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Technical Article

A Screening-Level Laboratory Method to Estimate Pit Lake Chemistry

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Abstract. An analog pit lake (APL) test has been developed to predict pit lake water quality following closure of an equatorial copper-gold mine. The juvenile (0-9 years after closure) pit lake (JPL) water budget will comprise 10% rainfall; 26% surface runoff; 40% wallrock runoff, and 24% deep groundwater inflow. The mature (>65 years after closure) pit lake (MPL) will consist of 39% rainfall; 29% surface runoff; 15% wallrock runoff; 3% deep groundwater inflow, and 1% shallow groundwater inflow, with the balance (13%) contributed by the JPL. Wallrock runoff due to incident precipitation was replicated in humidity columns, subaqueous wallrock leachate by leaching columns of each rock type with groundwater, rainwater by addition of sea salt to deionized water, and surface runoff by a sample from a local creek. The solutions were combined in aquaria and the appropriate fraction evaporated, 7% for the JPL and 36% for the MPL. Electron microprobe analysis of precipitates identified clays and Al, Cu, and Zn adsorbed to ferrihydrite surfaces. A preliminary pit design resulted in an acidic (pH 3.3) JPL containing 7 mg/L Cu. However, by modifying the design to exclude a potentially acid-generating andesite unit, the JPL water quality improves (e.g., pH 6.7; Cu 0.002 mg/L). The MPL pH with the andesite would be 6.1 (Cu = 2.2 mg/L), while the final design results in a pH of 7.1 and 0.22 mg/L Cu. The APL test can also be used to corroborate numerical models predictions and assess the efficacy of mitigation alternatives.

Key words: analog model; pit lake, wall rock, water quality

Introduction

Innovations in ore extraction techniques over the last 15 years have resulted in the development of large pits to extract low-grade ore, primarily in sulfide/limestone hosted settings. When the ore is exhausted, dewatering ceases and the cone of depression formed around the pit recovers, with groundwater discharging into the pit through the wallrock. While this issue has received attention in Europe (e.g., Schultze and Geller 1996; Geller et al. 1998) and Canada (Morin and Hutt 1995), pit lake water quality has only been studied relatively recently in the U.S. (Davis and Eary 1997; Shevenell et al. 1999; Eary 1999; Shevenell 2000). This interest has been heightened by the acidic (pH 3) high metal (Cu = 600 mg/L) condition of the Berkeley Pit lake (Davis and Ashenberg 1989) and concern that pit lake water quality will generally be poor (NRC 1999). This issue will continue to be important from the perspective of water quality and potential ecological impacts as open pit mining increases throughout the world, and in particular in the western United States. However, not all open pit mines are destined to be acidic, especially in terrain where the wall rock has substantial neutralizing capacity, and inflow through calcareous rocks (typically neutral pH with low metal concentrations) exceeds that through oxidized sulfide-bearing rock units (often low pH with higher metal concentrations). Indeed, existing pit lakes cover a wide spectrum of chemical conditions (Miller et al. 1996), ranging from benign (e.g., the Cortez Pit Lake) to those that exceed primary and secondary drinking water standards (e.g., the Berkeley Pit Lake). The range in chemistry is substantial, due to site-specific geologic, hydrologic, and geochemical variables that control the ultimate chemistry of the mature pit lake (Shevenell et al. 1999).

Predicting future pit lake chemistry has been the subject of intense research (e.g., PTI 1996; Geomega 2001; Ludwig and Balkenhol 2001) that has been necessitated by permitting and bonding requirements, securing funding for mining projects, and early definition of potential mitigation approaches in the event of potentially unacceptable water quality after mine closure. In this paper, we describe an analog pit lake (APL) test designed to quickly estimate pit lake water quality using site waters and wall rock, and its application to an actual site. Variations on the test could also be used for rapid screening of alternatives, e.g., the effect of modifying the pit design, infilling, and of amendments on pit lake water quality.

Geologic and Hydrogeologic Regime

We applied the APL test to the mining of a large equatorial copper-gold porphyry sulfide deposit. Mineralization is hosted in a tonalite intrusive complex, with diorite and metavolcanic (andesite) wallrock. The area contains numerous faults and joints, a result of three episodes of intrusions and associated faulting. A large diorite laccolith is the result of the first intrusive episode, itself later intruded by tonalite stocks and dikes during two later episodes (Figure 1). Chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4) with minor chalcocite

(Cu_2S) are the principle hypogene minerals, overlain by volumetrically insignificant supergene enrichment and by a gossan up to 85 m thick. The deposit is being mined using conventional open pit methods with ultimate pit walls ranging in height from 630-850 m. The mine will be located in steep terrain between the headwaters of two drainages about 10 km inland from the coast, with the highest point of the deposit at 555 m above sea level. Excavation of the pit will modify the local groundwater table by creating a sink during mining because of dewatering operations over the estimated mine life (30 years).

Oxidation of exposed sulfide minerals in the ultimate pit surface (UPS) wall rock will modify the initial groundwater seeping into the pit following facility closure. Near-surface sulfide oxidation occurs naturally in the area, as evidenced by acidic seeps and springs located near the top of the drainages, with 15 of the 87 exploratory pH measurements reported near the mine site between 3.6-6.0 (Figure 2) and with Cu in analyzed samples up to 3 mg/L (Table 1), similar to the chemistry of other streams emanating from volcanic areas (Delmelle and Bernard 1994). These data are also consistent with other reports of elevated dissolved metals and low pH in surface and ground water in contact with undisturbed mineral deposits throughout the world (Runnells et al. 1992).

The groundwater table mimics the topography, with the water table 50 m below ground surface (bgs) beneath the ridges, and 10 m bgs in the valleys. Infiltration of precipitation recharges the surficial groundwater system, some of which discharges into adjacent valleys. The remainder of the groundwater flows into a deeper regional system that discharges into lowland areas southeast of the site. The hydraulic conductivity of the unfractured rock ranges from 10^{-7}-10^{-4} cm/s, with diorite more permeable than andesite, while the hydraulic conductivity in the fault zones is higher (10^{-4}-10^{-3} cm/s). Hence groundwater inflow (estimated at 3E6 m^3/yr) into the ultimate pit will be predominantly fracture controlled. When the pit is full (~65 years after mine closure), overflow will enter the drainage to the east (Figure 1). The APL experiments simulate the juvenile pit lake (JPL) chemistry after 9 years (when the pit lake will be ~250 m deep and contain 16% of the total volume), and the mature pit lake (MPL), which will be ~540 m deep containing ~52.5E6 m^3 of water.

The Pit Lake Paradigm

The chemical composition of a pit lake depends on both hydrological and geochemical processes that may change over time as the pit fills, eventually reaching steady-state conditions (Figure 1). Hydrological processes are important because the water in the pit lake will be derived from a number of different sources including, 1) shallow and deep groundwater infiltration through perimeter wall-rocks, 2) runoff of incident precipitation from the pit walls, 3) artificial diversion of

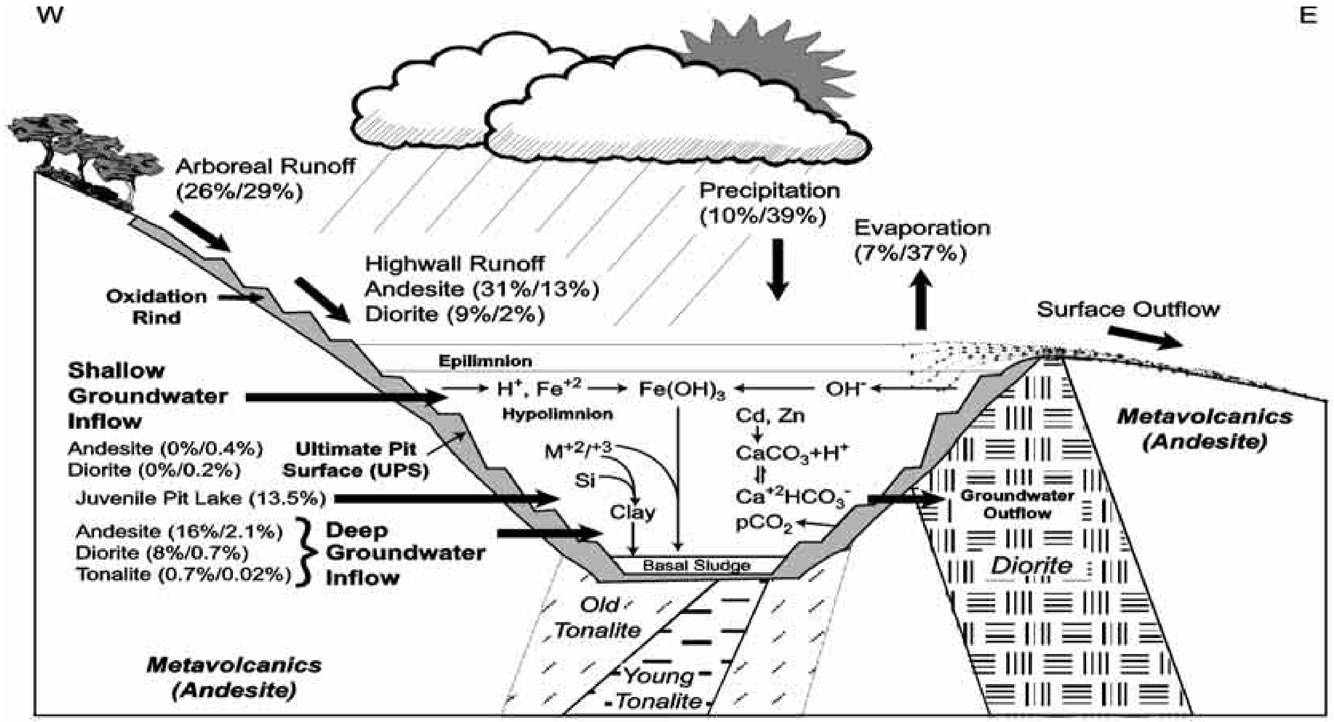

Figure 1. Schematic geologic cross-section, pit lake water budget and water column chemistry. The juvenile pit lake (JPL) contribution is represented by the numerator and the mature pit lake chemistry contributions by the denominator (Table 2). The JPL contributes 13.5% of the water to the mature pit lake.

Table 1. Geochemistry of background seeps and springs (A-F) collected in the footprint of the ore deposit prior to disturbance of the area (mg/L unless noted). See Figure 2 for well locations. Potassium was not analyzed in surface water but was typically <5 mg/L in groundwater with equivalent chemistry. MW 2-1 and MW-1-3P are shallow and deep wells, respectively.

Constituent	A	B	C	D	E	F	MW 2-1	MW-1-3P
pH (s.u.)	3.9	6.8	6.7	6.1	7.7	3.6	7.6	6.8
Cond (µS/cm)	380	240	200	150	250	430	400	610
Al	3.5	0.6	0.4	1.4	0.6	3.6	0.4	<0.3
Ca	6.9	14	11	5	23	20	38	62
Fe	5.6	3.5	0.8	0.08	0.02	7.7	0.03	1.1
K	n.a	n.a	n.a	n.a	n.a	n.a	1.3	1.1
Mg	17	13	6.1	2.2	8.1	10	12	20
Na	7.3	11	15	15	12	21	26	24
Cl	13	12	10	10	13	12	10	11
SO$_4$	110	75	65	50	42	150	48	170
NO$_3$-N	0.02	0.01	0.01	0.15	0.18	0.05	0.05	0.17
As (µg/L)	2	2	1	<1	1	2	7	5
Cu (µg/L)	107	1	180	303	14	660	3	<1
Mn (µg/L)	280	170	60	85	13	390	170	337
Ni (µg/L)	8	<2	2	<2	<2	5	<2	<2
Zn (µg/L)	81	13	23	82	6	191	<1	860

Table 2. Relative contribution of waters to juvenile and mature pit lakes

a) Juvenile Pit Lake

Fluid	Analog	Contribution (%)	Volume (L)
Deionized Water + Instant Ocean	Rainfall	10.2	0.51
Boulder Creek water	Arboreal Runoff	26.2	1.31
Humidity Cell 1 Effluent	Wall Rock Runoff	39.5	1.98
Tonalite Column Effluent	Deep Tonalite Inflow	0.7	0.04
Deep Andesite Column Effluent	Deep Andesite Inflow	15.6	0.78
Deep Diorite Column Effluent	Deep Diorite Inflow	7.8	0.39
	Total	100.0	5.00

b) Mature Pit Lake

Fluid	Analog	Contribution (%)	Volume (L)
Deionized Water + Instant Ocean	Rainfall	39.1	11.58
Boulder Creek water	Arboreal Runoff	28.7	8.50
Humidity Cell 2 Effluent	Wall Rock Runoff	15.3	4.53
Tonalite Column Effluent	Tonalite Inflow	0.02	0.005
Shallow Andesite Column Effluent	Shallow Andesite Inflow	0.4	0.13
Deep Andesite Column Effluent	Deep Andesite Inflow	2.1	0.62
Shallow Diorite Column Effluent	Shallow Diorite Inflow	0.2	0.04
Deep Diorite Column Effluent	Deep Diorite Inflow	0.7	0.21
Juvenile Pit Lake Water	Juvenile Pit Lake Water	13.5	4.00
	Total	100.0	29.62

surface runoff into the pit lake (arboreal runoff), and 4) direct precipitation into the pit lake. The lake chemistry will be a function of the flux and chemistry of these flows, on which is superimposed the geochemical processes that occur in the UPS. At this interface, exposed sulfidic rocks react with air, incident precipitation, and/or groundwater to produce solutions that are a function of: 1) the oxidizeable sulfide content of the wallrock, 2) the alkalinity of the infiltrating groundwater, 3) the buffering capacity (i.e., lithology)

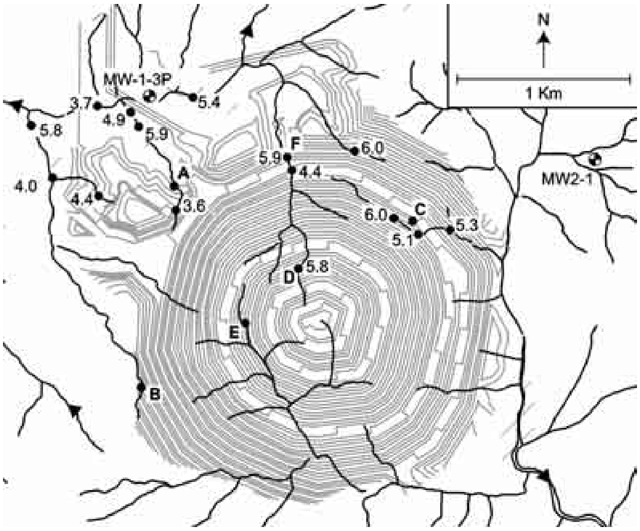

Figure 2. Configuration of the mine area showing shallow (MW2-1) and deep (MW-1-3P) monitoring wells and drainage features, with the ambient pH of previously existing seeps and springs (see Table 1 for chemistry) superimposed on the ultimate pit surface footprint. Designations A through F represent surface water sampling locations. Arrows on tributaries indicate prior surface water flow.

of the wallrock, 4) the extent of formation of amorphous ferric hydroxide [$Fe(OH)_{3(am)}$], 5) site-specific variables, such as moisture content and temperature, 6) the diffusion rate of oxygen into the wallrock (controls sulfide oxidation kinetics), and 7) the seasonal rate of lake overturn and oxygenation to depth (Davis et al. 2002).

Oxidation of sulfide minerals, particularly pyrite in the UPS, generates acidity in pit lakes following reaction chemistry that has been described previously (Nordstrom 1982; Fennemore et al. 1998). Conversely, in carbonate-buffered solutions, ferrihydrite precipitates on reactive pyrite surfaces, reducing reaction rates and the rate of formation of acid rock drainage (Nicholson et al. 1988). In practice, the acid-generating capacity of the pit wall rock is determined by the net carbonate value (NCV), which is the difference between the acid generation potential (AGP) and the acid neutralization potential (ANP). AGP and ANP are specified in terms of %S and %CO_2, respectively (Sobek et al. 1978), as measured on a carbon-sulfur analyzer after distinguishing the different carbon species, i.e., organic and carbonate, and between sulfate and sulfide sulfur (Newmont 1995). The AGP = 1.37 (S^{-2}), where S^{-2} is the % sulfide-S measured in the rock, and the 1.37 coefficient represents the formula weight of CO_2 divided by the atomic weight of S. The ANP = 3.67 ($C_{CO_3^{2-}}$), where $C_{CO_3^{2-}}$ is the % carbonate carbon measured in the rock. The 3.67 coefficient is derived from the formula weight of CO_2 divided by the atomic weight of carbon (the %CO_2 NCV can be converted to kg $CaCO_3$/1000 metric tons of rock by dividing by 0.044). When the ANP exceeds the AGP by a factor of >1.5, acid generation is inhibited, while at lower ratios, acid generation is likely (Lapakko 1992; Chapman et al. 2000), although the U.S. EPA (1994) asserts that ANP/AGP ratios of <3 represent a range of uncertainty. In contrast, long-term (>160 weeks) column tests indicate that an NNP:AGP of >2.7 should result in a net neutral pH condition (Chapman et al. 2000).

The UPS NCV of the deposit was characterized from 827 paired C and S analyses on a LECO 344 analyzer following the method of Newmont (1995). In the pit, approximately 75% of the UPS will consist of metavolcanics, with NCVs typically ranging from -2 to +2 (Figure 3). There is also potential for exposure of an acid-generating andesite unit (NCV –4 to –7) in the northeast perimeter of the highwall that could adversely influence the pit lake chemistry in the event of uncontrolled surface runoff into the pit. Indeed, one of the objectives of this study was to assess the nature of this impact as part of responsible mine planning.

The UPS wall rock contributing to the JPL consists of meta-andesite, tonalite, and hornblende diorite (Figure 3). The meta-andesite (n = 474; $\bar{x}$ ANP = 0.33, $\bar{x}$ AGP= 0.60, $\bar{x}$ NCV = -0.28) will occur at all UPS elevations (Figures 4a and 5a). Tonalite will only be exposed below –50 m, hence contributes to the JPL runoff but not directly to the MPL runoff. This unit consists of an old tonalite with a slightly negative to slightly positive (-1 to +1) NCV (n = 44; $\bar{x}$ ANP = 0.50%, $\bar{x}$ AGP= 0.50%, $\bar{x}$ NCV = -0.24), and a young tonalite (n = 48; $\bar{x}$ ANP = 0.44; $\bar{x}$ AGP = 0.38; $\bar{x}$ NCV = -0.15) (Figure 5b). The diorite unit (n = 261; $\bar{x}$ ANP = 0.18; $\bar{x}$ AGP = 0.56, $\bar{x}$ NCV = -0.42) NCV ranges from –2 to +2 (Figures 4b and 5c). Hence the NCV distribution was known as a function of depth for the entire UPS.

The contribution of the various hydrological and geochemical processes to the lake chemistry changes over time as the pit fills. As ground water discharges into the pit, acidity and iron will be flushed from the wall rock, facilitating precipitation of amorphous ferric hydroxide (AFH) in the water column (Figure 1). AFH sequesters metals in solution either by sorption or coprecipitation as it settles through the water column to form a metal-rich basal sludge (Miller et al. 1996) that limits metal solubility in the water column (depending on the system pH). For example, cation concentrations from closed basin lakes, existing pit lakes, and modeled pit lakes generally increase with decreasing pH, while anion concentrations are higher in more alkaline conditions (Davis and Eary 1997).

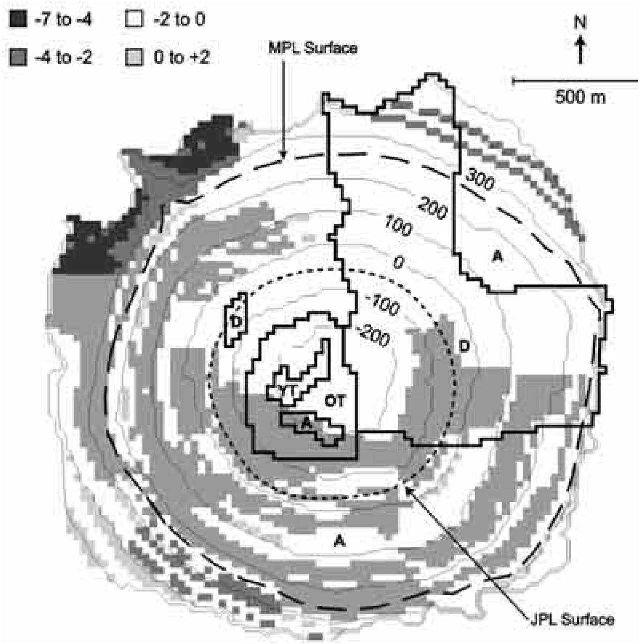

Figure 3. Distribution of NCVs in the UPS showing the Juvenile Pit Lake (JPL) and Mature Pit Lake (MPL) water surface elevations (above mean sea level); A = metavolcanics (andesite); D = diorite; YT = young tonalite, OT = old tonalite

Methods

The experiment consisted of initial simulation of JPL chemistry, followed by simulation of MPL chemistry. To simplify the experiments, wall rock was excluded from the APLs on the basis that reactivity had been accounted for during the leaching cycles, while the rubbleized base of the pit was assumed to be adequately represented by the crushed rock used in the column tests.

Relationship between Simulated Inflows and Analog Volumes

Water fluxes to the pit from the various sources were based on the results of a MODFLOW groundwater flow model (Golder 1995). The groundwater inflow rates to the pit through each unit were calculated by assigning a rock type to each model cell that intersected the UPS, and summing the fluxes to calculate the total flux into the pit for that rock type over time. Based on site-specific rain gauge data correlated with other local data, incident precipitation onto the pit lake surface and wall rock will be ~1.8 m/yr. Initial pan evaporation data indicates that evaporation from the pit lake will be ~1.3 m/yr, while arboreal runoff (calculated from a water balance study) will be ~0.7 m/yr (Golder 1995). Hence appropriate fluid volumes from humidity cells (representing high wall runoff) and the column effluent(representing groundwater discharge through the UPS) was mixed with precipitation in the appropriate ratios to simulate JPL and MPL influent solutions (Table 2).

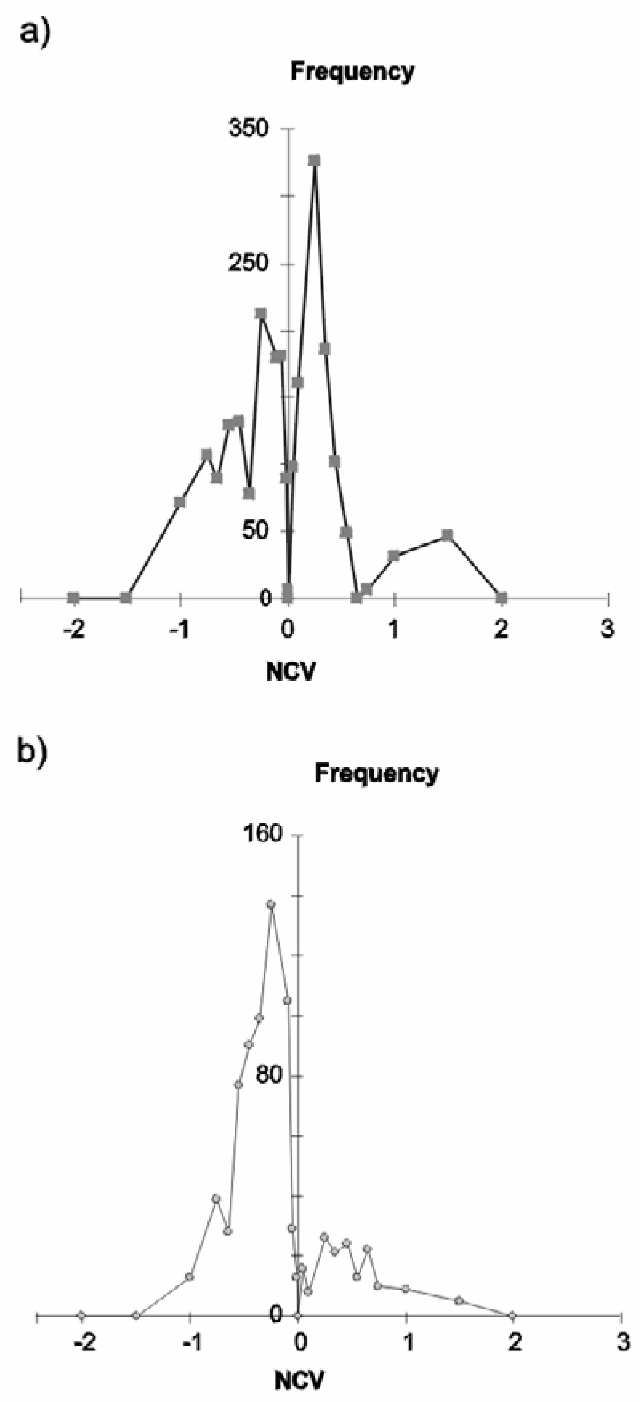

Figure 4. The NCV distribution and frequency by lithologic unit in the shallow (–50 to +278 m) interval of the UPS for a) meta-andesite and b) diorite

Generation of Characteristic Solutions

To obtain characteristic highwall runoff leachate, humidity columns were run following the protocols of Sobek et al. (1978) and ASTM (1996). The juvenile pit wall consists of 22% diorite and 78% andesite, while

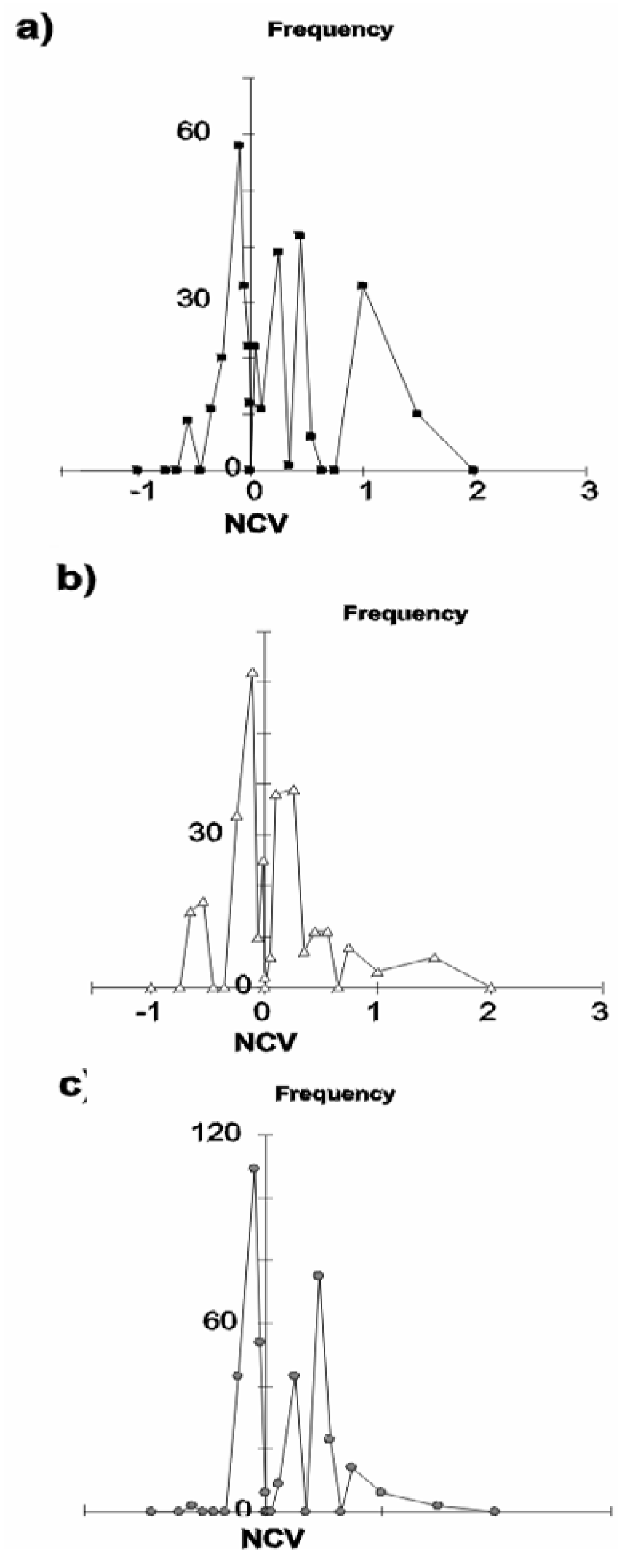

Figure 5. The NCV distribution and frequency by lithologic unit in the deep (–300 to –50 m) interval of the UPS for a) meta-andesite, b) tonalite (occurring in the UPS only below –50m), and c) diorite

the mature pit wall will comprise 13% diorite and 87% andesite (Table 3). The relative contributions by lithological NCV class were obtained from –10 mesh (2mm) drill core rejects and seeded with *Thiobacillus ferrooxidans* (cell density of 10^6–10^7/mL) to facilitate sulfide oxidation. The material was packed into columns in 10 separate lifts (tamped between lifts), and dry air pumped through each column for three days, followed by humid air (air bubbled through water) for three days. On the seventh day, 1L of deionized water was allowed to infiltrate by gravity through each cell. Geochemical parameters (pH, Eh, Fe^{+2}) were measured on each effluent aliquot, with the process continuing for 24 weeks (deemed adequate to assess the propensity for acid rock drainage; ASTM 1996) during which 21 samples were collected at approximately weekly intervals (Figure 6).

To determine the water quality discharging through each lithological unit into the pit, groundwater collected from shallow (MW2-1; 24-65m) and deep (MW-1-3P; 100m) monitoring wells from the site (Figure 2) was pumped through PVC columns. The columns (5 cm id x 36 cm) were packed with ~1kg of each rock type (Table 3) prepared as described previously. Initially, the rock material in the columns was allowed to oxidize (to simulate conditions at the exposed pit surface) by running a stream of air alternating from dry to humid through each column for 8 months, a period adequate to at least oxidize any peripheral sulfides. For context, humidity cells that have undergone oxidation cycles for 5 months are deemed to be representative of the long-term acid generation potential (ASTM 1996). Subsequently, deep and shallow groundwater collected from the site was pumped through the columns containing the deep and shallow rock types, respectively, at 40 mL/hr (representative of predicted groundwater discharge rates). Different volumes of groundwater were processed through each column depending upon the experimental requirements (Table 2) and the effluent from each individual column combined to generate the appropriate volume necessary for either the JPL or MPL test.

The rainfall component consisted of deionized water to which 1.9 mg/L of Instant Ocean (a synthetic sea salt) was added to simulate near-ocean rainfall, the amount determined by normalizing the amount of Na^+ to that in tropical near-ocean precipitation (De Carvalho and Leprun 1991). The arboreal runoff component consisted of water collected from Boulder Creek, a pristine mountain stream in Colorado, the chemistry of which (Table 4) was similar to arboreal runoff near the site (Table 1). The creek water contained 3.4 mg/L dissolved organic carbon and 9.4 mg/L of total inorganic carbon.

APL Deployment

Three 38 L glass-walled aquaria were used as pit lake analogs. Both the JPLs and MPLs included two

Table 3. Distribution of rock types and NCV values for leaching experiments

Aerial Exposure (Runoff)			**Sub-aqueous Exposure (Groundwater Discharge)**		
Juvenile Pit	%	NCV	Juvenile Pit	% Contribution	NCV
Diorite (22%)	12	-1.86	Tonalite	100	0
	70	-0.26			
	9	0.56	Diorite	56	-0.3
	9	-0.02		22	0.56
				22	-0.02
Andesite	16	-2.54			
	46	-0.71	Andesite	50	-0.37
	38	0.44		50	0.44
Mature Pit			Mature Pit		
Diorite (13%)	13	-1.86	Diorite	100	-0.26
	79	-0.26			
	4	0.56	Andesite	60	-0.37
	4	-0.02		40	0.44
Andesite	45	-2.54			
	31	-0.71			
	21	0.44			

replicates (J-1, J-2 and M-1, M-2), while the third (J-3and M-3) excluded the potentially acid-generating highwall andesite unit (AGHAU; Figure 3) by omitting the shallow runoff component from both these APLS. Hence J-3 and M-3 could simulate either mine plan modification or implementation of run-on and runoff control, e.g., routing up-gradient flow and incident precipitation on the -NCV AGHAU away from the lake through diversion ditches into an adjacent holding pond.

The volume of water representing each component was added to each JPL aquarium and heating pads placed under each to increase the water temperature to 25°C to enhance evaporation until the original volume decreased from 5L to 4.64L (93% of the original volume) over a 5-day period. Specific conductivity, pH, and temperature were measured regularly. The precipitate that settled to the base of the aquarium was separated from the supernatant by filtering the floc through a pre-weighed 0.45 µm cellulose acetate membrane filter. The filter was air-dried, weighed, and metal concentrations measured in both the precipitate [after digestion (U.S. EPA 1986)] and the fluid phase. Waters were analyzed for metals (inductively coupled plasma), for anions by ion chromatography (EPA Method 300.0), and alkalinity (EPA Method 310-1) (U.S. EPA 1993). Floc mineralogy was characterized by Electron Microprobe Analysis (EMPA), following the method of Davis et al. (1992).

The combined influents representing the MPL (M-1, M-2, and M-3) resulted in 29.6L in each aquarium (Table 2). Water from J-2 added to M-2 had 95% of the precipitate removed for EMPA, while the J-1 and J-3 water added to M-1 and M-3 contained the original amount of precipitate to simulate pit lake evolution in the presence of basal sludge. All MPLs were evaporated

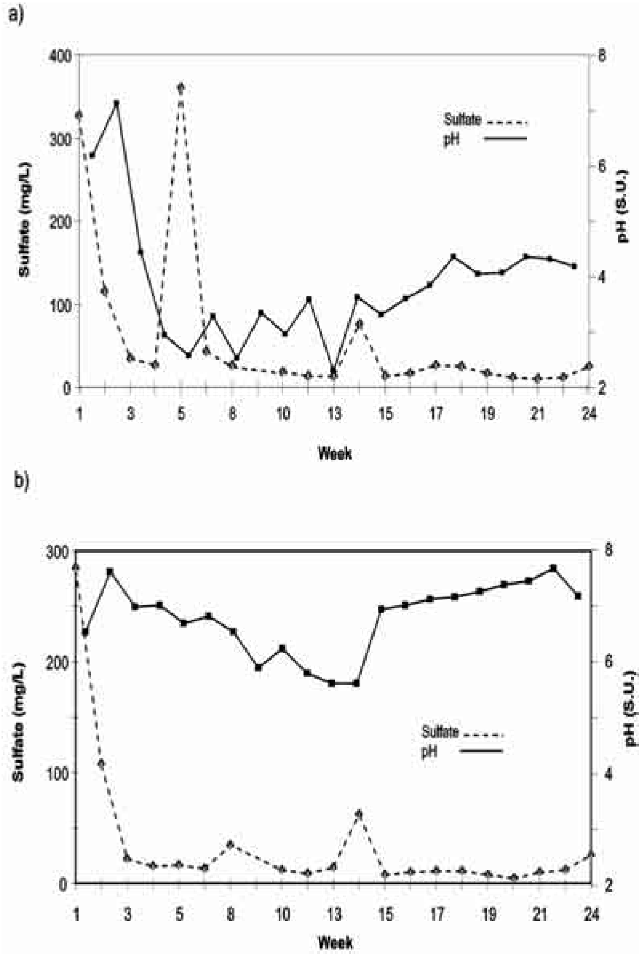

Figure 6. Humidity column pH and sulfate profiles for: a) the JPL UPS, and b) the MPL UPS; (13% diorite, 87% metavolvanics), NCV=1.25

Table 4. Selected geochemical parameters of the APL components and resulting geochemistry of the mixtures (mg/L unless otherwise noted) and precipitates

PIT LAKE COMPONENTS INFLUENTS	pH	Eh mV	Alk	SO_4	Al	Ca	Cu	Fe	K	Mg	Ni	Sr	Zn
Tonalite (gw)	6.9	-10	82	470	<0.008	38	0.08	<0.01	34	34	0.010	7.9	0.053
Deep Andesite (gw)	7.4	-13	92	147	<0.008	26	<0.002	<0.01	15	18	0.010	1.6	0.004
Shallow Andesite (gw)	7	-2	144	454	<0.008	35	0.013	<0.01	30	44	0.011	4.2	0.015
Deep Diorite (gw)	7.4	0	93	150	<0.008	29	<0.002	<0.01	13	13	0.010	3.3	0.007
Shallow Diorite (gw)	2.7	280	0	**	660	1260	1990	0.79	9	1020	0.133	47	195
Rainfall	6.7	-19	24	0.2	<0.008	0.03	<0.002	<0.01	0.04	0.04	0.010	0.08	0.002
Arboreal Runoff	6.6	-15	60	10	<0.008	11	<0.002	0.13	1	5.4	0.011	1.4	0.004
Juvenile WR Runoff$^{(1)}$	2.8	370	0	52	28	25	16	18.9	13	81	0.021	5	0.770
Mature WR Runoff$^{(2)}$	6.6	240	25	**	<0.008	12	<0.002	<0.01	2.4	2.3	0.011	0.59	0.006
APL TEST WATER MIXTURES	pH	Eh mV	Alk	SO_4	Al	Ca	Cu	Fe	K	Mg	Ni	Sr	Zn
J-1	3.3	118	0	102	12.2	23	7	1.06	9.9	17	0.016	3.3	0.41
J-2	3.3	107	0	65	11.7	22	6.6	1.11	8.6	15	0.016	3.2	0.38
J-3	6.7	-68	42	43	<0.008	16	<0.002	0.01	3.1	5.5	0.01	1.2	0.005
M-1	6.2	165	5	31	<0.008	22	2.2	0.01	4.2	9.5	0.011	1.7	0.26
M-2	6.1	160	3	29	0.057	22	2.4	<0.01	3.9	9.4	0.014	1.5	0.27
M-3	7.1	103	28	27	0.018	13	0.22	<0.01	2.4	4.8	0.011	0.93	0.089

PIT LAKE PRECIPITATES (mg/kg)

	S	Al	Ca	Cu	Fe	K	Mg	Ni	Sr	Zn
J-2	5200	29100	3600	860	OR	1400	15700	7	560	53
M-1	11500	102000	1400	18800	OR	600	2700	9	160	170
M-2	7600	73900	1700	9400	46600	2600	4100	22	240	160
M-3	1000	55400	4400	87400	66400	600	2200	280	1600	3400

OR: Over Range; **: analytical interference; (1) juvenile pit wall rock humidity cell (see Table 3); (2) mature pit wall rock humidity cell (see Table 3); gw = groundwater

to 18.8L (63% of their original volume) based on the calculated evaporative loss (Golder 1995). Geochemical parameters were measured routinely, and the water chemistry and precipitates in the 3 aquaria analyzed at the conclusion of the experiment (after 6 days).

Results and Discussion

UPS Wall Rock Runoff

The JPL wall rock humidity cells (representing runoff from the aggregate UPS) decreased to pH 2.3 after 13 weeks, recovering slowly to pH 4 after 18 weeks (Figure 6a) with Fe up to 115 mg/L. The aggregate water quality was acidic (pH 2.8), containing 16 mg/L Cu, 18.9 mg/L Fe, but only 52 mg/L SO_4^{-2} (Table 4). In contrast, the MPL wall rock humidity cell pH remained circumneutral (except for a temporary depression to 5.6 after week 13) with low Fe (<0.05 mg/L) and generally lower redox levels (Figure 6b) because of the reduced contribution from the shallow AGHAU in the MPL. Sulfate was initially leached from both cells, probably as a result of surface salt dissolution.

Groundwater Discharge

The groundwater passing through the exposed wall rock units that will contribute to the lakes had a pH between 6.9-7.4 (Table 4), except for the shallow diorite groundwater (2.7), which also contained 660 mg/L Al, 1990 mg/L Cu, and 195 mg/L Zn, but only 0.79 mg/L Fe.

APL Tests

Acidic juvenile wall rock runoff and shallow diorite ground water adversely affects the pit lake geochemistry (pH 3.3 for both J-1 and J-2), compared to

J-3 (AGHAU runoff excluded) with a pH of 6.7 (Figure 7). The difference in pH is reflected in the JPL metals concentrations, higher in J-1 and J-2 than in J-3 by a factor of 1.3 to >>1000. For example, Cu in J-1 and J-2 averaged 6.8 mg/L, compared to <0.003 mg/L Cu in J-3 (Table 4). The AGHAU has more impact than the diorite because the AGHAU contributed 31% to the JPL, compared to 0.2% from the shallow diorite groundwater throughflow (Figure 1). This effect carried over into the MPLs, where M-3 had a slightly higher pH (Figure 7) and lower dissolved metals (Table 4) than either M-1 or M-2.

Precipitates formed within 3 hours of mixing had settled to the bottom of the tank after 18 hours (J-1, 0.47g; J-2, 0.49g). The EMPA identified AFH and clay precipitates in both J-1 and J-2, while no precipitate formed in J-3, presumably because omission of the high wall runoff resulted in just 0.01 mg/L Fe in that APL test (Table 4) compared to > 1mg/L in the other two. Precipitation of AFH in M-1 (0.33g), M-2 (0.29g), and M-3 (0.20g) was consistent with the stability of AFH at the Eh/pH conditions of those fluids (Figure 8) and with leaching from the shallow diorite unit (0.79 mg/L Fe) by groundwater throughflow (Table 4).

The mineralogy of the precipitates forming in the APL test comprised amorphous metal-bearing precipitates rather than phases with ordered structure. For example, as postulated by others (Tempel et al. 2000), the JPL floc precipitating in acidic conditions primarily consisted of a mixed AFH and Mg-K-Al clay (Figure 9a), while the pH 6.1 MPL floc (including AGHAU runoff) was a mixed ferrihydroxide/basaluminite containing 4% copper (Figure 9b). In the absence of the AGHAU runoff, the pH of M-3 increased to 7.1, resulting in more effective attenuation of copper (0.22 mg/L) compared to J-1 and J-2 (averaging 2.3 mg/L Cu) and minimal sulfate in the ferrihydroxide matrix (Figure 9c; Table 4). The removal of solutes by precipitation reactions is generally consistent with those remaining in solution (Table 4) and with the measured pH and Eh in M-1, M-2, and M-3.

As a way of quantifying the removal of metals from solution by sorption/precipitation, Logarithmic Floc Enrichment Factors (pFEFs) representing the metal ratio in the floc compared to the fluid phase (Table 4) were calculated from:

$$\mathrm{pFEF_i} = \log_{10}[\mathrm{Floc_i}\ (\mathrm{mg/kg}) / \mathrm{Solution_i}\ (\mathrm{mg/L})]$$

The pFEFs ranged from 1.6 for Na, to 6.5 for Al (Table 5), generally increasing with pH. Most values were within the range of experimental distribution coefficients (Kd values) reported in the literature (Thibault et al. 1990; Table 5) or higher, due to co-precipitation with AFH.

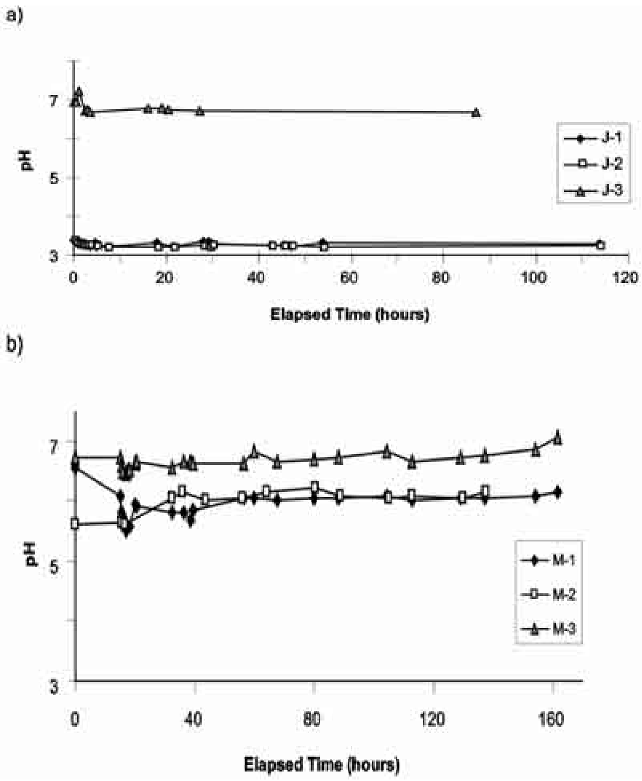

Figure 7. Evolution of pH with (J-1, J-2, M-1, M-2) and without highwall runoff (J-3 and M-3) in a) the JPL and b) the MPL

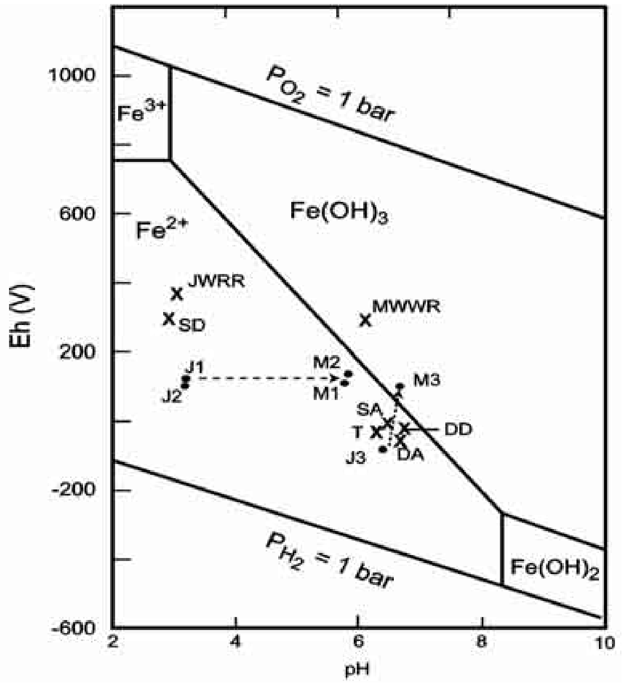

Figure 8. Influent leachate water (x) and APL test (●) Eh-pH data superimposed on the Fe-O-H system at 25°C and 1 bar; J=juvenile APLs, M = mature APLs, T= tonalite, DD = deep diorite, SD = shallow diorite, DA = deep andesite, JWWR = juvenile wall rock runoff, MWWR = mature wall rock runoff. The chemical evolution between the JPL and analogous MPL is designated by dashed arrows.

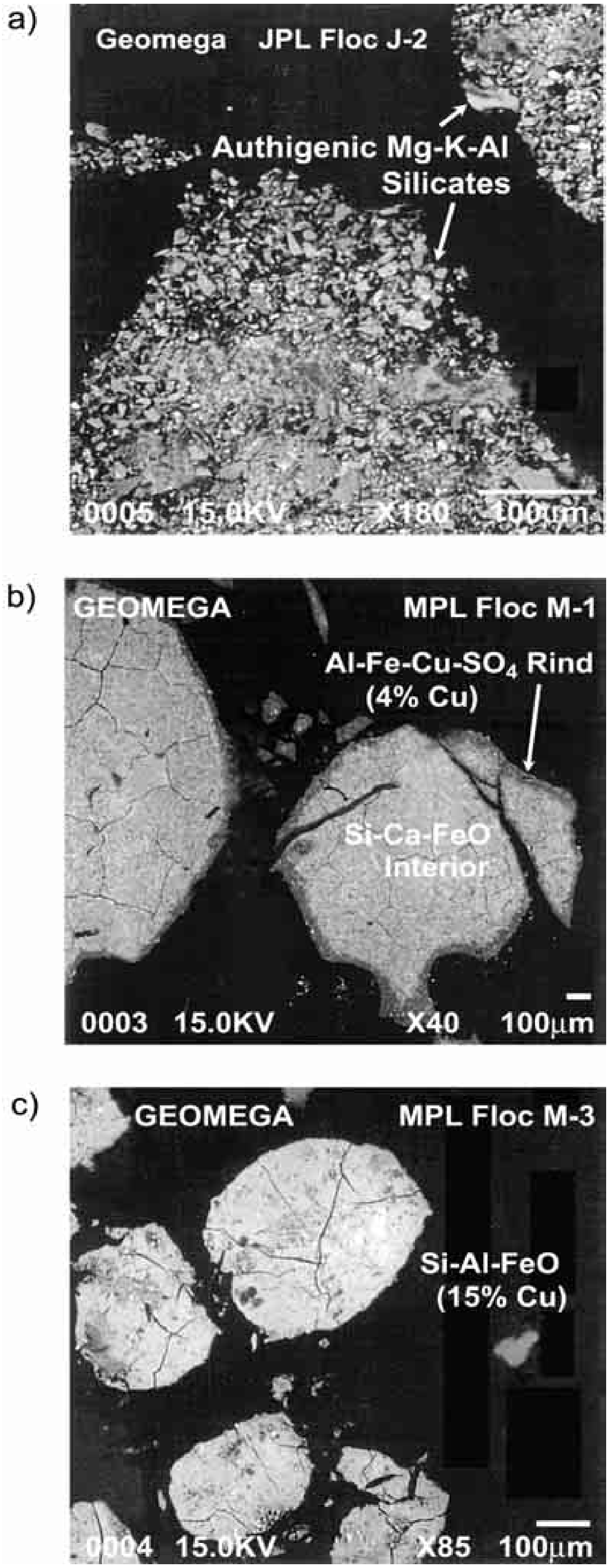

Figure 9. EMPA photomicrographs of: a) copious clay particles agglomerated in J-2; b) a Si-Ca-Fe oxyhydroxide bearing an Al-Fe-Cu sulfate rind containing up to 4% Cu; and c) Si-Al-Fe oxyhydroxide containing up to 15% Cu

Geochemical Modeling

The geochemical processes occurring in the experimental pit lake solutions were simulated using PHREEQC (Parkhurst 1995). The solutions were mixed in the appropriate proportions (Figure 1) and charge balanced by the addition or subtraction of Na^+, Cl^-, or SO_4^{-2}, then evaporated to 7% for the JPLs and 37% for the MPLs, and equilibrated with atmospheric partial pressures of CO_2 ($10^{-3.5}$ atm) and O_2 ($10^{-0.7}$ atm). The solutions were also allowed to equilibrate with solids that precipitated in the APL test or are known to form rapidly in acidic to slightly alkaline solutions, e.g., ferric oxyhydroxide (FeOOH), tenorite (CuO), barite ($BaSO_4$), basaluminite ($Al_4(SO_4)(OH)_{10}.5H_2O$), and micro-crystalline gibbsite [$Al(OH)_3$]. The mass of precipitated FeOOH was determined and then designated as a sorbing surface for ionic species, and the solutions re-equilibrated with the pertinent adsorption/desorption equilibria to compare with the analytical data.

The JPL solutions with high-wall runoff (J-1 and J-2) were similar to the measured values (Table 6) with the exception of SO_4^{-2} (used to charge balance the solutions). The MPL simulations, both with the andesite unit (M-1 and M-2) and in its absence (M-3) were also in good agreement with the measured values except for Cl (used to charge balance the solutions).

Conclusions

The APL test provides a rapid screening tool to estimate the evolving water quality of future pit lakes. As such, it augments the predictive capability of pit lake models (e.g., PITQUAL, Davis et al. 2002; MINEWALL, MEND 1995) by providing information on the precipitates that control metal solubility in pit lake water columns and identifying any pit lake components that may become of regulatory concern. This test resulted in a conservative estimate of pit lake water quality because the attenuation capacity of inundated UPS (which could be represented by a layer of representative rock on the base of the APL) was not included.

In addition, the test provides another method of predicting chemogenesis or validating numerical simulations of the aqueous chemistry as a function of time and infilling. Finally, the APL test could be used to assess the lake water quality of different pit shell designs intersecting variable lithological fractions, the effects of high wall failure on pit lake chemistry, and the efficacy of remedial alternatives designed to modify pit lake chemistry upon closure. These may include addition of alkaline tailings to potentially acid pit lakes, modification of the UPS to preclude acid-generating

Table 5. Floc enrichment factors (L/kg)

Log FEF	pH	Al	Ba	Be	Ca	Cd	Cu	K	Mg	Mn	Na	Ni	S	Sr	V	Zn
J-2	3.3	3.40	2.81	2.71	2.21	4.09	2.12	2.22	3.01	2.52	1.75	2.65	2.06	2.24	2.76	2.15
M-1	6.2	NDW	2.79	3.70	1.79	NDW	3.93	2.16	2.46	2.46	1.59	2.92	2.54	1.98	3.15	2.80
M-2	6.1	6.11	3.26	3.77	1.89	4.16	3.59	2.84	2.64	2.81	1.66	3.21	2.38	2.20	3.19	2.77
M-3	7.1	6.48	4.12	4.45	2.52	4.65	5.59	NDP	2.66	3.82	2.48	4.40	NDP	3.24	5.01	4.59
Low log Kd		NR	-.40	2.40	0.08	1.00	1.88	1.18	0.20	1.48	NR	1.00	NR	-0.30	NR	2.15
High log Kd		NR	4.95	3.48	1.95	3.00	2.42	2.30	1.13	4.89	NR	3.56	NR	3.92	NR	4.00

NDW: not detected in water; NDP: not detected in ppt (Kd = 0); Kd range reported in Thibault et al. (1990); NR: not reported

Table 6. Measured vs. modeled analytes in the APL test (mg/L); M-3 lacked the juvenile runoff component

Analyte	J-1	J-2	PHREEQC	J-3	PHREEQC	M-1	M-2	PHREEQC	M-3	PHREEQC
Al	12.0	12.0	12.0	<.008	0.01	<.008	0.06	0.04	0.02	0.11
Ca	23.0	22.0	20.9	15.7	10.3	21.8	22.2	17.0	13.0	15.6
Cu	6.99	6.61	6.67	<.002	0.00	2.18	2.42	2.61	0.22	0.04
Fe	1.06	1.11	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00
K	9.89	8.64	9.54	3.11	4.22	4.21	3.86	3.79	2.40	2.60
Mg	16.8	15.3	14.8	5.60	5.93	9.53	9.39	9.71	4.76	7.61
Mn	1.02	0.88	0.89	0.13	0.11	0.47	0.48	0.70	0.20	0.54
Na	22.1	21.0	20.2	14.5	15.4	10.7	9.33	13.57	10.12	9.89
P	0.60	0.59	1.05	0.59	0.41	0.59	0.58	0.48	<0.30	0.53
Sr	3.35	3.21	3.13	1.17	1.04	1.68	1.52	1.75	0.93	1.31
Zn	0.41	0.38	0.33	0.01	0.00	0.26	0.27	0.53	0.09	0.40
Cl	5.20	5.50	5.28	5.20	4.96	5.90	4.30	58.6	5.50	5.45
F	0.50	0.50	0.32	0.20	0.12	0.20	0.10	0.19	0.20	0.12
SO4	102	65.0	263	43.0	44.1	31.0	29.0	39.1	27.0	33.3
Alkalinity	0.00	0.00	0.00	51.0	44.5	6.00	4.00	0.56	34.0	26.6
pH (s.u.)	3.30	3.30	3.29	6.70	8.14	6.20	6.10	6.03	7.10	7.88

surfaces, and either partial or complete infilling through in-pit translocation of waste rock or backfilling.

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References

ASTM (1996) Standard test method for accelerated weathering of solid materials using a modified humidity cell. Standard D5744. American Society for Testing and Materials. West Conshohocken, PA 13p

Chapman J, Paul M, Jahn S, Hockley D (2000) Sulphide and carbonate availability and geochemical controls established from long-term column tests. Proc, 5th International Conf on Acid Rock Drainage, v 1, Denver, CO, IMWA, 581-590

Davis A, Eary LE (1997) Pit lake water quality in the Western U.S.: An analysis of chemogenetic trends. Mining Eng 6: 98-102

Davis A, Ashenburg D (1989) The aqueous geochemistry of the Berkeley Pit, Butte, Montana. Appl Geochem 4: 123-36

Davis A, Ruby MV, Bergstrom PD (1992) The bioavailability of arsenic and lead in soils from the Butte Mining district. Environ Sci Technol 26: 461-468

Davis A, Fennemore GG, Moomaw C, Buffington R (2002) Innovative Strategies in Remediating Mining Wastes. Ch 7 in Handbook of Complex Environmental Remediation Problems. CRC, Boca Raton, FL, USA

De Carvalho CN, Leprun JC (1991) Atmospheric deposition to a rural tropical site. Biogeochem 14: 99-112

Delmelle P, Bernard A (1994) Geochemistry, mineralogy, and chemical modeling of the acid crater lake of Kawah Ijen Volcano, Indonesia. Geochim Cosmochim Acta 58: 2445-2460

Eary LE (1999) Geochemical and equilibrium trends in mine pit lakes. Appl Geochem 14: 963-987

Fennemore GG, Neller WC, Davis A (1998) An improved method to predict pyrite oxidation in open pit mine wall rock. Environ Sci Technol 32: 2680-2687

Geller W, Klapper H, Salomons W (1998) Acidic Mining Lakes-Acid Mine Drainage, Limnology and Reclamation. Springer, Berlin, 435 pp

Geomega (2001) Twin Creeks In-Pit Translocation Program: Pit Water Quality. Prepared for Newmont Mining Co, Boulder, CO

Golder (1995) Technical Memoranda on Regional Hydrogeology and Regional Hydrochemistry. Golder Assoc, Denver, CO

Lapakko K (1992) Projection of the time required for neutralization potential depletion. Abstract, Mining, Exploration and the Environment '92, North Pacific Section, Soc of Mining, Metallurgy, and Exploration, Bellevue, WA

Ludwig B, Balkenhol R (2001) Quantification of the acidification potential of pyrite containing sediment. Acta Hydrochim Hydrobiol 29: 118-128

MEND (1995) MINEWALL 2.0. Programmer's Notes and Source Code. MEND, Ottawa, Ontario, Canada

Miller GC, Lyons WB, Davis A (1996) Understanding the water quality of pit lakes. Environ Sci Tech 30: 118A-123A

Morin KA, Hutt NM (1995) MINEWALL 2.0: A technique for predicting water chemistry in open-pit and underground mines. Conf on Mining and the Environment, Sudbury, Ontario, Canada

Newmont (1995) Carbon/sulfur mineral phases in solids by Leco 344 analyzer. Standard Operating Procedure AL0030 A-G. Newmont Gold Co, Denver, CO

Nicholson RV, Gillham RW, Reardon EJ (1988) Pyrite oxidation in carbonate-buffered systems: 1. Experimental kinetics. Geochim Cosmochim Acta 54: 395-402

Nordstrom DK (1982) Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. Acid Sulfate Weathering. Soil Sci Soc America, Madison, WI. pp 37-56

NRC (1999) Hardrock Mining on Federal Lands. Committee on Hardrock Mining on Federal Lands. NRC, National Academy Press, Washington D.C. 260pp

Parkhurst (1995) D.L. User's guide to PHREEQC-A computer program for speciation, reduction-path, advective transport, and inverse geochemical caculations, USGS Water Resources Investigation Report, pp 95-4227

PTI (1996) Predicted water quality in the Twin Creeks Mine pit lakes. PTI Environmental Services, Boulder, CO, prepared for the Santa Fe Pacific Gold Co

Runnells DD, Sheperd TA, Angino EE (1992) Metals in water: Determining natural background concentrations in mineralized areas. Environ Sci Tech 26: 2316-2323

Schultze W, Geller W (1996) The acidic lakes of the lignite mining district of the former German Democratic Republic. In: Reuther R (ed) Geochemical Approaches to Environmental Engineering of Metals, Springer, Berlin, pp 89-105

Shevenell L, Conors KA, Henry C. (1999) Controls on pit lake water quality at sixteen open-pit mines in Nevada. Appl Geochem, 14: 669-687

Shevenell L (2000) Cases and Solutions: Water quality in pit lakes in disseminated gold deposits compared to two natural, terminal lakes in Nevada. Env Geol 39: 807-815

Sobek AA, Schuller WA, Freeman JR, Smith RM (1978) Field and Laboratory Methods Applicable to Overburdens and Minesoils. EPA-600/2-78-054

Tempel RN, Balistrieri LS, Lengke MF, Shevenell LA, Stillings LL (2000) Proc, 5th International Conf on Acid Rock Drainage, Society for Mining, Metallurgy and Exploration, v 1, Denver, CO, pp 327-336

Thibault DH, Sheppard MI, Smith PA (1990) A critical compilation and review of default soil solid/liquid partition coefficients, Kd, for use in environmental assessments. Atomic Energy of Canada Ltd, Whiteshell Nuclear Research Establishment, AECL-10125

U.S. EPA (1986) Test methods for evaluating solid waste. SW-846, 3rd edit. Office of Solid Waste and Emergency Response, Washington, D.C.

U.S. EPA (1993) Methods for the Determination of Inorganic Substances in Environmental Samples. 600/R-93-100. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA (1994) Acid mine drainage prediction. 530-R-94-036. Office of Solid Waste Special Waste Branch, Washington, D.C.