An Empirical Comparison of Humidity Cell and Field Barrel Data to Inform Scale-Up Factors for Water Quality Predictions

Shannon Shaw[1] and Andrea Samuels[1]

[1]pHase Geochemistry Inc., North Vancouver BC, CANADA, sshaw@phase-geochemistry.com and asamuels@phase-geochemistry.com

Abstract
One of the biggest challenges for geochemists is the ability to confidently predict contact water quality associated with mine wastes. Uncertainties inherent in these predictions get proliferated through impact assessments, engineering evaluations and permitting that in part rely on these predictions. One of the greatest uncertainties is with the application of lab-based kinetic data and the process of scaling up assumptions applied to this type of data to predict contact water chemistry associated with larger mine waste management facilities. This paper presents results of samples from a proposed gold porphyry project subjected to both humidity cell testwork and field barrel trials. Similarities and differences in data are discussed and the scaling of humidity cell release rates to predict field barrel leachate provides an informative calibration of scaling factors on a relatively small scale with implications for further scale up for management facilities.

Key Words:geochemistry, mine waste characterization, kinetic testing.

Introduction
Application of kinetic test results commonly used in characterization programs to predict contact water quality of mine waste facilities is a key component of mine planning, effects assessments and permitting. Criticism of the reliability of these predictions has been widely circulated (Kuipers*et al* 2006). The reliability or validity of predictions are in large part related to changes in mine plans, variability in rock characteristics, the representativeness of geochemical samples, assumptions related to infiltration and unsaturated water flow and uncertainty related to scale-up of kinetic lab data. It is on the last point that this paper is focussed.

A set of four samples have each been subjected to kinetic testing by means of a standard humidity cell test and a field barrel test for slightly longer than one annual cycle. The results presented here focus on differences reflected in the different test procedures and implications for extrapolating the data to a larger scale.

Test Methods
Test methods utilized in this program included static characterization of the charge material as well as lab and field based kinetic test methods.

Each sample charge was characterized via acid-base accounting (ABA) by the modified Sobekmethod including sulphur and total carbon analysis by leco furnace, sulphate and total inorganic carbon by HCl leach, multi-element scan by aqua regia digestion with ICP-MS finish, whole rock chemistry by x-ray fluorescence (XRF), quantitative x-ray diffraction (QXRD) with Rietveldrefinement, optical petrography and grain size distributions via standard sieve analysis with the minimum aperature of -0.053mm (-270 mesh).

Humidity cell testing was conducted using standard humidity cell protocols as listed in MEND (1991). Each cell consisted of 1 kg (dry weight) of minus ~6mm material. Each cellwas initially flushed with 750 mL of deionized water, with the leachate re-circulated to the top of the cell for a period of 24 hours to maximize flushing of any stored oxidation products in the samples prior to testing. Subsequent cycles

followed the operating procedure consisting of circulation of dry air for 3 days, circulation of humidified air for 3 days, and then flushing with 500 mL of deionized water on day 7. Leachate from all cycles was collected and submitted for analysis of pH, electrical conductivity (EC), alkalinity, acidity, anions and metals.

Field Barrels were constructed using 116 L HDPE barrels fitted with a leachate collection drain at the bottom of each barrel that is overlain by a 5 cm layer of clean, washed quartz sand and a double layer of geotextile mesh. The collection system was comprised of a 10 L collection bottle contained within a 20 L covered pail. A drain on the bottom of each of the 20 L pails allowed leachate overflow to be directed to a 1000 litre overflow tank. The total weight of sample in each barrel was on the order of 280 kg. The barrels were located at the project site where they were subjected to local climatic conditions with an annual average precipitation in excess of 1200 mm falling in a distinct wet season and average annual temperatures of approximately 16°C. Leachate from the field barrels was sampled monthly subject to available leachate volume. Field parameters were measured including pH, conductivity, temperature, oxidation-reduction potential and alkalinity and water samples were collected, filtered through a 0.45 µm filter and placed in pre-charged sample bottles that were then submitted to an analytical laboratory for analysis of pH, EC, alkalinity, acidity, conductivity, redox potential, anions and nutrients (Cl, F, SO_4, NO_2, NO_3, P)and metals (Ag, Al, As, Ba, Be, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, U, V, Zn and Zr).

Sample Characteristics

Samples for the program were sourced from drill core and represented porphyritic intrusives and meta-sedimentary lithologies that are host rocks from a gold/copper porphyry deposit. Each sample was sourced from half core over a continuous 100 metre interval of drill core that had been drilled less than one year prior to sampling with negligible signs of secondary oxidation. The core was thenbroken by hammer while in sample bags such that the largest pieces were approximately 1 to 2 inches in diameter and all fines were retained. The entire interval was subjected to a cone and quarter method to produce a composited and homogenized split weighing approximately 5 kg. These sample splits were shipped to the analytical lab where samples were further homogenized and split for static characterization and humidity cell testing. The remaining broken core material including the fines component was loaded into the field barrels.

The four samples described in this paper are classified as potentially acid generating with very similar mineralogy, sulphide content and neutralization potential (Table 1).

Table 1.Summary characteristics of kinetic sample set.

Sample	Rock Type	Total S (%)	NP_{Carb} (kg $CaCO_3$/t)	NP/AP*	Mineralogy (by QXRD)			
A	intrusive	2.0	3	0.2	quartz (25%), plagioclase (25%), K-feldspar (15%), biotite (5%), chlorite (5%), muscovite (<5%), actinolite (<5%)	pyrite (2.5%)	-	calcite (1%)
B	intrusive	2.1	11	0.3			pyrrhotite (4%)	calcite (1%)
C	intrusive	1.3	8	0.3			-	calcite (1%)
D	meta-sediment	1.1	<1	0.3			-	-

Note:
* the NP/AP ratio used here represents the modified Sobek NP and AP calculated on sulphide sulphur.

Pyrite is the dominant sulfide, though one sample also contained significant pyrrhotite. Petrographic evaluations indicated pyrite was most typically disseminated and, for the intrusives also within quartz veinlets. Pyrite grains were typically anhedral but virtually all unaltered or rarely rimmed by an unknown red-brown Fe-ox aggregate. Pyrrhotiteoccurred as locally disseminated, anhedral and rarely rimmed and

partly replaced by unknown Fe-ox aggregate. Sulfate values were negligible and no sulfate minerals were noted in mineralogical evaluations.

Calcite was the dominant carbonate but was noted to be present in low amounts (nil to 1%). Petrographic analysis indicated calcite was present as 1) very fine grains and aggregates within quartz veinlets, 2) partly replacing plagioclase phenocrysts and matrix, and 3) associated with actinolite or chlorite-epidote alteration or partly replacing secondary K-feldspar. NP calculated on the basis of inorganic carbon is generally 20 to 30% of the modified Sobek NP with the remaining NP, limited as it is, attributed to gangue minerals such as feldspars and micas.

Results

The data set presented here represents data collected for a period just over 60 weeks. In that time, humidity cell leachate from the intrusive samples (samples A, B and C) remained buffered as did all but one of the field barrel intrusive samples, while the meta-sediment sample (sample D) dropped to acidic pH conditions in both the lab and field tests (Figure 1). Data shown in Figure 1 and in all subsequent time series plots illustrate field barrel data (annotated as FB series) as dashed lines and open symbols. Humidity cell data (annotated as HC series) are illustrated as solid lines and symbols.

There are two notable differences in the pH trends shown in Figure 1. Firstly, pH values in the acidic meta-sediment sample were approximately one pH unit lower in the leachate from the field barrel than from the paired humidity cell. Secondly, the intrusive sample A became acidic in the field barrel, but remained buffered in the humidity cell test, perhaps due to the higher alkalinity release rates in the humidity cell test (Figure 2).

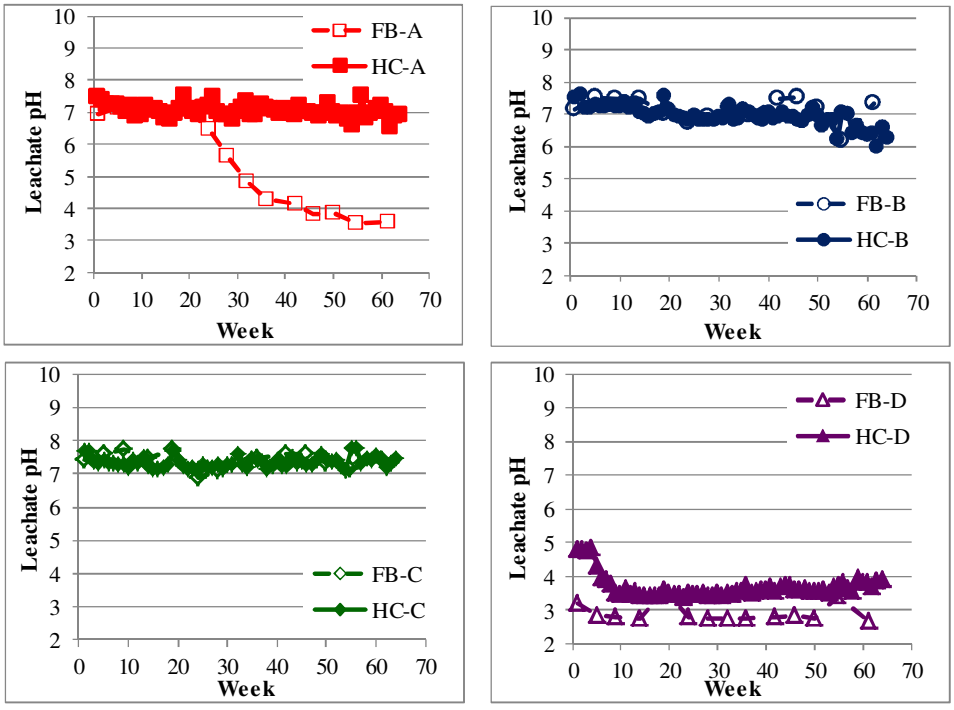

Figure 1. Lab pH in leachate from field barrels and humidity cells for samples A through D.

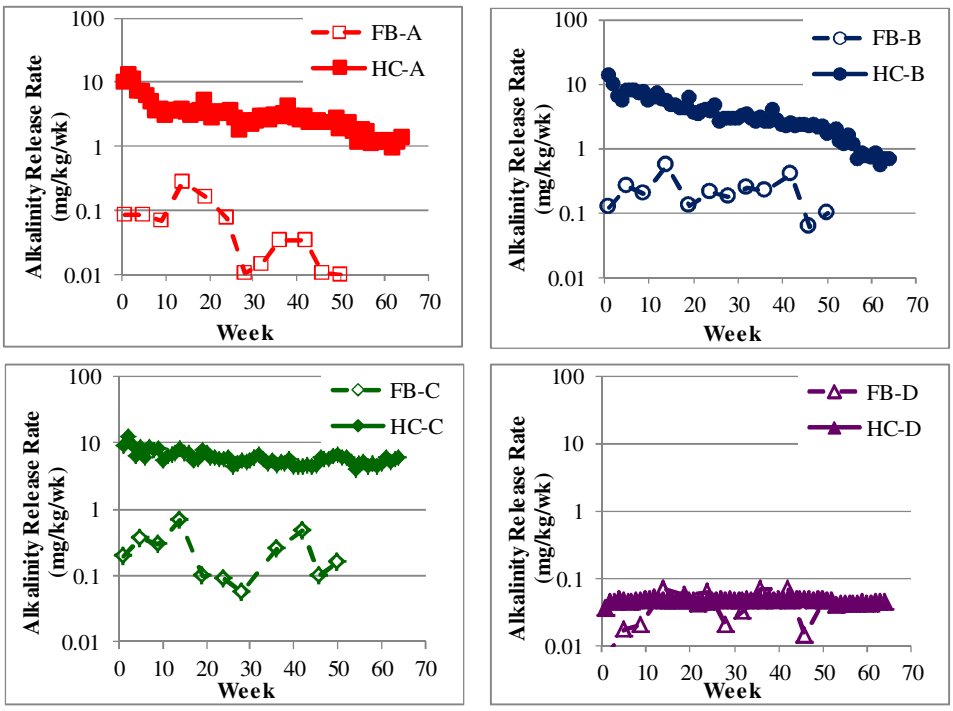

Figure 2.Lab measured alkalinity release rates from field barrel and humidity cells for samples A through D.

Concentrations of sulfate in the humidity cell leachates were generally on the order of 20 mg/L when buffered and up to 500 mg/L when acidic. Concentrations of sulfate from the field barrel samples were generally an order of magnitude higher with values on the order of 200 mg/L when buffered and up to 5000 mg/L when acidic. On a loading basis however (i.e. in units of mg/kg/wk), the humidity cell release rates were roughly an order of magnitude higher than from the field barrels despite pH differences (see Figure 3). Sample B which had notable pyrrhotite content, appeared to have higher sulfate release rates than the other samples with the same pH conditions, particularly in the humidity cell tests..

Average metal release rates were calculated using data once each individual test reported stable concentrations. A comparison of key average release rates from the humidity cells and from the field barrels indicate that humidity cell release rates are often, but not always higher than rates from the field barrels and a greater influence with respect to pH conditions may exist. Field barrel release rates for metals such as copper and zinc were higher than humidity cell release rates for sample A where pH conditions differed significantly between test methods (Figure 4).

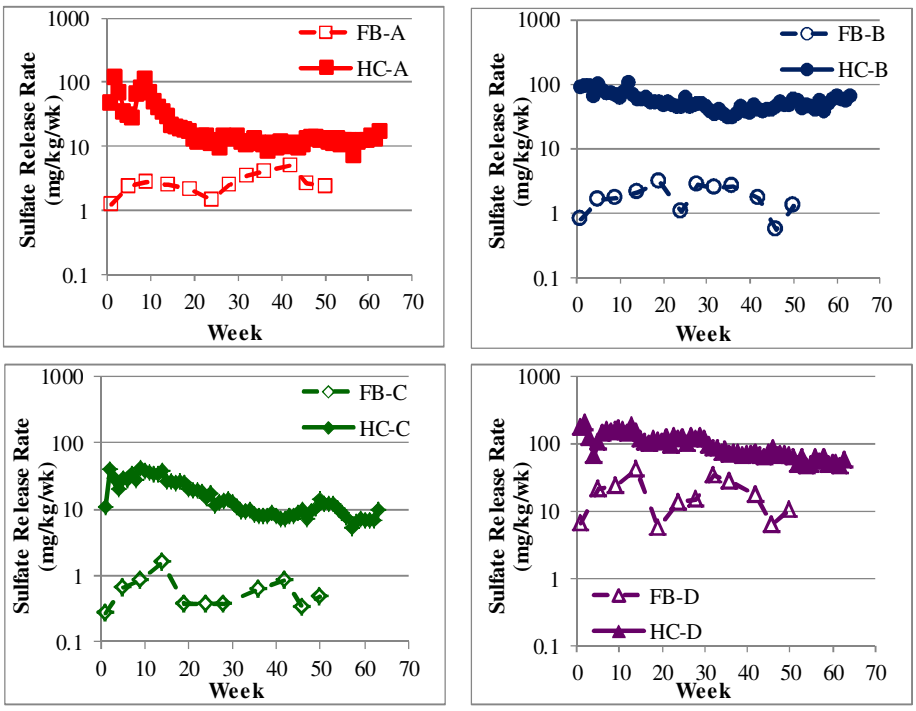

Figure 3. Sulfate release rates in field barrels and humidity cells for samples A through D.

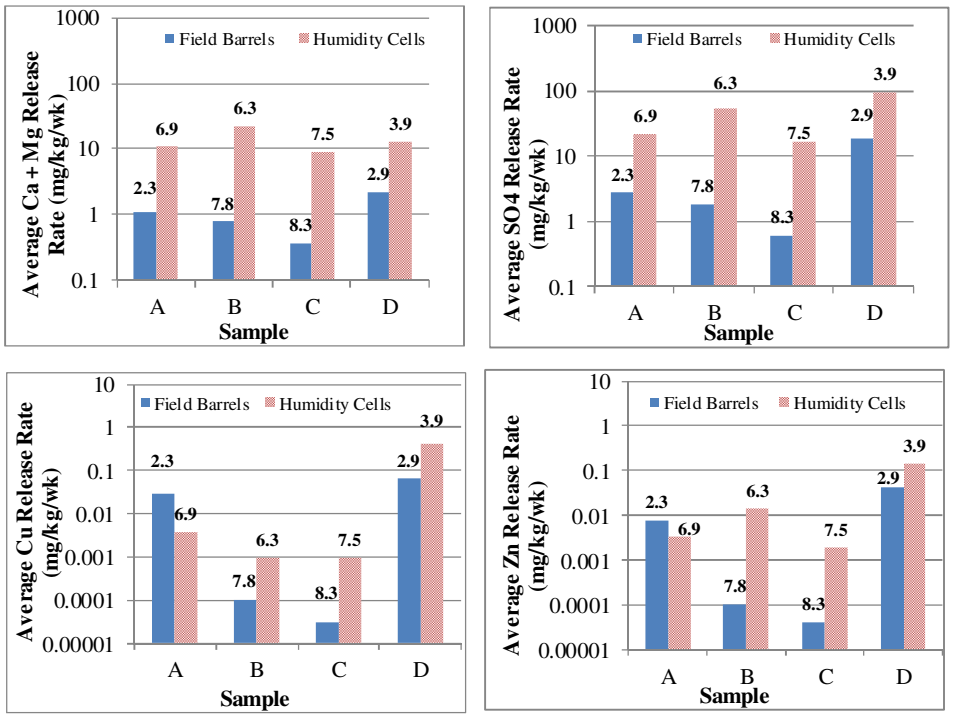

Figure 4. Average release rates for calcium+magnesium, sulfate, copper and zinc for both humidity cells and field barrels for samples A through D. Values of pH are provided for reference above each bar.

Figure 5 provides the average release rates for copper and zinc against pH with the symbol size proportional to average sulfate release rates and shows a much stronger correlation of metal release with pH than with sulfate release. The figure also shows a correlation with higher sulfate release rates and pH when looking at the field barrel results or humidity cell results independently. This effect however is largely masked by the influence of test method related release, i.e. greater leaching of sulfate from the humidity cell methodology.

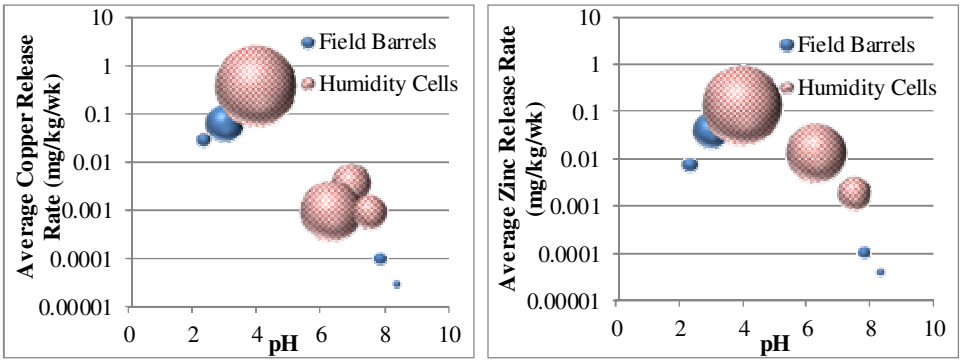

Figure 5.pH versus average release rates for copper and zinc from field barrels and humidity cells with symbol size proportional to average sulfate release rates.

Calculations

Depletion Calculations

One calculation often completed on humidity cell data is the depletion of neutralization potential and sulphide content. These calculations are often used to support estimates of lag time, or the time to onset of acidic conditions. For the four samples presented here, calculated neutralization depletion rates, based on the release of calcium and magnesium on a molar basis in units of kg $CaCO_3$/t/yr compared to the initial carbonate neutralization potential of the samples indicated that neutralization potential would persist for between 3 and 12 years under laboratory conditions for the samples that have remained buffered in the humidity cells. For sample A in particular, the field barrel sample went acidic after approximately 6 months of exposure. The discrepancy could in part be explained by greater liberation of carbonates in the humidity cell test sample than is available, or effective at the field barrel scale. It implies that at least in this case, calculations of depletion rates from humidity cells may over estimate lag time in the field.

Scale up Calculations

Another primary use of humidity cell data at the pre-operation phase of a project is to predict contact water quality. As a test of the approach commonly used, a calculation was conducted using the humidity cell release rates to predict the field barrel chemistry. Calculations were conducted usingEquation 1 below.

$$C_{FB} = (R_{HC} \times M_{FB}) / Q_{FB} \qquad \text{(Equation 1)}$$

Where:

C_{FB}= the predicted field barrel concentration (in mg/L)

R_{HC} = metal leach rate as observed by humidity cell testing (in mg/kg/wk)

M_{FB} = adjustment factor to correct for rock mass and material mixtures (in kg)

Q_{FB} = flows in contact with field barrel sample (in L/wk)

Scale-up calculations for mine storage facilities also often include adjustment factors for temperature, grain size differences and flushing, or the development of flow paths. Given the temperature and precipitation at the site and the size of the field barrels (i.e. considered small enough that flow path development would be somewhat limited), no corrections were considered appropriate for temperature or flushing effects. While grain size differences between the humidity cell sample and field barrel sample exist they are not as great as might be expected. Humidity cell samples generally reported 60% to 70% of the sample passing 6mm while the field barrel charges were estimated to be approximately 50 to 60% finer than 6mm.Further, applying an adjustment for grain size differences only exaggerated the differences in the predicted and monitored leachate quality for most parameters, i.e. more greatly under predicted chemistry. By not applying adjustment factors here, one can evaluate the strict scale up of humidity cell rates to field barrel quality as influenced by test size and water volume.

Using equation 1 above, predicted (scaled) values of parameters that should not be affected to a great extent by sulphide oxidation, carbonate dissolution or variations in pH, such as potassium or sodium, indicate that a strict scaling of humidity cell release rates to field barrel concentrations under predicts monitored field chemistry by approximately 2 to 4 times (Table 2). Parameters that are involved in mineralogical reactions during sample weathering, represented here by calcium (carbonate dissolution), sulfate (sulfide oxidation) as well as copper and zinc (metal leaching) illustrated larger variability as illustrated by the results provided in Table 3.

Table 2. Predicted (scaled) versus monitored results for selected "conservative" parameters in field barrels.

Sample	pH		Potassium (mg/L)		Sodium (mg/L)	
	HC	FB	Predicted	Monitored	Predicted	Monitored
A	7.0	3.5	3	13	1	4
B	6.5	6.5	4	7	1	3
C	7.5	7.0	1	2	2	4
D	3.5	2.5	9	19	2	9

Notes: Measured pH provided for reference, HC = humidity cell and FB = field barrel.

Table 3. Predicted (scaled) versus monitored results for selected "reactive" parameters in field barrels.

Sample	pH		Calcium (mg/L)		Sulfate (mg/L)		Copper (mg/L)		Zinc (mg/L)	
	HC	FB	Predicted	Monitored	Predicted	Monitored	Predicted	Monitored	Predicted	Monitored
A	7.0	3.5	2185	123	29	394	0.005	7	0.005	1
B	6.5	6.5	4563	89	70	214	0.001	0.008	0.02	0.01
C	7.5	7.0	3003	54	34	109	0.002	0.004	0.004	0.005
D	3.5	2.5	1929	113	137	2307	0.6	8	0.2	4

Notes: Measured pH provided for reference, HC = humidity cell and FB = field barrel.

Predicted calcium concentrations over predicted monitored field barrel leachate by approximately an order of magnitude, reflecting the excessive leaching of carbonates in the humidity cell procedure as compared to the field based test. Conversely, predicted sulfate values tended to under predict monitored values by approximately an order of magnitude, possibly in part due to pH variability between test methods, though even those sample pairs with similar pH values tended to be under predicted when sulfate was scaled.

Metals, as represented here by copper and zinc, were also under predicted. The degree to which they were under predicted was similar to the conservative parameters (e.g. potassium) when both tests had similar pH values. When pH differed between the humidity cell and field barrel however, larger discrepancies were seen. In general there is approximately an order of magnitude difference (under prediction) for each pH unit variance.

Summary and Conclusions

The results from four paired samples subjected to standardized lab based humidity cells and field based barrel tests presented here provide insight into the differences in the test conditions with implications to the use of kinetic data for scale-up calculations.

The primary differences in the two test methods compared in this evaluation are:

1.Sample size: 1 kg humidity cells versus 280 kg field barrels, and
2.Contact water to solid ratio: 0.5 L/kg in the humidity cells versus 0.01L/kg (average) in the field barrels.

It is the second variable, which is influenced by the first that appears to have a greater effect on results observed between test methods. The high flush rate associated with the humidity cell test meant to accelerate the weathering behaviour of material as compared to the field conditions has three distinct effects that may be contributing to these differences: (1) enhanced water dissolution and subsequent flushing of neutralization from the sample, (2) prevention of the development of 'hot spots' or acidic micro-environments where sulfur oxidizing bacteria tend to thrive, and (3) preclusion of secondary mineral precipitation and storage within the sample.

The combined effect may be that the ultimate pH reached in humidity cell leachate is not as low as can be developed in a test method that uses lower infiltration rates and does not develop as quickly as can be seen in the field environment. This effects predictions of pH-dependent variables including many metals of concern for mine wastes as well as estimates of lag time.

Observations conducted to date and calculations completed on these results suggest that scaling of humidity cell release rates to approximate the field barrel environment tended to over predict release of parameters associated with carbonate alkalinity (e.g. calcium) by an order of magnitude and under predict sulfate release, again by roughly an order of magnitude. A much more significant under estimate of metal concentrations occurred when pH values differed between test methods. In these scenarios, metal values were under predicted by approximately an order of magnitude for each pH unit difference.

Based on these observations, implications for scaling of humidity cell data to larger facilities should bear in mind two key factors: (1) alkalinity release rates in the humidity cell environment may not approximate field behaviour and (2) humidity cell data when used for scale-up calculations should be reflective of the ultimate evolved pH of the waste material for which it is meant to represent in order to best estimate metal concentrations.

References

Kuipers, J.R., Maest, A.S., MacHardy, K.A. and Lawson, G. (2006) *Comparison of Predicted and Actual Water Quality at Hardrock Mines: The reliability of predictions in Environmental Impact Statements*, Earthworks, Washington, DC.

MEND (1991). *Acid Rock Drainage Prediction Manual,* MEND Report 1.16.1b, March 1991.