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Geochemical modeling approach to predicting arsenic concentrations in a mine pit lake

Regina N. Tempel[a,*], Lisa A. Shevenell[b], Paul Lechler[b], Jonathan Price[b]

[a] *Department of Geological Sciences/MS 172, Mackay School of Mines, University of Nevada, Reno, NV 89557, USA*
[b] *Nevada Bureau of Mines and Geology, Mackay School of Mines, University of Nevada, Reno, NV 89557, USA*

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Abstract

Between 1968 and 1983, the North pit at the Getchell Mine, Humboldt County, NV, filled with water to form a lake. In 1983, water quality data were collected with the following results: As concentrations of 0.29 to 0.59 mg/L, pH of 7.1 to 7.9, SO_4 concentrations of 1490 to 1640 mg/L, and TDS of 2394 to 2500 mg/L. Using geochemical modeling techniques presented here, pit lake waters have been theoretically allowed to react for 8.5 a, the approximate time that the North pit had been completely full by 1983. Modeling results predict pH of 7.9 to 8.2, SO_4 concentrations of 1503 to 1644 mg/L, TDS of 2054 to 2366 mg/L, and As concentrations ranging from 0.57 in the hypolimnion to 96 mg/L in the epilimnion. In the epilimnion, model results do not match observed As concentrations, suggesting that mechanisms, such as precipitation of arsenate salts or adsorption to mineral surfaces, may control As levels in an actual pit lake system. Adsorption to Fe oxyhydroxide surfaces is questioned by the authors because of the low Fe content in the Getchell system, but adsorption to $Al(OH)_3$ (gibbsite) and clay mineral surfaces may be important in controlling natural As concentrations. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the most important environmental issues facing the Au mining industry in Nevada is the quality of water in newly formed pit lakes that results from interaction between pit waters and wall rocks over time. Among other components, As concentrations are elevated in ore minerals and in wall rocks in many mining districts (e.g. Tingley, 1992; Foo et al., 1996; Leonardson and Rahn, 1996). Water/rock interaction with As–sulfide wall rocks in an oxidizing environment can potentially result in high levels of As and metals and low pH, from oxidation of pyrite, in pit lake waters. Prediction of As is especially critical if the current US standard (0.05 mg/L) for drinking water is lowered, as is being proposed by the US Environmental Protection Agency (EPA) (Kaiser, 1998).

Prediction of As levels in future pit lakes requires a geochemical numerical modeling approach that utilizes an accurate conceptual model. To be accurate, the conceptual model must effectively link large-scale processes, such as wall rock weathering, local groundwater hydrology, limnology, and climate, to the molecular-scale effects of mineral dissolution and oxidation, reactivity of mineral surface areas, adsorption, and in situ pH and redox conditions. The principal hypothesis being tested by our work is that reasonable

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* Corresponding author. Fax: +1-720-784-1833.
E-mail address: gina@mines.unr.edu (R.N. Tempel).

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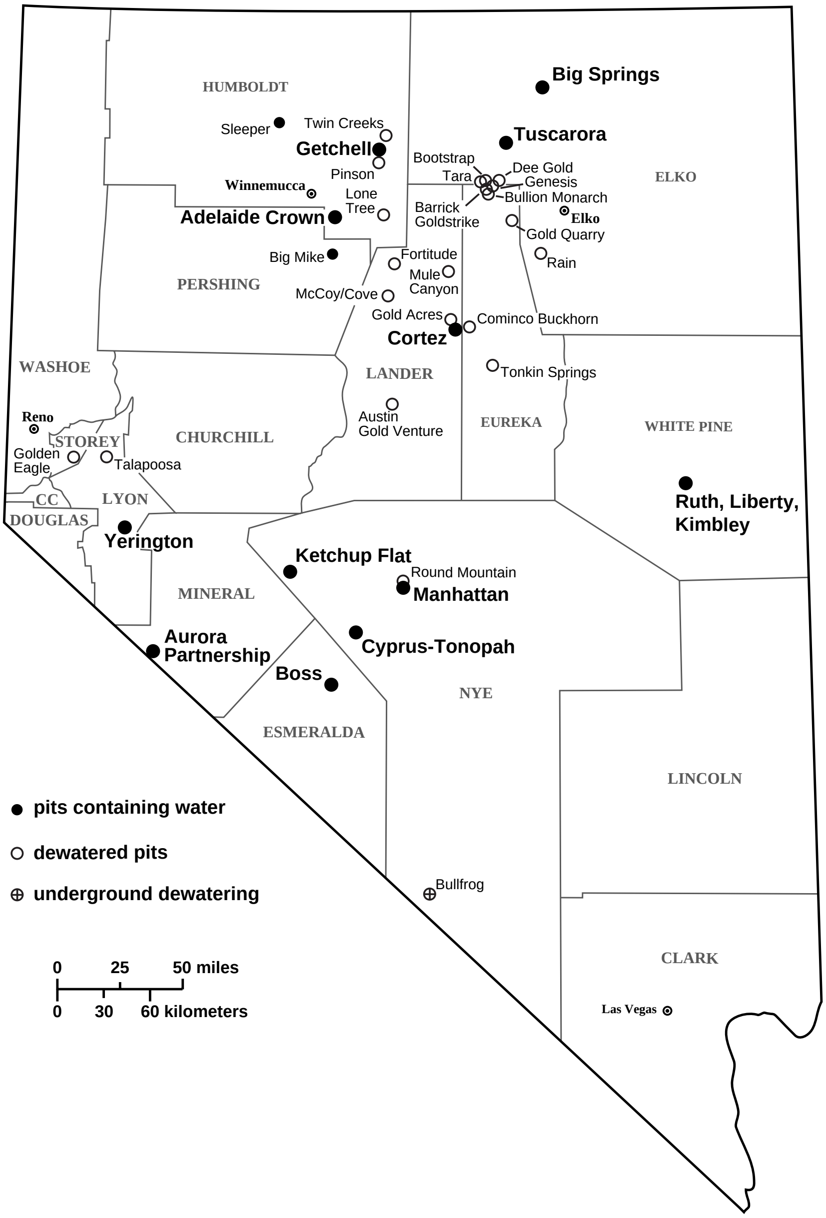

Fig. 1. Locations of current and future open-pit mines that will contain water upon cessation of mining activities. Filled circles indicate pits that currently contain water; open circles indicate pits that will contain water in the future (after Shevenell et al., 1999).

estimates of pH, As, and SO_4 concentrations can be predicted using existing datasets and geochemical codes coupled with a realistic conceptual model of a pit lake system.

One of the primary problems with modeling water quality in future pit lakes is that the few pit lakes in existence are either inaccessible or have not been in existence long enough to have attained steady state conditions either geochemically or hydrologically. However, the authors were able to obtain a relatively complete historical dataset from Getchell Gold Corporation in eastern Humboldt County, NV for 3 pit lakes that were in existence from 1968 to 1983. The importance of an historical dataset is that it can be used to calibrate a conceptual model of a mine pit lake environment.

The methods are applied to modeling water quality in the historical North pit lake on the Getchell Gold Corporation property. Mining operations in the North pit are currently inactive and the pit is pumped dry at

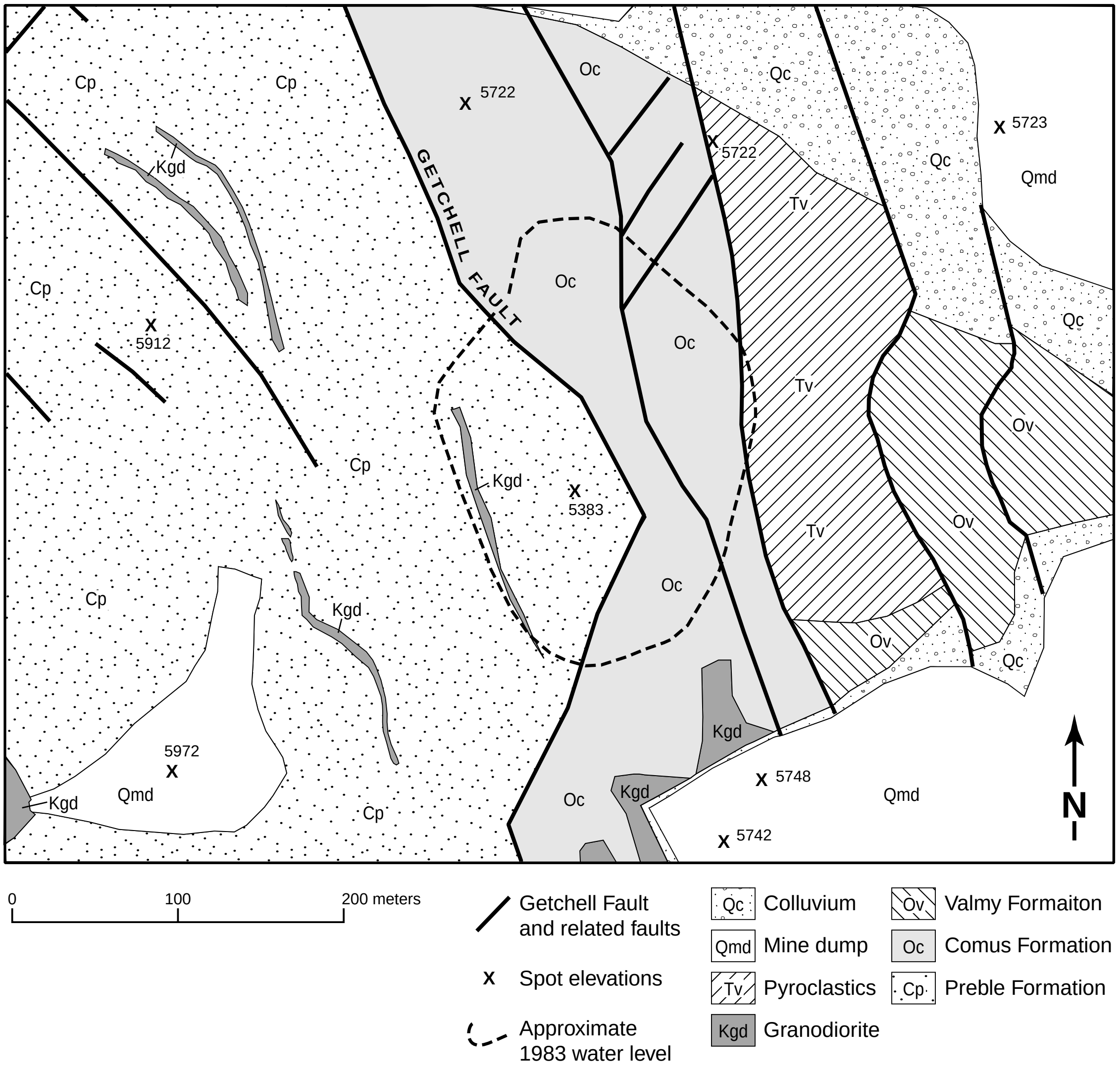

Fig. 2. Geological map of Getchell North pit as it exists at the present-day. Although the pit has been mined since 1983, the present-day geology does not differ significantly from 1968 to 83 geology, when the pit was filled with water. Approximate 1983 water level is shown on the map and is based on data from the 1996 USGS topographic map (an accurate topographic map circa 1983 was not available) and air photos taken during the time the pit was filled with water.

present to maintain dry operating conditions for underground mining operations. Future environmental concerns for this pit, as well as the other pits at Getchell, are focused primarily on the generation of high concentrations of As and SO_4 sulfate, as well as potentially low pH from oxidation of sulfide minerals. The Getchell Mine is well-known for its abundance of the As minerals, realgar, and orpiment (Hotz and Willden, 1964), and elevated concentrations of As have been measured in both the pit lakes and local groundwaters.

2. Background

2.1. Geology and mineralogy

The Getchell Mine is located in eastern Humboldt County, NV, northeast of the town of Winnemucca. The minesite is situated at the northern end of the Getchell Trend that includes other currently active open-pit mining operations for disseminated Au associated with As-bearing sulfide mineral phases (Fig.1).

The geology of the Getchell North pit is dominated by the Getchell fault zone, a N–S trending feature (Fig. 2), which has emplaced the Lower Cambrian to Lower Ordovician Preble Formation above the Ordovician Comus Formation. Tertiary volcanic rocks are exposed along the eastern flank of the North pit, and a small dike of Osgood Mountain granodiorite stock cuts the Preble on the western flank of the pit. The Preble and Comus Formations in the Osgood Mountains area are partly coeval and similar in lithology. The Preble Formation lithology is characterized by phyllitic shale and slate, interbedded limestone, and micaceous sublitharenite and quartz arenite. Comus lithologies are similar to Preble but lack regional metamorphism (Madden-McGuire, 1991) and are predominantly an alternating sequence of dolomite, limestone, and shale (Hotz and Willden, 1964).

Mineralogy of the Preble includes quartz, K-feldspar, calcite, muscovite, and pyrite. Greenstone-facies metamorphic rocks in the Preble consist of plagioclase, biotite, muscovite, and hornblende. Minerals observed in samples of Comus are quartz, calcite, calcic plagioclase, and muscovite. Tertiary volcanic rocks are composed primarily of quartz and feldspars with some biotite. Unaltered granodiorite consists of quartz, orthoclase, plagioclase and biotite. Main sulfide minerals at the Getchell Mine include realgar, orpiment, pyrite and arsenopyrite (Joralemon, 1951; Hotz and Willden, 1964).

2.2. Water levels and water chemistry

Getchell North pit lake attained a maximum depth of 34 m in 1983, and water was primarily contributed by groundwater with some surface water inflow. The premining water level is unknown, but assumed to be equivalent to the elevation of the water in the pit in 1983. Although no premining water levels are available at the site, water levels believed to be unaffected by dewatering operations have been measured in the vicinity of the North pit lake. One well (MMW5) is located upgradient of the pit, separated from the pit by one major fault and several minor faults and had a measured water level of 1851 m in February 1990. Another well (93-27) located just downgradient of the former pit lake had a measured water level of 1670 m in 2/93. Because the measured pit lake elevation in 1983 was 1697 m, a value that lies between the two water levels measured in nearby wells, it is likely that this 1983 value is very nearly equal to the premining water level in the pit area. Therefore, it is assumed that a water level elevation of 1697 m represents the steady state water level in the pit lake. The assumption of this near steady state water level is further supported by the measured water levels in the lake, which show only slight increases with time toward the end of the data record (Fig. 3).

Historical geochemical surveys from the North pit lake are either limited to reporting As, SO_4, TDS and pH, or the samples were composited over the entire depth profile of the North pit lake. No specific documentation was provided regarding procedures used to composite the historical samples except to state that equal proportions of pit waters were collected at 2 locations, one section at the south end and one section at the north end, and at 3 depths within the lake and mixed prior to sample analysis. The top sample was taken 5 feet below the surface, the bottom sample was taken 5 feet above the pit bottom, and the middle sample was taken at approximately mid–depth between the other two samples. These composited data are important in that they provide clues to water chemistry in the historical North pit lake and provide the basis for the model calibration.

The composited samples from January 1982 and April 1982 are complete for both major and minor ions. The analyses appear to be of high quality with electroneutrality for the two analyses at $<2\%$. Field measurements include pH temperature and conductivity. According to field notes, 2 composited samples were filtered and acidified (one with HNO_3 and one with H_2SO_4), and one sample was unfiltered and unpreserved. Although the size of the filter is not given in field notes, it is assumed to be a 0.45 μm filter. Analyses for the April 1982 samples were conducted at the Water Analysis Laboratory, Desert Research Institute, Reno, NV. Major cations, metals, and total As were measured on the filtered, acidified (HNO_3) sample and anions on the unfiltered, unpreserved sample using atomic absorption spectrometry. Total suspended solids and turbidity were measured on the unfiltered samples (Table 5) (M. Miller, Water Analysis Laboratory, Desert Research Institute, pers. comm.).

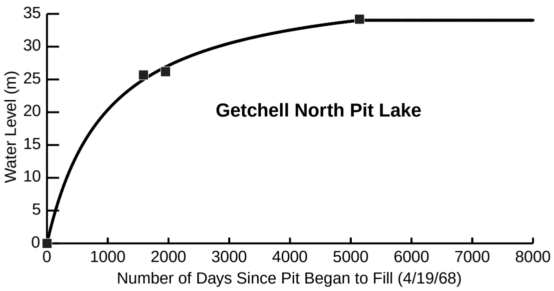

Fig. 3. Measured and curve fitted water level versus time for the North pit lake at the Getchell mine.

Table 1
Comparison of hydrologic properties of pit lakes with those of natural lakes

	Surface area (km^2)	Depth (m)	Surface area/depth ratio
Getchell mine			
North pit lake	0.023	34.15	0.67
Center pit lake	0.026	36.26	0.72
South pit lake	0.047	22.88	2.06
Natural lakes			
Walker Lake (Thomas, 1995)	164	55	2987
Pyramid Lake (Lebo et al., 1994)	438	102	4294

3. Conceptual model and method

3.1. Pit lake characteristics

Pit lakes possess several characteristics that distinguish them from natural lakes. Pit lakes generally have a greater depth relative to surface area than most natural lakes, a characteristic that influences circulation of the water column. Table 1 compares natural and pit lakes in Nevada and shows that pit lakes are consistently smaller than natural, closed–basin lakes and the surface area to depth ratios of pit lakes are >3 orders of magnitude smaller, a factor that can reduce the effect of evaporation on the total lake volume. Pit lakes exhibit thermal and chemical stratification and seasonal turnover, much like natural lakes, but the greater relative depth of pit lakes makes them more likely to develop a permanently stratified anoxic bottom layer or to be meromictic (Anderson et al., 1985; Doyle and Runnells, 1997). The hydrology of pit lakes differs from natural lakes because groundwater flow commonly dominates inflow, whereas surface water dominates inflow to natural lakes (Atkins et al., 1997).

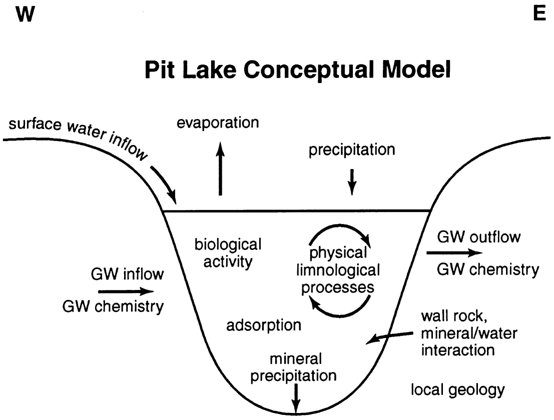

Fig. 4. Diagram illustrating the components of the pit lake conceptual model. In this study, the authors have considered local geology, groundwater (GW) chemistry, wall rock mineral/water interaction, physical limnological processes, and mineral precipitation.

Pit lake systems involve large-scale processes as well as micro-scale processes. Large-scale processes that affect water quality in a pit lake may include the evolution of background geochemistry of local groundwaters, seasonal stratification and turnover, and evaporation. Micro-scale processes that may affect water quality in a pit lake may include mineral surface area reactivity, dissolution and oxidation rates, and extent of wall rock reaction. Figure 4 links the macro- and micro-scale processes that are operative in a pit lake environment.

3.2. Hydrology

In order to evaluate the effects that pit lakes may have on water quality, knowledge of the water volumes and fluxes into and out of the lakes is required. Because the main hydrologic factor considered here in the geochemical conceptual model is the total fluid volume, details of the groundwater fluxes and losses via evaporation will be discussed elsewhere. Only the general water balance method is included here.

An analytical (spreadsheet) water balance method was employed in this work to model pit lake filling for the North pit lake at the Getchell Mine. Pit lake filling rates and water balances have been conducted previously and published for the Twin Creeks, NV open pit (HCI, 1996); hypothetical pit lakes in California and Nevada (Havis and Worthington, 1997); Voisey's Bay, Labrador pit lake (Bursey et al., 1997); and an unnamed pit lake (Naugle and Atkinson, 1992). Similar procedures were followed to estimate pit lake filling in the current work as in previous work. However, in the current work at Getchell, a known water level versus time curve could be constructed based on historical data (Fig. 3), and hence, water levels, volumes, and fluxes into the pit could be computed based on known rather than modeled water level values.

In order to determine the timing of lake filling, volumes of water in the pit at discrete times, and the

Table 2
Volumes and fluxes computed using simple water balance for Getchell's North pit lake. GW_i-GW_o is net groundwater flux

Lake volume (m^3)	387,699	vs. 401,620 m^3 from Conoco, 1982; 4% difference
Water level (m)	34.03	vs. 34.15 m measured; $<1\%$ difference
Top surface area (m^2)	22,746	
Precipitation (m^3/a)	5743	
Runoff (m^3/a)	2621	
Evaporation (m^3/a)	24,222	
GW_i-GW_o(m^3/a)	15,858	

potential inflow and outflow rates into and out of the pit lakes, a simple water balance was constructed for the lakes:

$$\Delta S = P - E + R + GW_i = GW_o \qquad (1)$$

where ΔS is the change in storage in the pit lake, P = precipitation, E = evaporation, R = runoff, GW_i = groundwater inflow to the pit, GW_o = groundwater outflow from the pit. Because it was assumed that steady state was reached when the pit was full in 1983, ΔS equaled zero for dates following 1983.

Precipitation data were acquired from the US Soil Conservation Service, and the data supplied were calculated using the PRISM method (Daly et al., 1993; Natural Resources Conservation Service, 1995). These data were queried in the current study to obtain representative precipitation data for the Getchell area. An empirical method was used to estimate potential evapotranspiration (PET) for the state of Nevada (Shevenell, 1996), in which a statewide GIS model was constructed that estimates PET on a 1 km grid for each of the 12 months of the year. These GIS grids were queried to determine the PET value associated with the pit lakes at the Getchell Mine. Following the methods of previous work at pit lakes (e.g. PTI, 1996), the HELP model (Schroeder et al., 1994) was used to estimate the evaporation from, percolation into, and runoff from the pit walls (R) between the lake surface at the current time step and the rim of the pit. All 3 of these parameters (P, E and R) were computed using the known water level, and hence, surface area of the top of the pit lake that was obtained from an equation describing stage-volume-surface area relationships (Fig. 3). Also from these relationships, the total volume of water in the pit at any time (and associated water level) was known.

Combined groundwater inflow minus outflow from the Getchell North pit lake was obtained by difference from Eq. 1 as a combined term:

$$(GW_i - GW_o) = (V_2 - V_1) - P - R + E \qquad (2)$$

where, V_2 and V_1 are the total volumes in the pit lake at two different time steps. Therefore, using a water level vs. time curve and the stage-volume-surface area relationships, P, R and E were computed using the known surface area at each time step (month). The pit lake volumes (V_1 and V_2) were also known from these relationships, and GW_i–GW_o, that must have entered the pit to obtain the known pit volume, were computed by difference at each time step.

Assumptions that were used in the water balance calculations are: (1) no evaporation from the lake occurs during months with average temperatures less than freezing; (2) no surface water inflow; (3) no runoff out of the lake was allowed (any excess water assumed to discharge as groundwater outflow from the lake); (4) calculations are updated on a monthly basis; (5) evaporation from the lake and precipitation inputs to the lake were allowed to occur over only the area represented by the surface area of the top of the pit lake as calculated from the previous time step.

The results of the water balance computations indicate the surface areas and annual volumes that can be anticipated when the North pit lake is full, and at steady state (Table 2). Using these volumes and fluxes, mean residence times within the pit lake can be estimated. The total possible inflow (GW_i) into the lake was estimated by multiplying the area upgradient of the pit lake to the groundwater divide by 15% of the precipitation falling over that area to obtain approximate recharge. At steady state, it is assumed that all recharge upgradient of the pit lake flows into the lake, and this volume is an estimated 33,000 m^3/a. Using this inflow, and the annual volumes gained and lost from Table 2, the North pit lake will flush within 9.4 a ($\approx$10% flushing/a). This indicates that 10% of the pit lake volume will be lost to evaporation and groundwater outflow, and 10% will be gained via groundwater inflow, precipitation and runoff from the pit walls. If it is assumed that all outflow from the lake is via evaporation, and none leaves the lake as groundwater outflow (i.e. $Q_2=0$ and only 15,858 m^3 enters the lake via groundwater inflow, which is 48% of the

Table 3
Comparison of historical pit lake to conceptual model. Total volume is reduced to 1000 cm^3 in conceptual model to accommodate geochemical model limitations. Relative depth of historical pit lake is maintained in conceptual pit lake

North pit lake	Max. depth	Top surface area	Rel. depth, %	Total volume
Historical	34.15 m	22,746 m^2	20	401,620 m^3
Conceptual	4 cm	250 cm^2	~ 20	1000 cm^3

computed value of 33,000 m^3), then the lake will flush every 16 a.

3.3. Geochemical conceptual model

Results from hydrologic model data are used to develop a small-scale geochemical conceptual model in which the total volume of the pit lake is 1000 cm^3, the same volume of fluid that is used in the reaction path model EQ3/6 (Wolery and Daveler, 1992). Table 3 compares the maximum depth, top surface area, relative depth (maximum depth to surface area), and total volume of the historical and conceptual pit lakes. Total surface area of pit wall rock in the conceptual small-scale model that is in contact with pit waters is $\approx 4.7 \times 10^{-3}$ m^2 and is defined for determination of the surface area of individual mineral phases in contact with pit waters.

3.3.1. Pit lake analogs

Because pit lakes do not currently exist on the Getchell property, analogs to the historical Getchell North pit lake have been used to estimate physical limnological conditions. Temperature and DO profiles in D pit lake and temperature profiles from B-zone pit lake, both located in northern Saskatchewan (Doyle and Runnells, 1997), and temperature and DO profiles from Aurora pit lake in western Nevada (Atkins et al., 1997) were used for comparison. D pit lake is 26 m deep and has a relative depth of 18%, which is closest to the 22% relative depth of Getchell North pit lake. B-zone pit lake is deeper than the maximum depth of Getchell North pit lake at 55 m. Aurora pit lake is 17 m deep and has been chosen as a second analog because it is affected by climatic influences most similar to Getchell North pit lake. Because the geology of each of these lakes is unique, other geochemical parameters, such as total As concentration and pH with depth, cannot be compared to historical Getchell North pit lake. DO profiles may also be a unique parameter, depending on wall rock mineralogy and degree of biological productivity.

Temperature and DO profiles were measured in the upper 15 to 20 m of the D pit lake and show turnover of the entire water column in spring and fall and stratification during the summer (Doyle and Runnells, 1997) (Fig. 5(a)). Thickness of the epilimnion (upper layer) from temperature data appears to be ≈8 m. The DO profile shows measured values that are approximately in equilibrium with the atmosphere throughout the thickness of the epilimnion during summer stratification (15-July-86), whereas DO values in the hypolimnion (layer below thermocline zone) are increasingly depleted (clinograde O_2 curve).

B-zone pit lake shows thermal stratification during the summer months and turnover during spring and fall (Doyle and Runnells, 1997) (Fig. 5(b)). The thickness of the epilimnion during summer stratification appears to range between 8 to 10 m. Depth profile plots of temperature and DO from Aurora pit lake also show summer stratification with the epilimnion layer developing in the upper 8 to 10 m of the pit lake. Seasonal turnover appears to occur in Aurora pit lake during spring and fall (Fig. 6(b)).

Considering studies of D, B-zone and Aurora pit lakes (Atkins et al., 1997; Doyle and Runnells, 1997), it is assumed that the historical Getchell North pit lake was dimictic (turned over twice yearly) and holomictic, meaning that the entire water column mixes during turnover. Temperatures for the North pit lake are estimated to be 17°C for the epilimnion and 4°C for the hypolimnion during summer stratification. Winter stratification is estimated to be isothermal at 4°C for both the hypolimnion and epilimnion. The epilimnion is estimated to comprise approximately 10% of the total pit lake depth with the hypolimnion comprising 90%.

3.3.2. Model assumptions

No direct measurements of redox potential within an existing pit lake have been reported using either redox couples or field Eh measurements. Because Eh does not correlate well with DO concentrations in natural lakes, DO cannot be used as a direct indicator of redox (Hutchinson, 1957). Redox potential of pit lake waters is perhaps the most important constraint on a model system, and lack of information on this aspect importantly affects model results. The authors have assumed that the redox state of the epilimnion is constrained by equilibrium with O_2 in the atmosphere, and that the hypolimnion is isolated from the atmosphere, so that its redox state is controlled primarily by interaction with wall rock minerals. Although the de-

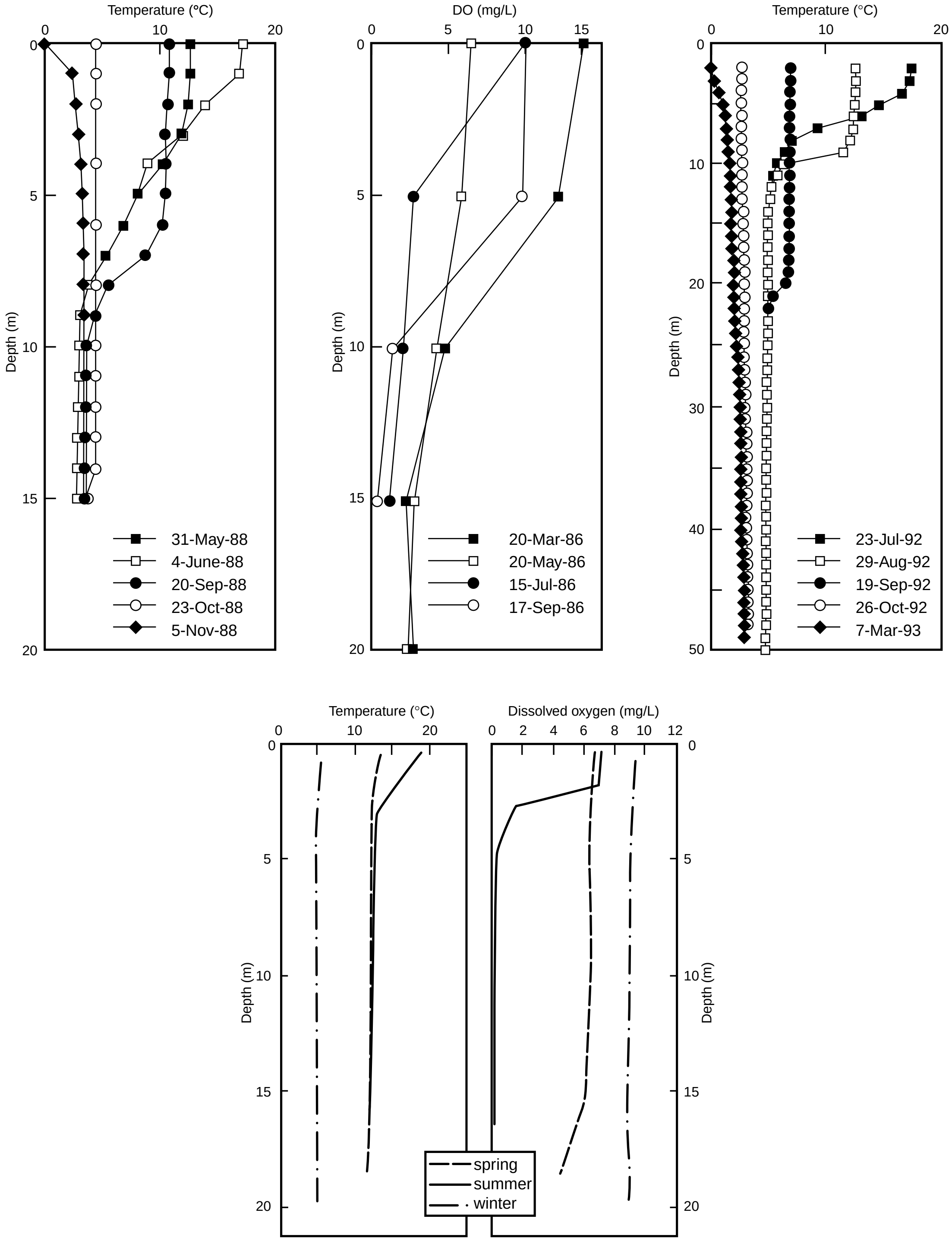

Fig. 5. Depth profiles of D pit lake and B-zone pit lake, both located in Saskatchewan, Canada and Aurora pit lake located in central Nevada. Depth profiles for D pit lake include temperature and dissolved O_2 (DO)(left diagrams in (a)), B-zone pit lake depth profile is temperature only (diagram on right in (a)), and Aurora pit lake depth profiles are temperature and DO (b). Profiles from D and B-zone pit lakes are modified from Doyle and Runnells (1997); data for the plots are taken from Saskatchewan Environment and Public Safety (1990). Aurora pit lake is modified from Atkins et al. (1997).

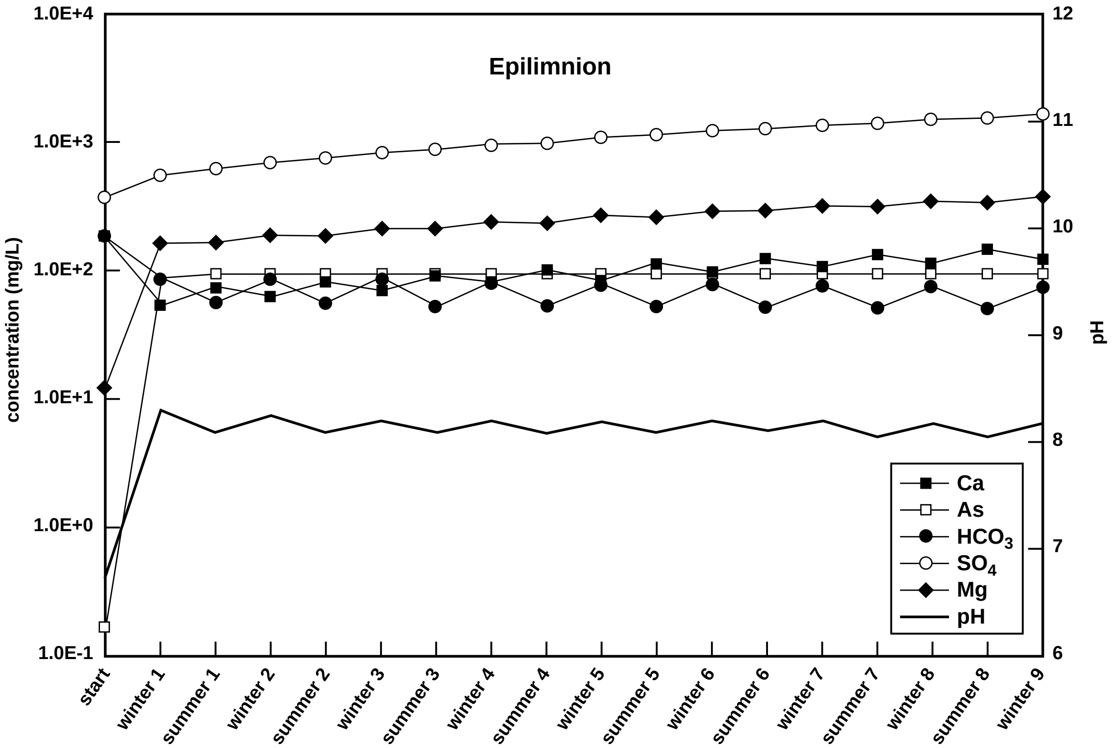

Fig. 6. Dissolved species concentrations estimated by simulations of epilimnion waters. Simulation starts in winter of year one (4/68) and continues through winter year nine (4/83). Summer conditions have been modeled at 17°C and winter conditions at 4°C.

Table 4

Absolute and relative dissolution rates and proportions of wall rock composition for reactant minerals used in simulations of Getchell North pit lake

Reactant minerals	Mol% wall rock	Log rate (mol/m^2/s)	Relative rate (×quartz rate)	References
Silicates				
Quartz	25	−13.39	1	Rimstidt and Barnes, 1980
Muscovite	20	−13.07	2.1	Lin and Clemency, 1981
Kaolinite	5	−13.28	1.29	Nagy et al., 1991; Carroll and Walther, 1988; 1990
Anorthite	5	−8.55	6.9×10^3	Fleer, 1982
Microcline	5	−12.50	7.8	Schweda, 1989
Annite	5	unknown	2.1	assumed muscovite rate
Carbonates				
Calcite	10	−6.0	2.5×10^7	Plummer et al., 1978; Svensson and Dreybrodt, 1992
Dolomite	5	−8.0	2.5×10^5	Busenburg and Plummer, 1987
Sulfides/Sulfates				
Pyrite	5	−9.4	1.0×10^4	Williamson and Rimstidt, 1994
Realgar	2	unknown	1.0×10^4	assumed pyrite rate
Orpiment	8	unknown	1.0×10^4	assumed pyrite rate
Arsenopyrite	4	unknown	1.0×10^4	assumed pyrite rate
Scorodite	1	unknown	1.0×10^4	assumed pyrite rate

Table 5
Comparison of modeled results after 8.5 a with a historical composited water analysis. Starting groundwater composition is also shown for comparison. Concentrations in mg/L, unless noted otherwise

	Composite 1/26/82	Composite 4/28/82	Modeled hypolimnion	Modeled epilimnion	Modeled turnover	MMW5 skarn/shale
Na	46	38.1	23.0	23.0	23.0	23.0
K	16	10.8	7.7	5.0	7.4	2.0
Mg	63	72.7	323	378	328	12.0
Ca	554	530	105	124	107	191.0
Fe	nd	0.16	0.1	< 0.001	< 0.001	0.21
Al	nd	0.2	1.0×10^{-8}	1.0×10^{-8}	1.0×10^{-8}	nd
As	0.14	0.38	0.57	96.3	10.1	0.17
HCO_3	127	119	74.0	75.7	73.7	195.2
SO_4	1610	1570	1503	1644	1518	380.0
SiO_2	12.8	11.0	0.45	0.32	0.43	20.7
pH	7.5	7.7	8.2	8.2	7.9	6.7
TDS	2465	2420	2054	2366	2085	854
TSS		24				
Turbidity		12 NTU[a]				

[a] Nephelometric turbidity unit.

composition of organic material and photosynthetic activity may also contribute to redox conditions, these processes have not been quantified in pit lakes and are not included in the preliminary simulations.

In modeling the epilimnion in a pit lake, the calculation proceeds under conditions of equilibrium with O_2 ($10^{-0.7}$ tm.) and CO_2 ($10^{-3.5}$ atm.) in the atmosphere. To represent such conditions, the fixed fugacity option is employed in EQ3/6 (Wolery and Daveler, 1992). The hypolimnion of a pit lake is modeled without the fixed fugacity option because the hypolimnion is separated from the atmosphere by the epilimnion and metalimnion (thermocline zone) and receives a limited supply of O_2 and CO_2. For simplicity, the metalimnion is neglected because it represents a zone of transition between the epilimnion and hypolimnion layers.

Model calculations have been conducted assuming two 6-month intervals per year representing summer and winter stratification events. Between each of the stratification events is a mixing event that represents spring or fall turnover. Water compositions that result from 6 months of pit water/wall rock interaction in both the epilimnion and hypolimnion are mixed in the approximate proportions that are estimated for the North pit lake (10% epilimnion; 90% hypolimnion). The water composition that results from the mixing event is used as input to the next winter or summer stratification event, and the sequence of calculations is repeated over several years. An assumption in model calculations is that turnover is instantaneous and that wall rock mineral reaction is negligible during a turnover event. The mean pit water residence time of approximately 10 a is considered to be the average time a liter of water resides in the pit lake reservoir. This simplifies the calculation by neglecting the $\approx 10\%$ groundwater inflow per year and is done to focus on the more dominant process of lake turnover.

3.4. *Mineral dissolution and oxidation rates*

Dissolution and oxidation rates of pit wall rock minerals are important in constraining the extent of water/wall rock reaction that takes place during the residence time of the pit waters. Dissolution and oxidation rates considered in this study are given in Table 4. The quartz dissolution rate is chosen as a reference rate because quartz dissolves slowest of any of the minerals used in the model, and rates of dissolution for minerals other than quartz are determined relative to the quartz dissolution rate. The oxidation rate for pyrite has been determined from the methods of Williamson and Rimstidt (1994) using a pH value of 7.5 and DO concentration of 3.0 mg/L. The pH value is the median of the values measured in the historical North pit lake waters. Because DO was not measured in the historical North pit lake, the concentration used in estimating the oxidation rate of pyrite was taken from measurements of the Aurora pit lake waters in Atkins et al. (1997). Oxidation rates for orpiment, realgar and arsenopyrite in the neutral pH range are not known (D. Rimstidt, pers. comm.), and thus the pyrite rate is assumed for these minerals. Using relative dissolution and oxidation rates in geochemical model calculations provides a convenient alternative to using absolute dissolution rates in some geochemical reaction path codes (i.e. EQ3/6, CHILLER), and can eliminate or minimize convergence problems.

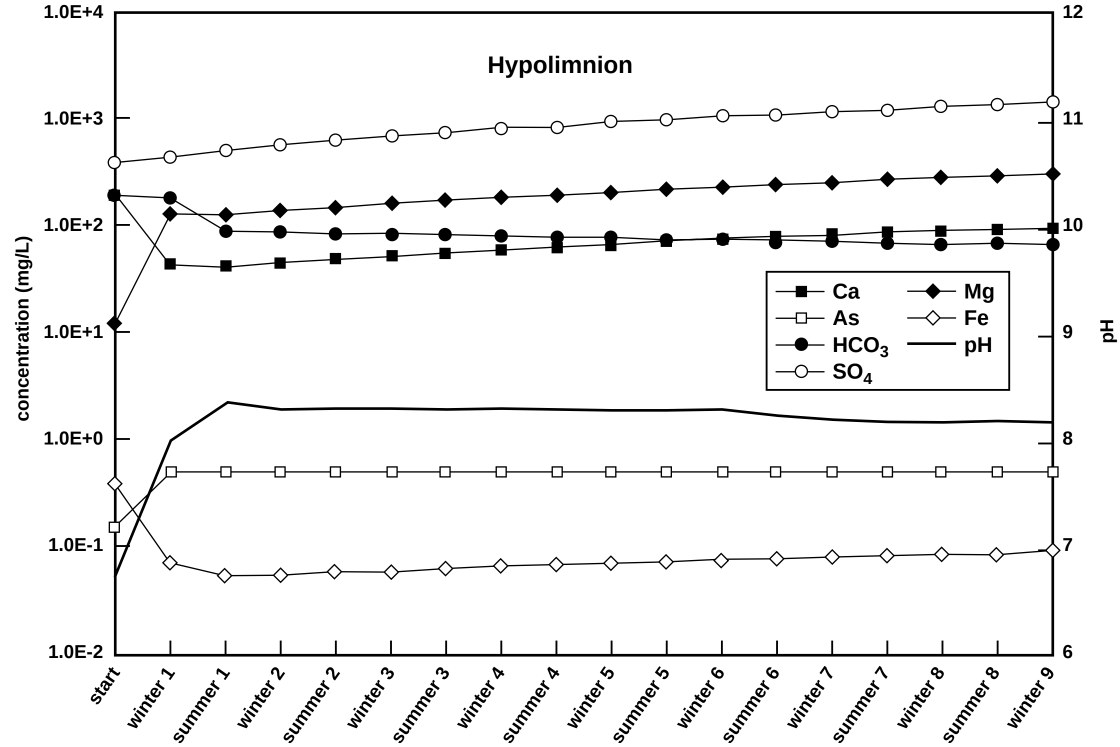

Fig. 7. Dissolved species concentrations estimated by simulations of hypolimnion waters. Duration of time is the same as in Fig. 6. Both summer and winter conditions are isothermal at 4°C.

Although mineral dissolution rates can be pH and CO_2 dependent, in the calculations dissolution rates are assumed to be constant over the range of geochemical conditions observed in Getchell North pit lake waters. This assumption is reasonable because historical pH measurements are near-neutral, and CO_2 levels in the epilimnion are controlled by the atmosphere.

3.5. Water chemistry and rock composition

Because inflow into the historical Getchell North pit lake was dominated by groundwater, it has been assumed that the geochemistry of North pit lake waters can be estimated by reacting wall rock minerals with the chemistry of a local groundwater. Contribution by surface waters is considered negligible here because little, but unknown quantities of surface water were noted to drain into the historical pit lakes. If surface waters were found to be important, the geochemical calculations would need to be modified because the addition of surface water would dilute pit waters.

A representative groundwater was collected and analyzed (Table 5) during January 1997 from groundwater monitoring well MMW5, located 0.25 km upgradient of the present-day North pit because historical groundwater analyses were not complete for major ions. The MMW5 groundwater is a $CaSO_4$ water-type with an As concentration of 0.17 mg/L that is in equilibrium with realgar.

In the conceptual model, the authors assume that the wall rock composition of present-day North pit is representative of the historical North pit lake wall rock. Although Getchell North pit has been mined since 1983, the exposed geology of the North pit was not modified significantly by mining based on historical and present-day geologic maps of the area (Fig. 2) (Hotz and Willden, 1964; Getchell Gold Corp, 1997).

Reactant minerals in the conceptual pit lake represent the various lithologies and the proportions of those lithologies in the wall rocks of the Getchell North pit. Table 4 lists the reactant minerals, percentages of wall rock composition, dissolution or oxidation rates used in the reaction path calculation, and the references from which the rate data were obtained. Scorodite ($FeAsO_4 \cdot 2H_2O$) has been included as a reactant mineral because it is a common weathering product of As-bearing ore deposits (Dove and Rimstidt, 1985) and is observed at Getchell (R. Bowell, pers. comm.). The EQ3/6 database has been modified to include scorodite using data obtained from Robins (1987).

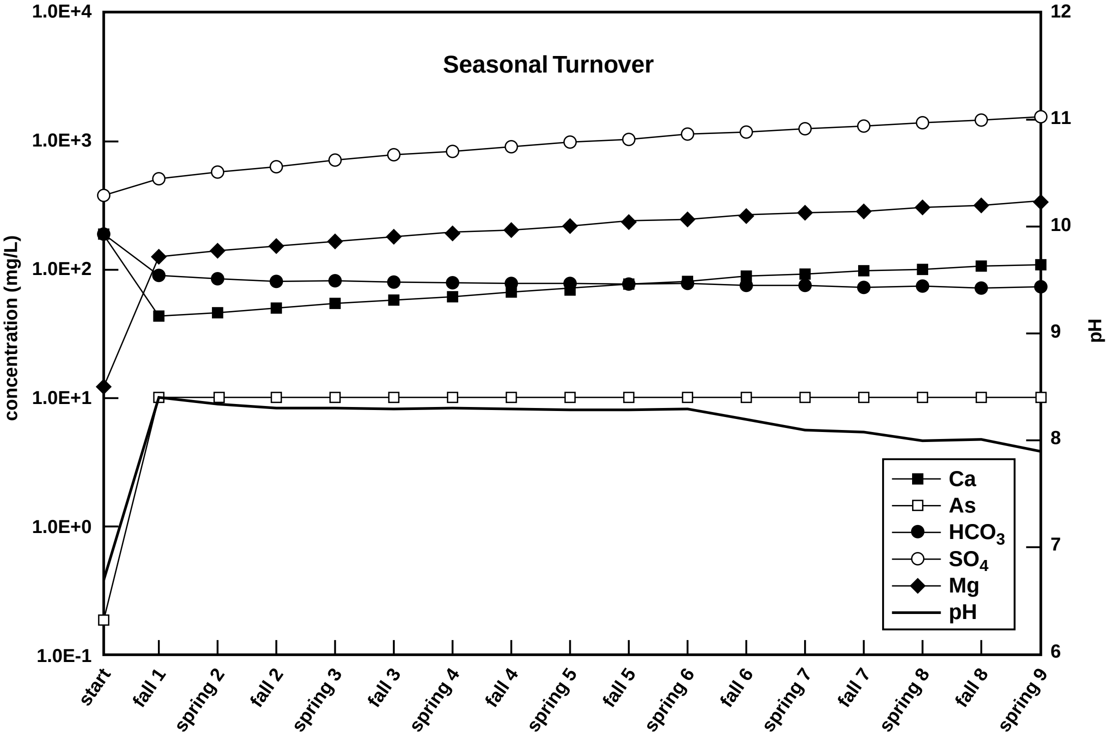

Fig. 8. Dissolved species concentrations resulting from simulations of spring and fall turnover of the entire water column.

3.6. Extent of wall rock reaction

The extent of wall rock reaction is a key component of the conceptual model and represents the amount of wall rock that is reacted with pit lake waters during a 6-month winter or summer season. The extent of wall rock reaction, or reaction progress (Helgeson, 1970), is based on the pit wall rock surface area in contact with the pit waters, dissolution rate of the reactant minerals, and the percentage of the reactant minerals in the pit wall rocks. Additionally, a reactivity factor represents the magnitude of effects, such as increased surface area due to fracturing of wall rocks and microbial mediation of sulfide oxidation rates, and is determined specific to a pit lake system. The expression for the extent of reaction is:

$$\text{Extent of reaction}_{(\text{mol of quartz})} = \text{wall rock surface area}_{(\text{m}^2)} \times \%\ \text{wall rock composition} \times \text{dissolution rate}_{(\text{mol/m}^2/\text{s})} \times \text{reactivity factor} \times \text{s}/6\ \text{months}$$

where wall rock surface area in the conceptual pit lake (cylinder) $= 4.7 \times 10^{-3}$ m^2; % wall rock composition is the reactant mineral (typically quartz); dissolution rate (typically quartz); a reactivity factor of 10^3 is used to account for the difference between estimated and observed values of dissolved species, and secs/6 months $= 1.6 \times 10^7$.

Table 6
Historical data from Getchell North pit lake with depth. Data for total dissolved solids, SO_4, and As are in mg/L

	Winter 1982					Spring 1982					summer 1983			
	3 ft	20 ft	40 ft	60 ft	75 ft	0 ft	5 ft	25 ft	50 ft	65 ft	5 ft	30 ft	55 ft	80 ft
pH	7.3	7.5	7.5	7.5	7.5	7.9	7.8	7.7	7.6	7.5	7.9	7.9	7.3	7.1
TDS											2455	2500	2394	2504
SO_4											1640	1520	1550	1490
As											0.55	0.59	0.29	0.44

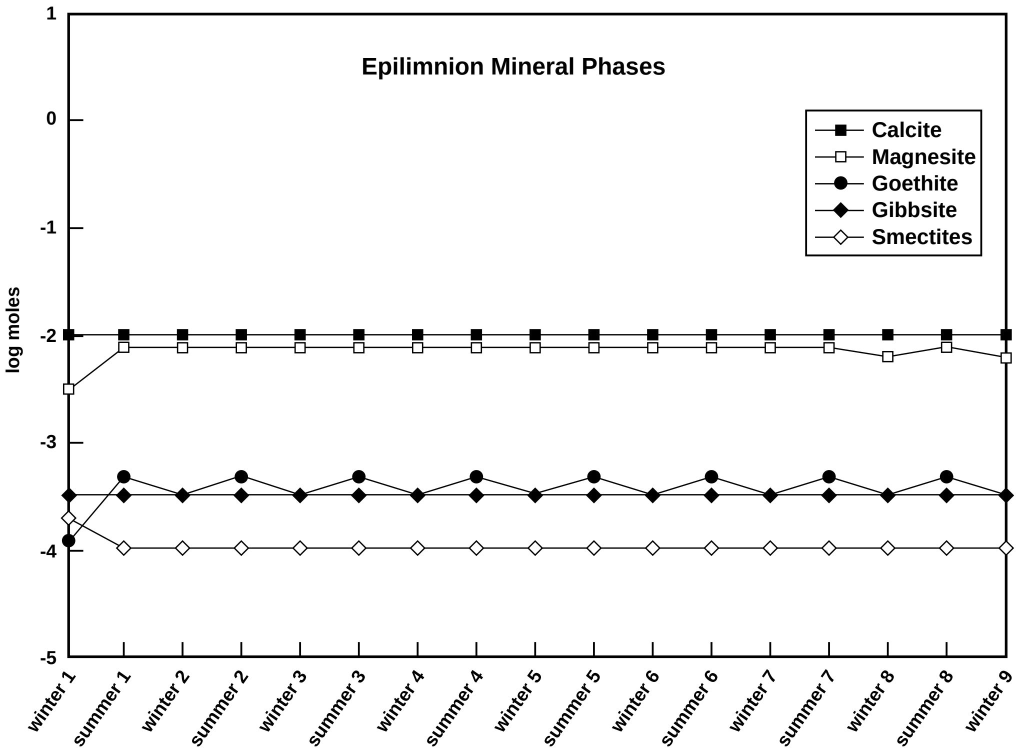

Fig. 9. Predicted mineral phase precipitation controlling water chemistry in epilimnion simulations.

3.7. Reactivity factor

Without a reactivity factor of 10^3, estimated SO_4 sulfate levels are an order of magnitude too low compared to observed values. Therefore, the extent of water/rock reaction in the actual pit lake is higher than that predicted using just the parameters of wall rock surface area, % wall rock composition, and dissolution rates given in Eq. 3 above. Of these 3 parameters, wall rock surface area and dissolution rate are the least well-known in field conditions. Factors that may influence wall rock surface area and dissolution rates are rock fracturing in the Getchell area, rock roughness, mineral surface reactivity, and microbial mediation. In the present conceptual model, the authors have considered the influences of these factors collectively as the reactivity factor, and once the factor has been computed, it remains constant in all simulations of the Getchell North pit lake.

Getchell North pit is located within the Getchell fault zone that was formed during uplift of the Osgood Mountains to the west. As a result of tectonic movements, the North pit walls are highly fractured, thus increasing the reactive surface area of the pit walls. Fracturing during blasting for mining may also contribute to the increase of reactive surface areas. Elsewhere, reactive surface areas in fractured rocks in contact with groundwaters are estimated to increase by a factor of ~10^3 to 10^5 (Paces, 1973; Torgersen et al., 1990), or for every square meter of wall rock surface on the pit walls, pit waters will be in contact with 10^3 to 10^5 m^2 of reactive rock surface along fractures.

Rock roughness enhances the reactivity factor by increasing the surface area of the wall rock that is in contact with pit waters. Mineral surface reactivity, related to numbers and types of surface dislocations, may decrease the % reactive surface area (100% mineral surface reactivity is assumed at present).

Microbial mediation of sulfide oxidation may increase the extent of water/rock interaction in a pit lakes system by increasing the dissolution rate parameter. Rates of oxidation of Fe sulfides are known to increase in lignites in the presence of *Thiobacillus ferroxidans* by about an order of magnitude (Pugh et al., 1984). At present, the influence of microbes on oxidation rates of As-sulfide minerals are not known or explicitly considered.

4. Results and discussion

Evolution of pit lake chemistry has been simulated using the described method over an 8.5-a period because that is the length of time that the historical pit

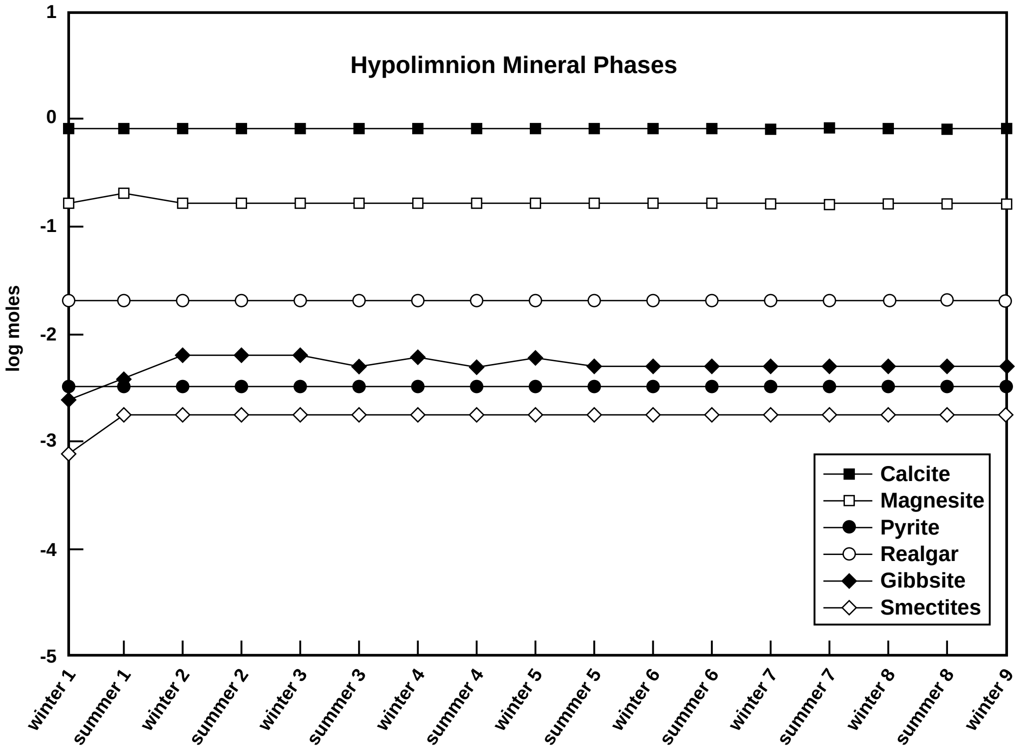

Fig. 10. Predicted mineral phase precipitation controlling water chemistry in hypolimnion simulations.

was approximately full of water. To simplify the calculations, it is assumed that both dimictic limnological conditions and water/rock interaction did not begin until the pit was completely full. Results are plotted against time for epilimnion, hypolimnion, and seasonal turnover conditions (Figs. 6–11), and include dissolved species in concentrations $>10^{-6}$ mg/L along with mineral phases controlling the dissolved species concentrations.

4.1. Comparison of pH values

Results of simulations in the epilimnion show that pH values fluctuate between 8.1 during the summer and 8.2 during the winter after year 1 (Fig. 6). Historical pH values in the upper 8–10 m (<33 ft.) of Getchell North pit lake ranged between 7.3 and 7.5 in winter of 1982 (equivalent to 7 a after 4/75, the estimated pit full date), ranged from 7.7 to 7.9 in spring of 1982, and was 7.9 in the summer of 1983 (equivalent to 8.5 a after pit full) (Table 6).

In the hypolimnion, simulated pH values drop to 8.2 after summer year 6 (Fig. 7). Observed values from historical data range from a high value of 7.6 (at 50 ft.) in spring of 1982 to a low value of 7.1 (at 80 ft.) in summer 1983 (Table 6). Estimated pH values from seasonal turnover simulations decline over time to a low of 7.9 by spring of year 9, and match observed values (Fig. 8).

pH in model calculations is controlled primarily by carbonate mineral equilibria. Throughout simulations of the epilimnion, hypolimnion, and seasonal turnover, calcite and magnesite precipitate as separate phases (Figs. 9–11). In a real system, calcite and magnesite would not precipitate as distinct phases, instead, they would precipitate as a Mg-calcite solid solution composition. The higher modeled pH values, especially in hypolimnion waters, may suggest that less carbonate wall rock was available in the historical pit lake than in the modeled pit lake system, or that groundwater or surface water input was higher than assumed in the model.

4.2. Sulfate concentrations

Observed SO_4 concentrations obtained during the summer of 1983 (Table 6) reached a maximum of 1640 mg/L from a sample taken in the epilimnion at 5 ft and a minimum of 1490 mg/L at 80 ft in a sample collected in the hypolimnion. Sulfate values estimated in the model epilimnion reach 1644 mg/L in spring of year 9 (Fig. 6) and match the observed values (0.2% difference) because the reactivity factor (Eq. 3) was adjusted to 10^3 to achieve the close match. Modeled

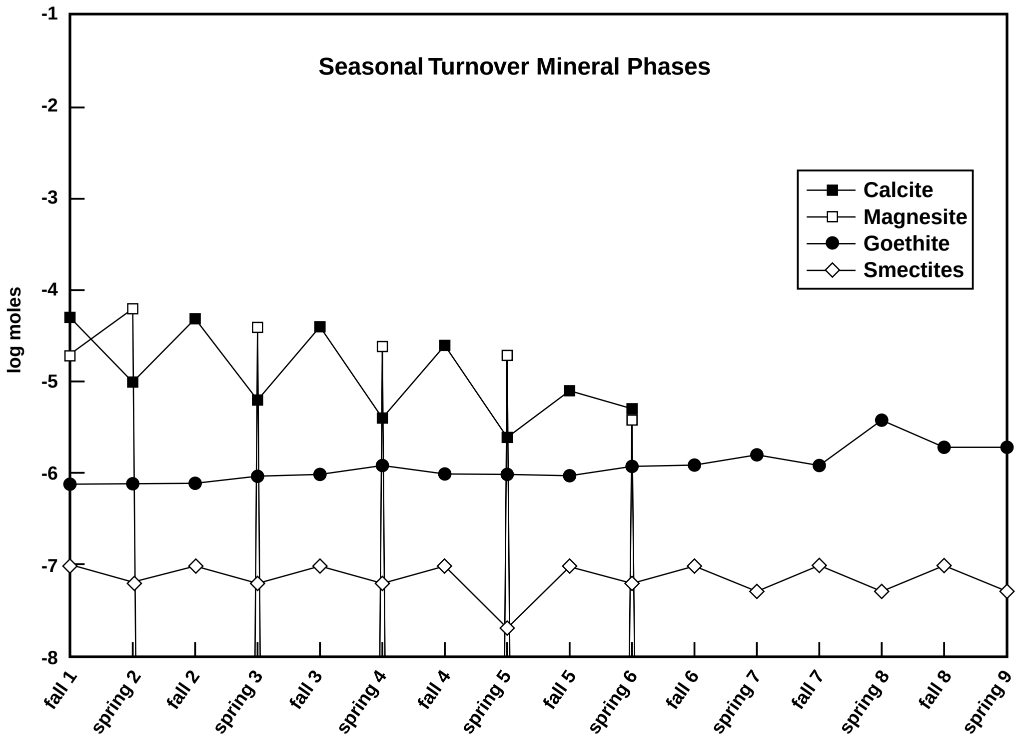

Fig. 11. Predicted mineral phase precipitation that results from mixing of epilimnion and hypolimnion waters in a 9:1 ratio twice yearly.

values from the hypolimnion and seasonal turnover are 1503 mg/L and 1518 mg/L, respectively (Figs. 7 and 8), and also match observed values closely (1490 to 1550 mg/L). Sulfate concentrations in the epilimnion simulations are not affected by mineral precipitation because sulfate minerals, including gypsum, are undersaturated. Gypsum is also undersaturated in model calculations of composited water analyses from the historical North pit lake. In comparison, SO_4 concentrations are controlled in the hypolimnion by reduction of SO_4 to sulfide and precipitation of pyrite and realgar.

4.3. TDS values

Differences between historical and modeled TDS values are small with an estimated epilimnion TDS value (2366 mg/L) at spring year 9 differing from historical measurements at an equivalent point in time (summer 1983; Table 6) by 3.6 to 5.4% (Fig. 6). Modeled TDS values (2054 mg/L) in the hypolimnion match less closely with observed measurements and differ by 14.2 to 18.0% (2394 and 2504 mg/L; Table 6);(Fig. 7).

Differences in observed and estimated TDS values are primarily the result of differences among Ca, Mg and HCO_3 concentrations in composited historical analyses and modeled results. Historical Ca, Mg and HCO_3 concentrations are only available in two composited analyses dated 1/26/82 and 4/28/82 that show high concentrations of Ca (554 and 530 mg/L, respectively), lower concentrations of Mg (63 and 72.7 mg/L), and HCO_3 concentrations of 127 and 119 mg/L (Table 5). By comparison, modeled Ca is lower than observed values in the epilimnion (124 mg/L) and in the hypolimnion (105 mg/L). Modeled Mg is higher in the epilimnion (378 mg/L) and in the hypolimnion (323 mg/L) than observed values, and estimated HCO_3 concentrations are lower than observed values at 75.7 mg/L and 74 mg/L in the epilimnion and hypolimnion, respectively (Table 5). Composited waters are slightly supersaturated with calcite, which is one reason that observed Ca values are higher than modeled Ca values.

Modeled Mg concentrations are higher than observed values because dolomite precipitation is suppressed in model calculations and the higher solubility of the solid solution endmember magnesite causes Mg to accumulate in pit waters. Slight supersaturation of calcite in composited waters is evidence that the kinetics of calcite precipitation in pit waters is a relatively slow process. The difference in the ratios of Mg/Ca in observed (0.14) and estimated (3.1) waters may be the result of poor thermodynamic data for Mg-bearing clay minerals that control Mg concentrations in the natural system.

Dissolved SiO_2 concentrations are 25 to 65 times higher in composited and MMW5 well waters than model water calculations (Table 5). This difference can be explained by the kinetically slow precipitation and resulting supersaturation of quartz or amorphous silica in natural waters. The calculated concentration of dissolved SiO_2 in equilibrium with quartz in pit lake and groundwater samples is approximately 1.9 mg/L.

Levels of Na and K are also lower in modeled waters compared to natural waters (Table 5). Sodium concentrations are essentially conservative in the calculations because Na-bearing mineral phases were not included in the reactant mineral assemblage. Geochemical analyses of both the Comus and Preble Formations, the predominant wall rock formations, showed only the presence of K-feldspar and Ca-plagioclase in small amounts. The granodiorite dike and the tuffaceous rocks (Fig. 2) contained some sodic feldspars, but the mol% of Na-feldspars in the overall pit wall mineralogy comprised $< 1\%$ and was, therefore, neglected in the reactant mineral assemblage. Considering the low Na concentration in modeled waters, a few mol% of a Na-bearing mineral phase, such as albite, should be included in future reactant mineral assemblages. Low K concentrations in modeled waters may also indicate that the mol% of K-bearing minerals in the conceptual model (muscovite, microcline, and annite) were lower than in the actual pit wall rock. Potassium concentrations in composited waters are in equilibrium with illite and stilbite, whereas in modeled waters K-bearing minerals are undersaturated.

Modeled Al concentrations are uniformly around 10^{-8} m and are held at such low values by precipitation of gibbsite and smectite mineral phases (Figs. 9–11). Actual Al concentrations from the North pit lake range from not detected to 0.2 mg/L (Table 5). The high measurement may be due to analysis of a poorly filtered sample.

4.4. Arsenic concentrations

Because the purpose of the work is to develop a method to estimate the As concentrations in pit lake waters over time, the comparison between estimated and observed As concentrations and interpretations of differences are of greatest concern. Interestingly, 15 a after the historical Getchell North pit lake began filling, observed As concentrations never exceeded about 0.6 mg/L (Table 6). In the model calculations, estimated As concentrations are nearly constant at 0.57 mg/L in the hypolimnion (Fig. 7), but epilimnion simulations resulted in estimated As concentrations as high as 96 mg/L (Fig. 6). Seasonal turnover simulations resulted in an intermediate estimate of about 10 mg/L (Fig. 8).

Estimated As concentrations are controlled in hypolimnion simulations at a nearly constant value of 0.57 mg/L by equilibrium with realgar (AsS) (Fig. 10). By comparison, in the epilimnion and seasonal turnover simulations, As is not controlled by equilibria with As-bearing minerals. In reality, As may be controlled in part in the epilimnion by equilibria with arsenate salts, but thermodynamic data for many of these minerals are not known, and therefore, they are not present in the reaction path model database. Scorodite may control As concentrations in nature in the epilimnion. However, scorodite is undersaturated in epilimnion simulations, primarily because of low Fe activity. Undersaturation for scorodite may also be due to an incomplete dataset for the Fe–As system in the model database (Doyle et al., 1994).

An alternative explanation to low observed As concentrations in the epilimnion is adsorption to probable hydrous oxide and clay mineral phases. While adsorption to hydrous Fe(III) oxides (HFO) may be an important mechanism elsewhere, its importance at Getchell needs further investigation primarily because of low Fe content in the Getchell system. Evidence for low Fe content in the system includes (1) paucity of Fe-bearing phases in host rocks; geochemical analyses show Fe_2O_3 contents of host rocks to be 4 wt% or less; and (2) low pyrite content in sulfide minerals; pyrite comprises about 20% of the sulfide minerals with As-bearing sulfide phases comprising the remaining 80% so that As content exceeds the Fe content by a factor of about 4:1 (Hotz and Willden, 1964).

Despite low Fe concentrations in the Getchell system, adsorption to other mineral surfaces, such as gibbsite and clay mineral phases, may be effective mechanisms in controlling As concentrations (e.g. Anderson et al., 1976; Frost and Griffin, 1977). Model calculations predict precipitation of both gibbsite and smectite in epilimnion simulations, and total suspended solids measured from unfiltered composited samples (along with 'dissolved' Al analyses of 0.2 mg/L) suggest that colloids may be important in the Getchell North pit lake system.

5. Summary

The work to date predicting As concentrations in a mine pit lake environment can be summarized as follows:

- Model results after 8.5 a compare favorably with pH, TDS, and SO_4 values measured in two historical composited waters and one depth profile.

- Modeled As concentrations compare favorably with observed As concentrations in the hypolimnion where model results suggest that realgar saturation controls As levels. In the epilimnion, model results do not match observed As concentrations which suggests that mechanisms, such as precipitation of arsenate salts (other than those included in the model database) or adsorption to hydrous oxide mineral surfaces, may control As levels in an actual pit lake system. Adsorption to HFO surfaces is unlikely because of the low Fe content in the Getchell system, but $Al(HO)_3$ (gibbsite) and clay mineral surfaces may be important in controlling natural As concentrations.
- The empirical reactivity factor is critical in model calibration and represents the increases in the extent of wall rock reaction caused by fracturing, rock roughness, mineral surface reactivity, and microbial mediation of mineral oxidation. More field studies are needed to quantify this factor for individual sites.

Continuing work will consider the effects of variable groundwater flux, evaporation, and adsorption to hydrous oxide mineral surfaces in controlling As concentrations in a mine pit lake environment. Additionally, the factors causing differences in Mg/Ca ratios between observed and modeled waters will be investigated.

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References

Anderson, M.A., Ferguson, J.F., Gavis, J., 1976. Arsenate adsorption on amorphous aluminum hydroxide. J. Colloid Interface Sci. 54, 391–399.

Anderson, R.Y., Dean, W.E., Bradbury, J.P., Love, D., 1985. Meromictic lakes and varved lake sediments in North America. US Geol. Survey Bull. 1607.

Atkins, D., Kempton, J.H., Martin, T., 1997. Limnologic conditions in three existing Nevada pit lakes: observations and modeling using CE-QUAL-W2. In: Proc. 4th Int. Conf. Acid Rock Drainage, Vancouver, BC, May 31–June 6, 1997, pp. 699–713.

Bursey, G.G., Mahoney, J.J., Gale, J.E., Dignard, S.E., Napier, W., Reihm, D, Downing, B., 1997. Approach used to model pit filling and pit lake chemistry on mine closure — Voisey's Bay, Labrador. In: Proc. 4th Int. Conf. Acid Rock Drainage, Vancouver, BC, May 31–June 6, 1997, 255–275.

Busenburg, E., Plummer, L.N., 1987. A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. US Geol. Survey Bull. 1578, 139–168.

Carroll, S.A., Walther, J.V., 1988. A surface complex reaction model for the pH-dependence of corundum and kaolinite dissolution rates. Geochim.Cosmochim. Acta 52, 2609–2923.

Carroll, S.A., Walther, J.V., 1990. Kaolinite dissolution at 25, 60 and 80°C. Am. J. Sci. 290, 797–810.

Conoco, 1982. Getchell Mine Pit Water Volumes. Inter-office Communication from J.T. McDonough.

Daly, C., Neilson, R.P., Phillips, D.L., 1993. A statistical–topographic model for mapping climatological precipitation over mountainous terrain. J. Appl. Meteor. 33, 140–158.

Dove, P.M., Rimstidt, J.D., 1985. The solubility and stability of scorodite, $FeAsO_4{\cdot}2H_2O$. Am. Miner. 70, 838–844.

Doyle, G.A., Runnells, D.D., 1997. Physical limnology of existing mine pit lakes. In: Mining Eng., pp. 76–80.

Doyle, T.A., Davis, A., Runnells, D.D., 1994. Predicting the environmental stability of treated copper smelter flue dust. Appl. Geochem. 9, 337–350.

Fleer, V.N., 1982. The dissolution kinetics of anorthite ($CaAl_2Si_2O_8$) and synthetic strontium feldspar ($SrAl_2Si_2O_8$) in aqueous solutions at temperatures below 100°C: with application to the geological disposal of radioactive nuclear wastes. Ph.D. thesis, Pennsylvania State University, University Park.

Foo, S.T., Hays Jr, R.C., McCormack, J.K., 1996. Geology and mineralization of the Pipeline gold deposit, Lander County, NV. In: Coyner, A.R., Fahey, P.L. (Eds.), Geology and Ore Deposits of the American Cordillera, Symp. Proc. Geological Society of Nevada, pp. 111–121.

Frost, R.R., Griffin, R.A., 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Am. J. 41, 53–57.

Getchell Gold Corp., 1997. Geological maps of the Getchell mine area.

Havis, R.N., Worthington, S.J., 1997. A simple model of the management of mine pit-lake filling and dewatering. In: Tailings and Mine Waste '97. Balkema, Rotterdam, pp. 549–557.

Helgeson, H.C., 1970. A chemical and thermodynamic model of ore deposition in hydrothermal systems. Miner. Soc. Am. Spec. Paper 3, 155–186.

Hotz, P.E., Willden, R. (1964) Geology and mineral deposits of the Osgood Mountains quadrangle, Humboldt County, NV. US Geol. Prof. Paper 431.

Hutchinson, G.E., 1957. A Treatise on Limnology. John Wiley and Sons, New York.

Hydrologic Consultants, Inc. (HCI), 1996. Hydrogeologic framework and numerical groundwater flow modeling of region surrounding Twin Creeks Mine, Humboldt County, NV. Prepared for Santa Fe Pacific Gold Corporation, HCI-822.

Joralemon, P., 1951. The occurrence of gold at the Getchell mine, NV . Econ. Geol. 46, 267–310.

Kaiser, J., 1998. Toxicologists shed new light on old poisons. Science 279, 1850–1851.

Lebo, M.E., Reuter, J.E., Goldman, C.R, 1994. Pyramid Lake: Nevada water quality study 1989–1993, vol. IV. Modeling studies. UC Davis Report.

Leonardson, R.W., Rahn, J.E., 1996. Geology of the Betze-Post gold deposits, Eureka County, NV. In: Coyner, A.R., Fahey, P.L. (Eds.), Geology and Ore Deposits of the American Cordillera, Symp. Proc. Geological Society of NV, pp. 61–94.

Lin, F.C., Clemency, C.V., 1981. The kinetics of dissolution of muscovites at 25°C and 1 atm CO_2 partial pressure. Geochim. Cosmochim. Acta 52, 143–165.

Madden-McGuire, D.J., 1991. Stratigraphy of the limestone-bearing part of the Lower Cambrian to Lower Ordovician Preble Formation near its type locality, Humboldt County, North-central, NV. In: Geology and Ore Deposits of the Great Basin. Geological Society of NV, pp. 875–894.

Nagy, K.L., Blum, A., Lasaga, A.C., 1991. Dissolution and precipitation kinetics of kaolinite at 80°C and pH 3. The dependence on solution saturation state. Am. J. Sci. 291, 649–686.

Natural Resources Conservation Service, 1995. PRISM briefing book and questionnaire, a description of the PRISM technique for spatially distributing observed precipitation.

Naugle, G.D., Atkinson, L.C., 1992. Estimating the rate of postmining filling of pit lakes. Mining Eng. 45, 402–404.

Paces, T., 1973. Steady state kinetics and equilibrium between groundwater and granitic rock. Geochim. Cosmochim. Acta 37, 2641–2663.

Plummer, L.N., Wigley, T.M.L., Parkhurst, D.L., 1978. The kinetics of calcite dissolution in CO_2–water systems at 5 to 60°C and 0.0 to 1.0 atm CO_2. Am. J. Sci. 278, 179–216.

PTI Environmental Services, 1996. Draft: Predicted water quality in the Twin Creeks Mine pit lakes. Prepared for Santa Fe Pacific Gold Corporation, January 1996, PTI contract No. CA1Q-0101.

Pugh, C.E., Hossner, L.R., Dixon, J.B., 1984. Oxidation rate of iron sulfides as affected by surface area, morphology, oxygen concentration and autotrophic bacteria. Soil Science 137, 309–314.

Rimstidt, J.D., Barnes, H.L., 1980. The kinetics of silica–water reactions. Geochim. Cosmochim. Acta 44, 1683–1700.

Robins, R.G., 1987. Solubility and stability of scorodite, $FeAsO_4{\cdot}2H_2O$: discussion. Am. Miner. 72, 842–844.

Saskatchewan Environment and Public Safety, 1990. Environmental monitoring investigation of the flooded 'D' pit at Cluff Lake, Saskatchewan.

Schroeder, P.R., Lloyd, C.M., Zappi, P.A., Aziz, N.M., 1994. The hydrologic evaluation of landfill performance (HELP) model, User's Guide for Version 3. EPA/600/R-94/168a.

Schweda, P.S., 1989. Kinetics of alkali feldspar dissolution at low temperature. In: 6th Int. Conf. Water–Rock Interaction. Balkema, 609–612.

Shevenell, L., 1996. Statewide evapotranspiration maps for Nevada. Nevada Bureau of Mines and Geology, Report 48.

Shevenell, L., Connors, K.A., Henry, C.D., 1999. Controls on pit lake water quality at sixteen open pit mines in Nevada. Applied Geochem. 14, 669–687.

Svensson, U., Dreybrodt, W., 1992. Dissolution kinetics of natural calcite minerals in CO_2–water systems approaching calcite equilibrium. Chem. Geol. 100, 129–145.

Thomas, J.M., 1995. Water budget and salinity of Walker Lake, western Nevada. US Geol. Surv., Fact Sheet FS-115-95.

Tingley, J.V., 1992. Mining districts of Nevada, Nevada Bureau of Mines and Geology, Report 47.

Torgersen, T., Benoit, J., Mackie, D., 1990. Controls on groundwater Rn-222 concentrations in fractured rock. Geophys. Res. Lett. 17, 845–848.

Williamson, M.A., Rimstidt, J.D., 1994. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. Geochim. Cosmochim. Acta 58, 5443–5454.

Wolery, T.J., Daveler, S.A., 1992. EQ6, A computer program for reaction path modeling of aqueous geochemical systems: theoretical manual, user's guide, and related documentation (version 7.0). Lawrence Livermore National Laboratory, UCRL-MA-110662.