Long Term Geochemical Evolution of the Highland Pit Lake

Final Report

Prepared for:

ExxonMobil

3225 Gallows Road Room 8B0607 Fairfax, Virginia 22037

Prepared by:

Tetra Tech

3801 Automation Way, Suite 100 Fort Collins, Colorado 80525 (970) 223-9600 Fax (970) 223-7171 Tetra Tech Project No. 180549

May 17, 2007

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1.0 INTRODUCTION

This report summarizes the evaluation of the geochemical evolution of the Pit Lake (Pit Lake) at the Highland Mine Site (Site). The evaluation was performed by MFG, Inc. (MFG), formerly Shepherd Miller. Inc. (SMI). This report was initially prepared on behalf of ExxonMobil This report was initially prepared on behalf of ExxonMobil Corporation (ExxonMobil) by MFG. Blasland, Bouck, and Lee, Inc. (ARCADIS BBL), has incorporated third party comments from the final draft, prepared by MFG, into this version for final submittal.

1.1 Background

In the late 1960s, Humble Oil and Refinery discovered a uranium deposit in the southern Powder River Basin of Wyoming and initiated mining activities that subsequently became known as the Highland Uranium Operations (Figure 1-1). The uranium occurred as a roll-front deposit that trended roughly northwest in the area of the Highland Mine Site (Site) (Langden and Kidwell, 1973). Multiple mining techniques were employed to extract uranium ore, including surface mining from a series of four open pits, beginning in 1970 and continuing through 1984 (Water Waste and Land [WWL], 1989). Overburden and waste rock removed during stripping operations were initially stockpiled and then used to backfill previously opened pits. The final two pits (Pits 3 and 4) were not completely backfilled and, beginning in March 1984, groundwater from the surrounding aquifer was allowed to discharge into the two pits, forming the Highland Pit Lake (Pit Lake).

Figure **1-1** Location Map Showing the Highland Ore Body and Major Geographic Features in the Powder River Basin

In the early 1980s, Exxon Production and Research Company (EPRC) conducted a study to predict the hydrologic and geochemical evolution of the Pit Lake for 2,000 years into the future (EPRC, 1983). During this initial phase of predictive modeling, radium-226 (radium) and total dissolved solids (TDS) were identified as the main constituents of potential concern (COPCs). Concentrations of radium and TDS were then estimated using a computer model in order to establish long-term conditions of the chemistry of the Pit Lake (EPRC, 1983). This work was completed before the Pit Lake began filling with water and was, therefore, completely predictive in nature.

Results of water-quality measurements obtained twice per year, after the Pit Lake began filling in 1984, indicated that, in addition to TDS and radium, concentrations of natural uranium (uranium) and selenium, at times exceeded the groundwater quality standards of 5 milligrams per liter (mg/L) and 50 micrograms per liter (ug/L), respectively, listed by the Wyoming Department of Environmental Quality (WDEQ)/Water Quality Division (WQD). Subsequently, the long-term hydrological and geochemical evolution of the Pit Lake was reevaluated by Shepherd Miller, Inc. (SMI, 1998). This modeling effort used a commercially available computer program (STELLA[®]) to create a dynamic systems model (DSM) of the Pit Lake and benefited from the availability of 14 years of water-quality data, which were used for model calibration. Thus, the SMI investigation extended the EPRC modeling effort to include uranium and selenium, and refined and extended predictions of chemical conditions in the Pit Lake based on the existing water-quality record and additional field measurements. While new field data were used for model calibration over the short term, hydrogeological assumptions previously used in the EPRC modeling effort (EPRC, 1983) were also incorporated into the revised model (SMI, 1998).

In 2003, MFG, Inc. (MFG, formerly SMI), at the request of ExxonMobil Corporation (Exxon), reevaluated the long-term groundwater and Pit Lake hydrology (MFG, 2003b). Estimates of pre-mining, steady-state groundwater conditions used in the revised model differed significantly from those used in previous studies (EPRC, 1983; SMI, 1998; Carovillano, 1998). Previous hydrologic evaluations had predicted that the Pit Lake would eventually develop into a flowthrough system (ERPC, 1983; Carovillano 1998; SMI, 1998). However, substantial revisions to the predicted groundwater flows indicate that the elevation of the Pit Lake will remain well below the elevation of the regional discharge area in North Fork Box Creek and its tributaries. As a result, the Pit Lake will not discharge flows to the groundwater system. These latest predictions of the local hydrology warrant a re-examination of the Pit Lake's chemical evolution.

The objective of this study was to evaluate the geochemical evolution of the Pit Lake based on the latest hydrological modeling. The latest geochemical model was created using STELLA[®] version 7.02, PHREEQC version 2.12, refined aquifer flows from MFG (2003b), and the most recent water-quality data. In addition, the DSM-produced predictions of bulk solution compositions were input to the PHREEQC geochemical model (Parkhurst and Appelo, 1999) to include the effects of geochemical reactions. concentrations of radium, selenium, uranium, and the major ions that form the bulk of TDS have been addressed. Many other metals, metalloids, and radionuclides, as discussed in Section 3.3, were not modeled because the concentrations of these constituents have historically been very low or below applicable method detection limits.

1.2 Report Organization

The remaining sections of the report are organized as follows:

- **"** Section 2: Summarizes the Site geology, hydrology, and the conceptual geochemical model.
- **"** Section 3: Presents the model inputs and assumptions.
- **"** Section 4: Discusses the long-term predictions of various water quality parameters from the revised model.
- **"** Section 5: Summarizes the sensitivity analysis performed on the revised model.
- **"** Section 6: Presents a summary of the work performed and conclusions from the revised model.

2.0 **SITE DESCRIPTION**

2.1 Site Geology

The Pit Lake lies within the geographic boundaries of the Powder River Basin in northeastern Wyoming (Figure 1-1). Geologic formations in the Powder River Basin are composed of a stacked sequence of sedimentary rocks that generally consist of interbedded sandstones and shales (Langden and Kidwell, 1973; EPRC, 1983). Deposits of coal and uranium are abundant in the Powder River Basin, which has a long history of mining.

The major geologic feature that defines the Powder River Basin is an asymmetrical syncline that trends approximately due north. Geologic formations on the east limb of the syncline (including the Site) dip gently to the west, toward the axis of the syncline. Thus, the geologic formations penetrated by open pit mining at the Site dip approximately west. In contrast, the topographic slope dips to the east in response to regional geologic uplift and to the evolution of the Cheyenne River drainage basin. Thus, the stratigraphic dip and the topographic gradient dip in opposite directions, resulting in groundwater flow paths that cross stratigraphic boundaries.

A generalized stratigraphic section of the major geologic formations present within the Powder River Basin at the Site is shown on Figure 2-1. The rock formations mined at the Site are found primarily in the Paleocene Fort Union Formation, which underlies the Eocene Wasatch Formation (Figure 2-1). Rock units potentially influencing the geochemical evolution and rate of filling of the Pit Lake include (Figure 2-2, from top to bottom):

- **"** Tailings Dam Sandstone (TDSS)
- **"** Tailings Dam Shale (TDSH)
- Ore Body Sandstone (OBSS)

Extensive uranium mineralization is found in the OBSS in three distinct layers: the upper, middle, and lower ore body sandstones (Langden and Kidwell, 1973). For the purposes of this investigation, the OBSS was treated as a single hydrogeochemical unit.

Uranium mineralization in the OBSS is closely linked to the geologic history of the sandstone formations. Sediments in the Fort Union Formation were deposited as part of a large-scale fluvial system (Houston, 1969; Langden and Kidwell, 1973). Thus, there are distinct zones within the OBSS that preferentially transport groundwater, and the highest-grade uranium mineralization occurs in these high-permeability zones as roll-front deposits. Mining at the Site focused on extracting the highest-grade uranium ore from the roll-front deposits.

NELSAS	SERIES	FORMATION	LITHOLOGY	DESCRIPTION
- œ œ \sim 884 ۳	ممه \equiv فعو ده \bullet ىب س \equiv فقة دے 0 ففه پ \mathbf{r} \bullet	≖ دے $\overline{}$ \mathbf{r} S \mathbf{r} \equiv \equiv 0 - æ \Rightarrow ► \approx 0 ш.		Soil and Weathered Zone
				Discontinuous Sandstones and Shales
				Sandstone: arain size varies from medium-grained sand to gravel, most commonly medium to very coarse-grained sand; beds vary from loose friable sand to well-cemented (carbonate) sandstones. (Does not contain uranium mineralization.)
				Siltstone and Claystone (shale): color varies from olive orange to gray green but generally gray green; may contain thin interbedded sandstones and lignite beds.
				TAILINGS DAM SANDSTONE: same as above (Does not contain uranium mineralization in Highland area)
				TAILINGS DAM SHALE: generally gray green with thin beds of sandstone
				UPPER ORE BODY SANDSTONE: same as above. (Ore bearing unit in Highland area.)
				Siltstone and Claystone (shale): generally gray green.
				MIDDLE ORE BODY SANDSTONE: same as above. (Major ore bearing unit in Highland area.)
				Siltstone and Claystone (shale): generally gray green; may contain thinbedded sandstone units.
				LOWER ORE BODY SANDSTONE: same as above. (Major ore bearing unit in Highland area.)
				Siltstone and Claystone (shale): generally gray green.
				Sandstone: same as above. (Does not contain economic amounts of uranium in Highland area.)
				Siltstone and Claystone (shale): same as above.

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(From EPRCO, 1983)

Figure 2-1 Generalized Stratigraphic Column, Highland Area

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Uranium roll-front deposits are formed by dynamic biogeochemical oxidation-reduction (redox) Uranium (and, typically, other metals), leached from minerals in hydrologically upgradient areas by oxygenated, high-carbonate groundwater, is subsequently transported downgradient and contacts zones that are geochemically reducing. Under reducing conditions, biological and/or chemical reduction cause the precipitation of various uranium minerals and a wide variety of other metal compounds along the interface between the oxidized and reduced zones (Figure 2-3) (Harshman, 1974; DeVoto, 1978; Langmuir, 1997; Lovley et al., 1991). Selenium minerals are commonly found in roll-front deposits on the upgradient side. Radium may also occur within or in association with the uranium minerals. The roll-front is a dynamic feature that migrates over geologic time, potentially resulting in high concentrations of metal compounds at the redox boundary. These processes formed the uranium roll-front in the OBSS that was mined at the Site.

(FROM **LANGDEN AND** KIDWELL **1973)**

Figure **2-3** Generalized Cross Section of the Highland Ore Body

Open-pit mining at the Site followed the general strike of the roll-front deposit. Therefore, portions of the Pit Lake walls have exposed the roll-front to oxidizing conditions (Figure 2-4). Under oxidizing conditions, uranium, radium, and selenium may be leached from the roll-front and transported in the groundwater system to the Pit Lake. Some areas of the Pit Lake walls were covered with backfill (EPRC, 1983). However, the backfill is unlikely to prevent leaching of mineralized zones in the Pit Lake walls. Therefore, the modeling effort for the Pit Lake included inputs of uranium, radium, and selenium from the OBSS and other source areas to the Pit Lake to account for leaching processes. The other primary source area for uranium, radium, and selenium is tailings seepage through backfill.

2.2 Site Hydrology

Groundwater near the Site generally flows from west to east in the OBSS and TDSS (EPRC, 1983). The OBSS and the TDSS contain groundwater separated by the TDSH, which acts as an aquitard. De-watering of the pit during active mining created a cone of depression in the regional groundwater potentiometric surface, thus causing groundwater to flow toward the Pit Lake. Because of de-watering, the flow of groundwater into the Pit Lake during refilling has occurred first from the lowest exposure of the OBSS and later from both the OBSS and the TDSS.

Other sources of water flowing to the Pit Lake include: (1) surface runoff; (2) direct precipitation; (3) discharge from a perched aquifer, and (4) seepage from the Tailings Basin. Outflow of water from the Pit Lake is limited to evaporation under the current hydrological model. A more complete discussion of lake and groundwater hydrology can be found in previous reports (MFG, 2003b; ERPC, 1983), and details of inflow and outflow calculations used in the **DSM** are provided in Section 3.0

2.3 Conceptual Geochemical Model

The concentrations of chemical constituents in the Pit Lake represent the combined effects of geochemical and hydrologic processes acting in the system. Figure 2-5 shows the basic conceptual model that guided the development of the computer model used to predict the geochemical evolution of the Pit Lake. Chemical mass is added to the Pit Lake as constituentbearing waters flow into it. Chemical mass loading for any given constituent is calculated

conservatively as the product of the flux of water into the Pit Lake times the concentration of the constituent in the water. In a complex limnological system, removal of chemical mass can occur via chemical and/or physical processes, such as adsorption and sedimentation, precipitation, or volatilization, which remove constituents from the water column. Adsorption and sedimentation processes could provide a mechanism for mass removal from the Pit Lake, but are not well characterized at this Site and, therefore, not included in the current model. A discussion of the potential significance and previous investigations into these processes is provided in Section 3.3.8.1. In contrast, as the concentration of constituents increases in the water column, due to the effect of evaporative concentration, the precipitation of various mineral phases will affect water quality in the Pit Lake. The PHREEQC geochemical model (Parkhurst and Appelo, 1999) was used to quantify the effects of mineral precipitation on predictions of future water composition in the Pit Lake.

Figure **2-5** Conceptual Model of Hydrology and Geochemistry Affecting Pit Lake Chemistry and Water Level at Highland

3.0 MODEL **INPUTS AND ASSUMPTIONS**

The Pit Lake is a relatively simple hydrologic system with a single water body and a limited number of hydrologic flows (Figure 3-1). In the **DSM** of Pit Lake, the mathematical expression for the change in Pit Lake volume with time is:

$$
\frac{dV}{dt} = \sum_{i=1}^{n} Q_i^{\text{Inflow}} - \sum_{j=1}^{m} Q_j^{\text{Outflow}}
$$
 [3-1]

where: V is the volume of water in the Pit Lake at time t

 Q is the discharge rate for an inflow (i) or outflow (i) (in units of volume per unit time) n is the number of sources of inflow

m is the number of sources of outflow.

The hydrologic Pit Lake is represented as a rectangle on Figure 3-1. Inflow and outflow to the Pit Lake are symbolized as flow pipes, and arrows on the pipes indicate the direction of positive flow.

Chemical mass is stored in a geochemical reservoir in the logical model of the Pit Lake. Each of the hydrologic flows transports constituents into or out of the Pit Lake in either constant or time-varying concentrations. The model calculates a chemical mass balance for each constituent using the following mathematical expression:

$$
\frac{d(C_k V)}{dt} = \sum_{i=1}^{n} C_{k,i} Q_i^{\text{Inflow}} - \sum_{j=1}^{m} C_{k,j} Q_j^{\text{Outflow}}
$$
 [3-2]

where: C_kV is the mass of constituent k dissolved in the Pit Lake water

 $C_{k,i(i)}$ are the concentrations of constituent k in the source of inflow i and source of outflow j (in units of mass per unit volume).

Separate chemical mass balance equations were written for uranium, radium, selenium, and the major ions for use in predicting future concentrations of these constituents and TDS. The massbased Pit Lake for each constituent is represented as a rectangle in the stack on Figure 3-1. Equation 3-2 demonstrates that the hydrologic and chemical models are linked by the following relationship: concentration = mass/volume. The mass of any constituent in the Pit Lake is the product of the hydrologic flow and the concentration in that flow. The details of the water and chemical mass balance sub-models are discussed in Sections 3.2 and 3.3.

3.1 Pit Lake Limnology

Previous studies of the Pit Lake have assumed that it stratifies seasonally and undergoes seasonal turnover, causing complete mixing of the water column. Seasonal turnover should cause the Pit Lake to be approximately chemically homogeneous (SMI, 1998). To determine the extent of chemical homogeneity, a field study was conducted on July 29, 2003 to obtain depth profiles of temperature, pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO). Measurements were made with a Hydrolab® multi-parameter probe. Water samples for analysis of uranium, selenium, radium, and sulfate were also collected at the surface and at a depth of 35, 65, 85, and 109 feet in the water column (Table 3.1).

Hydrology

- Hydrologic: Inflows
-
- * Surface Runoff
- * Groundwater discharge-from the Perched Aquifer
- Tailings Dam sandstone.and OreBody sandstone
- * Seepage from the tailings dam through the fill

Surface

Runoff

Drainage

Precipitatio

The hydrologic reservoir is represented as a rectangle labeled
"Reservoir Volume" The mass-*Reservoir Volume". The massbased reserVoir for each constituent of interest is represented as a rectangle in the stack labeled
"Geochemical Mass", Inflow and "Geochemical Mass". outflows to the reservoir are symbolized as pipes with arrows indicating the direction of positive flow. The circles and connectors convert inputs into outputs by

Geochemical Inflows Chemical Precipitation
Radioactive Decay (radium only)

Figure **3-1** Schematic Diagram of the Highland Pit Lake Dynamic Systems Model

Table **3.1** Results from July **2003** Sampling Event

Notes:

'C - degrees Celsius **D.O.** - dissolved oxygen $mV -$ millvolts pCi/L - picoCuries per liter Cond. - conductivity pS/cm - microsiemens per centimeter ORP - oxygen reduction potential s.u. - standard unit

Diss. - dissolved mg/L - milligrams per liter **%** - percent

The temperature profile observed in July 2003 is typical of a thermally stratified lake in the summer (Wetzel, 1975). The temperature in the surface water ranged from 22 to 23 degrees Celsius (°C) in the top 20 feet of the water column (Figure 3-2). The Pit Lake displayed a broad thermocline beginning at a depth of approximately 21 feet and extending down to a depth of approximately 60 feet. At the 65 feet depth, the temperature became approximately constant, with the temperatures in the hypoliminion ranging from 6.5 to 7.25 **'C.** In contrast, the chemical data from the study showed that the water column as well mixed with respect to pH and concentrations of dissolved oxygen, sulfate, uranium, and radium (Table 3.1, Figures 3-2 and 3- 3).

Figure **3-2** Temperature, **pH,** and Dissolved Oxygen Profiles from Highland Pit Lake, Measured July **2003**

Figure **3-3** Sulfate, Uranium and Radium Profiles from Highland Pit Lake, Measured July **2003**

The DSM uses a monthly time-step for its calculations. The monthly results were aggregated into yearly predictions of Pit Lake elevation and water quality. The assumption of chemical and physical homogeneity for time scales of a year or more simplifies the model by averaging seasonal variations in flows and is consistent with a lack of seasonal chemical stratification in the Pit Lake. The **DSM** was run for the time period from 1984, when the Pit Lake first started to fill, to 2984 for a total simulation period of 1,000 years.

3.2 Water Balance

3.2.1 Inflows

Six hydrologic flow components supply water to the Pit Lake:

- **"** groundwater discharge from the OBSS
- **"** direct precipitation
- **"** discharge from a perched aquifer in the Fowler Unit (located above the TDSS and below the alluvium found just beneath the surface)
- **"** groundwater discharge from the TDSS
- **"** surface runoff
- seepage from the Tailings Basin

The relative magnitude of each flow component in the water balance is described below and is depicted graphically on Figure 3-4. The flows used in the **DSM** were those determined in the hydrogeological study (MFG, 2003b). Because the flow component has a significant effect on mass loading, the sensitivity of the Pit Lake geochemical model to the rates of certain flow components was evaluated and is discussed in Section 5.0

3.2.1.1 Precipitation

The yearly average rate of precipitation in the Pit Lake area is 12.3 inches per year (in/year), with regional variations ranging from 11 to 14 in/year (EPRC, 1983). These averages were updated in 2003 (MFG, 2003b) to include recent precipitation data from the local weather stations, resulting in an average yearly precipitation rate of 12.06 in/year (Table 3.2). A rate of 12.06 in/year was used to represent the rate of precipitation inflow for the DSM. The volume of water added to the Pit Lake from direct precipitation is equal to the precipitation rate multiplied by the surface area of the Pit Lake. Therefore, the direct precipitation component will increase as the Pit Lake fills and the surface area increases. At steady state, precipitation in the second to largest source of water to the Pit Lake providing 27% (~12 acre-ft/month) of the total inflow.

Table **3.2** Highland Area Precipitation Areas

Notes:

From (MFG, 2003a) in/yr - inches per year

Figure 3-4 Rates of Hydrologic Inflows and Outflows

3.2.1.2 Surface Runoff

The amount of surface runoff entering the Pit Lake from precipitation events was estimated by several methods (EPRC, 1983) and is summarized in Table 3.3. The EPRO study included an evaluation of the results from each method and concludes that the average annual runoff to the Pit Lake is equal to 6% of the annual precipitation rate. In the DSM, the total volume of surface runoff is calculated as the product of the 6% runoff rate times the surface area contributing runoff to the Pit Lake. Surface runoff provides 10% of the Pit Lake's total inflow (4.3 acreft/month).

Table **3.3** Annual Surface Runoff Calculated as a Percentage of Average Annual Rainfall

Notes:

From EPRC, 1983 [as summarized in MFG, 2003b]

in - inches

USGS - United States Geologic Survey

% - percent

SCS - Soil Conservation Service

3.2.1.3 Perched Aquifer Flow

A small diversion dam located to the east of the Pit Lake directs the release of surface water away from the mine area. Water retained behind the dam is thought to recharge the normally dry Fowler Unit, creating a shallow, perched aquifer in the local area of the mine (Range, 1998). Groundwater flow in the perched aquifer follows the original alluvial channel that ultimately intercepts the southwest wall of the Pit Lake. The estimated flow rate, from field observations, was set to a constant value of 74 gallons per minute (gpm) (9.95 acre-ft/month) based on information from Range (1998). The inflow rate is equal to 23% of the total inflow to the Pit Lake.

3.2.1.4 Flow through the Ore Body Sandstone

The groundwater system in the area of the Site was dewatered from 1972 through 1983 to allow mining in the open pits that now comprise the Pit Lake. Dewatering rates typically exceeded 1,000 gpm and created a major disruption to the natural groundwater flow regime. In March 1984, dewatering of the remaining two open pits (Pits 3 and 4) ceased, allowing the Pit Lake to fill as the cone of depression in the potentiometric surface of the groundwater began to recover. As a result, the predicted discharge from the OBSS initially peaked at 66 acre-ft/month during the early filling of Pit Lake then decreased to a steady-state flow of 13 acre-ft/month over time (MFG, 2003b). Groundwater inflow from the OBSS is the largest source of water to the Pit Lake. These most recent estimates of groundwater discharge from the OBSS represent significant revisions from previous estimates, in part due to refined estimates of the initial static head parameter (MFG, 2003b). For comparison, the previous estimates suggested a decrease from a high inflow rate of 38 acre-ft/month to a steady-state inflow rate of 10 acre-ft month, (SMI, 1998). The revised flows from MFG (2003b) were used to represent the rate of water inflow to the Pit Lake from the OBSS (Figure 3-5).

3.2.1.5 Flow through the Tailings Dam Sandstone

Flows from the TDSS are estimated to have decreased from a high flow of 7 acre-ft/month during the initial period of Pit Lake filling to a steady-state discharge of 4.5 acre-ft/month (MFG, 2003b) (Figure 3-4). This component of flow makes up 10% of the Pit Lake's total inflow.

3.2.1.6 Tailings Basin Seepage

The hydrogeology at the Site has also been impacted by the placement of mill tailings from 1972 to 1984 in the unnamed tributary of North Fork Box Creek known as the Tailings Dam (Figure 3-6). The deposition of the tailings slurry over time created a groundwater mound beneath the impoundment that is evident in hydrographs from wells completed in both the TDSS and the 50-Sand (MFG, 2003b).

Several researchers have estimated the volume of groundwater impacted by the tailings impoundment (Table 3.4). These estimates do not represent the gallons of pure tailings solution in the strata underlying the tailings, but do include impacted water that is a mixture of tailings solution diluted with ambient groundwater. These studies provide estimates of several different volumes, including the total liquid volume and the total drainable volume of the entire plume, as defined by the area of elevated chloride concentrations in the groundwater. The chloride plume extends from all sides of the Tailings Dam. The studies also estimate the volume of total water and drainable water in the area west of the Tailings Basin between the Tailings Basin and the backfill area referred to as the "finger area." The volume of water contained in the finger area lies in the flow path between the Tailings Dam and Pit Lake and is the most probable portion of the plume that impacts water quality in the Pit Lake.

Figure **3-6** Highland Mine Site and Monitoring Well Locations

Table 3.4 Estimates of the Volume of Groundwater Impacted **by** Tailings at the Highland Mine Site

Notes:

CI - Chloride gal - gallons gal/min - gallons per minute WWL - Water, Waste, and Land

Early estimates of this groundwater mound suggested that the draindown from the tailings reached a maximum of approximately 180 gpm (34,500 cubic feet per day [ft³/day]) in 1984 as the Pit Lake initially began to fill, decreasing to 3.5 gpm (670 ft $3/$ day) by 1992 (WWL, 1984). Recent estimates suggest that the seepage mound under the tailings will naturally disappear in 20 to 60 years, and that a portion of the seepage mound water will flow through the TDSS and OBSS aquifers to backfilled areas of the Pit Lake, eventually reaching the Pit Lake itself (WWL, 1989).

The inflow of Tailings Basin Seepage (TBS) is represented in the DSM in a conservative manner, where it is assumed that seepage from the Tailings Basin flows at a rate of 30 gpm into the Pit Lake (4.03 acre-ft/month) for 20 years (WWL, 1989).

3.2.2 Outflows

Under the revised hydrological model, the operative pathway for water removal from the Pit Lake is through evaporation. The relative magnitude of this flow component of the water balance is described below and is depicted graphically on Figure 3-4.

3.2.2.1 Groundwater Outflow

Groundwater outflow from the Pit Lake would theoretically flow through the OBSS and TDSS if the water level in the Pit Lake reached an elevation greater than the elevation of the discharge
areas of North Fork Box Creek. Previous hydrologic modeling studies indicated that Previous hydrologic modeling studies indicated that groundwater outflow would eventually occur after a period of infilling. However, the most recent investigation of the local groundwater and surface water determined that it was unlikely that the Pit Lake would discharge groundwater and become a flow-through system based on a numerical analysis of the transient hydrologic conditions expected during the period of Pit Lake infilling (MFG, 2003b). The MGF (2003b) study determined that the Pit Lake will continue to fill until the water level reaches a steady-state elevation of approximately 5,060 feet in the year 2054, when the rate of inflows becomes equal to the rate of water loss by evaporation. The elevation of 5,060 feet is well below the elevation of the regional discharge area in North Fork Box Creek. Therefore, **MFG** (2003b) concluded that water would not be expected to flow out of the Pit Lake to the surrounding groundwater system. Instead, the Pit Lake will be hydrologic sink, with water loss occurring only by evaporation.

3.2.2.2 Evaporation

As noted by previous modeling efforts (EPRC, 1983; SMI, 1998), the Pit Lake is located in a semi-arid climate with a high rate of evaporation. The current hydrologic model indicates that evaporation is the only mechanism for water loss from the Pit Lake. Evaporation rates for the hydrologic model of the Pit Lake were well constrained by a suite of evaporation data collected in the region. The most recent pan evaporation data for the Site was obtained from the Department of Agricultural Engineering, University of Wyoming, Laramie's Design Information for Evaporation Ponds in Wyoming, published by the Wyoming Water Research Center (University of Wyoming, 1991). Using these data and the Kohler-Nordenson-Fox equation with a coefficient of 0.7, MFG (2003b) calculated an annual average evaporation rate of 45.2 in/year and a range of 40.2 to 54.5 in/year (Table 3.5). EPRC (1983) estimated that the evaporation rate ranges from 30 to 60 in/year, with an average of 45 in/year. This range and average is similar to that provided by **MFG** (2003b). Hence, an average rate of 45 in/year was used to represent evaporation in the DSM. Evaporation, like direct precipitation, is a function of the water surface area and will increase as the Pit Lake fills. For any one time-step, the DSM represents the total volume of water loss to evaporation from the product of the evaporation rates multiplied by the surface area of the Pit Lake.

Table **3.5** Annual Evaporation from Highland Mine Site Area **(SMI** Tech Memo, **1/8/2003)**

3.2.3 *Verification of Hydrologic Budget*

Chloride is a common constituent in most environments and is frequently used to calibrate or verify hydrologic flows because it is transported conservatively in most groundwater systems. At the Site, chloride is a particularly useful tracer because the concentration of chloride in the tailings solution is significantly elevated as compared to the concentration in regional groundwater. For example, the average chloride concentration in tailings solution is 217.5 mg/L (Table 3.6) compared to a range of 0.11 to 27.6 mg/L in other hydrologic sources in the area (Tables 3.7 and 3.8).

Notes: mg/L - milligrams per liter, pCi/L - picocuries per Liter

Notes: ^a**_ OBSS** fitted concentration is provided when applicable. First value is concentration used for early OBSS discharge. Second value is OBSS background concentration. Sodium and chloride concentrations were constant _ values.
^b - Uranium and Radium Activities in pico Curies per Liter (pCi/L); all others in micrograms per Liter (mg/L).
^c - Modeled TDS was calculated from the concentrations of individual constituents; TDS provided

 \degree - Modeled TDS was calculated from the concentrations of individual constituents; TDS provided only for reference in this table. TDS was not reported for precipitation.

Ksp - specific conductivity

OBSS - Ore Body Sandstone

TDSS - Tailings Dam Sandstone

Notes:
*Aerially weighted average of runoff from disturbed and undisturbed areas from ERPC (1983).

Ratio of U:Ra and Se:Ra in wells TDM 37, 38 and 39 used for estimation of uranium and selenium activity-concentration in runoff. Ratio of species: **TDS in wells TDM-9 and 41 used for estimation of species concentrations in runoff

Ca -Calcium

Cl - Chloride EPRC - Exxon Production and Research Company $HCO₃$ - Bicarbonate Mg - Magnesium Na - Sodium Ra - Radium Se - Selenium SO4 - Sulfate **TDS** - total dissolved solids U - Uranium

If the hydrologic flows provided by **MFG** (2003b), Range (1998), and WWL (1989) are valid, then the results from a chloride mass balance (calculated using representative well concentrations and the tailings solution composition multiplied by the respective flow) should reproduce the mass of chloride observed in the Pit Lake to date, as depicted on Figure 3-7. The chloride mass balance is calculated with Equation 3-3:

 $\text{Mass Cl}_{PL} = C_{PL}V_{PL} = Q_{ppt}C_{ppt} + Q_{PA}C_{PA} + Q_{T DSS}C_{T DSS} + Q_{O BSS}C_{O BSS} + Q_{SR}C_{SR} + Q_{TS}C_{TS} \quad [3-3]$

where: Subscripts: C_{XX} = CI concentration in the Pit Lake or inflows V_{PL} = Volume of the Pit Lake Q_{xx} = Inflow rates from individual sources PL = Highland Pit Lake ppt = precipitation

PA = perched aquifer TDSS = Tailings Dam Sandstone OBSS = Ore Body Sandstone SR = surface runoff

The average concentrations of chloride in the OBSS and TDSS aquifers for Equation 3-3 are listed in Table 3.7 and were determined BY averaging the available water quality data collected between 1986 and 2003 (Appendix C, Section 3.3.5). The methods for defining the concentrations of chloride in precipitation, surface runoff, and the perched aquifer listed in Tables 3.7 and 3.9 are described in Section 3.3. The chloride concentration in tailings seepage of 217.5 mg/L (Table 3.6) is from a sample collected at the mouth of the discharge tube leading to the Tailings Basin (EPRC, 1982).

Using the chloride concentrations from Tables 3.6 to 3.8 and the hydrologic flow rates described above, the mass balance calculations (with a flow rate of 30 gpm) from Tailings Basin seepage produced chloride concentrations that exceeded those described by a linear regression of measured chloride concentrations in the Pit Lake by 2 to 4 mg/L (Figure 3-8). The same calculation using a flow rate of 26 gpm for Tailings Basin seepage more closely matched the measured chloride concentrations coming within 1 to 1.5 mg/L of the concentrations (Figure 3- 8). These results indicate that the inflow rate from Tailings Basin seepage to the Pit Lake is probably within the range of 26 gpm (determined from the chloride mass balance) to 30 gpm (determined from the hydrologic analyses).

Table **3.9** Average Chemical Compositions of Groundwater from Monitoring Wells TDM **37, 9,** and 41

Notes:

mg/L - milligrams per liter

pCi/L - picoCuries per liter

TDS - total dissolved solids

Figure **3-8** Verification of Hydrologic Budget using Chloride

Conversely, because the major sources of chloride other than the tailings basis seepage are well constrained by hydrologic modeling (MFG, 2003b) and abundant monitoring well data, the quantity of chloride and flow rate of seepage from the tailings impoundment can be backcalculated for the first 20 years of the Pit Lake's history. To conduct this calculation, the sum of the masses of chloride from the OBSS, TDSS, perched aquifer, runoff, and precipitation was subtracted from the mass of chloride needed to reproduce the concentration of chloride in the Pit Lake. Chloride in the Tailings Basin seepage was set at the concentration of 217.5 mg/L, as reported by EPRC (1982) (Table 3.6), and flow rate from Tailings Basin seepage was set at 26 gpm. With these inputs, the mass-balance calculation indicates that 53% of the chloride in the Pit Lake is derived from Tailings Basin seepage.

3.3 Chemical Balance

Rates of chemical mass loading to the Pit Lake are calculated by Equation 3-2. The rates of hydrologic inflow to the Pit Lake are described above. This section describes the methods used to define the chemical compositions of the hydrologic inflows (Tables 3.7 through 3.9). The chemical compositions include concentrations of major ions (Ca, Mg, Na, K, Cl, SO₄, and HCO₃) and COPCs (U, Ra, and Se). Other dissolved solutes (Al, As, Ba, B, Cd, Cr, Co, Cu, F, Fe, Pb, Mn, Hg, Mo, Ni, Ag, Th, V, and Zn) that have been measured in the Pit Lake over time were not included in the model because the concentrations of these constituents have historically been very low and/or below the appropriate method detection limit. Measured concentrations of these constituents in the Pit Lake and monitoring wells are provided in Appendix C.

The modeling result also includes calculations of TDS concentrations for the Pit Lake. The **TDS** concentration is calculated from the following equation (Hem, 1985),

$$
[TDS] = [Ca2+] + [Mg2+] + [Na+] + [K+] + (0.4917)*[HCO3] + [Cl]+ [SO42]
$$
 [3-4]

3.3.1 Perched Aquifer

The chemical composition of groundwater in the perched aquifer was available from a single sample reported by SMI (1998) (Table 3.7). This reported composition has a much higher bicarbonate concentration than that found in other groundwater sources or the Pit Lake. The perched aquifer intersects the wall of the Pit Lake at elevations above the water level. Thus, the water inflow from the perched aquifer is expected to run down a seep face into the Pit Lake, allowing dissolved $CO₂(g)$ to be lost as it equilibrates with the lower partial pressure of $CO₂(g)$ in the atmosphere. The perched aquifer composition was also found to be oversaturated with calcite solubility. Thus, prior to use in the DSM, the perched aquifer water composition was equilibrated with calcite solubility at the atmospheric partial pressure of $CO₂(q)$ of 10-3.5 atmospheres (atm). This equilibration resulted in a removal of 69 and 85% of calcium and bicarbonate from solution, respectively, because of the combined effects of calcite precipitation and $CO₂(g)$ degassing. The equilibrated solution composition was used as input to the DSM to represent the perched aquifer.

3.3.2 Precipitation

SMI (1998) compiled water-quality data for precipitation from the National Atmospheric Deposition Program (NADP) records for the Snowy Range Site located in south-central Wyoming (Table 3.7; Appendix D of SMI, 1998). Uranium, radium, and selenium are not reported and are assumed to be below detection limits. These data were used to represent the chemical composition of precipitation for the DSM.

3.3.3 Surface Runoff

Reclamation around the Pit Lake has resulted in a potential total surface drainage area of 840 acres composed of both mine-disturbed areas and undisturbed areas. EPRC (1983) collected surface runoff samples from both areas, but reported analytical results only for radium and TDS. The radium activity and TDS concentrations from runoff samples collected in disturbed areas averaged 4.6 picocuries per Liter (pCi/L) and 836 mg/L respectively (EPRC, 1983). For the undisturbed areas adjacent to the Pit Lake, radium averaged 1.3 pCi/L and TDS averaged 169 mg/L (Table 3.8). After weighting these activity/concentrations by the areas of each drainage, the surface-water runoff was estimated to contain 2.2 pCi/L radium and 345 mg/L **TDS** during the initial filling of the Pit Lake (EPRC, 1983). It was assumed that, after 20 years, re-vegetation efforts would shift these runoff concentrations toward the composition of the undisturbed drainage (Table 3.8).

In the current modeling effort, the activity of radium reported by EPRC (1983) was initially used for surface runoff. The activity of uranium and the concentration of selenium in surface runoff were calculated from the previously reported activity of radium using the ratio of uranium to radium and the ratio of selenium to radium measured in wells completed in the backfill (Tables 3.8 and 3.9).

The constituents of TDS in the surface runoff were estimated in the same manner as uranium and selenium. The water quality of the surface runoff for the disturbed drainages was assumed to be the same as runoff from backfilled areas of the Site. The concentrations of the major ions that were estimated from the ratio of each ion to TDS measured in wells completed in the backfill (Tables 3.8 and 3.9). After 20 years had elapsed in the model runs, the concentrations of all constituents were reduced to the undisturbed concentrations to account for the effects of re-vegetation at the Site.

3.3.4 Tailings Seepage through Backfill

The current hydrological model indicates that seepage from the tailings impoundment have reached the Pit Lake through backfilled areas. To determine whether uranium, selenium, and radium would be transported conservatively (like chloride), data from monitoring wells were used to represent chemical composition of the tailings solution that would actually reach the Pit Lake. Averaged chemical data from well TDM 37 are used to represent tailings seepage, because this well is completed in the backfill and has high concentrations of radionuclides compared to other wells that lie within the flow path between the Tailings Basin and the Pit Lake (Table 3.9). Chloride was represented by its concentration in pure tailings solution, as shown in Table 3.6. Using the concentration of sodium observed in well TDM 37 with other background levels of sodium resulted in an excess of predicted sodium in the Pit Lake (Table 3.9). The concentration of sodium measured at TDM 37 was reduced by 50% in order to better reproduce the measured concentrations.

3.3.5 TDSS and OBSS Aquifers

The presence of the Tailings Dam to the east of the mine pits complicates the geochemistry of groundwater entering the Pit Lake from the TDSS and OBSS. Previous assessments of Tailings Basin seepage suggest that seepage would flow toward the Pit Lake potentially affecting water quality in both the TBSS and OBSS aquifers (WWL, 1989). Water-quality results for the local groundwater come from monitoring wells in the TDSS and OBSS located on the periphery of the Pit Lake. The concentrations of chloride and sulfate have been used to distinguish wells representing background water quality from wells that have been affected by Tailings Basin seepage. The previous water-quality analysis of tailings contribution (SMI, 1998) was updated in the current investigation to include the most recent well data. Concentration plots, as well as scatter diagrams of chloride and sulfate, indicate that wells RM1, RM2, RM3, RM4, EM 5, TDM 40, and TDM 48 have not been impacted by Tailings Basin seepage and are representative of baseline water quality in the TDSS (Figure 3-9). Other wells completed in the **TDSS** show evidence of mixing between background water and seepage from the Tailings Dam. Water-quality diagrams for the OBSS indicate that wells DW 18, DW 41, DW 46, DW 47, and DW 35 have not been impacted by Tailings Basin seepage and are representative of background water quality (Figure 3-10). Average concentrations for calcium, magnesium, chloride, sodium, sulfate, and bicarbonate were calculated for these two groups of background wells using the available water-quality data collected between 1986 and 2003 (Table 3.7).

Figure **3-9** Chloride vs. Sulfate Scatter Diagrams from **TDSS** Monitoring Wells

Figure 3-10 Chloride vs. Sulfate Scatter Diagrams from OBSS Monitoring Wells

Using the average background concentrations of calcium, magnesium, and sulfate in the OBSS inflow produced a close but slightly underestimated reproduction of measured concentrations. Increasing these constituents to the slightly higher concentrations observed in background well DW-47 for the early years of the simulation (less than 10 years) produced a closer fit to measurements (Table 3.7, Figures 3-11 and 3-12).

Figure **3-12** Measured vs. Modeled Calcium, Bicarbonate and Magnesium Concentrations in Highland Pit Lake

^Achloride-mixing model was developed to evaluate the extent that tailings seepage has infiltrated the TDSS and **OBSS** aquifers. As noted above, chloride is used for this purpose because it is transported conservatively, and levels of chloride in tailings pore waters are elevated compared to regional groundwater. Key wells representing the end member compositions for tailings water (TDM 9 and TDM 41) and background water for the TDSS (TDM 48, RM1 and RM2) and OBSS (DW-35) were chosen from time-series plots of major ions and the scatter diagrams of chloride vs. sulfate (Figures 3-9, 3-10, 3-13). Using the same set of diagrams, well TDM 11, completed in the OBSS, and well TDM 35, completed in the TDSS, were identified as wells receiving both background and tailings water. Both wells are located in the flow path between the Tailings Dam and the Pit Lake and are used to estimate the extent and duration of Tailings Basin water seepage in the aquifers from east of the Pit Lake (Figure 3- 13).

Figure **3-13** Chloride Concentrations Over Time in Highland Monitoring Wells

Using the available average annual chloride concentrations from the end member wells, the proportion of Tailings Basin water to background water between 1986 and 2003 was determined for wells TDM 11 and TDM 35 using the following equation:

$$
R_v = \frac{V_1}{V_2} = \frac{(C_2 - C_m)}{(C_m - C_1)}
$$
 [3-5]

where: V_1 , and C_1 are the volume of water and concentration of chloride in the Tailings Basin water

> V_2 and C_2 are the volume of background water and the concentration of chloride in the background water, respectively

 C_m is the concentration of chloride in the well with a mixed composition.

Chloride mixing results for the TDSS indicate that the proportion of tailings water reporting to well TDM 35 increased from 1990 through 1999 and, from 1999 to 2002, has represented between 65 and 68% of the flow at this location. Sixty-eight percent was used as the maximum impact to Well TDM 35 (Figure 3-14), with sensitivity studies conducted at 95% (Section 5). The duration of the mixing of plume and background water was modeled at 20, 40, and 60 years in accordance with estimates for seepage duration (WWL, 1989).

Figure 3-14 Tailings Seepage Mixing Curves for **TDSS** Well TDM **35**

Results from well TDM 11, completed in the OBSS, indicate that the contribution of tailing seepage water to the OBSS inflow from the west reached a maximum of 14% between 2000 and 2001. The contribution of tailings seepage to OBSS water quality appears to have reached a maximum, as shown by data collected in 2002 and 2003 (Figure 3-15). Future and past contamination are forecasted using the following best-fit polynomial curve of:

$$
y = -3x10^{-6}(X^2) + 0.0012(X) (R^2 = 0.6239)
$$
 [3-6]

where: X is time in months and y is the percentage of tailing water in well TDM 11.

The chloride-mixing model indicates the extent to which seepage has infiltrated two key wells in the aquifer but does not indicated the percentage of the larger drainage basin that is impacted with tailings water. In order to estimate the aerial extent of tailings seepage, the 1,000 mg/L TDS contour (SMI, 1998) from the Tailings Basin was intersected graphically in geographic information system (GIS) with the 5,085-foot groundwater contour surrounding the Pit Lake (Figure 3-16). An estimated 20% of the immediate basin is potentially impacted by tailings seepage. In the baseline model, chloride at a concentration of 218 mg/L (equivalent to that in pure tailings solution) is added at a rate of 30 gpm through the TBS flow. Hence, it was not necessary to add additional chloride to the background concentrations in the OBSS and TDSS for model calibration.

Figure 3-15 Tailings Seepage Mixing Curve for **OBSS** Well TDM **11**

Figure **3-16** Aerial Extent of Tailings Basin Seepage **(1000** mg/L **TDS** Contour Map, **1998)**

3.3.6 Uranium, Radium and Selenium Calibration

Uranium, radium, and selenium activities/concentrations in Site monitoring wells are quite low compared to the concentrations measured in the Pit Lake (Table 3.10). Initial DSM simulations that used measured concentrations from the monitoring wells in the modeled groundwater inflow underestimated the concentrations of these three constituents compared to measured levels in the Pit Lake. One geochemically plausible explanation for the discrepancy between observed and modeled results is that groundwater entering the Pit Lake from the OBSS contacts oxidized portions of the roll-front deposits adjacent to the pit walls, enriching the influent groundwater with radionuclides and selenium. While historical well data from the OBSS in the vicinity of the Site (EPRC, 1983) suggest that the activities of uranium and radium were quite high in the excavated area, none of the current monitoring wells penetrate the un-mined ore body that occurs in close proximity to the Pit Lake to provide an estimate of the potential enrichment.

Notes:

mg/L - milligrams per liter **OBSS** - Ore Body Sandstone pCi/L - picoCuries per liter TDSS - Tailings Dam Sandstone

A second plausible source for these constituents is the tailings impoundment to the east of the Pit Lake. Previous studies and reports (EPRC, 1983; Coal and Minerals Company [Exxon], 1994) indicate that a considerable mass of these constituents was deposited into the Tailings Basin during mine operations. Because there are two very plausible potential sources for uranium, selenium, and radium that could account for the higher levels observed during the early history of the pit, both options for calibrating the DSM were considered.

3.3.6.1 Calibration to OBSS Ore Zone Leaching

To better reproduce the observed conditions in the Pit Lake, radium and selenium were calibrated against the approximately 20 years of available Pit Lake water-quality data. Historical data, which showed the higher activities for radium in the OBSS (ERPC, 1983), were used to set model influent levels for the early history of the Pit Lake. The initial activity of radium in the OBSS flow was set to the average activity reported for the lower and middle units of the OBSS (ERPC, 1983) and decreased to the measured activities observed in the previously identified OBSS background wells (Table 3.7). A comparison of predicted radium concentrations to measured data is shown in Figure 3-17. Historical measurements of selenium were not available. Thus, an initial selenium concentration of 0.6 mg/L was determined by iterative model runs to provide the best match to early monitoring data for the Pit Lake. This initial concentration was used to represent only the first year of input to the Pit Lake. For subsequent years, the selenium concentration was reduced over time until it reached the levels reported for the OBSS background wells (Table 3.7). The resulting model predictions for selenium are compared to the observed water quality in the Pit Lake in Figure 3-18.

Figure **3-17** Measured vs. Modeled Radium Activities in Highland Pit Lake

In contrast to radium and selenium, the uranium concentrations observed in the Pit Lake are not reproducible assuming a short-term early flush of high uranium entering the pit similar to selenium. Instead, results from calibration simulations indicate that approximately 2,000 pCi/L of uranium in the OBSS inflow is needed to reproduce the uranium concentrations measured in the Pit Lake observed between 1986 and 2002. To estimate the flux of uranium from leaching in the OBSS, the mass of uranium entering the pit for the first 20 years was calculated using the modeled Pit Lake volumes and the measured uranium concentration in the Pit Lake. Subsequent simulations used the line of best fit from this calculation to specify the amount of uranium entering the pit from the OBSS:

$$
y = 2x10^{11}e^{-0.006x} \quad (R^2 = 0.995)
$$
 [3-7]

where: **X** is the simulation month

Once the activity/concentration predicted by this curve approaches the background activity/concentration observed in local monitoring wells at approximately 145 years, the measured concentration from the wells is used until the end of the simulation. The resulting model predictions are compared to the observed uranium concentrations in the Pit Lake on Figure 3-19.

Figure **3-19** Measured **vs.** Modeled Uranium Activities in Highland Pit Lake

3.3.6.2 *Evaluation of Potential Mass Contribution from the Tailings Basin*

A significant mass of TDS components, radionuclides, and selenium was deposited in the Site tailings impoundment during mining operations. The amounts of several constituents (all COPCs were not reported) originally deposited in the Tailings Basin were estimated from operational data in order to constrain the maximum possible contribution of the tailings solution to the Pit Lake. In addition, a series of sensitivity simulations were constructed to evaluate the impact that seepage from the Tailings Basin could have had on the early chemical evolution of the Pit Lake.

The mass of COPCs originally deposited in the Site tailing impoundment was estimated from operational data. The Highland mill processed 10.5 million tons of material, with a resulting tailings makeup of 35% solids by weight (Exxon, 1994). These quantities indicate that 30 million tons of slurry containing 19.5 million tons of water was deposited in the Site tailings impoundment. If the entire 19.5 million tons of tailings solution entered directly into the Pit Lake, then the calculated flow rate would be 445 gpm distributed over 20 years. If the draindown period is extended over 60 years, then the resulting flow rate would be 148 gpm. These two flow rates provide approximate bounds for the expected rates of flow from the tailings impoundment to the Pit Lake.

Chloride, a conservative element that exhibits minor attenuation in most geochemical sediments, was used to refine the volume of the available tailings water that potentially entered the Pit Lake. A chloride concentration of 217.5 mg/L was determined for the tailings solution by EPRC (1982) (Table 3.6). Assuming that the chemical composition of the tailings solution was constant throughout the deposition of the impoundment, the basin would have received 3.85 x 106 kilograms (kg) of chloride, 1.61 x **10⁵**kg of uranium, and 2.23 x **103** kg of selenium in the solution phase. The radium content of the tailings solution was not reported.

To reproduce the measured concentrations of chloride in the Pit Lake, 4.19 x **10⁵**kg of chloride must be added to the lake over the first 20 years in the DSM. Assuming that the tailings impoundment contained 19.5 million tons of water with a chloride concentration of 217.5 mg/L, the impoundment contained 3.85 x **106** kg of chloride. Only 11% of the impoundment's chloride is needed to satisfy the total mass requirement of the Pit Lake. Aside from the tailings solution, the background OBSS and TDSS aquifers and the perched aquifer are other important sources of chloride based on the reported concentrations and flows (Table 3.7 and Figure 3.4).

The chloride mass-balance calculation described in Section 3.2.3 indicates that 53% of the chloride in the Pit Lake comes from the tailings solution via seepage from the Tailings Basin. During the mass balance calculations, simulated flows from the Tailings Basin of 26 to 30 gpm provided a good match for measured chloride in the Pit Lake (Figure 3-8). Therefore, a flow rate of 26 to 30 gpm of Tailings Basin seepage was applied to estimate the possible mass contribution of uranium and selenium from the tailings solution to the Pit Lake. During these simulations, it was assumed that there was no attenuation of uranium and selenium; thus, the concentrations of these constituents in the tailings solution reaching the Pit Lake are equal to those measured in the pure tailings solution. Geochemical modeling supports this assumption, indicating that greater than 95% of the uranium and selenium in the groundwater system would be present as anionic or neutral complexes; therefore, somewhat conservative behavior may be anticipated. Using flows of 26 to 30 gpm of pure tailings solution, 24 to 27% of the uranium and 10 to 11% of the selenium in the Pit Lake are likely derived from the tailings solution.

3.3.6.3 Model Simulated Comparison of Mass Fluxes

The baseline DSM simulation (as discussed in Sections 3.2 and 3.3.1 to 3.3.6.1) and additional simulations discussed in this section were developed using WWL's (1989) estimate that the worst-case seepage rate from the Tailings Dam would be 30 gpm for 20 to 60 years. This flow rate is slightly higher than the rate of 26 gpm for 20 years that was calculated using a chloride mass balance in Section 3.3.6.2 and the 26.6 gpm rate derived from Carovillano's (1998) highest estimate that the total volume of liquid contained within the finger area is 280 million gallons (Table 3.4). These volumes of seepage are considerably higher than the volume of liquid in the finger area that Carovillano (1998) and Exxon (1998) have estimated is actually mobile (Table 3.4). To examine the effects of the higher rate of 30 gpm, a set of simulations was conducted for uranium, selenium, and sulfate to define the probable bounds for tailing seepage contributions to the Pit Lake. In these simulations, it was assumed that there is no attenuation of chemical species on the flow path between the Tailings Basin and the Pit Lake. Monitoring data for uranium, selenium, and sulfate were not available for the Pit Lake for the first 2 years of filling (1984 and 1985). Hence, the simulation results are compared to monitoring data from 1986 on.

3.3.6.3.1 Uranium

Model calculations indicate that, if tailings seepage is represented by 30 gpm for 20 years with a uranium activity of 6,078.8 pCi/L (9.1 mg/L), then a uranium activity of 1,750 pCi/L in the OBSS inflow is needed to match the available water-quality data for the Pit Lake (Figure 3-20). In this scenario, the tailings seepage provides 24% of the total influent uranium to the Pit Lake. However, data from monitoring wells completed in the tailings and backfill (e.g., TDM 37) do not support the input of uranium at an activity as high as 6,078.80 pCi/L. If the activity of uranium in the modeled tailings seepage component is reduced after 2 years from 6,078 pCi/L, present in pure tailings solution, to 432 pCi/L (0.65 mg/L), the concentration measured at well TDM 37, then an activity of 2,000 pCi/L for the OBSS inflow is needed in the OBSS inflow to match the data (Figure 3-21). In this scenario, the tailings seepage provides 4% of the total influent uranium to the Pit Lake. Each of these simulations provides a reasonably good fit to the actual Pit Lake water quality (Figures 3-20 to 3-21).

Figure **3-20** Model Simulated Comparison of Uranium Mass Fluxes, 20 Years of Pure Tailings Solution

Figure **3-21** Model Simulated Comparison of Uranium Mass Fluxes, 2 Years of Pure Tailings Solution

Because of the limited number of wells between the tailings and the Pit Lake, the limited data set for tailings solution, and the potential for preferential groundwater flow paths that may transport greater concentrations of constituents than measured in well TDM 37, the total contribution of uranium attributable to TBS is likely somewhere between 4 and 24%. However, mass balance calculations for chloride indicate that assuming a conservative transport of **Cl**and a flow of 26 gpm provides a good fit for the chloride mass measured in the Pit Lake. Under the conditions present in the groundwater between the tailings and the Pit Lake (i.e., circumneutral pH and an elevated bicarbonate concentration) uranium would also be expected to be complexed with carbonate and, therefore, to be very mobile and to demonstrate conservative transport behavior. Thus, based on the geochemistry of uranium and the chloride mass balance calculations (Section 3.3.6.2), it is expected that the contribution of uranium from the tailings would be nearer to 24% than 4%.

3.3.6.3.2 Selenium

A set of model calculations with selenium similar to those for uranium described in the preceding section was also conducted. If tailings solution is represented by a flow rate of 30 gpm for 20 years with a selenium concentration of 0.126 mg/L (e.g. equivalent to pure tailings solution), then an initial pulse of 0.45 to 0.5 mg/L selenium from the OBSS is needed to match the observed water-quality data for the Pit Lake (Figures 3-22 and 3-23). In this scenario, the tailings seepage provides 10 to 11% of the total selenium mass to the pit in the first 20 years. However, groundwater data from monitoring wells completed in the tailings (wells TDM 9 and TDM 41) and the backfill (TDM 37) do not show selenium concentrations as high as those used in this calculation. Thus, in a second model calculation, the selenium concentration in the tailings seepage was reduced to 0.003 mg/L, which is the average concentration observed in local monitoring well TDM 37. In this case, 0.45 to 0.5 mg/L of selenium in the OBSS inflow were needed to match the observed selenium concentrations in the Pit Lake data (Figures 3-22 and 3-23). In this scenario, the tailings solution provides 1.2 to 1.7% of the total selenium to the Pit Lake. Based on these model calculations, the percentage of selenium in the Pit Lake that originated from tailings seepage is expected to be between 1.2 and *11%.*

Figure 3-22 Model Simulated Comparison of Selenium Mass Fluxes, OBSS Background Selenium is 0.5 mg/L

However, under the oxidizing, near neutral pH conditions in the local groundwater, selenium is expected to be present primarily as the oxidized selenate ion, which is transported

conservatively under these conditions. Thus, as with the uranyl ion (discussed above), it is likely that the actual amount of selenium in the Pit Lake that originated from the Tailings Basin is nearer the **11%** value.

3.3.6.3.3 Sulfate

The potential contribution of sulfate from tailings solution was also conducted because sulfate is the largest component of TDS in the Pit Lake. As with uranium and selenium, no groundwater data from the tailings area were available for the first 2 years of Pit Lake filling. Hence, the modeled sulfate input for the first 2 years assumes that 30 gpm of tailings solution with a sulfate concentration of 7,580 mg/L reaches the Pit Lake. In this simulation, the DSM overestimates the concentration of sulfate in the Pit Lake. The excess of sulfate predicted in the modeled results occurs because the DSM does not account for the precipitation of sulfate-bearing mineral phases, such as gypsum as the acidic solution passes through the neutralizing carbonate-rich aquifers. Gypsum precipitation was observed by EPRC (1982) in laboratory titrations of the tailings solution with a calcium hydroxide solution. If the average level of sulfate in wells TDM 9 and 41 (3,922 mg/L) is, instead, used for the first 6 years and then reduced to the level in TDM 37 (415 mg/L), the DSM closely matches the available Pit Lake measurements (Figure 3-24). In this latter scenario, the tailings seepage accounts for 30% of the sulfate in the pit during the first 20 years.

Figure 3-24 Model Simulated Comparison of Sulfate Mass Fluxes

3.3.7 Pit Lake Geochemical Processes

Geochemical processes occurring within the water column of the Pit Lake have the potential to affect water quality. These processes include the mineral-water equilibria reactions adsorption and sedimentation, and radiogenic decay specifically for radium.

3.3.7.1 Mineral-Water Equilibrium Processes

A limitation of the DSM used to simulate water compositions for the Pit Lake, based on rates of chemical inflow from different hydrologic sources, is that the solutes are treated conservatively (i.e., no changes in concentration because of geochemical reactions are included in the DSM simulation). However, geochemical reactions, such as mineral precipitation, can be expected to affect solute concentrations in pit lakes over long time frames. Hence, the bulk chemical compositions predicted by the DSM were input to the PHREEQC geochemical model (Parkhurst and Appelo, 1999) and equilibrated with appropriate chemical reactions.

The approach for determining the appropriate chemical equilibria involved the following procedure. The measured solute concentrations (Ca, Mg, K, Na, SO₄, Cl, HCO₃, pH, U, Se, and Ra) for the Pit Lake for the period from 1986 to 2005 were averaged to obtain a depiction of the current water composition (Appendix A and C). The average composition was entered into the PHREEQC geochemical model and speciated to determine the saturation state of the Pit Lake water. The speciation results indicated that Pit Lake water has had an average $CO₂(g)$ partial pressure of 10.2.82 atm or about 4.8 times the normal atmospheric C0 2(g) level of **10-3.5** atm over the period of monitoring. Also, the model results indicated that the calcite saturation index (log ratio of the ion activity product divided by the solubility product for calcite) for the average Pit Lake is 0.05. This small positive value indicates that the average reservoir composition is normally slightly oversaturated compared to calcite solubility. The average reservoir composition was not oversaturated with the solubilities of any other minerals.

To conduct the long-term simulations, the yearly bulk compositions produced by the DSM simulations were entered into the PHREEQC model and equilibrated according to the constraints determined from the PHREEQC speciation results for the measured average reservoir composition, assuming that the current saturation state of the Pit Lake will be maintained in the future. These equilibria include setting the $CO₂(q)$ partial pressure at 10^{-2.82} atm and the saturation state for calcite at 0.05. An additional constraint of gypsum solubility was also specified because preliminary model runs indicated that the bulk compositions became oversaturated with gypsum after about 2,550 years because of evapoconcentration. Oversaturation with other minerals did not occur over the 1000-year simulation period. With these equilibria specified, the PHREEQC model was applied to the yearly bulk solution compositions output by the DSM. The only dissolved constituents that are affected by mineral equilibrium processes are calcium, bicarbonate, sulfate, pH, and TDS. The equilibrated solution compositions from the PHREEQC model calculations comprise the long-term predictions of water quality for the Pit Lake.

3.3.7.2 Adsorption and Sedimentation Processes

In addition to mineral precipitation, other chemical and physical processes could potentially reduce the concentrations of uranium, radium, and selenium in the Pit Lake. Selenium may associate with calcite and then coprecipitate, but the extent of association depends on the redox state of selenium, with selenite $(SeO₃²)$ being preferentially adsorbed (Cowan et al., 1990). Radium has a fairly strong affinity for fine-grained sediments (e.g., Fetter, 1993) and should partition onto fine-grained sediments that either wash into the Pit Lake or are generated by inlake processes and removed via sedimentation. Thus, there are geochemical mechanisms, such as coprecipitation or adsorption and sedimentation, that may lead to chemical mass removal from the water column, and such removal may exert a control on the long-term chemical evolution of the Pit Lake. However, sedimentation rates and coprecipitation reactions that might affect uranium, selenium, and radium levels in the Pit Lake and other water bodies have not been well documented.

The limited data on sedimentation rates in the Pit Lake available from a previous investigation (SMI, 1998) offer contradictory results. Sediment cores and dredge samples collected in 1997 suggested that there was a large flux of sediments into the Pit Lake during the year following a widespread fire that swept through the area in 1996. An estimated concentration of total suspended solids (TSS) of 500 mg/L in the Pit Lake following the fire was inferred from the sediment core data. This is a concentration that is much higher than those typically observed in other reservoirs and lakes (Wetzel, 1975). However, analysis of water-quality data during this period indicates that this large sedimentation event had very little effect on the concentrations of uranium, selenium, or radium in the Pit Lake water column, indicating that removal of these constituents via adsorption to fine-grained sediments and subsequent sedimentation is not a significant mechanism for mass removal.

In contrast, data from sediment traps placed in the Pit Lake in 1997 suggested that the cumulative removal of radium by sedimentation was an important process, possibly removing an average of 36% per year of the total mass of radium in the water column (SMI, 1998). These data also suggested that removal of uranium and selenium from the water column via sedimentation was likely a relatively unimportant mechanism, possibly contributing to an average mass loss of 0.3 and 1.7%, respectively. Estimates of chemical mass removal were obtained by converting the concentrations of constituents from a volumetric basis to an aerial basis. This interpretation, however, assumes that all or most of the mass of the constituents in the sediments was removed from the dissolved phase in the water column and, further, that the removal of radium was associated with calcite precipitation. An alternative interpretation is that a portion of the mass of each constituent measured in the sediment traps was not removed from the dissolved phase (e.g., from the water column) but rather entered the system in the solid phase. This interpretation is supported by the data, which show that a greater mass of each of these constituents is deposited in the sediment traps during the winter, when erosion and transport of sediments into the pit during snowmelt are important. Furthermore, while the flux of calcium carbonate to the traps appears to be greatest during the summer, typical of many lakes and reservoirs (Wetzel, 1975), there is a poor correlation between the concentration of radium and the weight percentage of carbonate in the sediment traps during the summer, suggesting that integration of radium into calcite forming in the water column is of minor importance.

In combination, these results suggest that the removal of these constituents from the water column of the Pit Lake by sedimentation is not an important process, and, as such, these three constituents (uranium, selenium, and radium) were modeled without sedimentation and/or precipitation/coprecipitation controls.

3.3.7.3 Radiogenic Decay

Radium-226 is a radiogenic element with a half-life of 1,600 years. Therefore, because the modeled period was for 1,000 years, the radiological decay equation for radium was incorporated into the DSM.

4.0 PREDICTED **LONG** TERM WATER **QUALITY**

The model created for the Pit Lake was used to predict the time-dependent evolution of water quality for a specific set of hydrologic and geochemical constraints for 1,000 years. Long-term estimates of TDS, uranium, radium, and selenium concentrations and activity/concentrations are discussed in the following sections.

4.1 Long-Term Estimates of **TDS**

The concentrations of major ions that comprise **TDS** are predicted to increase steadily as chemical mass continues to be added by hydrologic flows, while evaporation removes pure water from the Pit Lake (Figure 4-1). After 1,000 years, the TDS concentration is predicted to be 10,310 mg/L. The largest component of TDS is sulfate, which reaches 7,208 mg/L after 1,000 years. This predicted **TDS** concentration is substantially greater than those predicted in earlier modeling efforts (3,500 mg/L [SMI, 1998] and 4,100 mg/L [EPRC, 1983]) after 2,000 years. The difference in predictions is attributable to the difference in the expected hydrologic conditions. The earlier modeling efforts were conducted with the expectation that the Pit Lake would be a flow-through hydrologic system over the long term, whereas the results described here are based on the expectation that the Pit Lake is a hydrologic sink over the long term.

Figure 4-1 Long-term **TDS** Predictions for Highland Pit Lake

The effects of evapoconcentration on TDS over the long term are modified to a small extent by the precipitation of calcite, which removes calcium and bicarbonate from solution and causes these solutes to remain relatively constant over time (Figure 4-1). The precipitation of gypsum starting at about year 2550 causes additional removal of Ca and S04 from solution. The combined effects of calcite precipitation of fixed partial pressure of $CO₂(q)$ produce a relatively small range of pH values (7.75 to 7.85), which is consistent with monitoring data. All other solutes are unaffected by chemical equilibria for 1,000-year time period considered in the modeling.

The modeling results are consistent with the known effects of evapoconcentration on lakes that have chemical compositions with 2^{\ast} [Ca] > [HCO₃], where the brackets refer to molal concentrations. Known as the theory of "chemical divides" (Eugster and Hardie, 1978), lakes that fall into this category will precipitate calcite until the bicarbonate is reduced to the point that calcite precipitation becomes negligible or stops. After that, Ca and other soluble ions will continue to increase in concentration with continued evapoconcentration until the solubility limit of another Ca mineral is reached. Most commonly, the next Ca mineral that reaches saturation is gypsum, as occurs in the Pit Lake. The end result of this evaporation pathway is a nearneutral Na-Ca-SO₄-(±Cl) solution (Drever, 1982; Eary, 1998; Eugster and Hardie, 1978). The results of the PHREEQC modeling for the Pit Lake are consistent with this type of chemical evolution over the long term.

4.2 Long-Term Estimates of Uranium and Radium

Model simulations indicate that uranium and radium concentrations will increase slowly to approximately 3,034 pCi/L (4.54 mg/L) and 4.5 pCi/L, respectively, after 1,000 years (Figures 4- 2 and 4-3). Dissolved uranium and radium are not expected to be strongly affected by mineral precipitation, adsorption, or sedimentation processes within the Pit Lake that would remove these constituents from solution. Hence, the long-term simulations indicate that uranium and radium concentrations increase slowly over time because of evapoconcentration, although the increase for radium is moderated by radioactive decay. The very slow increase in concentration over the long term is due to the fact that, after the initial influx of uranium and radium from the Tailings Basin seepage, the hydrologic inflows have very low concentrations (Table 3.7). As a result, the rates of addition of uranium and radium to the Pit Lake are very small fractions of the masses already existent in the lake, thereby producing only small increases in concentration over time. This behavior is different from the major solutes (TDS) for which concentrations in the hydrologic inflows continue to input proportionately larger masses of dissolved constituents from the hydrologic sources throughout the simulation period, thereby producing comparatively greater increases in concentration because of evapoconcentration.

Figure 4-2 Long-term Uranium Predictions for Highland Pit Lake

Figure 4-3 Long-term Radium Predictions for the Highland Pit Lake

4.3 Long-Term Estimates of Selenium

The concentration of selenium is predicted to increase from its current level of 0.09 mg/L to 0.14 mg/L after 1,000 years (Figure 4-4). Previous modeling efforts predicted that selenium concentrations would decrease to less than 0.05 mg/L within approximately 60 years. However, those previous predictions were based on a model that included the removal of selenium from the water column by sedimentation processes and the assumption that the Pit Lake would become a flow-through system in which the high initial concentrations of selenium in the Pit Lake would eventually be displaced by lower concentrations flowing in from groundwater. As discussed in Section 3.3.7.2, removal of constituents via the sedimentation process is not well defined in the Pit Lake; therefore, for the model simulations presented here, the removal of selenium from the water column is not incorporated into the DSM. As a result, selenium concentrations increase over time because of evapoconcentration similar to uranium. Also similar to uranium, the rate of increase in selenium concentrations for the Pit Lake is very slow after the initial influx of Tailings Basin seepage because the hydrologic inflows have very low concentrations compared to those already present in the Pit Lake.

Figure 4-4 Long-term Selenium Predictions for Highland Pit Lake

5.0 SENSITIVITY ANALYSIS

Numerous factors can potentially contribute to uncertainty in long-term predictions of geochemical conditions, as simulated by dynamic system models such as Stella™. Results of the baseline modeling presented above are based on the currently available data in combination with relevant scientific theory and professional experience. However, because it is extremely difficult to determine the absolute levels of constituents in various aqueous streams and or flow volumes, a series of sensitivity simulations were created using the baseline dynamic system model of the Pit Lake to determine the relative influence of the parameters included in the model. A summary description of each simulation and the resulting final concentrations at 1,000 years are listed in Table 5.1.

5.1 TDSS and **OBSS** Total Water Quality

The model was not sensitive to concentration changes in the TDSS but was highly sensitive to the alteration of concentration for the OBSS component. Model sensitivity to the concentrations of constituents in the TDSS and OBSS was evaluated by doubling the baseline levels and reducing the levels by 50%. Doubling the concentrations of the constituents from both Doubling the concentrations of the constituents from both background flow and tailings seepage in the TDSS inflow primarily impacted radium and selenium, whose final activity/concentrations reached 6.11 pCi/L and 0.153 mg/L. Decreasing the influent concentrations by half reduced the final activity-concentrations of radium and selenium to 3.72 pCi/L and 0.137 mg/L respectively.

Doubling the concentrations of the constituents from both background flow and tailings seepage in the OBSS aquifer had a significant effect on the final levels of radium, uranium, and selenium. The final activity/concentrations of these elements reached 6.41 pCi/L, 7.84 mg/L, and 0.267 mg/L, an increase of 42%, 71% and 88% respectively (Table 5.1). Decreasing the influent concentrations by half reduced the final activity-concentrations of radium, uranium, and selenium to 3.57 pCi/L, 2.96 mg/L, and 0.080 mg/L respectively. The concentrations of these constituents had been fitted to match measured water-quality data for the Pit Lake, and changes to the OBSS chemistry resulted in a large discrepancy between early model results and the observed water-quality data for the Pit Lake, suggesting that the baseline levels most accurately reflected the mass flux from the OBSS (Figures 5-1 through 5-3).

5.2 Tailings Basin Seepage through Backfill

The model results were not very sensitive to changes in the duration or rate of flow of tailings seepage through the backfill. Recent estimates suggest that the seepage mound under the Tailings Dam at the Site will naturally disappear in 20 to 60 years at an "extreme worst-case" flow rate of 60 years of flow averaging 30 gpm (4.03 acre-f/month) (WWL, 1989). Several sensitivity scenarios were created to test the sensitivity of the model to tailings seepage through the backfill (Table 5.1). Simulations were conducted with 20, 40, and 60 years of tailings seepage at 30 gpm. These scenarios also lengthened the duration of the maximum impact of tailings water on the TDSS aquifer. The differences between the final concentrations of COPCs were minor, with the largest impacts seen in uranium, whose final concentrations ranged from 4.59 to 4.68 mg/L, an increase from baseline of less than 2%.

A second set of simulations evaluated the effect of decreasing and increasing the rate of seepage from the Tailings Basin through the backfill by 50%. Adjusting the flow rate had a smaller impact on the ultimate concentrations than changing the duration of draindown, as discussed above (Table 5.1).

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			Final Concentrations (1,000 years)			Baseline Description
			Ra-226	\mathbf{U}	Se.	
Туре	Simulation	Description	pCi/L	mg/L	mg/L	
Final	Final DSM of Highland Pit Lake	Final DSM of Highland Pit Lake	3.72	4.54	0.143	
Baseline		Baseline Simulation used for Sensitivity Analyses	4.51	المتوحم كالمتعارض $4.59 -$	0.143	
Tailings Dam Impacts	CI mixing model	60 year OBSS keywell at 25%; 40% impacted area; TDSS keywell 99% impacted for 60 years	4.58	4.68	0.143	OBSS key well 13% impacted
	TD Seepage through backfill	50% lower TD Seepage Flow in Backfill (2.02 Acre-foot/month)	4.51	4.57	0.143	4.03 Acre-foot/month
	TD Seepage through backfill	50% higher TD Seepage Flow in Backfill (6.05 Acre-foot/month)	4.52	4.61	0.143	4.03 Acre-foot/month
	TD Seepage through backfill	Concentration in TD Seepage x 2	4.52	4.64	0.143	
Perched Aquifer	Perched Aquifer Flows	10% higher flow (10.95 Acre- foot/month)	4.26	4.42	0.135	9.74 Acre-foot/month
	Perched Aquifer Flows	20% higher flow (11.94 Acre- foot/month)	4.03	4.27	0.127	9.74 Acre-foot/month
	Perched Aquifer Flows	10% lower flow (8.96 Acre- foot/month)	4.79	4.76	0.151	9.74 Acre-foot/month
	Perched Aquifer Flows	20% lower flow (7.96 Acre- foot/month)	5.09	4.95	0.161	9.74 Acre-foot/month
	Perched Aquifer Chemistry	Concentrations x 2	4.57	5.58	0.144	
Runoff	Runoff flow rate	Runoff calculated as 2.4% of Rainfall	4.56	5.15	0.162	6% of Rainfall
	Runoff flow rate	Runoff calculated as 13% of Rainfall	4.36	3.78	0.115	6% of Rainfall
	Runoff Chemistry	U, Ra, Se from Table 3.6	4.51	4.49	0.143	U, Ra, Se from TDM37
	Runoff Chemistry	Runoff Concentrations x2	5.53	4.89	0.15	See Table 3.6 for TDS: U. Ra. Se from TDM37; decrease over time
	Runoff Chemistry	Highest initial concentrations from key wells	4.51	4.59	0.143	See Table 3.6 for TDS; U, Ra, Se from TDM37: decrease over time

Table **5.1** Results of Sensitivity Analysis (continued)

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Notes:

 $\frac{a}{a}$ - Runoff was calculated as in baseline case as 6% of 12.06 in/yr annual precipitation

Cl - chloride

DSM - dynamic systems model

in/yr - inches per year

mg/L - milligrams per liter

OBSS - Ore Body Sandstone

% - percent

pCi/L - picoCuries per liter

Ra - Radium

Se - Selenium

TDSS - Tailings Dam Sandstone

U - Uranium

Figure **5-1** Sensitivity: Measured vs. Modeled Radium

Figure **5-2** Sensitivity: Measured vs. Modeled Uranium

Figure **5-3** Sensitivity: Measured vs. Modeled Selenium

5.3 Tailings Basin Seepage in the **TDSS** and **OBSS** Aquifers

The chloride-mixing model described in Section 3.3.5 includes multiple parameters that were sensitivity tested, including the maximum percentage of tailings water impacting the key wells, the length of draindown, and the percentage of the drainage basin impacted by tailings seepage.

As discussed in Section 3.3.6, the early influx of radium, uranium, and selenium to the Pit Lake through the OBSS is fitted at concentrations higher than those observed in the tailings seepage. Consequently, changes introduced in these sensitivity simulations had minimal influence on the concentration of these constituents, as shown in Table 5.1.

The model was not sensitive to changing the seepage concentrations of radium, uranium, and selenium in the TDSS between the average concentrations observed in wells TDM 9 and TDM 41 and the highest average values from well TDM 37 (Table 3.9). In all simulations varying the radionuclides in the seepage with the maximum percentage of tailings water in the TDSS and the duration of the draindown or the percentage of the basin impacted, the final activityconcentrations of radium, uranium and selenium were 4.5 pCi/L, 4.6-4.7 mg/L, and 0.143 mg/L respectively (not shown in Table 5.1).

5.4 Perched Aquifer Flow and Water Quality

Groundwater flow in the shallow alluvial aquifer was estimated from field observations as 74 gpm (9.95 acre-ft/month) (Range, 1998). Because this flow is not well documented, the rate was changed by $\pm 10\%$ and $\pm 20\%$ to examine the sensitivity of the model to the perched aquifer discharge. The resulting concentrations for the COPCs changed slightly (Table 5.1). Radium ranged from 4.03 to 5.09 pCi/L, uranium ranged from 4.27 to 4.95 mg/L, and selenium ranged from 0.13 to 0.16 mg/L. Doubling the concentrations of the constituents in the perched aquifer inflow primarily impacted the long-term concentration of uranium, resulting in a final concentration of 5.58 mg/L, an increase of 21%.

5.5 Surface Runoff Rates and Water Quality

The amount of surface runoff entering the Pit Lake from precipitation events was estimated by several methods (EPRC, 1983), as summarized in Table 3.3, and averaged 6%. Sensitivity runs were conducted using the high- and low-end percentages from these methods. When runoff was increased to 13% of rainfall, radium, uranium, and selenium decreased by dilution to 4.36 pCi/L, 3.78 mg/L, and 0.12 mg/L respectively. When runoff was reduced to 2.4% of rainfall, radium, uranium, and selenium increased to 4.56 pCi/L, 5.15 mg/L, and 0.16 mg/L.

The water quality of the runoff was also tested because no field measurements exist. As described in Section 3.3.3, in one simulation, the activity of radium reported by EPRC (1983) was initially used for surface runoff. The activity of uranium and the concentration of selenium in surface runoff were calculated from the previously reported activity of radium using the ratio of uranium to radium and the ratio of selenium to radium measured in wells completed in the backfill (Table 3.8). The modeled concentrations/activities of all constituents were reduced over time from the weighted prevegetation values to the undisturbed values to account for the effect of revegetation at the Site. The results from this simulation are listed in Table 5.1. A second conservative simulation was created where the early activity-concentrations of uranium, radium, and selenium were set to the values observed in well TDM 37, the well in the flow path between the Tailings Dam and Pit Lake that exhibits the highest concentrations of radionuclides (Table

3.9). This simulation is the baseline scenario listed in Table 5.1. The primary impact of this change was a slight increase in uranium.

The sensitivity of the Pit Lake to the water quality in the runoff was examined in a series of simulations listed in Table 5.1 including unrealistic worst-case scenarios in which the water quality of the runoff was set at the highest observed concentrations from the monitoring wells with no decrease for 1,000 years. The activity/concentrations of radium and uranium under this simulation increased to 9.31 pCi/L and 6.92 mg/L, respectively, with no significant change in the concentration of selenium.

5.6 Precipitation and Evaporation Rates

The Pit Lake was modeled using the average rates for precipitation (12.06 in/year) and evaporation (45.2 in/year) documented by **MFG** (2003a). One thousand years is a sufficient period to realistically expect variations in the local and regional climate to affect the Pit Lake. A period of drought or excessive precipitation could affect both short- and long-term conditions through changes in direct surface runoff and evaporation rates. Extended climatic changes could also impact the rates of recharge to the local groundwater flow system. Drought conditions would be expected to magnify the effects of evapoconcentration and thus increase the concentrations of the COPCs. A shift towards a wetter climate would be expected to dilute the Pit Lake and thus decrease the concentrations of the COPCs.

Future climate changes are, at best, extremely difficult to predict and quantify, and this type of sensitivity testing is not attempted by this study. Instead, the sensitivity of this DSM of the Pit Lake to rainfall and evaporation rates was evaluated using the minimum and maximum rates reported by **MFG** (2003a) and listed in Tables 3.2 and 3.5. Groundwater inflows and runoff rates were not altered despite the potential changes in recharge. The results listed in Table 5.1 illustrate the sensitivity of the model to a change in precipitation or evaporation at the extreme ends of the reported ranges.

6.0 SUMMARY **AND CONCLUSIONS**

Due to recent revisions of the Site groundwater concept and the availability of additional groundwater and Pit Lake water-quality data, a revised DSM was developed to simulate the dynamic hydrologic and geochemical evolution of the Pit Lake. Long-term predictions were made for the concentrations of TDS and selenium and for the activity-concentrations of uranium and radium. The computer model was developed using water-quality data collected during the past 19 years. Historical water-quality measurements the Pit Lake provided a tool for calibrating the computer model prior to extending the modeling time to 1,000 years.

The following conclusions can be drawn based on the results obtained from the computer modeling:

- Water-quality measurements from the Pit Lake during the first 19 years of filling indicate that leaching of constituents to the OBSS groundwater system from exposed uranium roll-front deposits, and seepage from the Tailings Basin have resulted in elevated levels of radium, selenium, uranium, sulfate, and TDS in the Pit Lake.
- Calibrations of the computer model for uranium, radium and selenium required that a \blacksquare source term be included to account for leaching of constituents from the exposed and oxidized portions of the remaining mineralized zone. The major source terms incorporated into the **DSM** were input as an early flushing of constituents from the remaining oxidized ore body and seepage from the Tailings Basin. This approach provided a good fit of modeled to existing water-quality data. The potential contribution of the Tailings Basin was also evaluated.
- **"** The disposal of tailings to the east of the Pit Lake, structurally elevated by as much as 200 to 400 feet, affected the level of TDS during the early history of the Pit Lake r. For example, in the first 20 years of the filling of the Pit Lake, mass balance calculations indicated that 53% of the chloride and a maximum of 30% of the sulfate came from the tailings impoundment.
- Under current conditions, the primary source of chemical mass entering the Pit Lake is from the OBSS. Specifically, uranium, radium, and selenium are leached from the remaining mineralized zone exposed in the pit walls. However, seepage from the Tailings Basin has also contributed a significant mass of constituents to the Pit Lake. Model simulations indicate that as much as 24% of the uranium and 11% of the selenium in the Pit Lake could come from the tailings impoundment.
- Evaporation of water from the Pit Lake constitutes the sole hydrologic outflow and, therefore, has a significant effect on the long-term evolution of chemistry in the Pit Lake due to evapoconcentration of Pit Lake constituents.
- **"** The predicted concentration of TDS at year 1,000 is approximately 10,310 mg/L. Sulfate levels exert the primary control on TDS, which increases to a maximum modeled concentration of 7,208 mg/L at 1,000 years.
- The precipitation of calcite imposes limits on the concentrations of calcium and bicarbonate in the lake.
- **"** The predicted activity/concentrations of uranium and radium after 1,000 years are 4.54 mg/L (3,034 pCi/L) and 3.7 pCi/L, respectively.

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APPENDIX A DYNAMIC SYSTEMS/PHREEQC GEOCHEMICAL MODEL RESULTS: WATER CHEMISTRY

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APPENDIX A

DYNAMIC SYSTEMS/PHREEQC GEOCHEMICAL MODEL **RESULTS:**

Geochemical Modeling Approach

The dynamic systems model (DSM) used to predict the geochemical evolution of the Highland Pit Lake is based on a mass balance approach. The DSM calculates a chemical mass balance for each solute using the following mathematical expression:

$$
\frac{d(C_k V)}{dt} = \sum_{i=1}^n C_{k,i} Q_i^{\text{Inflow}} - \sum_{j=1}^m C_{k,j} Q_j^{\text{Outflow}}
$$

where C_kV is the mass of solute k in the Highland Pit Lake and $C_{k(ii)}$ are the concentrations of solute k in the source of inflow i and source of outflow j (in units of mass per unit volume). The DSM was run for 1000 years (1984 to 2984) and bulk solution compositions were output on a yearly basis.

A limitation of the DSM is that solutes are treated conservatively, that is, no changes in concentration because of geochemical reactions are included in the DSM simulation. However, geochemical reactions, such as mineral precipitation, can be expected to affect solute concentrations in pit lakes over long time frames. Hence, the bulk chemical compositions predicted by the DSM were input to the PHREEQC geochemical model (Parkhurst and Appelo, 1999) and equilibrated with appropriate chemical reactions.

The approach for determining the appropriate chemical equilibria involved the following procedure. The measured solute concentrations (Ca, Mg, K, Na, SO₄, Cl, HCO₃, pH, U, Se, and Ra) for the Highlands Pit Lake for the period from 1986 to 2005 were averaged to obtain a depiction of the current water composition (Table A.1). The average composition was entered into the PHREEQC model and speciated to determine the saturation state of the Pit Lake water. The speciation results indicated that Pit Lake water has had an average $CO₂(g)$ partial pressure of 10-2-82 atm or about 4.8 times the normal atmospheric C0 2(g) level of **10-35** atm over the period of monitoring. Also, the model results indicated that the calcite saturation index (log ratio of the ion activity product divided by the solubility product for calcite) for the average reservoir is 0.05. This small positive value indicates that the average reservoir composition is normally slightly oversaturated compared to calcite solubility. The average reservoir composition was not oversaturated with the solubilities of any other minerals.

To conduct the long-term simulations, the yearly bulk compositions from the DSM results were entered into the PHREEQC model with the equilibria constraints determined from the PHREEQC speciation results for the measured reservoir composition, assuming that the current saturation state of the reservoir will be maintained in the future. These equilibria include setting the C0 2(g) partial pressure at **10-2.82** atm and the saturation state for calcite at 0.05. An additional constraint of gypsum solubility was also specified because preliminary model runs indicated that the bulk compositions became oversaturated with gypsum after about 2550 years because of evapoconcentration. Oversaturation with other minerals did not occur over the 1000-year simulation period. With these equilibria specified, the PHREEQC model was applied to the yearly bulk solution compositions output by the DSM. The PHREEQC results comprise the long-term predictions of water quality for the Highland Pit Lake.

Summary of Results

The results of the long-term modeling are given in Table A.2. A comparison of the DSM bulk compositions to the PHREEQC equilibrated solutions shows that calcite precipitation removes Ca and HCO₃ from solution. The precipitation of gypsum starting at about year 2550 causes additional removal of Ca and S04 from solution. The combined effects of calcite precipitation of fixed partial pressure of $CO₂(g)$ produce a relatively small range of pH values of 7.75 to 7.85, which is consistent with monitoring data. All other solutes are unaffected by chemical equilibria for 1000-year time period considered in the modeling.

The modeling results are consistent with the known effects of evapoconcentration on lakes that have chemical compositions with 2^{\star} [Ca] > [HCO₃] where the brackets refer to molal concentrations. Known as the theory of "chemical divides" (Eugster and Hardie, 1978), lakes that fall into this category will precipitate calcite until the bicarbonate is reduced to the point that calcite precipitation becomes negligible or stops. After that, Ca will continue to increase in concentration along with other soluble ions with continued evapoconcentration until the solubility limit of another Ca mineral is reached. Most commonly, the next Ca mineral that reaches saturation is gypsum as occurs in the Highland Pit Lake. The end result of this evaporation pathway is a near-neutral, Na-Ca-SO₄-(\pm CI) solution (Drever, 1978; Eary, 1998; Eugster and Hardie, 1978). The results of the PHREEQC modeling for the Highland Pit Lake are consistent with this type of chemical evolution over the long-term.

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Table A.2. Summary of yearly compositions for the Highland Pit Lake output from the DSM and after equilibration with PHREEQC

Table A.2. Summary of yearly compositions for the Highland Pit Lake output from the DSM and after equilibration with PHREEQC (continued)

The dynamic systems model (DSM) does not produce a solution pH. The predicted pH is from the PHREEQC modeling results mg/L **=** milligrams per liter

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Table A.2. Summary of yearly compositions for the Highland Pit Lake output from the DSM and after equilibration with PHREEQC (continued

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Table A.2. Summary of yearly compositions for the Highland Pit Lake output from the DSM and after equilibration with PHREEOC (continued)

**TDS = Ca + Mg + Na + K + Cl + SO_4 + 0.4917*HCO₃

DSM = dynamic systems model

 $mg/L =$ milligrams per liter

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APPENDIX B DYNAMIC SYSTEMS MODEL RESULTS: WATER BALANCE

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APPENDIX B WATER BALANCE

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OBSS - Ore Body Sandstone TDSS - Tailings Dam Sandstone

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APPENDIX C MEASURED WATER QUALITY: HIGHLAND PIT LAKE AND GROUNDWATER MONITORING WELLS (CD)

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