyrite	+ 19.6386	+ 19.3567
SiO_2	-37.8987	-30.0417

[1] Redox state.

[2] Millimoles of reactant or product per kilogram of final water, except for Initial 1 and Initial 2, which are mixing ratios that sum to 1.0.

6-type water. This mixing provides a large component of infiltration water that would respond to precipitation events rapidly and a smaller component that would provide continual flow. The saturation index of gibbsite is consistent with the dissolution shown in the model. Pyrite oxidation, with a molar ratio of FeS_2 to O_2 of 3.67, lowers the pH (table 2), and secondary mineral formation controls iron concentrations. Gypsum is formed, which is consistent with the differences in saturation indices for the three waters. Even though calcite was included in the input parameters, it does not appear in the models. The mass balance solution requires only loss of carbon dioxide to balance the difference in alkalinity seen in the input. Hydrogen ions are not included in BALANCE, so pH control is observed only indirectly.

Because other minerals are known to be in the waste rock, different minerals were investigated (table 6). Anorthite and dolomite were substituted for diopside and calcite. The change to dolomite from calcite forced the dissolution of more carbonate in the models, since dolomite is the only source of magnesium. This is probably a more reasonable control on pH than the one seen in previous models. The mixing ratios are identical to those in previous models, which supports accepting the flow path from well 1S to Boyd Seep with mixing of infiltration water of a type similar to that found at well 6.

In summary, even though the water level in pit 3 was higher in elevation than that at Boyd Seep, no model was found consistent with the hydrologic response of the system that could produce the water with concentrations found at the Boyd Seep when the model included water from pit 3. The preferred model combines two types of waters that originate upslope from the seep. A portion of the flow originates in deeper waste rock that produces water throughout the year. Infiltration of rainwater through surface wastes provides a larger component that responds rapidly to precipitation events. Mixing water with concentrations similar to those found at wells 1S and 6, combined with dissolution of minerals found in the waste rock, produces water with the concentrations measured at Boyd Seep.

Pit 3

As described earlier, pit 3 is the largest open pit on the mine property. The water level has been getting higher because of precipitation, overland flow, groundwater flow, and pumpback of water from the pollution control pond, which includes water from the pumped seeps (figure 1). The BLM has collected data on the quantity of water pumped back to pit 3 and the total volume of water accumulated in pit 3 from 1985 through 1991. On the basis of calculations from these data, the pumpback system contributes about 60 ±10 pct of the increase in the volume of water in pit 3. To evaluate the relative contributions of pumpback water and infiltration water, BALANCE was used to evaluate the mixing of 6-type water with water from the pollution control pond. Input and output files are shown in table 7.

The model was used to calculate a mixing ratio of approximately 54 pct pollution control pond water to 46 pct infiltration water, which is close to the ratio calculated from pumping records. The minerals incorporated in the model were similar to those used to produce acid water using water from well 6.

The concentration values in water from the pollution control pond input to BALANCE were higher than those from pit 3, indicating that infiltration water to pit 3 must be diluting the water pumped back from the pollution control pond. However, the output from the program shows that some minerals must also be dissolved by infiltration water to achieve the concentrations measured in pit 3. It is apparent that any reclamation activities will to have to deal with water infiltrating pit 3. As this model shows, the water may contain products of acid water formation. As pit 3 is dewatered, the infiltration water will need to be monitored to determine if treatment is required before it is discharged.

Table 6.--Input and output files from BALANCE evaluating mixing of water from well 1S with well 6-type water to obtain water similar to that found at Boyd Seep, millimoles per kilogram.

Element	Final, Boyd Seep	Initial 1, well 1S	Initial 2, well 6	
Al	2.904	0.0003709	0.01112	
C	.001646	5.603	.6671	
Ca	11.860	.2939	.1868	
Fe	.004317	.0008190	.0004298	
K	.3057	.08702	.002558	
Mg	14.790	.1099	.1088	
Mn	1.499	.001359	.0001238	
Na	2.836	10.100	.179	
S	36.350	2.332	.06621	
Si	.5083	.2932	.3662	
RS[1]	218.100	36.340	3.066	
MINERAL AND GAS INPUT DATA				
Albite	+Na 1.0	Al 1.0	Si 3.0	
Anorthite	+Ca 1.0	Al 2.0	Si 2.0	
CO_2 gas	- C 1.0	RS 4.0	RS 21.0	
Dolomite	+Ca 1.0	Mg 1.0	C 1.0	RS 8.0
Gibbsite	+Al 1.0			
Goethite	- Fe 1.0	RS 3.0		
Gypsum	- Ca 1.0	S 1.0	RS 6.0	
Kaolinite	- Al 2.0	Si 2.0		
K-feldspar	+K 1.0	Al 1.0	Si 3.0	
MnO_2	+Mn 1.0	RS 4.0		
O_2 gas	+RS 4.0			
Pyrite	+Fe 1.0	S 1.0	RS 0.0	
SiO_2	Si 1.0			
OUTPUT DATA, MODEL 6A[2]				
Initial 1	0.2678			
Initial 2	.7322			
Anorthite	+ 1.3076			
CO_2 gas	-31.3492			
Dolomite	+ 14.6809			
Goethite	- -20.0067			
Gypsum	- -4.3440			
K-feldspar	+ .2805			
MnO_2	+ 1.4985			
O_2 gas	+ 73.5405			
Pyrite	+ 20.0105			
SiO_2	-3.2952			

[1] Redox state.

[2] Millimoles of reactant or product per kilogram of final water, except for Initial 1 and Initial 2, which are mixing ratios that sum to 1.0.

Table 7.--Input and output files from BALANCE comparing mixing ratios of infiltration water and pumpback water from pollution control pond to produce water found in pit 3, millimoles per kilogram.

Element	Final, pit 3	Initial 1, pollution control pond	Initial 2, well 6
Al	1.857	3.728	0.01112
C.	.000164	.001647	.6671
Ca	9.948	11.65	.1868
Fe	.02228	.0188	.0004298
K	.1114	.1799	.002558
Mg	9.166	16.99	.1088
Na	2.341	1.735	.179
S	25.61	38.53	.06621
Si	.3774	.6824	.3662
RS[1]	153.67	231.18	3.066

MINERAL AND GAS INPUT DATA

Albite	+Na	1.0	Al	1.0	Si	3.0
Calcite	+Ca	1.0	Mg	1.0	RS	4.0
CO_2 gas	- C	1.0	RS	4.0		
Diopside	+Ca	1.0	Mg	1.0	Si	2.0
Gibbsite	Al	1.0				
Goethite	- Fe	1.0	RS	3.0		
Gypsum	Ca	1.0				
K-feldspar	+K	1.0	Al	1.0	Si	3.0
O_2 gas	RS	4.0				
Pyrite	+Fe	1.0	S	2.0	RS	0.0
SiO_2	Si	1.0				

OUTPUT DATA, MODEL 7A[2]

Initial 1		0.5365
Initial 2		.4635
Albite	+	1.3272
Calcite	+	3.6109
CO_2 gas	-	-3.9208
Gibbsite		-1.4892
Goethite		-2.4415
K-feldspar	+	.0137
O_2 gas	+	9.1948
Pyrite	+	2.4535
SiO_2		-4.1810

[1] Redox state.

[2] Millimoles of reactant or product per kilogram of final water, except for Initial 1 and Initial 2, which are mixing ratios that sum to 1.0.

Table 8.--Saturation indices for selected minerals from WATEQ4F using data from pit 4 and pit 3 seep.

Mineral	Formula	Saturation index	
		Pit 4	Pit 3 seep
Albite	$NaAlSi_3O_8$	-1.375	-0.817
Allophane (amorphous)	$Si_3Al_4O_{12}\cdot nH_2O$	-.549	-.035
Anorthite	$CaAl_2Si_2O_8$	-2.721	-2.326
Calcite	$CaCO_3$	.218	-.164
Ca-montmorillonite	$Ca_{0.25}Si_4Al_{1.5}Mg_{0.5}O_{10}(OH)_2$	1.955	3.849
Diopside	$CaMgSi_2O_6$	-.579	-1.105
Dolomite	$CaMg(CO_3)_2$	-1.114	-3.067
Ferrihydrite	$Fe(OH)_3$	1.994	2.259
Gibbsite (crystalline)	$Al(OH)_3$	.449	1.113
Goethite	FeOOH	7.885	8.150
Gypsum	$CaSO_4\cdot 2H_2O$	-.920	-.567
Jarosite K	$KFe_3(OH)_6(SO_4)_2$	-5.064	-1.729
Kaolinite	$Al_2Si_2O_5(OH)_4$	3.005	4.633
K-mica	$KAl_3Si_3O_{10}(OH)_2$	6.859	8.616
Manganite	MnOOH	2.354	.583
Silica (amorphous)	SiO_2	-.679	-.529

Pit 3 Seep

Pit 4 lies in the northern third of the mine site. Mining operations ceased in pit 4 before they were halted in pit 3, so water that accumulated in pit 3 was pumped into pit 4. Although no water has been pumped into pit 4 since 1982, the water elevations continued to rise in pit 4 until approximately 1988. Since that time, the water elevation in pit 4 has remained relatively constant except for minor seasonal fluctuations. The stability of the water elevation suggests that the pit may be in dynamic equilibrium with the local groundwater flow system. That is, the amount of water recharging the pit is equal to the amount of water evaporating and being discharged as ground water.

The flow path of the ground water discharging from pit 4 is not well understood, but at least two discharge paths are plausible. Either the ground water discharges through the ancestral West Drainage or through the central part of the mine site toward pit 3. The flow may be split between the two flow paths.

Seeps are seen in the north headwall of pit 3, and it is proposed that these seeps originate at least in part from leakage out of pit 4. To evaluate this possible flow path, WATEQ4F was run using water quality data from pit 4 and the seeps at pit 3 (pit 3S) to evaluate the solubility controls on solution concentrations.

The WATEQ4F data for pit 4 and pit 3S show that many of the common minerals are undersaturated (table 8). In particular, calcium concentrations appear to be in equilibrium with calcite or possibly dolomite, but not gypsum. Iron concentrations are very low, and Fe^{3+} species predominate in the solution. Iron concentrations appear to be supersaturated with respect to ferrihydrite. Manganese concentrations are in apparent equilibrium with the solid phases pyrolusite and manganite.

Judging from the appearance of the seeps when sampling, part of the discharge originates where the alluvium and the waste rock contact bedrock and part is probably fed via fractures in the metasedimentary rock. A model was developed in which water flowing from pit 4 (water with concentrations equivalent to water typically sampled in pit 4) (table 2) was mixed with water infiltrating through the surface materials (as represented by well 6) to produce water with the characteristics of pit 3S. Previously, a model had been developed that described a flow path from pit 4 to pit 3S with no mixing,[4] but the mixing model better reflects field observations.

Using the input given in table 9, four mass balance solutions were found, two of which are presented. The major difference is in the mixing ratios for the initial waters. When a larger proportion of infiltration water is used (model 9A), more minerals are dissolved. More goethite and silica are formed, which matches the concentrations measured in pit 3S water. Gypsum was not used in the model, since gypsum was shown to be unsaturated in all three waters. Well 6 water is unsaturated for manganese, which would account for the dissolution of pyrolusite seen in the model. The oxygen-to-pyrite ratio is about 3.65, which is near the theoretical value.

In an attempt to decide which of the two models might best describe the proposed flow path, other models were developed using the same aqueous input but different mineral phases. Anorthite was substituted for diopside, which provides a different silica-to-calcium ratio. As a source of magnesium, dolomite was substituted for calcite.

Two models were produced that satisfied the mass balance constraints; one of these models (9C) is given in table 9. The models differ only in whether or not the silica and aluminum concentrations are controlled by silica and kaolinite or by silica and gibbsite; the mixing ratios are the same. The saturation indices indicate apparent control by silica and gibbsite (table 8). The mixing ratios agree closely with model 9B, indicating that the ratios of waters mixing to form the seeps may be about 89 pct pit 4 water to 11 pct infiltration water.

From the field observations and models, it is reasonable to believe that a hydrologic connection exists between pit 4 and the pit 3 seeps, and that part of the water in pit 4 discharges to the seeps in the headwall of pit 3. However, the amount of this discharge is small, from 0.9 to 1.9 gal/min. Thus, discharge from pit 4 is probably draining to other areas that should be studied in subsequent phases of the site investigation.

Well 4

Well 4 was completed next to a protore pile, allowing water in two zones to be sampled (figure 1). Analysis of water from this well provides information on the impact of protore on the ground water. This protore pile has been identified as containing some of the most reactive material on the mine site. Temporal variations in water elevation and water quality indicate that chemical reaction products were being flushed from sites in the waste rock and moved downgradient.

Water elevation varied by approximately 1 ft (0.3 m) throughout the year, reaching a minimum in the winter and maximum during the spring and summer. In addition, while water quality was initially poor, pH decreased from 5.5 at the beginning of the study to almost 4 during the winter and spring of 1991. At the same time, concentrations of many ions increased (figure 5).

For example, sulfate and magnesium concentrations showed two types of temporal variation. First, they varied annually in response to changes in water elevation, indicating infiltration by snowmelt and rain. Second, they increased steadily over the duration of the study. These two types of variation indicate that well 4S is being impacted by reaction products from the protore pile. The steady increase in concentrations of uranium, zinc, and iron also support this hypothesis.

Calcium concentrations are controlled by gypsum saturation as shown by the saturation index calculated by WATEQ4F (table 10). Seasonal variations stopped after December 1990; at that time, sulfate concentrations had

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[4] Mineralogical analyses were performed by Dr. Charles N. Alpers under an interagency agreement between the Bureau and USGS.

Table 9.--Input and output files from BALANCE evaluating possible flow path from pit 4 to pit 3 seep with mixing of 6 water, millimoles per kilogram.

Element	Final, pit 3 seep	Initial 1, pit 4	Initial 2, well 6
Al	0.010	0.000	0.000
C.	1.401	.9003	.6671
Ca	5.015	2.916	.1868
Fe	.001156	.0004838	.0004298
K	.0969	.08957	.002558
Mg	3.473	1.185	.1088
Mn	.3170	.007286	.0001238
Na	1.080	.7530	.1790
S	8.338	4.114	.06621
Si	.4306	.3081	.3662
RS[1]	55.632	28.285	3.066

MINERAL AND GAS INPUT DATA

Albite	+Na	1.0	Al	1.0	Si	3.0
Calcite	+Ca	1.0	C	1.0	RS	4.0
CO_2 gas	C	1.0	RS	4.0		
Diopside	+Ca	1.0	Mg	1.0	Si	2.0
Gibbsite	- Al	1.0				
Goethite	- Fe	1.0	RS	3.0		
Gypsum	- Ca	1.0	S	1.0	RS	6.0
Kaolinite	- Al	2.0	Si	2.0		
K-feldspar	+K	1.0	Al	1.0	Si	3.0
MnO_2	+Mn	1.0	RS	4.0		
O_2 gas	+RS	4.0				
Pyrite	+Fe	1.0	S	2.0	RS	0.0
SiO_2	Si	1.0				

OUTPUT DATA[2]

Mineral	Model 9A	Model 9B	Model 9C
Initial 1	0.5142	0.8857	0.8857
Initial 2	.4858	.1143	.1143
Albite	+ .6058	+ .3926	+ .3926
Calcite	+ .6140		
CO_2 gas		.5274	-4.2947
Diopside	+ 2.8108	+ 2.4111	
Dolomite			+ 2.4111
Gibbsite			- -.4011
Goethite		- -2.3427	- -2.3423
Kaolinite	- -.3251	- -.2005	
K-feldspar	+ .0496	+ .0173	+ .0173
MnO_2	+ .3132	+ .3105	+ .3105
O_2 gas	+ 11.2931	+ 8.4768	+ 8.4769
Pyrite	+ 3.0952	+ 2.3434	+ 2.3430
SiO_2	-6.8433	-5.5349	-1.1139

[1] Redox state.

[2] Millimoles of reactant or product per kilogram of final water, except for Initial 1 and Initial 2, which are mixing ratios that sum to 1.0.

increased to the point where gypsum saturation and subsequent precipitation occurred. Since that time, there have been only minor variations in calcium levels.

Conclusions

Geochemical modeling has advanced the understanding of the hydrogeology of the Midnite Mine by delineating possible flow paths on the basis of hydrochemical changes in water quality between sampling sites. Even though the system is continually changing, computer models based on thermodynamic equilibria are useful in describing solubility control of solution species.

Acid water is being produced in protore piles, waste rock, and other spoils piles because of the oxidation of sulfide-containing minerals, such as pyrite, associated with the ore and waste materials. The acid water dissolves minerals in the piles, which may raise pH or may increase concentrations of toxic metals in the water.

Seasonal flushing of contaminated water occurs at the Midnite Mine. Water containing high concentrations of toxic metals is produced when rainwater moves through the waste rock and migrates downgradient to emerge at a seep. Concentrations of toxic metals increase as the flow rate increases. This indicates that soluble products that accumulate in the pore space of the waste rock during the dry season are being dissolved by infiltration water.

The volume of water in pit 3 is continually increasing as a result of precipitation, groundwater flow, overland flow, and pumpback of water from the pollution control pond. On the basis of geochemical modeling of concentrations of major cations and anions from various sources, the water entering pit 3 from infiltration and runoff is being degraded and may require treatment before it is discharged from the site.

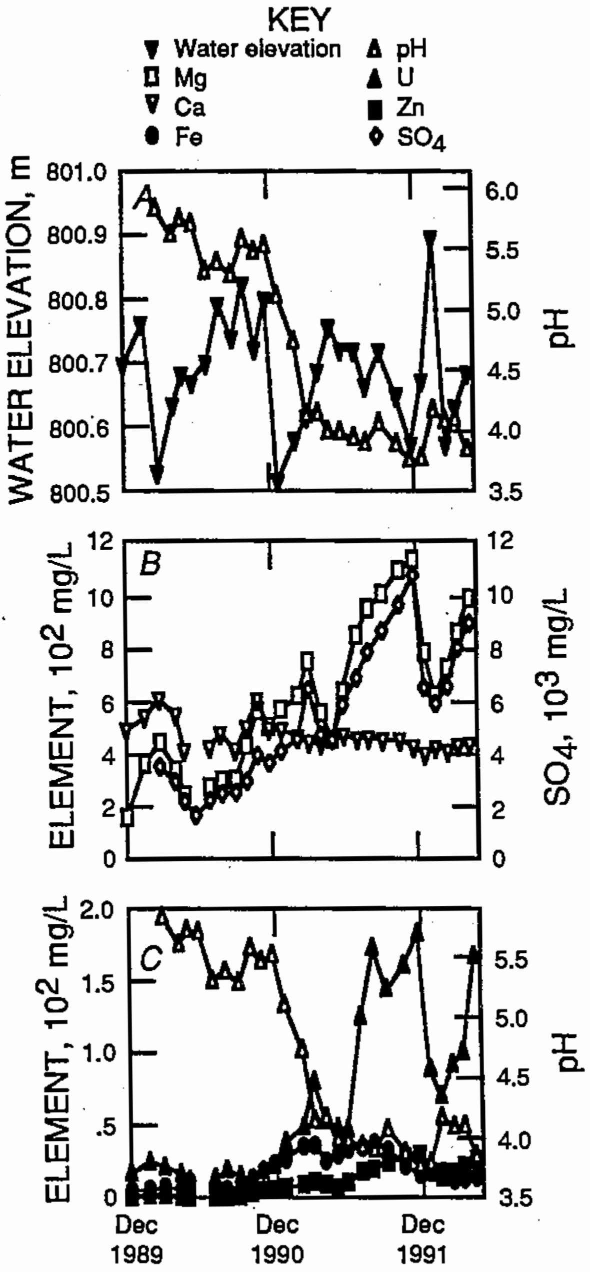

Figure 5.--Temporal variations in groundwater quality at well 4S. *A*, Water level and pH; *B*, calcium, magnesium, and SO_4; *C*, uranium, zinc, iron, and pH.

Ground water emerging at Boyd Seep is probably a mixture of water similar to the ground water sampled by well 1S and water infiltrating the waste rock just above the seep. A mixture of water from these sources would explain the seasonal fluctuations in flow and metal concentrations measured at the seep, as well as account for the continual flow at the seep during the summer months. Although a flow

Table 10.--Saturation index for selected minerals from WATEQ4F using analytical data from well 4S.

Mineral	Formula	Saturation index
Albite	$NaAlSi_3O_8$	-6.345
$Al(OH)_3$		-3.764
Allophane (amorphous) . . .	$Si_3Al_4O_{12}\cdot nH_2O$	-.988
Anorthite	$CaAl_2Si_2O_8$	-13.688
Ca-montmorillonite	$Ca_{0.25}Si_4Al_{1.5}Mg_{0.5}O_{10}(OH)_2$	-2.170
Diopside	$CaMgSi_2O_6$	-16.906
Ferrihydrite	$Fe(OH)_3$	-7.704
Gibbsite (crystalline)	$Al(OH)_3$	-.938
Goethite	FeOOH	-1.812
Gypsum	$CaSO_4\cdot 2H_2O$	.038
Jarosite K	$KFe_3(OH)_6(SO_4)_2$	-20.192
Jurbanite	$Al(OH)SO_4\cdot 5H_2O$	1.306
Kaolinite	$Al_2Si_2O_5(OH)_4$	.507
K-mica	$KAl_3Si_3O_{10}(OH)_2$	-.978
Manganite	MnOOH	-13.824
Pyrolusite	MnO_2	-25.768
Quartz	SiO_2	.810
Silica (amorphous)	SiO_2	-.555

path may exist between pit 3 and Boyd Seep, the hydrochemical models indicate that such a flow path is unlikely.

A hydraulic connection between pit 4 and the seeps on the north headwall of pit 3 is probable. The hydrochemical models describe the water from the seeps as predominantly pit 4 water with a smaller component of infiltration water. The quantity of water being discharged, however, is very small.

Concentrations of those ions that indicate acid water production have increased significantly in the ground water impacted by a protore pile since November 1989. Concentrations of toxic metal ions have also increased. This finding indicates deterioration of water quality at the Midnite Mine can be expected to continue until the causes of acid water production are controlled.

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