

D-3

TDRSA Water Chemistry

TECHNICAL MEMORANDUM

DATE: 7 November 2005

TO: Kennecott Eagle Mining Company

FROM: Mark J. Logsdon (Geochimica)

SUBJECT: Water Quality from the Development Rock Storage Pad During Operations

BACKGROUND

The water-quality model for the Development Rock Stockpile in the Phase II Geochemistry Report (Geochimica, 2005) is for a full-scale pad that contains the entire volume of development rock that will ultimately be placed there before backfilling begins. The model results in the report assume no amendment of the stockpile with limestone. The hydraulic portion of the analysis is based on effective infiltration of 20% of the average annual precipitation, estimated from long-term data at Marquette. This memorandum describes and produces the results for a water-quality model for the Development Rock Stockpile, including the expected geochemical effects of amending the development rock with limestone to extend the lag period for the onset of possible acidification. This analysis uses the most recent and complete data for simulated weathering in column tests, received in August 2005.

TECHNICAL APPROACH

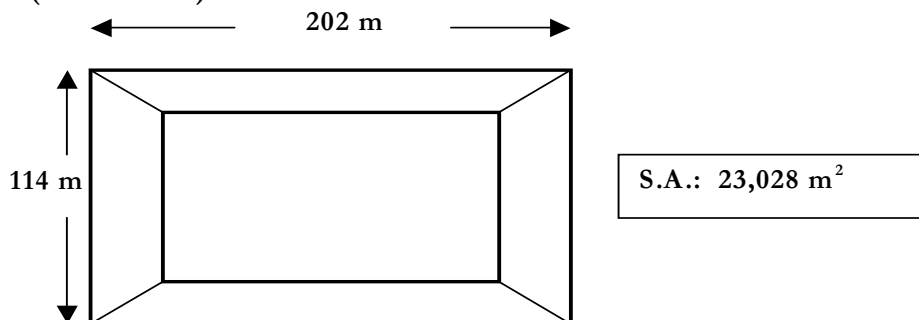
Based on current mine planning, KEMC will produce a total of approximately 379,000 tonnes¹ of development rock that will be stored on a rectangular pad with plan dimensions of approximately 200 m by 100 m for periods of up to seven years at the surface. Mid-way through the mine life (beginning about Mine Year 4), development rock will be returned to the underground workings as cemented backfill, and by Mine Year 7 all development will be backfilled into the deep underground.

At this stage of the geochemical investigations, one can develop a simple model of a development rock stockpile undergoing surficial weathering in the vadose zones with rinsing by infiltrating meteoric waters (rain and snowmelt) typical of average annual precipitation in the Upper Peninsula. One uses the results of the ongoing kinetic tests and available data on site hydrology to characterize the system behavior. The basic conceptual model for a development-rock stockpile undergoing surficial weathering is illustrated in Figure 1.

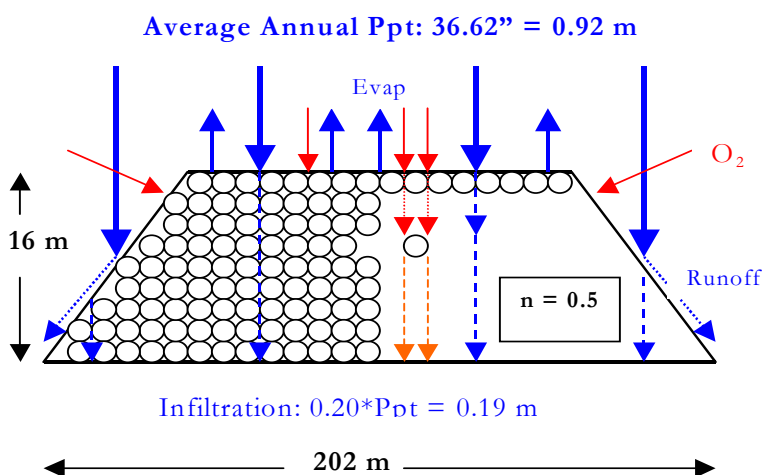
¹ Tonne is a metric ton, 1000 kg, or 2200 pounds (1.1 US short ton).

Figure 1 Conceptual Model for a 379,000-tonne Development-Rock Stockpile

Plan (not to scale):



Section (not to scale):



The model assumes that the development rock stockpile would be an equal mixture of Intrusive and Country Rock that has been well represented by the Phase I and Phase II kinetic tests. For each rock group, we have considered high-sulfur and low-sulfur samples from the kinetic tests. In this most recent version, we have used data from both the Phase I and II tests because Phase II samples represent a higher-sulfur range and show more sign of reactivity. Sulfide oxidation in the stockpile occurs because O₂ migrates into the pile; this model does not depend on the specific mechanism of gas transport, but does assume that oxygen is not limiting. Water needed for the reactions and also for transport through the pile comes from annual precipitation that is intercepted on the plan surface area of the pile. The average-annual precipitation value, 36.6 inches (0.92 m) per year is the long-term average from Weather Service records at Marquette. For the calculation, we assume that 20% of average annual precipitation infiltrates through the pile on a steady-state basis. The bulk porosity of the pile is assumed to be 50%, and the mean diameter of rock particles in the pile is assumed to be 10 cm (0.1 m). Leach rates for weighted average country-rock and intrusives are calculated in terms of mass per unit surface area per unit time from the kinetic column tests, with the surface areas calculated from the sieve analyses of sample splits

measured before the leach testing begins. Because the rock on the full-scale pad will include much more coarse rock than can be tested in the columns, the column leach rates are then scaled to field conditions for the surface area of the total pad. The spreadsheet model used to calculate expected water quality is provided in Appendix F to Geochimica (2005), and also includes a thermodynamically-based geochemical model of the estimated solution to account for precipitation and sorption reactions that could be expected within the pile prior to discharge.

The basis for the mass-balance calculation is as follows:

- Compile basic data on the column tests (mass of charge; particle-size distribution of the fragments; weekly effluent volumes)
- Compile column test effluent chemistries for a representative period over which chemistries are essentially constant. Because natural rain water is compositionally close to de-ionized water, the conceptual model of the column tests is apt, and the effluent chemistries can be taken as representative, for the experimental conditions of the columns.
- Convert the observed concentrations to release rates in units of mass/unit surface area/unit time.
- Calculate the total surface area for rock in the stockpile based on a model of particle size distribution for the rock.
- Calculate the equivalent annual mass released from weathering of the full stockpile, assuming that release rates per unit surface area in the columns is equivalent to release rates per unit surface area of the full-scale pile.
- Calculate the volume of infiltration expected to report through the pile on an annual basis.
- Divide the mass released by the amount of water available to carry the mass. This has units of concentration (Mass solute/Volume solvent).
- Finally, evaluate the mass-balanced chemistry in terms of equilibrium with geochemically credible phases (e.g., gypsum; ferrihydrite), and the pH is calculated for the resultant solution as controlled with atmospheric CO₂.

LEACHATE CHEMISTRY IN MODEL INPUT

In the conceptual model for the Development-Rock Stockpile, there is no ore-grade rock (Massive Sulfide Unit or Semi-Massive Sulfide Unit). Based on advice from mine planners, the total access development is modeled as 50% unmineralized intrusive and 50% country rock. Both types of development rock are assumed to include both high-sulfur and low-sulfur rocks, represented by the range of samples that have been weathered in KEMC's ongoing column-test program. To represent this conceptualization, we take long-term (40 –

70 week) data from the most recent column-leach tests for the unmineralized intrusives and country rock. When input data are less than the limit of detection, they are entered in the model as ½ the limit of detection.

Table 1 Input Leachate Chemistry for Development-Rock Stockpile during Operations (mg/L except pH in su and Alkalinity in mg CaCO₃/L)

Parameter	Values	
	Country Rock	Intrusive
pH	6.1	7.1
Alkalinity	6.8	8.4
Total Dissolved Solids	145	164
Calcium	12	9
Magnesium	8	16
Sodium	2	3
Potassium	2	6
Bicarbonate	5.5	6.9
Sulfate	72	82
Cl	0.5	0.6
F	0.07	0.09
Aluminum	0.32	0.62
Antimony	0.0004	0.0002
Arsenic	0.01	0.001
Barium	0.007	0.015
Boron	0.03	0.13

Parameter	Values	
	Country Rock	Intrusive
Cadmium	0.0020	0.0021
Chromium, Total*	<0.0005	.0009
Cobalt	0.111	.053
Copper	0.40	1.13
Lithium	0.007	.009
Lead	0.007	.019
Iron	2.51	4.77
Manganese	0.48	0.17
Mercury *	<0.00005	<0.00008
Molybdenum	<0.0004	<0.0001
Nickel	0.63	1.65
Selenium	0.0005	0.0032
Silver*	<0.00002	<0.00001
Strontium	0.104	.09
Thallium*	<0.0001	<0.0001
Vanadium	<0.001	.0015
Zinc	0.32	0.18

*: Values less than the detection limit are entered in model as ½ detection limit for calculational purposes

DEVELOPMENT-ROCK STOCKPILE MODEL RESULTS

The results of the equilibrated model are presented in Table 2 for the same parameters that are shown for input waters in Table 1. In cases where input data were less than detection, output data are modeled using a value of one half the largest detection limit in the set. For additional detail and discussion of specific geochemical reactions, readers are directed to the Phase II Geochemistry Report (Geochimica, 2005).

Table 2 Modeled Water-Quality for Development-Rock Stockpile – No Limestone Addition (mg/L except pH in su and Alkalinity in mg CaCO₃/L)

Parameter	Value	Parameter	Value
pH	7.1	Cadmium	0.0002
Alkalinity	66	Chromium, Total**	0.00045
Total Dissolved Solids	865	Cobalt	0.0008
Calcium	79	Copper	0.29
Magnesium	88	Lithium	0.019
Sodium	19	Lead	0.0004
Potassium	29	Iron	0.005
Bicarbonate	54	Manganese	0.005
Sulfate	575	Mercury **	0.00004
Cl	11	Molybdenum	0.0015
F	2	Nickel	8.33
Aluminum	0.001	Selenium	0.004
Antimony	0.0004	Silver**	0.00005
Arsenic	0.083	Strontium	0.50
Barium	0.03	Thallium**	0.00005
Boron	0.58	Vanadium**	0.00075
		Zinc	1.90

** : Input values less than the detection limit were modeled as 1/2 detection limit for calculational purposes

The mass-balanced values were adjusted in the geochemical model REACT (Bethke, 2005) for solubility controls. Geochemically credible phases that affect the solution chemistry included barite [Ba], ferrihydrite [Fe], gibbsite [Al], manganite [Mn], malachite [Cu], and amorphous silica [Si]. The model considered the solution for solubility with gypsum [CaSO₄·2H₂O], but found the waters somewhat undersaturated. The geochemical model

predicts extremely low values (<0.001 mg/L for Al, Fe and Mn). For this evaluation, we have adjusted them slightly upward to account for sub-part per million levels of these metals observed in almost all natural groundwaters that have TDS values greater than a few hundred mg/L.

No pure-metal solubility controls in low-temperature waters were found for trace metals and metalloids such as As, Sb, B, Cd, Cr, Pb, Ni, Se, or Zn. Because the input values for Hg in both rock types are less than detection, the model returns less-than-detection values for Hg; concentrations of other trace metals (Cr, Ag, Tl and V) also are limited by the non-detect values in one or both of the input parameters. It is expected that there could be sorption controls on some of these metals and metalloids, especially As and Hg. Near pH 7, sorption of B, Cd, Ni, Se and Zn would be slight; relatively little is known about the sorption behavior of Sb, but it probably behaves somewhat like As. Although the model solution is saturated in ferrihydrite, the amount of ferric hydroxide precipitated is so small that sorption onto the ferric hydroxide precipitated would be minimally effective at pH near 7.

DISCUSSION

General Results

Table 2 shows that important aspects of the effluent chemistry in the stockpiled development rock, especially the concentrations of sulfate and trace metals, will be dominated by the reactivity of the minor to trace levels of sulfides that are exposed during operations. The mineralogy of these rocks is described in detail in the Phase II Geochemistry Report (Geochimica, 2005).

The specific values shown in Table 2 derive from the specific assumptions (e.g., 50% proportions of both country rock and intrusives; volume of development rock on the stockpile; infiltration rate) used in the model. If other modeling assumptions had been used, the concentrations would have differed. However, the general outcome of the modeling (neutral pH; slightly elevated sulfate; part-per-million concentration for Ni) would be repeated for any plausible combination of assumptions that are based on the existing test data. Thus, we consider that the model successfully represents the major chemical conditions expected in the development rock storage pad so that water-management and treatment options can be evaluated.

Column-test data indicate that the neutralization potential measured in the static tests (Phase II report, Geochimica [2005]) are sufficiently available to overcome the acidity, averaged over the tested samples, released from oxidation of the minor to trace amounts of sulfide minerals for generally extensive periods. The parameters that are noticeably different from common water-quality criteria are boron, sulfate and nickel. Boron derives from leaching of the intrusive rocks, all of which have elevated concentrations of B. The slightly elevated sulfate is due to oxidation of pyrite and pyrrhotite in both rock types, and nickel will be released during the incipient oxidation of sulfide minerals (probably largely pyrrhotite) in the development rock. Unlike some other transition metals (e.g. Fe), there is no plausible solubility control for Ni once it has been released, so its elevated concentration during operational conditions is entirely expected.

Unlike groundwater flowing into the workings that will have reacted with bedrock over thousands of years and will already have a solute load, the water infiltrating the development rock stockpile will be a very low and poorly buffered rain water or snow melt. Therefore, the outcomes from this modeling exercise do not need to be understood as incremental concentrations, but rather can be taken as estimates of effluent from the development-rock stockpile.

Effects of Adding Limestone to Extend Lag Period for Onset of Acidification

The initial modeling of the Development-Rock Stockpile, although producing a pH of 7.1 (Table 2), is slightly undersaturated in calcite (CaCO_3). This suggests a possible strategy for simply amending the system with readily-available High-Calcium limestone. This would have two, closely related functions:

- Add additional acid-neutralization capacity, in a readily available form, to the pad, thereby extending the lag period for potential onset of acidification.
- Raise the pH of effluent water, further reducing concentrations of pH-sensitive metals such as Cu and stabilizing the ferric hydroxide (ferrihydrite) that would precipitate and sorb other trace metals.

The effect of adding limestone was evaluated by simulating the reaction of the modeled effluent with calcite (CaCO_3 , the principal component of limestone). A source of limestone being considered by KEMC has an analyzed content of 98% CaCO_3 (personal communication, KEMC, September, 2005), so this is a fair assumption regarding the mineralogy. The simulation is conducted using the numerical model REACT (Bethke 1996; 2005). In the simulation, only a small amount of limestone (600 mg CaCO_3 ; 0.22 cm³ of calcite) is required to bring each kg of modeled effluent into equilibrium with calcite. The results are provided in Table 3.

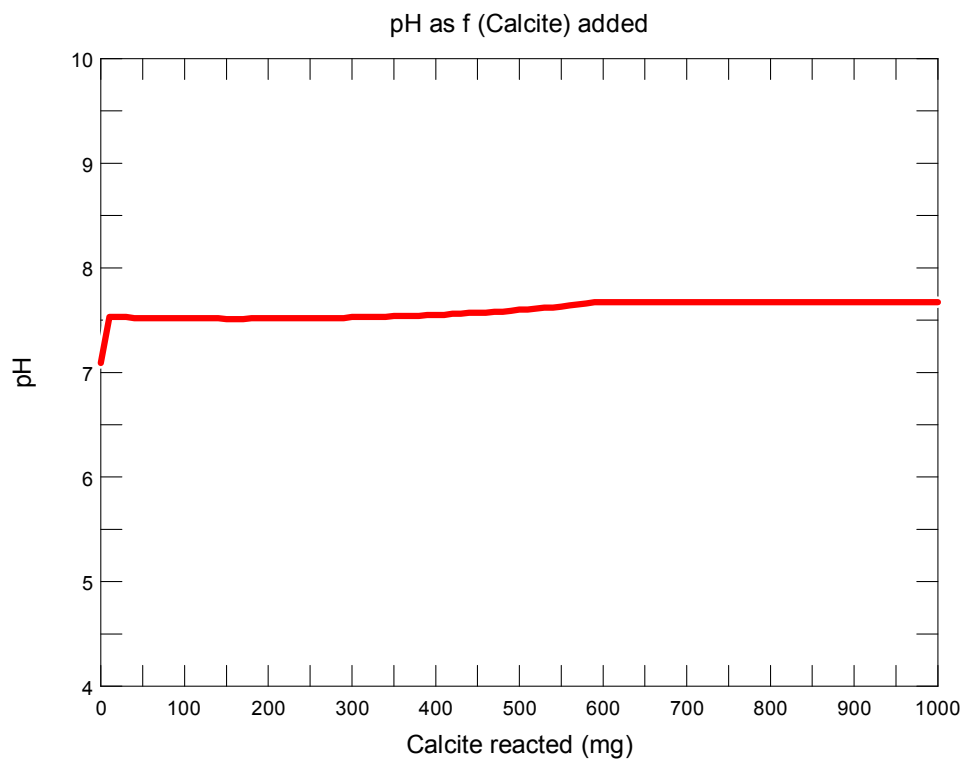
Table 3 Modeled Water-Quality for Development-Rock Stockpile with Limestone Addition (mg/L except pH in su and Alkalinity in mg CaCO₃/L)

Parameter	Value	Parameter	Value
pH	7.6	Cadmium	0.0002
Alkalinity	72	Chromium, Total**	0.00045
Total Dissolved Solids	932	Cobalt	0.0008
Calcium	199	Copper	0.06
Magnesium	18	Lithium	0.019
Sodium	19	Lead	0.0004
Potassium	29	Iron	0.002
Bicarbonate	59	Manganese	0.0005
Sulfate	575	Mercury **	0.00004
Cl	10	Molybdenum	0.0015
F	0.5	Nickel	8.33
Aluminum	0.001	Selenium	0.004
Antimony	0.0004	Silver**	0.00005
Arsenic	0.083	Strontium	0.20
Barium	0.03	Thallium**	0.00005
Boron	0.58	Vanadium**	0.00075
		Zinc	1.90

** : Input values less than the detection limit were modeled as ½ detection limit for calculational purposes

The principal change is an increase in pH and Ca, and a reduction in Cu. The solution remains undersaturated in gypsum. The pH increase, modeled to be to 7.6, is not sufficiently high to precipitate Ni as a hydroxide, so the Ni concentration remains unchanged. The solution does reach equilibrium with fluorite, so there is a small decrease in the concentration of F. At the point in the simulation where calcite reaches saturation, the mineralogical control on Ba changes from barite (BaSO₄) to witherite (BaCO₃), according to the thermodynamic factors, however, there is no significant change in Ba concentration expected. Major trends in the geochemistry if limestone were added to the pile are illustrated in Figures 2 and 3.

Figure 2 pH Change as a Function of Calcite added.



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The main points of Figure 2 are that the pH (a) rises slightly and (b) stays nearly constant, implying the increase in buffer capacity from the additional calcite in the system.

Figure 3 Mineral Precipitation During Calcite Addition

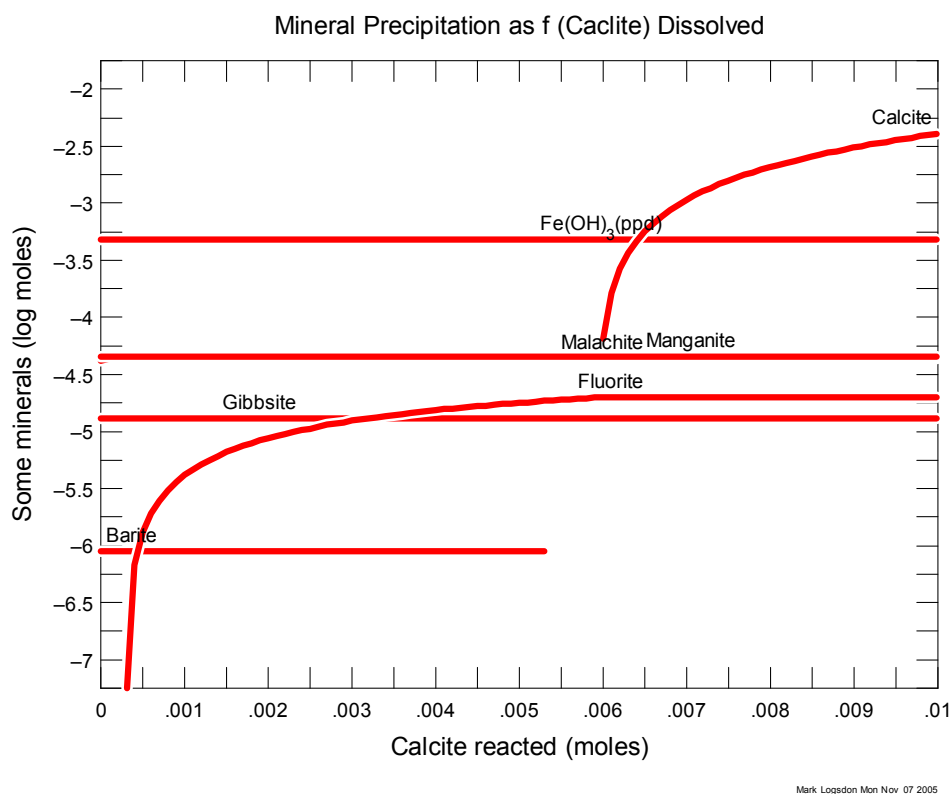


Figure 3 shows the succession of mineral precipitation reactions expected as calcite is added to the solution. Barite (controlling Ba and SO₄ very slightly), Gibbsite (Al), Malachite (Cu), Manganite (Mn), and Ferrihydrite (Fe) all were saturated when the simulation began. As explained above, the termination of barite merely means that witherite (BaCO₃) is stable once sufficient carbonate alkalinity is available. The rise of fluorite (CaF₂) is notable, adding a control for F. The appearance of calcite after dissolution of 0.006 moles (600 mg) of calcite indicates that calcite has reached equilibrium and additional calcite would then be available as additional Acid Neutralization Capacity.

ESTIMATING LIMESTONE ADDITION

The best available point estimate of ARD risk is the Net Neutralization Potential. Using either medians or means, the best estimate of NNP for the whole of the Development Rock stockpile is approximately (–10) tonnes CaCO₃ eq/kt (Phase II Report, Geochimica (2005)). If one assumes that the underground workings would re-flood quickly (either under natural gradient or by intentional flooding), then the long-term acidification potential would be controlled by the inundated condition. Therefore, KEMC could consider an alkaline addition to either the stockpile or the backfill sufficient to meet the average Maximum Potential Acidity demand, assuming that if that amendment were readily available for dissolution, it would be adequate to offset the reaction rate of the backfill and wall rock until

the flooded conditions can predominate. Note that this estimate assumes that it would be sufficient to bring the stoichiometric NNP value to precisely 0.

For 379,000 tonnes of Development Rock, an incremental NP of 10 t CaCO₃eq/kt would require about 3800 tonne CaCO₃ eq. The amount of limestone that would be needed is greater than this because of several sources of inefficiency.

- Firstly, natural limestones are rarely pure CaCO₃. Based on assays of available metallurgical-grade limestone, one may assume a 98% CaCO₃ eq content.
- Secondly, a great deal of field experience shows that only a portion of the actual potentially-effective CaCO₃ will react, either because of inefficiencies in mixing or because some of the limestone is blinded by secondary precipitates like gypsum or iron oxides. For current planning, we recommend that KEMC assume that the average availability would be 70%.
- Therefore, the total availability of neutralization potential from the limestone would be estimated at 68.6% (70% of 98%).

Therefore, a reasonable planning basis if KEMC were to strive for an even acid-base balance across the whole of the Development Rock Stockpile would be approximately 5540 tonne of limestone. If KEMC wished a factor of safety of 1.2, the value would be 6650 tonne, and for a FOS of 1.4 (the Nevada DEP factor), 7760 tonne of limestone would be needed.

If the minimum recommended value of 5540 tonne of limestone were added, this would comprise 2.31E+09 cm³ of calcite ($\rho = 2.4 \text{ g.cm}^{-3}$). If, as indicated by the numerical simulations described above, the calcite equilibrium requires 0.22 cm³ of calcite per kg of effluent, then the design-basis limestone would be capable of neutralizing 1 E+10 kg of effluent. Based on the conceptual model illustrated in Figure 1, total effluent production would be approximately 4.38E+3 m³.a⁻¹. For a fluid density of approximately 1E+3 kg.m⁻³, the total annual mass of effluent would be 4.38 E+6 kg.a⁻¹. Thus, there would be a very large excess of limestone in the pile, compared to that required to buffer pH to levels suggested by Table 3. Therefore, there should be sufficient calcite present to both ensure that the solution is not net acid-generating and also to buffer the pH and control metals concentrations to levels such as those estimated in this model (Table 3).

REFERENCES

- Bethke, C.M. 1996. *Geochemical Reaction Modeling*. New York: Oxford University Press.
- Bethke, C.M., 2005. *The Geochemist's Workbench, Release 6.0, Users' Guide*. Urbana-Champaign, IL: University of Illinois.
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