

New Insights on Factors Controlling Pit Lake Chemistry

Andy DAVIS, Maggy F. LENGKE

Geomega Inc., 2525 28th Street, Boulder, Colorado 80301, USA, andy@geomega.com

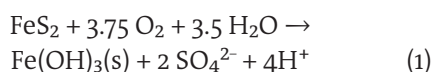
Abstract Pit lake chemistry has not always been as predicted due to several issues. For example, the pit lake surface at the rock/water interface has a ≈ 2 ft (0.6 m) capillary zone that enhances oxidation of available pyrite. If the redox boundary is above the pit lake surface, accumulation of spill material on benches results in sulfides becoming reactive if the pit lake reaches that bench. From a remedial perspective, with initiation of deeper pit lakes, it is apparent that pit lake hydraulics, including is important. However, from an ecological risk perspective, a slightly acidic (pH 4.5) pit lake does not appear to result in an unacceptable ecological risk.

Keywords pit lake, ecological risk, pyrite, predictive modeling

Introduction

Cessation of dewatering activities at open pit mines results in the creation of a "pit lake" if the pre-mining groundwater table elevation is higher than the bottom of the pit after it is decommissioned. As part of the environmental assessment process, it is necessary to determine the environmental impacts of future pit lake chemistry on potential receptors including, 1) groundwater quality adjacent to the pit (in the case of a through-flow pit lake), and 2) the food web.

Pit lake chemistry is influenced by the nature of the wall rock, its mineralogy, alteration and the location of the redox boundary. Many gold deposits are rich in sulfides, commonly pyrite (FeS_2). When pyrite reacts with atmospheric oxygen and water, sulfuric acid is generated (Nordstrom and Alpers 1999), *i.e.*:



Coal deposits, except for those with very low sulfur contents, commonly contain substantial pyrite or its polymorph, marcasite. Organic-rich shales that are mined for phosphate fertilizer may also contain pyrite (Gammons *et al.* 2009). Uranium deposits may or may not contain significant pyrite, but the radionu-

clides from the ore can present their own problems. Pits producing metals, industrial minerals, and solid fuels may all generate acid pit lakes depending on the lithologic setting.

Consequently, environmental regulators require mining companies to estimate post-mining water quality predictions as part of the permitting process. Such analyses can also guide mine managers to develop site closure plans that minimize negative impacts and optimize the value of the pit lake as a future water resource.

Pit lake chemistry prediction for mine permits is usually based on site-specific groundwater hydrogeology, background groundwater chemistry, pit lake water balance, wall rock acid-base accounting and mineralogy, pit wall surface area, and wall rock kinetic humidity cell or column tests. Model verification may rely on laboratory or field analogs (Davis *et al.* 2006) and pre-existing pit lake data (*e.g.* Tempel *et al.* 2000) where it is available. Where such information has been collected during an interlude between mining eras, *e.g.* from the South and Center pit lakes at the Getchell mine (Davis *et al.* 2006) and the Liberty and Kimbley pit lakes at Robinson (Miller *et al.* 1996), it may shed light on pit lake chemogenesis subsequent to new pit expansion and then closure.

When mining ends, the resulting pit lake chemistry has not always been as predicted. The goals of this paper are to describe the pit lake modeling process and identify perceived data and conceptual gaps which are ripe for additional research to assist in developing more accurate predictive tools.

Modeling Pit Lake Chemogenesis

Pit lake water chemistry predictions typically combine the output from a groundwater flow model (e.g. MODFLOW), background groundwater chemistry, the extent of wall rock reaction, and solute releases based on kinetic humidity cell or column tests data for related formations exposed on the pit wall. (fig. 1).

Pit wall runoff of solutes into the pit lake during storm events may also affect the chemistry but is usually considered inconsequential compared to groundwater/wallrock interactions. Wall rock reactivity is a key component of the conceptual pit lake model, the extent of which is based on the pit wall surface area in contact with pit water and a reactivity factor. The pit wall surface area is usually calculated using geographic information system (GIS) software, by superimposing the geology on pit elevation contours.

Wallrock solute release to be well represented by humidity cell tests (HCTs) run on crushed rock representative of the exposed lithologies (ASTM 2007). HCTs appear repre-

sentative of wall rock conditions due to the combination of moisture, air, heat and sulfides in the capillary zone. Curves fit to the effluent chemistry provide chemical release functions allowing cumulative mass of any parameter per surface area to be calculated as a function of time.

A finite difference groundwater model, e.g. MODFLOW (HydroGeoLogic 1996) is used to predict the infilling rate of the pit lake resulting in an estimate of the rate-of-rise of the pit lake with time. The same model is used to estimate the dewatering schedule to maintain a dry pit base during mining, any impacts to seeps and springs based on the extent of the ten-foot drawdown cone resulting from dewatering, and potential compaction due to withdrawal of water from the aquifer until recovery of the pre-mining groundwater elevation. The infilling rates from the groundwater model are correlated with the pore volumes passed through the HCTs as a function of the pit lake hydrograph, which describes the volume of water passing through any zone in the wall rock over time.

For non-reactive rock, standard equilibrium geochemical programs suffice to quantify mineral dissolution and precipitation reactions. However where there is substantial pyrite as well as other sulfides the kinetic dissolution rate becomes important, especially if these minerals are at higher elevations in the

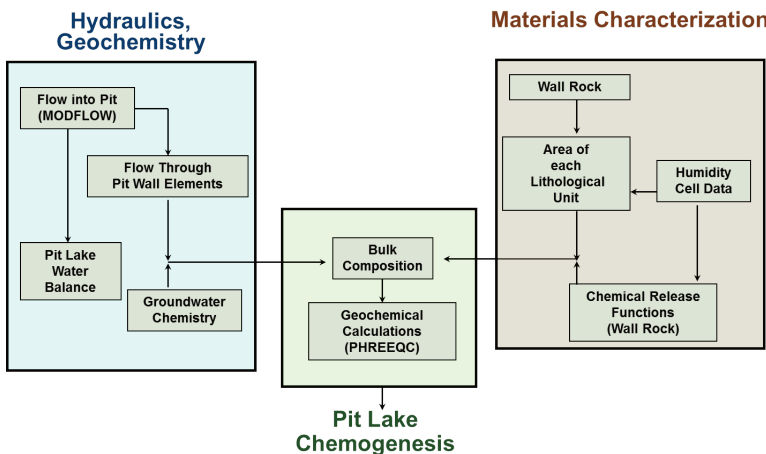


Fig. 1 Typical pit lake chemistry modeling approach

pit wall where infilling rates slow and there is a greater residence time for reactions prior to inundation by the rising pit lake. In these cases a reactivity factor has been used to predict pit lake chemistry (Geomega 2010). This factor acts as a calibration parameter (akin to variable hydraulic conductivity in the groundwater model) to incorporate factors such as increased surface area due to fracturing of wall rocks, slough material and the kinetics of sulfide oxidation.

Mechanisms Requiring Additional Attention

Rock Spalling

Open-pit mines result in benches that are usually 7 to 15 m high, depending on the size of the machinery in use and the stability of the high



Fig. 2 Rock spall on pit benches.



Fig. 3 A landslide covering several pit benches.

walls. The frequency and amount of spalling is a function of weathering rates, the type of rock, and inherent structural weakness. Benches collect rubble (fig. 2) resulting in an increase in reactive surface area as the infilling pit lake reaches this material. This factor is usually not incorporated into pit lake chemistry predictions. If the spall rocks are abundant and mostly acid-generating, then it may affect the pit lake pH.

Land Slides

A land slide results in spalling of the pit wall (fig. 3) due to slope instability. Although designed with an allowable safety factor, slides do occur. For pit lake chemistry predictions, the land slide factor is usually not included, but depending on the acid-generating capacity of the wall rock it may be relevant in acute pit lake chemical evolution.

The Capillary Zone

At several pit lakes we have observed a 1–2 foot (0.3–0.6 m) capillary zone above the air/pit lake interface (fig. 4). When the pit lake infilling rate is rapid during early recovery of the draw-down cone, the oxidation of pit wall sulfides is limited due to, 1) inadequate time for oxidation before the sulfide is inundated, and 2) sufficient alkalinity to offset any acid generation from soluble acid salts. As pit infilling slows, there is increasing time for sulfide oxidation



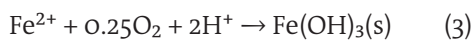
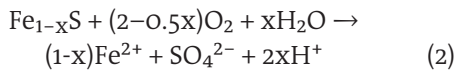
Fig. 4 Capillary zone during pit lake infilling.

to be initiated in the capillary zone due to the availability of oxygen, heat, and moisture.

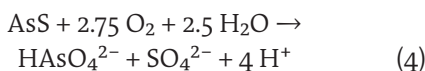
Sulfide oxidation (fig. 3) is indicated by the red iron oxide/hydroxide in the capillary zone. Abiotic pyrite oxidation rates increase over time (Lizama and Suzuki 1989) and under acidic conditions even more so if bacteria, *e.g. thiobacillus ferrooxidans* are present (Nordstrom 1982). This process indicates that reaction rate kinetics may be an important component of pit lake chemistry prediction in such settings, precluding the use of equilibrium geochemical programs (*e.g.* PHREEQC, MINTQA2). The kinetic reactivity is usually not built into pit lake predictions, but it has been applied as part of pit lake predictions for the Getchel mine, Nevada, USA (Tempel *et al.* 2000) and the Martha mine, New Zealand (Castendyk and Webster-Brown 2007).

Mineralogy and Kinetic Reaction Rates

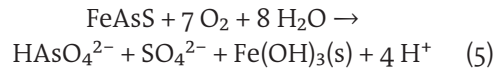
Pyrite is generally considered to be the sulfide engendering acidity. However, other iron sulfides such as pyrrhotite and marcasite can be equally or more problematic so that understanding wallrock mineralogy is an important geochemical variable. Pyrrhotite has a non-stoichiometric composition (Fe_{n-1}S_n with n≥8), resulting in structures from Fe₇S₈ to Fe₁₁S₁₂. The oxidation reaction of aqueous pyrite or marcasite by dissolved oxygen is written in the above reaction (1) and the oxidation reaction of pyrrhotite is:



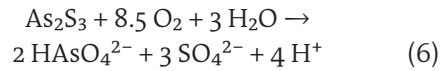
In addition, arsenic sulfides may have similar reactivity to iron sulfides depending on arsenic species in solution. For example, dissolution of realgar generates the same number of protons as pyrite, *e.g.*:



as does each mole of arsenopyrite:



and orpiment :



The kinetic rate laws for oxidation of pyrite (Williamson and Rimstidt 1994), marcasite (Asta *et al.* 2010), and orpiment/realgar (Lengke and Tempel 2009) demonstrate that rates generally increase at higher pH values with increasing dissolved oxygen. However, the reaction of orpiment and realgar in the laboratory has not shown a complete oxidation reaction of arsenic and sulfur species (Lengke and Tempel 2009). The oxidation rate of pyrite by dissolved oxygen is much lower than marcasite at pH 2–3 and pyrrhotite at pH 2.8 while the pyrite oxidation rate is slightly higher than realgar and orpiment (fig. 5).

In a ferric iron-mediated system, the oxidation rate of pyrrhotite increases by one order magnitude at pH 2.8 (Janzen *et al.* 2000), while the oxidation and dissolution of arsenopyrite increases by approximately one to two orders of magnitude at pH 1.8 over non-ferric iron systems (Lengke and Tempel 2009).

Sulfide oxidation by iron- and sulfur-oxidizing bacteria facilitates oxidation of Fe²⁺ to Fe³⁺ or of elemental sulfur to sulfate, respec-

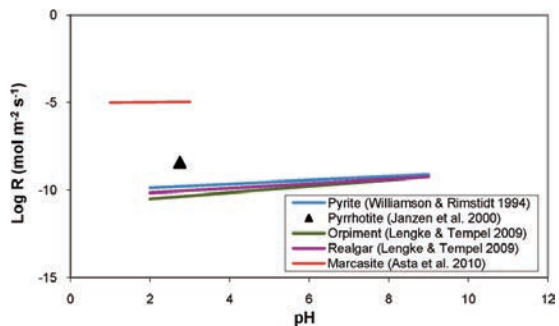


Fig. 5 A comparison of Fe- and As-bearing sulfide oxidation as a function of pH.

tively (Lengke and Tempel 2009). Because Fe^{3+} in solution can rapidly attack the sulfide surface, these minerals will be oxidized as rapidly as the bacteria can generate Fe^{3+} . In addition, increasing acidity as elemental sulfur is oxidized to sulfate may cause an increase in oxidation rates.

Pit Lake Hydrodynamics

An emerging field in pit lake chemistry is the evolution of the thermal (and chemical) profile as the pit lake fills. This phenomenon has been described previously in the Berkeley pit lake (Davis and Ashenburg 1989).

Where pit lakes are acidic and mitigation is necessary, this issue is consequential because of the need to manage liming over the course of yearly cycles of thermal stratification and breakdown. In addition, pits are often asymmetric in structure, such that evolving thermal and chemical conditions in deep portions of the pit lake can lag behind shallow areas.

Modeling pit lake hydrodynamics is complicated by these factors and also because the requisite data to calibrate the models is rarely available.

Integrating Ecological Risk with Pit Lake Predictions

A screening-level ecological risk assessment (SLERA) evaluates potential ecological risks as-

sociated with the actual range of pH and chemistry in a mine pit lake, specifically to wildlife attracted to the water. In the SLERA, a set of species representative of the food web is identified then the pit lake water concentration compared with different toxicity thresholds, *e.g.* the no- or the lowest-observed adverse effects threshold, the NOAEL or LOAEL, respectively, to ascertain the potential for risk.

A SLERA can also be used to develop a critical pH at which there should be no adverse impacts to biota. For example, the lowest pH at which Al is \geq NOAEL (4.5 mg/L) is 4.0. Using a LOAEL (45 mg/L) the highest pH at which Al \geq LOAEL is 3.3 (fig. 6).

Conclusions

Predicting pit lake chemistry is not simple, and ultimately the accuracy of the prediction should be evaluated by comparing modeled pit lake chemistry to observed lake water chemistry during the post-mining period. Factors controlling pit lake chemistry such as rock spalling, land slides, and pyrite oxidation kinetics in the capillary zone may have significant impacts on pit lake chemistry that have not been incorporated into conceptual models. Ongoing monitoring of post-mining pit lakes is an important element of understanding pit lake chemogenesis that will improve our scientific understanding and lead to more

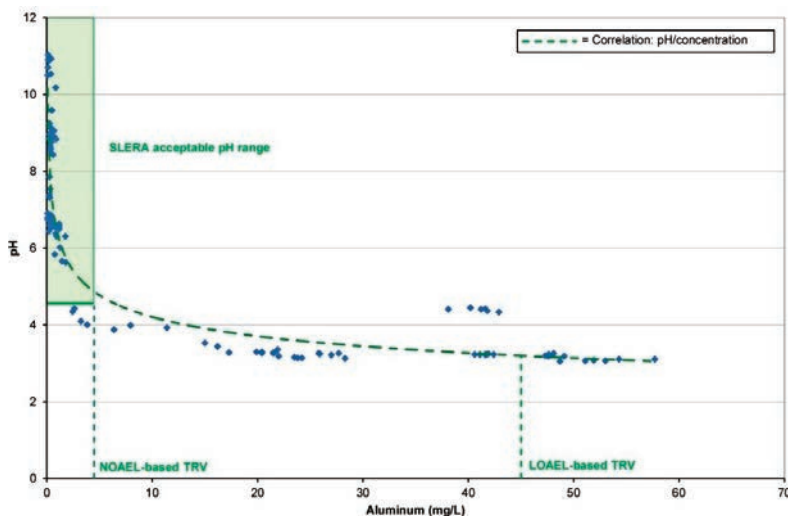


Fig. 6 Determination of the relationship between Al concentrations in the pit lake over the period of record as a function of pH. The equivalent LOAEL Al values and the corresponding "safe" pH can be determined at the interception point with the dashed line.

accurate predictions, and where necessary improve mitigation planning in the future.

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