Appendix A21

“Geochemical Evolution of Water Quality During Re-filling of the Homestake Mine”, Geochima, Inc, 13 June 2003

GEOCHEMICAL EVOLUTION
OF WATER QUALITY
DURING RE-FILLING
OF THE HOMESTAKE MINE

June 13, 2003

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GEOCHEMICAL EVOLUTION OF WATER QUALITY DURING RE-FILLING OF THE HOMESTAKE MINE

Prepared for:
Homestake Mining Company
Lead, South Dakota

Prepared by:
Geochimica, Inc.
206 North Signal Street, Suite M
Ojai, California 93023

June 13, 2003

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INTRODUCTION

1.0 INTRODUCTION

1.1 BACKGROUND

While planning closure of the Homestake Mine (Lead, S.D.), Barrick have continued pumping water from the mine workings. At this time, the mine is dewatered to the 8150 Level, however, Homestake stopped pumping below the 5000 Level on 10 June, 2003, and the mine will re-inundate.

Barrick's Senior Hydrogeologist developed a physical model for re-flooding that accounts for (a) groundwater flow to each level of the mine, (b) infiltration from surface, and (c) surface water that will be captured by the mine workings (Zhan, 2002). The flow model indicates that the underground workings will re-saturate, with water levels expected to rise approximately 7,350 feet to the base of the open cut (800-Level) in 27 years. Once waters accumulate in the open cut, water level rises much more slowly, with the steady-state elevation (approximately the 300-Level) approached in approximately 180 years. The long, slow rise in the open cut, in contrast to the relatively rapid rise in the underground workings, is due to three factors:

- The limited flow of groundwater as the hydraulic gradient decreases over time;
- The large open-space volume of the open cut compared to the small space of mine workings;
- Evaporation from the surface of the water body that accumulates in the open cut.

As part of its closure-planning process, Homestake Mine personnel have collected water chemistry from approximately 38 locations underground. The water-chemistry stations are located vertically over most of the extent of the underground workings (Figure 1). In addition, Homestake have water-quality data for surface-water samples that can be used to evaluate the overland-flow portions of inflow to the Open Cut during the later stages of mine re-flooding.

As is common in the mining industry, relative vertical position within the mine is routinely specified in terms of a depth (in feet, ft) below an arbitrary datum at the ground surface (Figure 1). The elevation of datum at the Homestake Mine is 5231 ft amsl (above mean sea level). The principal levels (and their elevation equivalents) used in this memorandum include:

Table 1. Inundation levels evaluated in this study

Mine Level	Elevation (ft amsl)	Significance
300	4931	Steady-state water level in open cut; reached in 179 years
800	4431	Base of open cut; water level after 27 years of refilling
1100	4231	Water level after 20 years of refilling
3050	2181	Water level after 10 years of refilling
5000	231	Base of Yates Shaft; water level after 3.6 years of refilling
6950	-1719	Water level after 1 year of refilling
8150	-2919	Lowest exposed level of mine; current water level

1.2 PURPOSE AND OBJECTIVES

The purpose of this report is to provide initial estimates of water chemistry in both (a) the underground mine workings below the base of the open cut (i.e., over the first 27 years of re-filling) and (b) the Open-Cut Mine (i.e., from model years 27 to 179).

Specific objectives of this evaluation include:

- Describing a conceptual model for re-filling over time;
- Identifying the major types of water chemistry that will report to the underground workings;
- Elaborating the conceptual flow model into a conceptual model of water chemistry during the re-filling process;
- Estimating potential changes in water chemistry as the underground workings re-fill. The changes in water chemistry in the underground mine are evaluated for the following times (and mine levels):
    - Re-Filling Year 1 (6950 Level)
    - Re-Filling Year 3.6 (5000 Level)
    - Re-Filling Year 10 (3050 Level)
    - Re-Filling Year 20 (1100 Level)
    - Re-Filling Year 27 (800 Level; Base of the Open Cut)
- Estimating potential changes in water chemistry as the Open Cut re-fills. The changes in water chemistry in the Open Cut are evaluated for the following times (and mine levels):
    - Re-filling Year 27.6 (800 Level)
    - Re-filling Year 38.5 (700 Level)
    - Re-filling Year 60 (600 Level)
    - Re-filling Year 95 (500 Level)
    - Re-filling Year 147 (400 Level)
    - Re-filling Year 179 (300 Level)
- Documenting the computations and results.

1.3 TERMS OF REFERENCE

Mr. Todd Duex (Barrick – Homestake Mine) asked Geochimica to develop a model of the hydrogeochemical evolution of the water in the underground mine during re-flooding of the workings to the base of the open cut. Barrick provided (1) the water-balance model for re-filling of the mine (Zhan, 2002) and (2) water-quality data for subsurface flows. All chemical data and conditions considered in this evaluation are inorganic.

Geochimica has relied on the data and information provided by Barrick. Although we have applied some simple checks for internal consistency of the chemical data, we have not tried to independently validate the water-chemistry data in detail. Mark Logsdon (Geochimica) has been to the Homestake Mine on several occasions and is generally familiar with the site geology from literature references, discussions with Homestake staff, and from hand-sample and field observations.

Neither Geochimica, Inc. nor Mark Logsdon personally (including through members of his family) has any financial interest in Homestake Mining Company or Barrick Gold. Geochimica was not involved in any planning or decision-making that led to the decision to stop pumping and allow the workings to flood. Geochimica has in the past performed consulting assignments for Homestake Mining Company, and Geochimica now is engaged in other geochemical studies related to mine closure.

2.0 EVOLUTION OF WATER CHEMISTRY IN THE UNDERGROUND WORKINGS FROM 8150-LEVEL TO BASE OF OPEN CUT

2.1 ISSUES IN THE UNDERGROUND WORKINGS

- At what rates will ground and surface water report to the underground workings during re-filling?
- What are the data on chemistry of inflows, and how can these be represented in a hydrogeochemical model?
- How can flows and chemistries be combined to represent the integrated chemistry of the re-filling mine pool over time?
- What is the expected chemistry of the mine pool as the underground workings re-fill?
- How can estimates of future water chemistry during re-filling be checked?

2.2 CONCEPTUAL MODEL FOR GEOCHEMCAL EVOLUTION OF UNDERGOUND WORKINGS

2.2.1 Conceptual Model of Re-Filling the Underground Workings

Flow that reports to the underground workings arises from two basic sources:

- Local infiltration above the workings and surface water flows that are captured by the open cut. Seepage from the Grizzly Gulch tailing system that is captured by Shaft 5 is a special case of local infiltration.
- Groundwater flow, driven by regional flow gradients, to the cone of depression created by mine dewatering.

The conceptual and theoretical bases for the flow model are described in detail in Zhan (2002). Dr. Zhan's re-filling model accounts explicitly for both sources of water, accounting each flow as a function of depth. The average surface-derived flows remain constant throughout the re-filling of the underground workings, but Dr. Zhan's model accounts for the decreasing flux of ground water inflow during re-filling, due to declining lateral hydraulic gradients as the water level rises. Note that Shaft 5 is connected to the underground workings only from the 7700 Level to the 2000 Level, implying that inputs to the workings from Shaft 5 are part of the mixture only during this phase of the re-filling process.

The basic conceptual model of re-filling is very simple: Water flows from higher levels to lower levels; as open space fills, water level rises. Three physical factors suggest that the saturated water column probably will be well mixed over most of the mine:

- There is a distinct thermal gradient between the deep workings (temperatures near 40 °C) and shallow zones (temperatures near 10 °C). Surface-water inflows during snowmelt periods will be colder yet. Because temperature is the predominant influence on water density until salinity becomes quite high (typically > 50,000 mg/L), the temperature gradients imply density gradients that will tend to mix the water column.
- The large potential energy differences between shallow inflows and the deeper workings will be converted to kinetic energy as water flows downward to the slowly rising water level. The kinetic energy of the flowing waters will tend to cause mixing with the static waters below.
- Pressure conditions measured by HMC in the deep system indicate that there will be an upward-directed, fresh-water hydraulic gradient over much and perhaps most of the re-filling (T. Duex, personal communication, April, 2003).

During the late-stage refilling, there may be a tendency for waters in the upper part of the workings (perhaps from the 800 Level to the 1100 Level (i.e., stages that re-filled during Years 20 – 27) to be slightly less dense than the deeper waters, leading to long-term waters near the base of the open cut that are closer to the shallow-system inflows than to the lower well-mixed system. On the other hand (see Results and Discussion sections, below), the successful calibration of predicted Year 27 values for a well-mixed system (expect for temperature) to observed water chemistry in the 800 Level in early 2003 suggests that the well-mixed model is a reasonable approximation for purposes of planning and decision-making.

2.2.2 Conceptual Model of Hydrogeochemistry during Refilling the Underground Workings

Table 2 compiles the available water-quality data for subsurface flows.

As shown in Table 2, one may classify the observed underground flows collected close to points of seepage or flow from fractures into three, basic hydrogeochemical types:

- Calcium-sulfate [$Ca\text{-}SO_4$] waters, which typically are observed in seeps and flows from the 800 Level to approximately the 3050 Level.
- Magnesium-sulfate [$Mg\text{-}SO_4$] waters, which typically are observed in seeps and flows from approximately the 3050 Level to approximately the 5000 Level.

- Sodium-bicarbonate [Na-HCO_3] waters, which are observed in seeps and flows in the deepest parts of the mine, from approximately 5000 Level to total depth.

There are two additional flows to be considered:

- Surface water captured by the Open Cut. Because no separate samples of surface-water inflow are available, we have assumed that this component has the Ca-SO_4 signature of shallow ground water. This perhaps is slightly conservative (i.e., overestimates concentrations) because the contact time between surface water and rock probably is somewhat less than that between infiltration and shallow groundwater and rock through which it must seep.
- Flow down Shaft 5. This component is evaluated separately because Barrick/HMC have identified that the Shaft 5 seepage includes a signature – specifically, low but discernible levels of total-CN and very low concentrations of wad-CN - that appears to be due to seepage from Grizzly Gulch tailing facility. The Shaft 5 flows report to the combined underground flows from the 7700 Level to the 2000 Level only.

Key chemical characteristics that help distinguish the major water types are summarized in the Table 3, based on median values for all water samples in each class of water type[1]. (The pH is repeated intentionally in Table 3 to help clarify context of results in each part.) The meaning and significance of waters sampled in mine sumps is discussed immediately after Table 3.

Table 3 Median Chemistry for Major Water Types (mg/L, except pH in su).

Water Type	**pH**	**TDS**	**Na**	**Ca**	**Mg**	**SO_4**	**HCO_3**	**CN-tot**	**CN-wad**
Ca-SO4	8.0	472	16	83	28	120	250	<0.010	<0.010
Mg-SO4	7.9	4670	317	323	475	3146	318	0.015	<0.010
Na-HCO3	7.8	837	301	12	7	40	792	<0.010	<0.010
Shaft 5	7.8	2197	206	287	90	1372	146	3.85	0.278
Mine Sumps	8.0	2441	232	169	239	1502	374	0.020	<0.010

Water Type	**pH**	**F**	**NO_3**	**Al**	**As**	**Cu**	**Fe**	**Mn**	**Zn**
Ca-SO4	8.0	0.36	0.07	<0.05	<0.005	<0.005	<0.050	0.19	<0.050
Mg-SO4	7.9	1.55	0.35	<0.05	0.044	0.012	0.093	0.69	<0.050
Na-HCO3	7.8	6.12	0.03	<0.05	0.006	0.003	0.050	<0.050	<0.050
Shaft 5	7.8	1.19	3.80	<0.05	<0.005	0.020	0.591	6.95	0.35
Mine Sumps	8.0	1.84	1.76	<0.05	0.024	0.018	<0.050	0.21	<0.050

Sump water deep in the mine integrates long-term flows through mined ground over a large range of water flow paths that include both rapid and slow flows. Water samples from the

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[1] For a normal distribution, both the mean and the median are unbiased estimators of central tendency. However, for any sample that is not normally distributed (and in particular for polymodal samples, which are common in mining systems because of geologic controls on mineralization), the mean will be biased, whereas the median will not. Therefore, as a first approximation from samples for which the underlying distribution is not known and in particular when a spatial range associated with volumetric contribution is implicated, the median is the preferred estimator.

deep sumps show concentrations and ratios of concentrations that differ from the three principal groundwater end-members. We interpret these differences as reflecting reactions between the three principal water types and minerals that occur on the surfaces of the fractured rock in the mine workings. Some components (e.g., SO_4) increase in concentration, whereas others (e.g., Alkalinity) decrease. Because of the large amount of carbonate minerals present in the mined formations (especially, but not exclusively, in the Homestake Formation), pH is well buffered in the neutral to mildly alkaline range despite the ranging values of alkalinity. Because of the heterogeneous distribution of both primary lithologies and secondary minerals, it is not practicable, given the state of the art in geochemical modeling and practical limitations on sampling to try to construct a "forward model" (using a thermodynamically-based computer model to quantitatively simulate reacting water with minerals in known proportions over time; e.g., Alpers and Nordstrom, 1999).

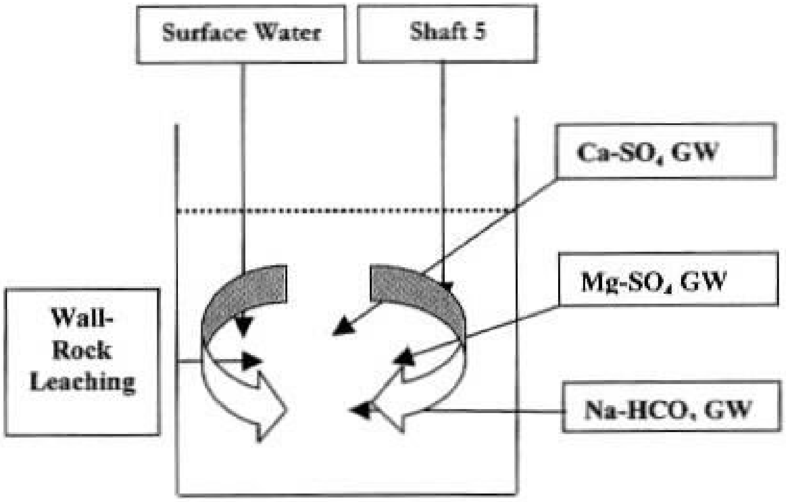
The conceptual model for calculating the evolution of water chemistry during refilling of the mine, based on the underlying arithmetic of a mixing cell, is illustrated in Figure 2.

To account for reactions with the mine walls, we have empirically evaluated the changes in chemistry between water-balanced proportions of the three principal water types and the median chemistry of the integrated "mine water" samples. We assume that the currently observed differences arise from interactions that have occurred over the entire 8150-foot interval of de-saturated rock reporting to the deep sumps. We infer that the extent of reaction depends on the residence time in the system, which is, to a first approximation, proportional to the average distance from ground surface to the ambient water table. Therefore, we calculate the proportional impact, as water levels rise, by taking ratio of the median elevation of water in the filling interval to the full 8150-foot, initial interval, and then apply that ratio to the observed difference over the full 8150-foot, initial interval. The incremental mass associated with these interactions is added to the end-member-mixing model at each stage.

For example, the modeled increment of SO_4 concentration between the Year 1 model (based on the three end-member waters) and the observed Mine Water is 836 mg/L. This represents an incremental 0.103 mg/L of SO_4 per foot of depth (given a total depth of 8150 feet). The end-member mixing model for Year 1 has a concentration of SO_4 of 681 mg/L, so the inferred total SO_4 at Year 1 (for which the median filling depth is 7550 feet) is (681 + ((7550/8150)* 836) mg/L, or 1455 mg/L. The median value for all mine-sump waters is 1517 mg/L. The Relative Percent Difference (RPD) between observed seep water and modeled concentration is 4%, indicating a very close match of modeled to observed sulfate concentration. As the water rises from the 5000 Level (Year 3.6) to the 3050 Level (Year 10), the median filling level is the 3950 Level. The end-member Model SO_4 for Year 10 is 497 mg/L, and the incremental mass is (497 + ((3950/8150)*(836) mg/L), or 902 for the incremental flow from year 3.6 to Year 10. The mine pool at Year 3.6 had an estimated SO4 concentration of 1,436 mg/L, and the incremental flow is 57.5% of the total water between Year 0 and Year 10 (see Attachments 1 and 2). Therefore, the modeled SO_4 for the well-mixed system at Year 10 (water level at the 3050 Level) is 1,129 mg/L.

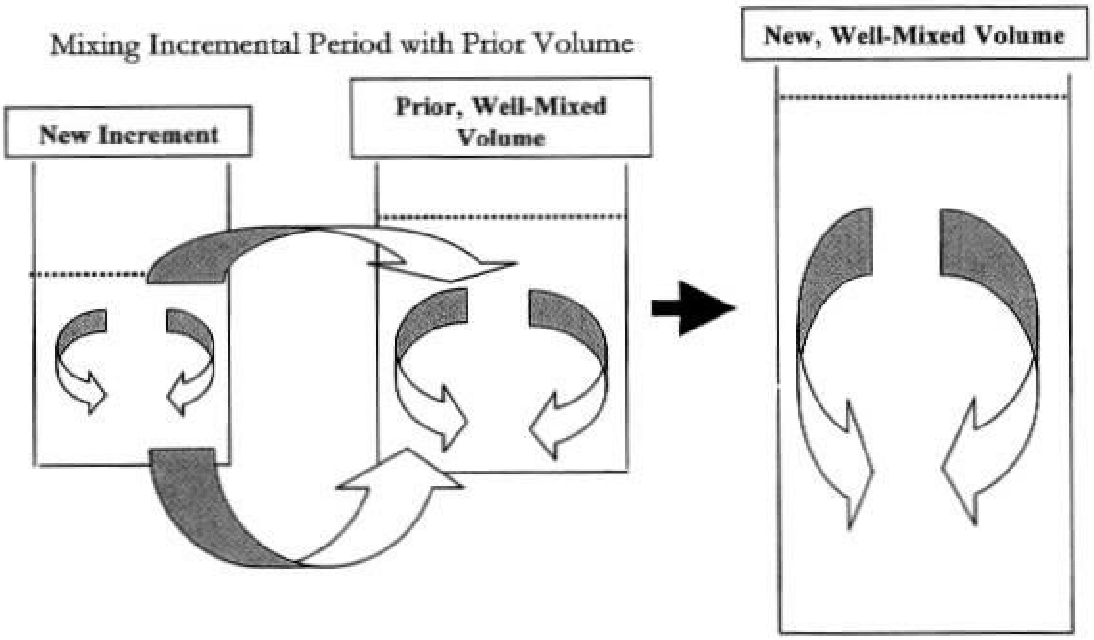
Figure 2 Conceptual Model of Mixing Cell Model for Re-filling of Underground Workings

A. Mixing in an Incremental Period of Filling:



There is a flow proportion and chemistry for each of the 5 flows and an incremental mass for wall-rock leaching. Initial model is a mass balance, adjusted (if necessary) for thermodynamic controls.

B. Mixing Incremental Period with Prior Volume



Assume that fluid volume is conserved in mixing. Again test mass-balance for equilibrium after mixing.

The initial mixing model is a straightforward mass-balance using the proportions of flow and concentrations of the model inputs. For example, consider SO_4 at Year 1. The end-member mixing-model includes:

Water Type	Flow Proportion	SO_4 (mg/L)
Ca-SO_4	0.489	120
Mg-SO_4	0.187	3,146
Na-HCO_3	0.308	40
Shaft 5	0.016	1,372

The flow-weighted average SO_4 concentration using the three end-member waters would be 681 mg/L. (The equivalent flow-weighted average is used for each chemical parameter.) As shown above, to this one needs to add the estimated additional SO_4 dissolved as water flows along regional flow paths and local infiltration from surface to depth, approximately 774 mg/L, for a total modeled estimate sulfate concentration of 1455 mg/L.

2.2.3 Selection of Periods for Evaluation in the Underground Workings

The methods used in this analysis could be applied to any period between the initiation of pumping and 27-years later when the water level reaches the base of the open pit. In terms of planning and decision-making, there is no good reason to do it for each year. We selected the 5 intervals shown in Table 1 for simple reasons:

- Year 1: An obvious choice in order to understand how water quality would evolve in the first year of refilling;
- Year 3.6: It will take 3.6 years for water level to reach the base of the Yates Shaft at the 5000 Level. The Yates Shaft is the principal access to the deep part of the mine and the locus of major, subsurface infrastructure.
- Years 10 and 20: Arbitrary time intervals in the interval over which most of the re-filling will occur.
- Year 27: The time at which the flow model predicts water levels to reach the base of the Open Cut at the 800 Level.

2.3 DATA FOR FLOW AND WATER QUALITY

Zhan (2002) developed a water-balance model for re-filling of the underground workings. The final water-balance model for re-filling, used in this hydrogeochemical evaluation, is presented in Attachment 1 and summarized in Figure 3.

Barrick/HMC undertook a special campaign of underground water sampling during 2001-2003. The special sampling campaign has collected water from all points at which there is both access and sufficient flow to obtain a sample (T. Duex, HMC, personal communication, 2003). We have used all data provided to us by the mine (Table 2 and Attachment 2). In addition to data, Attachment 2 presents sampling information, photographs, and other relevant information.

2.4 RESULTS FOR THE UNDERGOUND WORKINGS

Attachments 1 and 3 provide the complete set of spreadsheet models for re-filling (Attachment 1) and mine-pool (Attachment 3) chemistry. The chemical data used in Attachment 3 are taken from the analytical data presented by HMC in Attachment 2. Attachment 4 is the output from the mass-transfer geochemical model for year 27 (800 Level). Attachment 5 presents results for the sensitivity study of arbitrarily substituting Mg-SO_4 water fro Ca-SO_4 water across a very wide range of alternatives.

Speciation modeling and subsequent equilibrium thermodynamic modeling of the Year 27 results shows that, when the partial pressure of CO_2 is allowed to equilibrate with atmosphere, the waters will precipitate a small volume of calcite, $CaCO_3$ (Attachment 4)[2]. The equilibrium pH for the mass-balanced estimate at the 800 Level would be pH 8.7 if the system is closed to CO_2 (e.g., during refilling), or pH 8.1 if open to CO_2 (e.g., if there is enough air-flow between the 800 level and the atmosphere of an unfilled Open Cut). For comparison, the mass-balance model produces an estimated pH of 8.0, and the observed pH of the February 2003 sample from the 800 North Raise was 8.6. The total buffer capacity (i.e., accounting for both dissolved carbonate and solid calcite) is indifferent (see also Stumm and Morgan, 1996). The concentrations of other species are sufficiently low in the mass-balance models and the pH sufficiently well buffered that there is no good reason to try to adjust calculated water chemistry for equilibrium precipitation. Therefore, the estimated concentrations from these simple models are expected to overestimate future, observed concentrations for constituents such as Mn, which might precipitate over time in an oxidizing environment as birnessite or another Mn-oxide or hydroxide (see also Attachment 4). In addition, the model does not account for biogeochemical transformations that could be expected to deplete the waters of dissolved NO_3.

The relative humidity in a flooding underground mine without ventilation is very high, and evaporation consequently low. For the underground mine, we have ignored the effects of evaporation. The effects of evaporation on both concentration of dissolved solids and alkalinity (thence pH) are evaluated explicitly for the Open Cut, where evaporation is expected to be a much more significant factor than in the underground.

Figure 3 (from Zhan, 2002) summarizes the expected re-filling of the Homestake Mine.

Table 4a and Figure 4a summarize the expected concentrations of major species in the underground pool at Years 1 (6950 Level), 3.6 (5000 Level), 10 (3050 Level), 20 (1100 Level), and 27 (800 Level, base of the Open Cut). Table 4a and Figure 4b summarize the expected chemistry of minor and trace metal species at the same times.

Note that some trace metals and other constituents are expected to be below limits of detection at these time intervals (Table 5). These species (Al, Cd, Cr, Hg, Pb, Se, Ag, Zn, and wad-CN) are not included in the summary figures because all modeled values for these species are below the analytical detection limits.

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[2] All geochemical modeling in this study was done by Geochimica, Inc. using the path-seeking, thermodynamic model, React from the Geochemist's Workbench suite of models (Bethke, 1996, 2002).

Based on data that can be collected in the mine today, it is possible to check the reasonableness of the modeled results for two time periods of the re-filling. Predictions of the first-year's re-filling can be checked against current data for the main lower-mine sumps, which are integrating the full flow, from various water sources. Table 5 compares the predicted chemistry at Year 1 with (a) a single, specific analysis of mine sump water (May, 2002 data for the Yates Shaft Sump) and (b) the median data for all "Mine Water" samples.

During periods of high flow, water accumulates in the workings of the 800 Level faster than it can drain. Table 6 compares the predicted chemistry for Year 27 (800 Level, base of Open Cut) with data for a February, 2003 sample collected from the 800 North Caledonia vertical raise. The terminus of the raise is immediately below the open cut.

2.5 DISCUSSION OF THE UNDERGOUND CHEMISTRY

2.5.1 Basic Issues in Geochemical Modeling and Selection of Modeling Approach

Although it has become common for environmental evaluations - including evaluations for regulatory purposes - to use models, there remain concerns, both practical (e.g., Zhu and Anderson, 2002) and theoretical (Oreskes et al., 1994; Bethke, 1996), about what models are and how best to use them. The most focused discussion of geochemical modeling applied specifically to mining environments is a recent contribution from Alpers and Nordstrom (1999); the authors are senior scientists with the Water Resources Division of the U.S. Geological Survey, specializing in the environmental geochemistry of mineral deposits. Alpers and Nordstsrom present a very useful definition for the basic term "model" in geochemistry:

> "We adopt the following definition for a model: 'a **testable** idea, hypothesis, theory or combination of theories that provides … insight or a new interpretation of an old problem.' A chemical model is a theoretical construct that permits the calculation of physicochemical processes and properties of substances…; a geochemical model is a chemical model developed for geologic systems." (Alpers and Nordstrom, 1999, p. 289. Emphasis in original).

A supplementary notion that also may be useful comes from a paper prepared by staff for the Division of Waste Management, U.S. Nuclear Regulatory Commission:

> "… [A] model should be an analog of the real system and should reproduce the studied behavior of the system to the required level of accuracy and precision when its input parameters and conditions are specified." (Emphasis in original; Logsdon, 1984)

Alpers and Nordstrom provide detailed discussions of different general kinds of geochemical modeling approaches – statistical, mass-balance, speciation, and both inverse and forward modeling using thermodynamic approaches - and review specifics of several computer-based programs that implement numerical models. This report, in common with many and perhaps most modern environmental studies, includes aspects and provides results of statistical, mass-balance, speciation and forward thermodynamic modeling. Alpers and Nordstrom describe "forward" modeling thusly:

> "Forward models generally describe geochemical and hydrogeologic systems with sets of initial and boundary conditions and march forward either with respect to time or reaction progress, resulting in a predicted future state." (Alpers and Nordstrom, 1999, p. 304).

The general approach of this study has been to use the results of a mass-balance model for water flow to the underground workings (Zhan, 2002, e.g., Figure 3) together with a mixing-cell model for geochemistry (Section 2.2.2 above). Taken together, these modeling assumptions define the analog with the subsurface system. Statistics were used (in a simple fashion for the small data sets) to define the chemical inputs. The underlying hypothesis is that the chemistry of subsurface waters can be adequately described by the mixing of solutions, supplemented by an incremental mass flux that derives from reaction between solutions and wall rock or backfill (E.g., Figure 2). This is a testable hypothesis of future geochemical conditions and processes if there is, as HMC plans to do, on-going monitoring of water chemistry during the re-filling process, thus meeting the Alpers and Nordstrom definition. The structure of the calculation scheme reproduces the expected behavior of the system when parametric results for flow and chemistry are used as inputs, this meeting part of the Logsdon definition. Section 2.5.7 below argues that the accuracy and precision are adequate for the purposes of this study.

The alternative to this approach would be a fully coupled flow and reactive-transport model. Such models, which are at the frontier of geochemical research today, require detailed description of initial conditions throughout the modeling domain and boundary conditions that control the flux of fluids (e.g., Blowes et al., 2000). Zhan (2002) discusses the reasons for not attempting the hydrogeologic portion of such a coupling. Blowes et al. (2000) describe the data needs for the geochemical aspects of such a coupled model. With respect to the current understanding of the Homestake underground mine, such a modeling approach cannot be implemented. In particular, we do not know the secondary mineralogy of the backfilled tailing and wall rock or the flow paths for water through the backfill, much less the details of the spatial distribution of secondary minerals with respect to water flow. Without knowledge of both the primary and secondary mineralogy, it is not possible to develop the underlying geochemical model (equilibrium and/or kinetic), and without being able to match spatial distributions of flow and mineralogy, the very coupling that makes the reactive-transport model theoretically appealing is lost. As emphasized by all experienced modelers, such earth-science models are inevitably non-unique (e.g., Alpers and Nortdstrom, 1999, Bethke, 1996; Zhu and Anderson, 2000). This is true also of the simpler model we have developed. However, when the basic elements of the model are unavailable, all choices of values would be arbitrary - if not also capricious, and the ensuing results could not be justified at all.

Therefore, we have elected to model the geochemistry use a relatively simple approach, one that is consistent with the level of information available to describe the flow and geochemistry. However, whatever the apparent simplicity of the approach, we emphasize that this model is testable. In this case, as shown below, the model is testable not only through future data, but also – to a limited, but helpful degree – using data that actually already are available (Table 5 and 6, above, and Section 2.5.4 below). In addition, we have completed sensitivity studies that examine aspects of uncertainty about leachable As and the possibility that Ca-SO_4 waters will evolve over time into Mg-SO_4 waters (Section 2.5.5 below). In that section on uncertainty we also discuss the potential impacts in water quality (both positive and negative) of changes in the redox conditions of the subsurface after flooding. Finally, this report puts forward a context for decision-making into which this, or any other model, can be placed (Section 2.5.6).

2.5.2 General Chemistry in the Underground Workings

The modeled results and trends for major chemical parameters follow one's intuition based on trends in relative proportions of flow. There are no identified flows of acidic water, so there are no significant acid-base reactions. The dissolved Fe and Al concentrations in all flows are low to non-detectible, so there are no issues of mineral acidity. Because the redox-sensitive species (As, Cu, Fe, Mn, NO_3) all are low, potential changes in chemistry due to variations in redox conditions during filling also are minor or negligible[3]. Consequently, the mass-balance calculations presented here provide a good, first approximation of expected chemistry from mixing different proportions of waters. The major outcomes include:

- The pH of the mine waters is expected to remain near 8 throughout the refilling from the 8150 level to the base of the Open Cut. During the slow filling of the pool in the Open Cut, it is likely that the pH will rise, at least slightly, as usually is observed in natural, terminal lakes with high alkalinity as the water exchanges CO_2 with atmosphere. Examples of such lakes in the U.S. include Great Salt Lake, UT, Walker Lake, NV, and Mono Lake, CA. The central portion of the Green River Basin includes the famous, commercial soda-ash deposits that are the geologic record of such processes at very large scale.

- Alkalinity falls slightly over time because the most alkaline waters in the system are the deep, Na-HCO_3 groundwater flows (median: 650 mg $CaCO_3$ eq/L), which become volumetrically insignificant with time. However, even at Filling Year 27, the model estimates that water at the 800 level immediately below the Open Cut still will have alkalinity in excess of 200 mg $CaCO_3$/L. This high bicarbonate alkalinity buffers the system pH to the slightly alkaline range.

- TDS, Sulfate, Magnesium, and Sodium concentrations fall over time during the refilling process because (a) Na-HCO_3 water characteristic of the deepest parts of the groundwater flow system and (b) high –TDS, Mg-SO_4 water at intermediate depths become minor contributors to incremental flows. In addition, incremental mass-loading from reactions with wall-rock decreases as both the groundwater flows decrease and the exposure of oxidized walls decreases during filling. As usually is the

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[3] In terms of equilibrium chemistry, sulfur also is a redox-sensitive species. However both laboratory and field studies show that SO_4 will remain the principal, though metastable, species of dissolved sulfur unless sulfate-reducing bacteria were abundant. Although we expect the deep part of the flooded workings to become anoxic, it is not clear that there is sufficient organic matter present to allow the system to actually become and remain sulfidic. Even if this did happen, the result would be to reduce the modeled estimates of sulfate concentration and probably also to provide additional controls on solubility of metals, another potential outcome that would be more favorable than predicted here.

case in mine waters, on a mass-basis, sulfate is a major proportion of the TDS in several of the mine-water flows, notable the Mg-SO_4 groundwater and the Shaft 5 and mine-sump samples. In the modeled, mixed waters SO_4 is about 70% of the total dissolved solids. Over the modeled period, expected values for sulfate in solution fall from slightly less than 1,500 mg/L to near 1,000 mg/L in simulations of well-mixed waters.

- Calcium, Potassium, and Chloride concentrations remain nearly constant or decline slightly over time, especially after the water levels rise above the 5000 Level. There is relatively little variance between different water types for these major ions, although K is somewhat higher in the Na-HCO_3 waters than in other water types.

2.5.3 Minor and Trace Constituents in the Underground Workings

Because the pH is near 8 for all input waters, there are only very low concentrations of dissolved metals at any time in the evolution of the system. Because the pH is well buffered by the aqueous alkalinity (which in turn is controlled by the large inventory of solid carbonate minerals in the wall-rock system), the trend of low dissolved metals is very unlikely to change over time.

- Manganese (Mn) is the only metal that is an apparent exception to this, as shown on Figure 4b. However, close examination of the data in Table 4b and that figure show that the maximum predicted concentration of Mn is only 0.38 mg/L for well-mixed systems, expected around Filling Year 10. By Year 27,the incremental-flow concentration is Mn is modeled to be down to 0.18 mg/L, and the February 2003 datum from the 800 North Caledonia raise shows 0.052 mg/L Mn. The slightly elevated persistent of Mn in these waters, compared to Fe, which is typically not detected as a dissolved species, is consistent with the Eh-pH characteristics of Mn (e.g., Hem, 1985).

- Total cyanide (but not weak-acid-dissociable cyanide) and nitrate are the only apparently anomalous minor species in the waters. The data in Tables 2 and 3 clearly show that total cyanide is associated with the low flows from Shaft 5, which enter the mine workings only between the 7700Level and the 2000 level. Median concentration for total cyanide in Shaft 5 water is 3.85 mg/L; wad-cyanide concentration is only 0.28 mg/L. The dissolved Fe concentration in Shaft 5 water is the highest of any inflow, by about an order of magnitude or more, 0.59 mg/L. This suggests that most of the total cyanide value is complexed with Fe and will remain biologically unavailable (because exposure to ultraviolet light, the only plausible mechanism for transforming Fe-cyanides to wad- or free-cyanide forms, will not occur for the underground waters). The low concentrations of dissolved Cu (0.02 mg/L) and Zn (0.35 mg/L) are consistent with the observed wad-cyanide concentration, indicating that truly "free" cyanide (HCN or $CN^-_{(aq)}$) is not an issue. Based on the location, we consider that total cyanide represents small infiltration flows from the Grizzly Gulch tailing impoundment captured by drainage to Shaft 5.

There is no other plausible source, and the Fe-cyanide signature of the dissolved constituent is consistent with tailing seepage, too.

The Shaft 5 flow is estimated at a constant rate of 10 gpm, compared to cumulative flows of 700 gpm when water is at the 8150 Level and 250 gpm when water level is near the 2000 level. The constant Shaft 5 flow, over a filling period in which the rest of the groundwater flow component is declining, implies that the Shaft 5 proportion to incremental mixed waters rises as water levels rise to the 2000 Level. As water levels rise above the 2000 level, there is no longer a pathway from Shaft 5 waters to the incremental mixing zones, so the contribution of shaft 5 drops to 0 above that level. The result (Table 4b, Figure 4b) is total CN that rises to Filling Year 20, then declines sharply. Incremental flows in Filling Year 27 have a modeled total cyanide concentration lower than the analytical detection limit (< 0.010 mg/L), and measured total cyanide values in the 800 North Caledonia Raise also are < 0.010 mg/L. It is very likely that there will be no detectible total cyanide (and certainly no wad-Cyanide) when water levels reach the base of the Open Cut.

- Nitrate concentrations are somewhat elevated in the deep-mine sumps (1.76 mg/L) and the Shaft 5 flows (3.80 mg/L) compared to other waters. These values do not exceed water-quality criteria. Slight elevations of nitrate in waters contacting mined rock usually are due to dissolution of minute quantities of residual blasting compounds (e.g., ammonium nitrate); in gold tailing or heap-leach systems, nitrate may be an oxidation product of cyanide (Logsdon et al., 1999). The modeled values (maximum < 2 mg/L) do not rise to concentrations that impair beneficial uses of water. The low values for nitrate seen in the 800 North Caledonia Raise sample in February 2003 indicates that NO_3 will not persist in this system.

2.5.4 Verification of Modeled Results Against Field Observations

At this time, the Homestake Mine is de-watered to the 8150 Level. All computer simulations of the re-flooding of the workings must, necessarily, relate to future conditions. Therefore, verification, in the sense that the word is used for modeling situations such as groundwater flow systems is not strictly possible. However, there are two sets of water-quality data available today that are relevant to two of the time periods modeled in this study. Firstly, we make predictions for the first year of refilling, during which Dr. Zhan's flow model predicts flooding will raise the water level to approximately the 6950 Level. The zone between the 8150 Level and the 6950 Level is the elevation zone serviced by most of the deep-mine sumps. We have used water chemistry from these sumps to evaluate the additional mass gained (or lost for some parameters like alkalinity) by water flows from interactions with the wall-rock system. Thus it is appropriate to compare the predicted water chemistry for water flowing to the mine workings as it rises from 8150 to 6950 Levels with the observed "mine water" samples. This comparison is documented in Table 5 for two sets of mine-water chemistry. Table 5 first compares the Year 1 modeled results to one specific deep-mine sump sample, from the Ross Shaft. The second comparison is for Year 1 predictions against the median value for all deep-mine sump waters.

When judged against the median of the deep mine waters, the Filling Year 1 model results have RPD[4] values less than 10% for all parameters except CN-total. The RPD for CN-total is 16.9%, but the absolute difference is only 0.009 mg/L. When measured against a single mine-water sample such as the Ross Shaft sump, the RPD values are somewhat higher for some parameters, but the absolute differences remain very low. Assuming that the absolute accuracy of each measured values is +/- 10% (a generous analytical assumption for trace parameters), values with RPD < 20% can be considered analytically equivalent. By this measure only As (RPD 32%) and Mn (RPD (77%) are distinguishable. However, the absolute difference for As is only 0.009 mg/L (Ross Shaft observed 0.032 mg/L vs. modeled 0.023 mg/L) and the absolute difference for Mn is 0.12 mg/L (Ross 0.095 mg/L vs modeled 0.215 mg/L). The other available quality checks, ion balance and modeled versus calculated TDS show that the modeled results are internally consistent.

Table 6 provides data for the second comparison of modeled to measured values. During infiltration of high-flow events (snow melt or high intensity storms), shallow water accumulates at the base of the Open Cut and in and near the 800 Level before infiltrating deeper into the mine. HMC recently (May 2002 and February 2003) sampled flows in the 800-Level Vertical Shaft, which collects water from immediately below the Open Cut[5]. These waters can be seen as samples that are related to the predicted water quality when water levels have risen to the 800 Level. The comparison is provided in Table 6 for all measured parameters for the May 2002 sampling event only. The two sampling events have very similar data (Table 2), with the principal difference being that the Mn value in the February sample, 0.35 mg/L) is greater; using the February sample value would decrease the apparent difference between modeled and observed value for Mn.

The parameter match (in terms of RPD) is < 20% for the following parameters:

- pH, TDS, Alkalinity, CN-tot, CN-wad, F, Cl, SO_4, Al, Cd, Pb, Hg, Se, Ag and Zn

Of the other parameters, T is not relevant, as the 800 Level sample is for a one-time (winter) sample that is expected to have a lower temperature than an "average" annual value would show. For each of the other parameters, the modeled value is higher than the observed value, indicating that the model is conservative with respect to decision-making. For all the remaining parameters, the absolute differences are low, especially with respect to values that are significant to potential water use:

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[4] RPD: relative percent difference: (Value 1 – Value 2)/[1/2 * (Value 1 + Value 2)]

[5] In earlier drafts of this study, the May 2002 sample was incorrectly identified in sampling records as "North Caledonia vertical raise". An audit of this study by HMC has identified the error and verified that the two samples are for the same location (T. Duex, HMC, personal communication, 2003).

Parameter	**mg/L**		
	Model	**800 Level Vertical Shaft**	**Difference (1)**
Nitrate	0.97	0.06	0.91
Na	95	25	70
Ca	138	195	57
As	0.013	<0.005	0.010
Ba	0.05	0.03	0.02
Cr	<0.001	0.002	0.002
Cu	0.010	<0.005	0.008
Mn	0.30	0.05	0.25
K	19	8	11

(1) When one value is < lod, the difference is calculated assuming that value is ½ lod

It is reasonable to expect that the uncertainties in modeling would propagate as the water levels rise, if only because of the assumed mixing processes. Additionally, the assumption that surface water inflow has the same chemistry as shallow Ca-SO$_4$ groundwater becomes increasingly important as one approaches the ground surface and this becomes a larger proportion of the total flow. Finally, the "test" is to a single-valued estimator, one specific water sample collected on a given winter's day, whereas the modeled values assume "average annual" flows and chemical conditions. Given these issues in modeling from small data sets, the match between thee modeled and observed values for the 800 Level are considered very close.

2.5.5 Uncertainties in the Model and Results

Outside reviewers for the State of South Dakota have expressed concerns about modeling uncertainty arising from three principal sources:

- Progressive inundation of backfilled tailing as water level rises. State reviewers identified the possible mobility of As released during long-term oxidation of sulfides as a special concern.
- Potential for geochemical evolution of the shallow Ca-SO4 water to a signature much more like the Mg-SO4 water currently seen deeper in the system.
- Effects on geochemical stability as the redox conditions of the mine change from oxic (under the fully drained state) to anoxic or even sulfidic after inundation.

This section of the report addresses these data and modeling uncertainties in at least a preliminary fashion.

Sensitivity of Model to Arsenic Release

The base-case model described above assumed that the representative value for As in the mine sumps was the median value, 0.024 mg/L dissolved As. Even using this assumption, more than half the As in the mine sumps must be due to releases from wall rock and backfill, because the apparent mass-balance value would be 0.011 mg/L (Attachment 3).

It is not possible to systematically sample and test the leachable geochemistry of the backfilled tailing. Most of the mass, the placement of which occurred over many decades, is physically inaccessible (largely for reasons of safety). Statistically representative sampling of the huge volume in the subsurface from surface is technically infeasible.

To test the sensitivity of overall model results to the amount of As released from the solids, we modified the base-case model to assume that the representative value were 0.060 mg/L, at the extreme upper end of observed values (T. Duex, HMC, personal communication, 2003). Two samples of seepage from backfilled stopes are available in the database (Attachments 2 and 3): 0.015 mg/L and 0.291 mg/L. The apparent range from ca. 0.01 mg/L to ca 0.10 mg/L is also observed in samples from the pore water of Grizzly Gulch tailing and many samples from the Whitewood Creek system (T. Duex, HMC, personal communication, 2003). Given that the hydraulic conductivity of compacted tailing is usually quite low, it is reasonable that the total As load in the mine sumps (and in future mine waters) will not represent 100% flow derived from leaching of backfilled tailing. Thus a sump-water value of 0.060, while well above the mine-sump median, is perhaps a fair estimate of the maximum As that might be observed if a flow-weighted sample were actually available.

This factor of nearly 3 increase in leachable input was then carried through the rest of the modeling process and the resulting changes in As concentration calculated. The results are summarized in Table 5 and Figure 5. The sensitivity study shows that whereas the early-time results are sensitive to the assumed As input from leaching, the late-time results are very insensitive. By the time the water level in the underground workings approaches the base of the Open Cut, the incremental leaching of backfill and wall rock has declined to the point where the mass flux from this source no longer is a major contributor to the overall water chemistry. In part this is a consequence of the specific manner in which we have modeled the incremental mass flux, but the overall result is quite surely correct: the total surface area of exposed, oxidized rock (including backfill) must decrease as the water level progressively inundates the system. The maximum exposure, and therefore the maximum proportional contribution, occurs when re-flooding begins, and that declines to zero as the water level reaches it's ultimate equilibrium level.

This sort of sensitivity study could be performed using any arbitrary assumption for starting As concentration. The absolute values would change, but the general shape of the curve for As concentration as a function of rising water level would be similar. There is no technical basis for choosing an initial value that is greater than the observed maximum, so results that differ significantly from those evaluated by this sensitivity study are not expected.

Sensitivity of Model to Increasing Proportions of Mg-SO_4 Water Relative to Ca-SO_4 Water

The base-case model of Section 2 supposes that the three major water types are characteristic of groundwaters arising due to some, currently unspecified geologic controls, and that such flows would persist in space, at least for the next 27 years while water levels rise to the base of the Open Cut.

Although 27 years is not a very long time for major changes in hydrogeochemistry (the current mine has evolved over 125 years), we do not have long-term water-quality data of high quality to show the time-series evolution of underground waters. For example, one might hypothesize that the observed Mg-SO_4 waters in the zone from approximately 3000 Level to 5000 Level represent the long-term evolution of shallow, Ca-SO_4 waters as (a) progressive oxidation of sulfides releases additional SO_4, and (b) Mg concentration increases due to reactions between incipient acidity and Mg-bearing carbonates. Coherent geochemical reactions can be written to show the inherent plausibility of this idea.

The principal differences that may be significant for groundwater quality between the Mg-SO_4 and the Ca-SO_4 waters are the higher TDS (due largely to SO_4) and As of the Mg-SO_4 waters. To evaluate these and other water quality changes, we elected to use a classical sensitivity analysis: arbitrary increases in the proportion if Mg-SO_4 (and consequent decreases in proportion of Cas-SO_4), leaving all other modeling assumptions constant. We prepared 3 alternative models (called Models 05a, 05b and 05c, to distinguish them from earlier evolutions of the basic mass-balance model). The incremental changes were entirely arbitrary and do not represent any mechanistic geochemical scenarios. In Model 5a, we increased the proportion of Mg-SO_4 by 10% of total flow and decreased the Ca-SO_4 proportion by 10% at all modeling steps. In Models 5b and 5c the changes were 25% and 40%, respectively, at each step. In relative terms, these are huge changes in proportions of flows, in fact introducing significant flows of Mg-SO_4 throughout the vertical extent of the underground workings, although there is no field evidence for this after 100 years of mining. The changes to flow in the four models of this sensitivity study are summarized in Figure 6. Figures 7 (SO_4) and 8 (As) illustrate the outcomes. These and additional results (TDS, Mg, CN-total, and Mn) are included in Attachment 5.

As expected, there are discernible changes in SO_4 and As concentrations, and the impacts increase over time. The relative change over time represents the increasingly harsh assumption of substituting Mg-SO_4 for Ca-SO_4, which is the dominant flow type for waters above the 3000 Level in the base-case model. Although the modeled differences are discernible, the absolute values for the cases do not range into concentrations that would be problematic for water quality. I particular, note that the concentration of As never rises above 0.05 mg/L. In fact, the changes of 25% and 40% (representing total swings of 50% and 80%) are not very realistic for a time period of only 27 years, and it is likely in our view that if this substitution mechanism occurs at all, the change would be close to the 10% change, if not less. Note that the proposed mechanism depends on continuing oxidation of sulfides, which would not occur at any appreciable rate once zones are progressively inundated, so the risk of this process decreases with time.

We conclude from this sensitivity study that evolution of Ca-SO_4 water to Mg-SO_4 water, if it happens at any appreciable rate, during the 27 years it is expected to take water levels to reach the 800 Level would have a small to negligible effect on groundwater quality within the inundated workings.

Geochemical Impacts of Redox Changes

Reviewers have suggested that the generation of reducing conditions in the subsurface after flooding could adversely affect groundwater quality. At this time, we address this concern only by discussion, as the quantification of any effects would require assumptions (such as redox equilibrium) that cannot be justified quantitatively.

The effects of reducing conditions in the subsurface are not simple to predict. On the one hand, ferric minerals (e.g., ferric hydroxides, nominally $Fe(OH)_3$) might, depending on the actual redox state and pH, become undersaturated and begin to dissolve as some (unknown) kinetically-controlled rate. This would cause the concentration of ferrous ion to increase. Dissolved Mn also might increase for the same underlying reason. Metals and metalloids that are adsorbed to these iron and manganese minerals would be desorbed if this process occurred.

On the other hand, as the redox state of groundwater falls, pyrite, pyrrhotite and other sulfides would become more stable, and the risk of oxidation and subsequent acidification would fall to negligible levels. Note, too, that if Fe(II) were the stable iron valence, then hydrolysis of ferric ion, the principal source of excess H^+ during ARD, would not occur. Additionally, the risk of pyrite oxidation by ferric ion would be negligible if Fe(III) were negligible. Under these conditions, primary As (i.e., arsenic in arsenopyrite or arsenian pyrites, would not be released, nor would other trace metals that are associated with sulfides (e.g., Cd, Cu, Hg, Pb, Zn). Finally, if additional sulfide oxidation is inhibited, the existing alkalinity of the groundwaters would be preserved, buffering the solutions in a decidedly alkaline range at which the acidophilic bacteria that are the biota primarily implicated in catalysis of iron oxidation would be severely disfavored ecologically, further reducing risks of long-term sulfide oxidation and metals release.

At this time, it is not possible to make meaningful, quantitative estimates of the effects of these competing issues in redox geochemistry. Long-term monitoring will reveal the actual outcome, at which point detailed geochemical analysis may help understand the relative influences of different processes, but forward-looking predictions are not possible.

2.5.6 An Approach to Evaluating Water-Chemistry Models: "What Counts as an Answer?"

The overall problem addressed by this portion of the study can be summarized in a simple statement such as:

> "What will be the chemistry of water in the underground workings of
> the Homestake Mine as the working progressively flood to the base
> of the Open Cut?"

In order to answer this (or any) question in a way that is satisfactory to all parties to the question, there must be some agreement as to *what counts as an answer*. This is not as simple a matter as it may seem in general (Belnap and Steel, 1976), nor for the specific matters of mine-waste geochemistry (Logsdon and Miller, 2000). However, if all parties with standing in subsequent evaluations cannot agree on criteria that would be acceptable as a basis for a evaluating the mine-water chemistry to support subsequent decisions, moving forward on substantive plans will be difficult if not impossible.

In dealing with the analytical chemistry of geochemical samples, there are well-established criteria for determining whether results are sufficient for a given purpose. Accuracy and precision are well-defined notions in analytical chemistry, and it is normal to establish decision-making criteria for chemical analyses, for example the Data Quality Objectives process described in SW-846 for CERCLA and RCRA projects.

In terms of modeling into the future – especially using limited databases - to estimate something like the water-quality conditions in an underground mine after pumping ends, the situation is not so straightforward. It is clear that the actual underground chemistry will depend on at least three principal matters:

- The proportional flows of different chemical types of waters;
- The chemistry of each of those water types;
- Chemical reactions that may occur during or after mixing and between the water and the solids that bound the mixing volume.

All three of these fundamental factors may vary over time or possibly range in space, or both. It now is generally agreed in groundwater and geochemical modeling that unique solutions to modeling problems are rare, if not intrinsically impossible (e.g., Oreskes et al, 1994; Bethke, 1996; Nordstrom and Alpers, 1999). How then, is one to deal with modeling estimates, such as these for a (currently) hypothetical re-flooding of the Homestake Mine? What counts as an answer, for purposes of evaluating technical conditions, to the question of future water chemistry in a flooded Homestake Mine?

To help address this absolutely fundamental question, we pose the following assertion:

One can evaluate the environmental risk to ground water, and also evaluate management alternatives, provided one can accurately place water-quality projections in a simple evaluation matrix such as that shown in Table 7:

Table 7 Example Evaluation Matrix for Water-Quality

PH	**Alkalinity**	**Acidity**	**TDS (SO_4)**	**Metals [$Me_{i,j,k\ldots}$], where $Me_{i,j,k}\ldots$ are specific, identified metals or metalloids**
6.5 < pH < 9	> 100	Nil	10 – 500 (10-250)	[Mei,j,k…] on order of 0.001 – 0.1 mg/L
4.5 – 6.5	25- 100	Nil – 25	500 – 3000 (250 – 2000)	[Mei,j,k…] on order of 1 mg/L
3 – 4.5	Nil – 25	25 – 100	3000 – 7500 (2000 – 5000)	[Mei,j,k…] on order of 10 mg/L
< 3	Nil	> 100	> 7500 (> 5000)	[Mei,j,k…] on order of 100 mg/L or greater

The specific structure and classes of values within cells in the matrix may differ from site to site, and perhaps according to specific management or regulatory issues, however the notion of quantifiable, water-quality classes to evaluate significance is very general. Provided one can accurately place future water quality into classes such as these, both mine managers and regulators would have very clear ideas about how to consider the water-quality conditions. In addition, managers would have clear direction to provide engineering with respect to water-quality management. Great precision within the classes is not important for basic technical evaluation: whether pH were 3.2 or 3.9, or 6.8 or 7.2 would make little difference. But the difference between waters with pH 3.6 and pH 7.0 is fundamental.

Given the uncertainties in data, conceptual models, or coupled issues like groundwater flow or future climates, great precision in geochemical modeling of dynamic flow systems is simply not predictable. However, the basic controls on aqueous chemistry (general flow proportions; redox conditions and acid-base relationships) usually can be defined sufficiently that one can estimate general chemistry into classes such as those shown in Table 7.

For the underground flows at Homestake Mine, the matrix shown in table 7 can be prepared as shown in Table 8:

Table 8 Evaluation Matrix for Water-Quality – Homestake Mine to Base of Open Cut (mg/L. except pH in su and Alkalinity/Acidity in mg $CaCO_3$ eq/L)

Model Filling Year (Mine Level)	**pH**	**Alkalinity**	**Acidity**	**TDS (SO_4)**	**Metals [$Me_{i,j,k...}$], where $Me_{i,j,k...}$ are specific, identified metals or metalloids**
Year 1 ***(6950 Level)***	7.9	311	Nil	2368 (1458)	[i] ~ 0.01 mg/L: ***CN-t; As, Cu, Fe*** [j] ~ 0.1 mg/L: ***Mn***
Year 3.6 ***(5000 Level)***	8.0	260	Nil	2364 (1473)	[i] ~ 0.01 mg/L: ***CN-t; As, Cu, Fe*** [j] ~ 0.1 mg/L: ***Mn***
Year 10 ***(3050 Level)***	8.0	220	Nil	2264 (1424)	[i] ~ 0.01 mg/L: ***As, Cu, Fe*** [j] ~ 0.1 mg/L: ***CN-t; Mn***
Year 20 ***(1100 Level)***	8.0	212	Nil	1884 (1151)	[i] ~ 0.01 mg/L: ***As, Cu, Fe*** [j] ~ 0.1 mg/L: ***CN-t; Mn***
Year 27 ***(800 Level)***	8.0	211	Nil	1717 (1030)	[i] ~ 0.01 mg/L: ***CN-t; As, Cu, Fe*** [j] ~ 0.1 mg/L: ***Mn***

2.6 CONCLUSIONS AND RECOMMENDATIONS FOR UNDERGROUND WORKINGS

This study has combined the site hydrogeologic model for re-filling of the underground workings with site-specific data on water chemistry in different parts of the mine to develop a hydrogeochemical model of the chemical evolution of the mine waters during refilling from the 8150 Level to the 800 Level at the base of the Open Cut. Subsequent modeling with trace the evolution of water chemistry while the Open Cut fills to the steady-state elevation at the 300 Level.

The current model generates estimates of water chemistry in re-flooded portions of the mine for 5 intervals:

- Filling Year 1 (6950 Level, -1719 ft amsl)
- Filling Year 3.6 (5000 Level, +231 ft amsl)
- Filling Year 10 (3050 Level, + 2181 ft amsl)
- Filling Year 20 (110 Level, +4131 ft amsl)

- Filling Year 27 (800 Level, +4431 ft amsl – base of Open Cut)

The modeled water-quality estimates have been tested against site-specific monitoring data for the Filling Years 1 and 27. The modeled values match the observed data very well.

Throughout the refilling period, the modeled water remains in a narrow range of water chemistry with respect to decision-making:

- pH near 8
- Alkalinity > 200 mg $CaCO_3$ eq/L. In this range, the pH would be well buffered
- TDS 1400 – 2400 mg/L
- SO_4 850 – 1500 mg/L
- A small and consistent set of trace components:
  - CN-t, As, Cu, Fe on the order of 0.01 mg/L
  - Mn on the order of 0.1 mg/L
  - All other trace metals and metalloids < analytical detection limits

Inflow waters become more dilute as the water level in the mine rises. Infiltration from the Grizzly Gulch tailing impoundment is the source of the low concentrations of total cyanide. Shaft 5 flow (approximately 10 gpm) enters the underground workings only between Levels 7700 and 2000.

Because the well-buffered pH is mildly alkaline and dissolved species are relatively low, there is unlikely to be any significant change in modeled water chemistry were thermodynamic equilibrium constraints to be applied. This has been tested for water at the 800 Level, and the changes are very small. By not considering precipitation reactions at this time, the current water-quality estimates will be conservative compared to more elaborate modeling approaches.

3.0 EVOLUTION OF WATER CHEMISTRY DURING FLOODING OF THE OPEN CUT

Most of the approaches, and many of the modeling issues, for the Open Cut are the same as matters discussed at some considerable length above for the underground workings. In most respects, the Open Cut is a more straightforward modeling problem, and there seems no purpose in reiterating materials already discussed. Section 3 will focus on differences.

3.1 ISSUES IN THE OPEN CUT

- At what rates will ground and surface water report to the Open Cut during re-filling?
- What are the data on chemistry of inflows, and how can these be represented in a hydrogeochemical model?
- How can flows and chemistries be combined to represent the integrated chemistry of the re-filling water body in the Open Cut over time?
- What is the expected chemistry of the water body as the Open Cut re-fill?

3.2 CONCEPTUAL MODEL FOR GEOCHEMCAL EVOLUTION OF THE OPEN CUT

3.2.1 Conceptual Model of Re-Filling the Open Cut

Flow that reports to the Open Cut arises from four basic sources:

- Surface-water run-on from the catchment of the Open Cut.
- Runoff from precipitation that intercepts the pit walls.
- Direct precipitation onto the surface of the water body in the Open Cut.
- Groundwater flow, driven by regional flow gradients, to the cone of depression created by mine dewatering.

There also is evaporation from the water body; in this model, we treat the net result (which is net precipitation on an annual basis) as the relevant flow component.

The conceptual and theoretical bases for the flow model are described in detail in Zhan (2002). Dr. Zhan discusses the use of a water-balance approach in detail. His re-filling model for the Open Cut accounts explicitly for both sources of water, accounting each flow as a function of depth (relative to Mine Levels). Surface-water run-on from the catchment is constant (because average annual precipitation and the surface area of the catchment are constant), but Dr. Zhan's model accounts explicitly for (a) the decreasing flux of ground water inflow during re-filling, due to declining lateral hydraulic gradients as the water level rises; (b) decreasing pit-wall precipitation as water-level rises, and (c) increasing net precipitation onto the water-body surface as water level rises (i.e., as surface-area of the pond increases).

During the early stages of re-filling the Open Cut, it is likely that the waters will be well mixed, largely due to the mechanical energy of water flowing down the walls. Most long-term water bodies, if they are more than a few tens of meters deep, ultimately will stratify if there is not a significant through-flow component. (By analogy, cranberry juice over ice will, when the ice melts, stratify into a clear layer of water and a deeper layer of red juice, although the apparent densities of water and cranberry juice are quite similar.) At mid-latitudes (such as that for Lead), it is often observed that lakes and reservoirs will mix seasonally to annually over depths of not more than about 20 m – 30 m, due to solar energy and wind action. In the case of the Open Cut, wind action will be limited by the remaining high walls, which also will affect solar energy to the surface, especially during winter. However, because we are trying to evaluate the water body over a long period (on the order of 200 years), it seems reasonable to assume that, from time to time, there will be mixing to some depth, which might be on the order of 20 m (50 feet). Below this depth, it may be that, in the long run, there will develop a chemocline (and perhaps a thermocline). However, given the severe winter conditions that sometimes affect the area and the possibility of snow-melt running off both the catchment and pit walls, it may be that there will be sufficient input of dense water to cause large-scale turn-over of the water body in some years.

It is not possible at this time to make definitive statements about whether the water body will or will not stratify on a permanent basis. In any event, there are no good models for how rapidly stratification of the water body may develop. Therefore, at this stage in planning, we have modeled the water body in the Open Cut on both a fully mixed and a shallow-stratified basis.

3.2.2 Conceptual Model of Hydrogeochemistry During Refilling the Open Cut

As with the underground system, we need to assign nominal chemistry to each of the four water types:

- Groundwater flowing to the Open Cut is expected to have the Ca-SO_4 signature seen today in the shallow portions of the underground workings.
- Following closure and reclamation activities, most, if not all of the surrounding catchment will be re-vegetated with native species and the terrain is expected to approximate the natural conditions. Therefore, we model the surface water run-on from the surrounding catchment as having a water quality that is similar to an up-gradient surface water today. We have selected a typical analysis from Sampling Station SW-08.
- The pit walls, of course are variably mineralized. Precipitation falling on the pit walls therefore will encounter mineralized rock similar in most important geochemical regards to waste rock. To represent this run-off component we have selected water from the underdrain system of the East Waste Rock Facility (Sampling Station BTUD).
- Finally, direct precipitation (or net precipitation) falling directly onto the surface of the water body in the Open Cut will be very dilute. Without great loss of generality, this water could be taken as pure H_2O. However, we have chosen to model it as including some dissolved components, using the average of three published analyses (Berner and Berner, 1996) for the general region (stations in South Dakota, North Dakota and Montana).

The conceptual model for the combined geochemical interactions in the Open Cut is as for the underground: a mass-balanced, mixing cell model in which each stage is well mixed. We also calculate a well-mixed model for the cumulative stages. In addition, we present results for the final increment of flow to the water body, representing proportions if flow characteristic of the flows reporting between Mine Levels 350 and 300. This shallow-flow component is taken to represent the shallow waters that might exist if the pool develops a significant degree of stratification at depth. After calculating the mixing cells, we allow the partial pressure of CO_2 in the water to equilibrate with atmospheric P_{CO2}, and recalculate the pH. As discussed in Section 2 above, this causes the pH to drift slightly higher, toward about pH 8.5, as is very commonly seen in terminal lakes in the western U.S. when there is a significant input of alkaline water.

3.3 DATA FOR FLOW AND WATER QUALITY

Zhan (2002) developed a water-balance model for re-filling of the underground workings. The final water-balance model for re-filling used in this hydrogeochemical evaluation is presented in Attachment 1 and summarized for the Open Cut in Table 8.

Barrick/HMC provided data for samples from SW08 and BTUD. The values used for precipitation are from Berner and Berner (1996). The Ca-SO_4 water used for groundwater flows is the same set of median values used in the underground analysis. Table 9 summarizes the input values for the four water types.

3.4 RESULTS FOR THE OPEN CUT

Attachment 6 provides the full mixing-cell model for the Open Cut. The results are presented in Table 10 for Major, Minor and Trace components. Note that, for the Open Cut at all filling levels, there is a very large suite of trace components that are predicted to be below detection levels at all times. This suite includes: Al, As, Cd, Cu, Cr, CN, Fe, Pb, Hg, Se, Ag and Zn.

The time-series predictions for Major and Minor species are illustrated in Figures 9 and 10, respectively. These figures show the results for both (a) the well-mixed models and (b) a hypothetical shallow-stratified case (at a nominal Mine Level 350 in Table 10 and Figures 9 and 10). For the various minor species except NO_3, there is not enough difference between the shallow case and the trend of the well-mixed case to be distinguishable at the scale of these figures. For detail, the reader is advised to consult the tabulated values in Table 10 or to go to the full model in Attachment 6.

As with the speciation and equilibrium modeling discussed for the 800 Level in the underground model, the effects of trying to apply thermodynamic modeling to these cases is somewhat subtle. Differences in pH (and therefore in the saturation state of Mn) depend on how one assumes the dissolved gases behave. It is likely that, at least in the long-run, dissolved CO_2 will equilibrate with the atmosphere, as often is seen in shallow waters. (However, if an algal or other plant community establishes itself on the water body, the P_{CO2} and pH of shallow water will vary diurnally and seasonally as photosynthesis proceeds, so average annual conditions are only an approximation.) Given the alkalinity of groundwater and the presence of carbonates in the pit walls, it is highly likely that the pH in the water body will range between about 8 and about 8.5 at almost all times.

3.5 DISCUSSION OF OPEN-CUT CHEMISTRY

3.5.1 General Trends

The expected chemistry of the Open Cut is quite straightforward and flows directly from the basic structure of the flow model. As the water level moves toward its equilibrium elevation, the lateral hydraulic gradient decreases; groundwater flow becomes a smaller and smaller component of the mixture over time. The second highest TDS component is runoff from the pit walls. This too, decreases as an absolute flow and proportionally over time because the surface area of exposed pit walls decreases as water level rises. This leaves the two lowest TDS waters – direct precipitation and background surface-water run-on as increasingly important contributors to the water balance. Therefore, the fundamental water-quality trend is toward a more and more dilute water body.

Unlike lakes in more arid zones like Nevada, the water balance for Lead indicates that there always will be an annual net precipitation. Therefore, one will not see extreme evapo-concentration effects that typify both natural terminal lakes (e.g., Mono and Great Salt Lake) or have been predicted for pit lakes in some Southwestern locations.

Because the lake will have a pH near 8, well buffered by carbonate alkalinity values near 100 mg/L, metal solubilities will be severely limited. The available data and modeling indicate that the pH is unlikely to rise high enough to cause enhanced solubility for amphoteric species like As and Se. In the portion of the system that is well-mixed (routinely the uppermost 50 feet or so of the system, except when the water is frozen), the water probably will be sufficiently oxidized to stabilize ferric hydroxides that can scavenge any small amounts of trace metals or metalloids that may report to the shallow water. Waters deeper in the system are unlikely to provide a complete exposure pathway to any ecological receivers.

There is nothing in the existing information that suggests that waters, if they were to discharge from the Open Cut, would adversely affect surface-water uses. In any event, if these predictions are incorrect, there will be many decades of monitoring data available to allow Homestake to develop and execute a surface-water management plan.

3.5.2 Uncertainty Analysis for Open-Cut Model

There are three major sources of uncertainty with respect to the geochemical evolution of Open Cut:

- Water quality associated with runoff from the pit walls.
- Possible full-lake turn-over.
- Inability to calibrate the Open-Cut model against any existing site-specific data.

The East Waste Rock Facility contains a large volume of rock developed from the Open Cut. Infiltration of rain and snow-melt through the facility provides a long-term, full-scale field simulation of natural precipitation contacting such rocks. Therefore, although the BTUD data seems a reasonable basis for estimating the chemical loads from waters generated by contact with the pit walls, it is hard to say at this time that the data are unique. Absent empirical data on flows from the walls, it will be impossible to do other than estimate this flow component. There is some evidence, from secondary precipitates that form locally on rock surfaces in the pit walls, that there is incipient oxidation of sulfides, and it is possible that some local, seasonal seeps may be acidic. However, the same lithologies and mineralogies are present in the East Waste Rock facility, and the sulfate load of BTUD (1728 mg/L, Table 9) shows that sulfide oxidation is occurring there, too. Yet the pH from BTUD is 7.74, and the water has greater than 250 mg/L bicarbonate alkalinity. From these results, we infer that the bulk rock has sufficient available carbonate neutralization potential to buffer the acidity released by localized concentrations of oxidizing sulfides. We consider that the situation in the walls of the Open Cut would be analogous. Additionally, as discussed above, the relative contribution of this flow component decreases over time, as the walls become inundated, so this uncertainty is mitigated by the natural hydrology of the system. HMC are pursuing additional geochemical studies of waste-rock and pit-wall geochemistry that will allow new estimates of run-off chemistry to be formulated in the future. At this time, it seems very unlikely that there would be large-scale acid generation from the pit walls; the large mass of carbonate present in the system is a mitigating factor and the walls have had many years to oxidize already without widespread acidification. However, this matter is being pursued explicitly and actively through field studies and laboratory testing.

In making the flow calculations, we have implicitly assumed that there will be surface-water management for the general run-on so that catchment surface water is directed into the pit at some number of discrete and controlled locations, rather than willy-nilly across the highwalls. This certainly can be managed as closure planning proceeds.

Although physical turnover of shallow lakes (e.g., Great Salt Lake) does occur, the likelihood of this in a deep pit-lake is quite small. If such turnover were to occur, then there would be a tendency for reduced materials from the sediment/water interface to be re-oxidized and the mass subsequently redistributed in the water body. In deep waters, the amount of energy needed to cause physical turnover and mixing to the surface is sufficiently great that it is much less likely to happen than in a shallow water body. In our view, the risks, even if this mixing were to occur, are quite small in the case of the Open Cut. Firstly, there is not a significant flux of metals or metalloids flowing to the water body to be potentially sequestered. Secondly, by modeling the well-mixed system and then not using geochemical modeling top "remove" mass by hypothetical precipitation reactions, the modeling of this study already assumes that complete mixing can and will occur. The results of the well-mixed models, while discernibly higher than for the predicted shallow, stratified values also are very low. The only metal predicted to be measurable tin the well-mixed system is Mn, and that at concentrations less than 0.1 mg/L. Even the sulfate concentrations are low: 300 mg/L to 350 mg/L across the filling cycle, with TDS commensurately low (400 – 650 mg/L).

Finally, unlike the underground model (which can be tested partially for modeled results for Year 1 and 27), there are no comparable data that can be used to test the model predictions for the Open Cut. This is a true forward model that is testable, but when long-term monitoring data become available. Fortunately, it will be many decades before water levels in the Open Cut approach elevations at which impacts to surface waters would be physically possible.

4.0 CONCLUSIONS

We have combined numerical results for inflows of different types of waters with chemistries that are representative of those flow types. For both the underground and Open Cut portions of the Homestake Mine it is possible to develop strong estimates of future water quality. Based on the best available data, both underground and surface waters in this system are expected to remain neutral to slightly alkaline in pH. Metals and metalloids will be low, and even sulfate values will not be very high. The best-estimate models indicate that water-quality in both the underground and Open Cut systems will meet water-quality criteria for groundwater and later for surface water in the Open Cut.

There remain uncertainties about specific inputs to the model and also to about details of groundwater flow. Some of these uncertainties can be evaluated through sensitivity studies, and those show there is little likelihood that the current modeling results are too inaccurate to allow decision-making. Some other uncertainties can be discussed only qualitatively at this time.

As almost always is the case for environmental models of any kind, it will be important to establish and maintain monitoring programs to test the current models, serve as a basis for updating these or other tools, and finally to help design long-term closure and contingency plans. Because the water level is not expected to reach the base of the Open Cut for 27 years(and the equilibrium elevation ion the Open Cut will not be reached for nearly 180 years), there is a great deal of time in which Homestake can further advance it understanding on the basis of solid, empirical information for the full-scale system.

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