Geochemical Processes in a Column: Modeling Humidity Cell Test Results

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Abstract Humidity cell tests (HCTs) are used to evaluate the potential for mined materials to leach constituents during operation and closure with an emphasis on sulfide oxidation. Our work evaluates the ion balance of the leachate results, emphasizes secondary mineral weathering and the "early flush" of solutes, and uses two types of geochemical modeling approaches to help understand reactions occurring throughout the tests. Secondary salt dissolution lasted for up to ~60 weeks and overlapped with peak sulfide oxidation. In all tests, sulfide oxidation dominated over a limited time that was rarely apparent at the end or the beginning of the test. Unlike early flush behavior in the laboratory, secondary salt dissolution in the field repeats continually and is linked to precipitation events. Early flush and maximum sulfide oxidation results from HCTs should be retained and used in environmental models and facility design.

Key words humidity cell tests, geochemical modeling, secondary minerals

Introduction

Humidity cell tests (HCTs) are long-term (weeks to years) laboratory leach tests conducted on mined materials (drill core, mine wastes, or wall rock) under oxidizing conditions for estimating the leachate quality of mining materials and wastes. The most common method used is ASTM D5744-13 (ASTM 2013). The purpose of this study is to examine humidity cell leachate chemistry in terms of the underlying geochemical processes and to apply geochemical modeling to HCT results from three U.S. mining projects to determine how this approach might address questions including whether pyrite (or other sulfide) oxidation rates can be distinguished from rates of other processes, such as secondary mineral dissolution and precipitation, and how HCT data could be used for improved predictions. Metal sulfate salts commonly form as efflorescent crusts on sulfide deposits and mine wastes (Nordstrom 1982; Nordstrom and Alpers 1999; Jambor et al. 2000) during periods of evaporation. These salts are rarely considered in mine waste characterization studies, and their effect on water quality can be important when interpreting HCT results.

The HCT results selected for this study are from one active mine and two proposed mining projects in the United States. The geologic settings span a range of rock and mineralization types including a granodioritic intrusion (Pebble Project in Alaska), a metamorphosed sedimentary and volcanic deposit (Buckhorn Mine in Washington State), and a mafic intrusion (PolyMet Project in Minnesota). Samples from each project were selected based on their neutralizing potential (to examine the onset of acidic leachate), the length of the test (one year or longer), the completeness of geochemical analyses on the leachate, and the availability of electronic data. Results from a Pebble Project field test pile are also presented.

Methods

Data sources used for the HCT results were: Pebble, PLP (2011); Buckhorn, Washington State Department of Ecology (2005); and PolyMet, SRK Consulting (2007). The following methods and approaches were used:

- Geochemical modeling using WATEQ4F for aqueous speciation and saturation indices
- Evaluation and correction of charge imbalances
- Calculation of oxidation and dissolution rates
- Inverse modeling of early flush HCT results using PHREEQC
- Comparison and evaluation of field results for two sites.

If the speciated charge imbalances (CIs) in WATEQ4F (Ball and Nordstrom 1991; with database updates) were greater than ±20 to 25% (Nordstrom et al. 2009), the direction of the CI (positive or negative for the CI) and the conductivity imbalance ($\boldsymbol{\delta}\mathbf{K}_{25}$; comparing measured and WATEQ4F-calculated conductivity values, also positive or negative) were examined to determine if cations or anions needed to be adjusted, and in which direction, using the protocols established by McCleskey et al. (2011), and the program was re-run until charge imbalances met the criteria. Using adjusted ORP values (corrected for Eh, available for all samples), Fe aqueous species and saturation indices were calculated in WATEQ4F. Uncertainties in Eh values could affect Fe speciation and saturation index results.

Maximum Fe sulfide oxidation rates were obtained from the change in dissolved SO_4 concentrations over the time that both Fe and SO_4 concentrations were increasing most rapidly. Mineralogic information, as available, and measured molar concentrations of Fe, Cu, and SO_4 were used to infer the most likely sulfide minerals responsible for the observed changes in concentration. Early flush, maximum, and “steady state” SO_4 release rates were calculated using measured HCT concentrations, sample volume, and solid sample mass.

The inverse modeling routine of PHREEQC (Parkhurst and Appelo 2013) was used to estimate the moles of dissolved minerals needed to produce the observed solute concentrations in early-flush HCT samples. Measured major and minor solute concentrations, including metals if present in concentrations $\geq 10^{-5}$ m, were evaluated. Uncertainty was set at 1.0, and the WATEQ4F thermodynamic database was used because it has hydrated sulfate salts. Possible sulfate, chloride, oxide, and carbonate minerals dissolving were selected in the inverse modeling program based on the available phases in PHREEQC and known field occurrences from the literature; choices also needed to be consistent with the solution chemistry, and the SI values from WATEQ4F were used as a guide.

Pebble Limited Partnership initiated a series of field barrel HCTs in 2007 using composited Pre-Tertiary Pebble West Zone core materials from intrusive and mudstone units (see PLP 2011, Appendices 11J and 11C). The HCTs were also run on the same composited Pre-Tertiary Pebble Zone West intrusive and mudstone materials following unmodified ASTM protocols.

Results and Discussion

A subset of the results from each site and method are presented. Typical HCT SO_4 trends in partially weathered, sulfide-bearing samples subjected to a regular leaching sequence show initially elevated SO_4 concentrations (early flush – Ca, Cu, Ni, and other metal concentrations may also be elevated (Price 2009; Jambor et al. 2000)), rapidly decreasing concentrations, later increases in SO_4 concentrations, and then a leveling off of concentrations. In samples that produce acidic drainage, pH values typically start in the neutral range and drop to values below approximately 6, when Fe and SO_4 concentrations increase. Redox potentials often increase as soluble Fe and low pH values create enough Fe(II) and Fe(III) to be electroactive with respect to redox electrodes.

Charge and conductivity imbalances: The CI and the δK_{25} exceeded ±25% in one HCT sample for each of the three sites. These samples should have been re-run and were rejected for our evaluation of salt dissolution and inverse modeling. Using the McCleskey et al. (2011) approach, cations, CI, and $\boldsymbol{\delta K_{25}}$ were too high for the Pebble and Buckhorn samples, whereas anions, CI, and $\boldsymbol{\delta K_{25}}$ were too high for the rejected Polymet sample. The results indicate that analytical measurements for HCT leachate samples should be evaluated more carefully.

Oxidation-reduction reactions and rates: Figure 1 shows the changes in Fe speciation, dissolved Cu concentrations, pH, Eh, and ferrihydrite SI over the course of the test for one of the Pebble samples. Sulfate concentrations are shown only for the period when Fe and SO_4 concentrations were increasing most rapidly. After the pH dropped below 4 (about week 60), ferrihydrite was consistently undersaturated. In general, Eh values do not become meaningful until pH values drop below about 4 (Nordstrom 2011). The Fe(III) concentrations and pH were inversely correlated for the most part, and when pH values dropped below 3 for the first time (about week 100), Fe(III) concentrations rose in response to the oxidative dissolution of Fe sulfide. The Fe(II) concentrations remained low as the Eh rose and Fe(II) was converted to Fe(III). Dissolved Cu concentrations were elevated in the early-flush sample and later peaked around 120 weeks, and Fe concentrations peaked around week 150. Measuring Eh in samples with pH values <4 can improve interpretation of Fe behavior and improve charge balances by adjusting the distribution of Fe(II) and Fe(III). For all samples, Fe concentrations quickly dropped after they peaked, suggesting that Fe oxyhydroxides could be at least partially coating the available sulfide minerals and limiting further dissolution.

Depending on where in the HCT results the reaction or release rates are derived, the time to acid production and other variables can vary widely (Table 1). Maximum SO_4 release rates were 2 to 3 times higher than steady-state rates, and sulfate release rates were even higher during early flush conditions. Similar trends in SO_4 release rates were seen by Lapakko and Trujillo (2015). The maximum sulfide oxidation rate for the Buckhorn sample was about 25 times faster than for the Pebble sample. Iron sulfide in the PolyMet sample took the longest time to oxidize, and maximum sulfide oxidation rate for the Buckhorn sample was about 6.5 times faster than for the PolyMet sample (Table 1). In general, laboratory rates for single-sulfide mineral experiments are faster than those in the HCTs examined, as expected. However, the maximum Fe sulfide oxidation rate for the Buckhorn sample, in which pyrrhotite is the likely dissolving phase, is similar to that found for pyrrhotite by Nicholson and Sharer (1994). Sulfide mineral oxidation rates are strongly dependent on the presence of Fe-oxidizing bacteria, which are not monitored in HCTs. Because of the lack of information on microbial activity in the HCTs, one should look for these rapid increases in Fe and SO_4 concentrations that indicate pyrite or pyrrhotite oxidation and assume that would be a worse-case scenario for application of laboratory rates to field conditions.

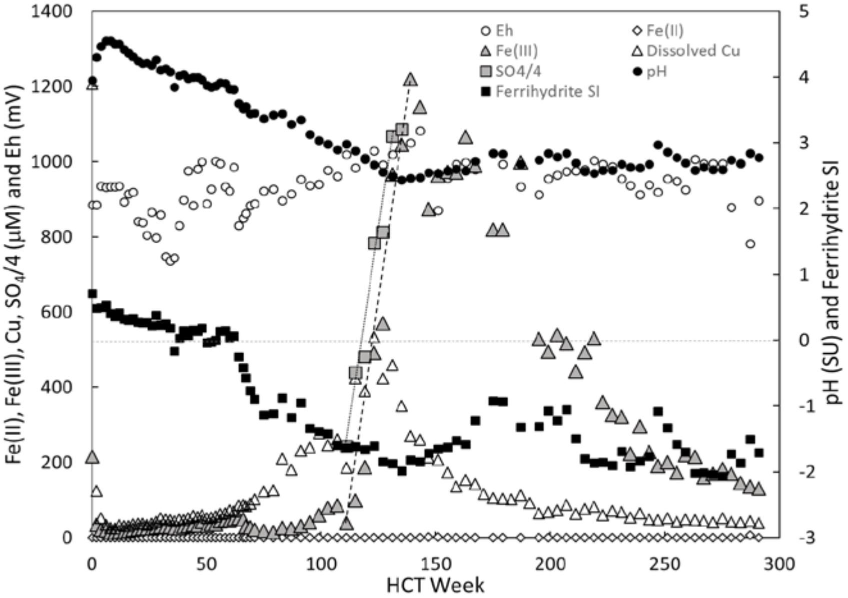

__Figure 1__. Dissolved Fe species, ferrihydrite saturation index (SI), SO4 (only during rapid increase), dissolved Cu, and Eh for Pebble sample 3069-0927-0947. Horizontal dashed line is SI=0, and the near-vertical dashed and solid lines represent the data used to calculate Fe sulfide dissolution rates.

__Table 1__. Sulfate release rates and conditions during early flush, maximum Fe sulfide oxidation, and "steady-state" conditions[1] for the Pebble, Buckhorn, and PolyMet project HCTs

Mine or Project, Location (USA)	Units	Maximum Early Flush	Maximum Fe Sulfide Oxidation	Mean Steady-state
Pebble Project, Alaska	$mg_{SO_4}\ kg_{material}^{-1}\ wk^{-1}$	513	206	68.7
Buckhorn Mine, Washington	$mg_{SO_4}\ kg_{material}^{-1}\ wk^{-1}$	201	429	168
PolyMet Project, Minnesota	$mg_{SO_4}\ kg_{material}^{-1}\ wk^{-1}$	32.0	62.9	36.3

1 last five weeks of HCT with Fe and SO_4 data, or weeks with most stable release rates
Pebble: granodiorite 2.44%S; Buckhorn: magnetite skarn 1.91%S; PolyMet: anorthositic troctolite 1.83%S

Salt dissolution and inverse modeling: Elevated early-flush HCT results are typically ignored when interpreting the results (Price, 2009). In the field, however, sulfide oxidation weathering products can be present intermittently and repeatedly from year to year and have a strong effect on mine drainage quality. Inverse modeling using PHREEQC with the WATEQ4F database identified gypsum as the dominant dissolving phase for the Pebble and the Buckhorn early-flush samples, with melanterite also identified for the Pebble sample. For the Buckhorn sample, epsomite, halite, and dolomite were possible dissolving phases. For the PolyMet sample, halite, calcite, and epsomite were more important than gypsum. The results suggest that sulfate, chloride, and carbonate salts can explain a substantial portion of the observed solute concentrations in the early flush samples.

The major common cations and anions and the Ca:SO_4 molar ratio for the PolyMet sample during the first 60 weeks of testing are shown in Figure 2. The PolyMet sample was less controlled by gypsum dissolution early in the test, but Ca and SO_4 concentrations tracked each other starting in week 6 and remained linked throughout the remaining approximately 50 weeks of testing. Results suggest that gypsum solubility can mask sulfide dissolution and oxidation because of the elevated SO_4 concentrations, as noted by Price (2009) and others, and testing was needed for at least one year. More frequent analysis especially in the first several weeks of the test would help distinguish sulfate salt dissolution from rapid SO_4 increases that signal sulfide oxidation.

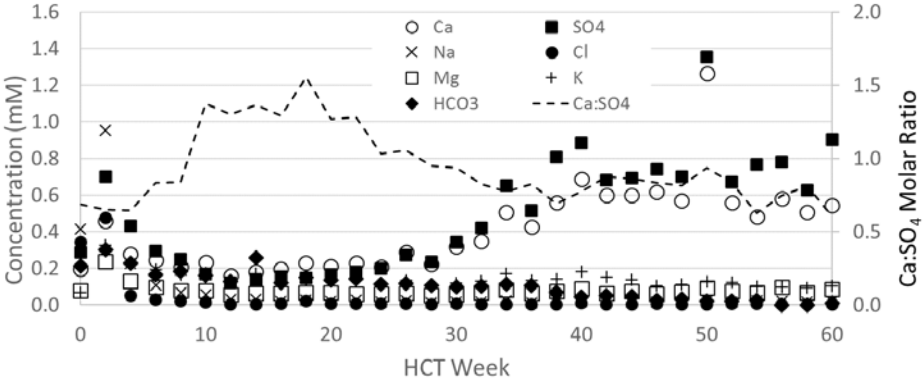

Figure 2. *Major ions for the first 60 weeks of HCT testing for PolyMet Project sample 26027(616-626)*

Field barrel and HCT comparisons – Pebble Project, Alaska, USA: The Pebble Project field barrels and their related HCTs were as identical in composition and particle size as compositing and sub-sampling allow. The Pebble barrel tests followed ASTM protocols, and were sampled only six to 11 times over a two-year period, mostly in fall and winter (Sept. 2007 to Oct. 2009), and the volume of leachate collected was not noted. Therefore, the effects of snowmelt and rain events on leachate characteristics cannot be fully evaluated. For the intrusive rock samples (Figure 3.a), pH values in most field barrel leachate samples were substantially lower than those early in the HCTs; HCT results never dropped below 6.85, but field values were as low as 5.2. Mudstone samples (Figure 3.b) had HCT pH values that were eventually substantially lower that barrel-test values after day 600, suggesting that the HCTs could have accelerated weathering and acid generation – possibly because of the lower temperatures in the field in Alaska.

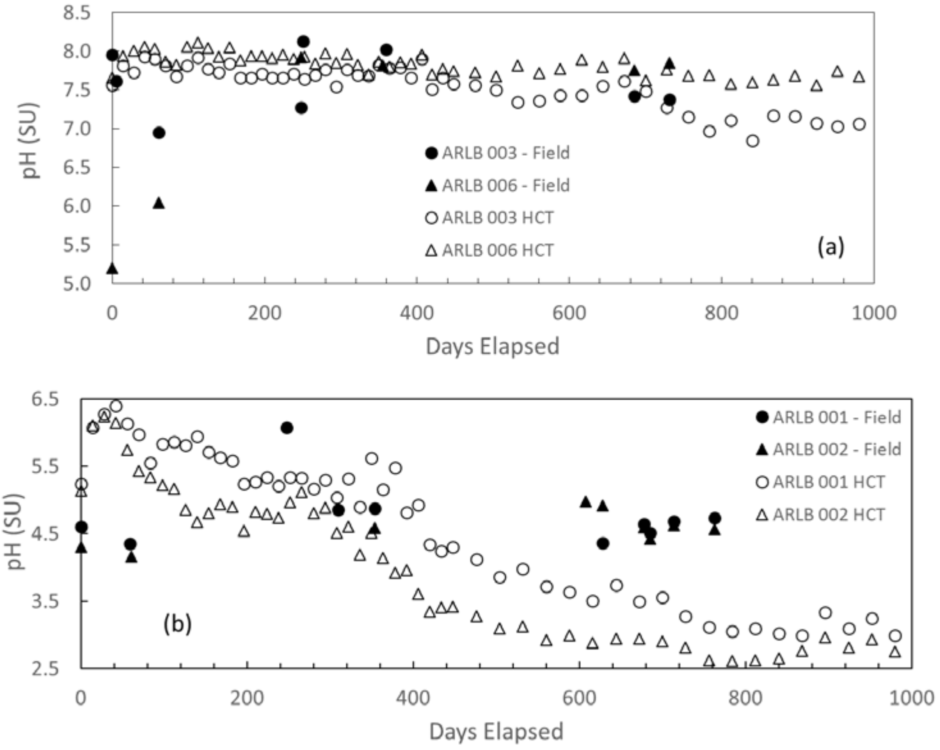

***Figure 3**. Changes in pH over time for Pebble field barrel vs matched HCTs for Pebble West Zone Pre-Tertiary (mineralized) (a) intrusive rocks (003 and 006), and (b) mudstones (001 and 002). Data source: PLP, 2011, Appendix 11J (field barrel) and 11C (HCTs).*

Summary and Conclusions

Early-flush HCT concentrations are ignored in predictions of field pH and solution chemistry. Dissolution and flushing of acidic, metal-rich salts from field tests and waste piles can occur seasonally or after rain or snowmelt events and have a strong effect on leachate and receiving stream chemistry. Early flush and maximum sulfide oxidation results from HCTs should be retained and used in environmental models and facility design. Improved guidance is needed for more consistent interpretation of the results of HCTs that relies on identifying the geochemical processes, the mineralogy, including secondary mineralogy and mineral coatings, the available surface area for reactions, and the influence of hydrologic processes on leachate concentrations in runoff, streams, and groundwater before mining begins. Linked field and laboratory tests should be conducted far more commonly than they are, and reactions involving secondary minerals should be identified and evaluated in the laboratory and the field.

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