Comparison between Long-Term Humidity Cell Testing and Static Net Acid Generation (NAG) Tests: Potential for NAG Use in Preliminary Mine Site Water Quality Predictions

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ABSTRACT

Kinetic testing is one of the key tools for predicting the long-term weathering of mine waste materials and their potential environmental impacts. The standard methodology commonly undertaken for kinetic testing of mine waste is the ASTM D 5744 humidity cell test procedure. However, this test requires a significant time period to generate representative data, with typical test duration in excess of 40 weeks. In some cases, it may even require years before suitable information is obtained. This long lead time can have significant impact on mine development schedules especially if the data is required by environmental regulators for the permit application procedures. Due to the time constraints of mine development programs, it is highly desirable to identify complimentary test methods that are able to deliver the required data for water quality predictions in a shorter period of time. One of the more promising methods is the use of hydrogen peroxide (H_2O_2) leach test (a common variant being the Net Acid Generation or NAG tests). The resulting NAG leach solutions can potentially be scaled to field conditions to allow for a preliminary prediction of mine waste seepage water quality. This paper compares results from NAG testing and long term humidity cell testing, including correlations between the two data sets to show whether NAG leaching is an appropriate method for preliminary rapid assessment of mine site drainage water quality.

Keywords: NAG test; Humidity Cell; Seepage prediction

INTRODUCTION

Exposure of sulfide minerals during mining results in gradual oxidation of these minerals and the associated release of solutes and acidity to the environment. This is commonly referred to as acid rock drainage (ARD) and metal(loid) leaching (ML) or ARDML. ARDML can result in significant detrimental ecological impacts which makes the prediction of water quality from mine sites one of the most critical aspects of the evaluation of mine design for permitting and/or closure applications. Prediction of ARDML and associated water quality impacts have become mandatory for studies in many mining jurisdictions and/or where international bank financing is required.

One of the primary objectives of an ARDML study is to determine if contaminants will be released and to predict the rate at which they will be released from each mining waste type. In order to do this, it is necessary to undertake a series of characterization tests. These tests can generally be classified into two types (MEND, 2009):

- Static tests – rapid testing procedures that deliver information on the finite materials characteristics, for instance, if the material is potentially acid generating, if it is enriched in certain elements of concern, what the immediate mobility of such elements are, and the potential for long term release of certain elements if the samples are fully oxidized.
- Kinetic tests –laboratory or field column tests that are used to determine the rate at which acidity is generated and solutes are released. Kinetic tests require a longer time period than static testing, and are usually run for 40 weeks or more.

Kinetic testing methods vary based on the particular scenario that is being examined and the required test outcome. The most commonly used kinetic test is the ASTM D 5744 Humidity Cell Test (HCT) (ASTM, 2013). This is an optimized weathering test in which a sulfidic material is exposed to alternating dry and humid air cycles followed by weekly flushing with deionized water at a high liquid to solid ratio. The test is intended to ensure that appreciable oxidation and solute release is achieved and is not designed to directly simulate field conditions.

The long lead time between the initiation of the tests and the time at which the test matures i.e. when the data obtained from the test is suitable for use in long term water quality predictions, can be many months (eg. Sexsmith et al, 2015). This is especially applicable with materials which are slow reacting and demonstrate a significant lag time to the onset of persistent acidic leaching conditions at which solute mobility and release from the cell is at its highest and most representative of long term weathering.

In many cases, the significant maturation time of kinetic testing does not fit in with the mine development schedule where timely water quality predictions are essential in order to ensure that the most suitable and cost effective mitigation measures are designed into the project at the earliest possible opportunity. In order to avoid such situations, it would be beneficial to develop a complementary methodology that can be used to undertake preliminary predictions of water quality far in advance of that provided by kinetic tests.

One of the most promising methods to address these needs is the use of solute release data obtained from Net Acid Generation (NAG) test. NAG tests are commonly used as a complimentary method to Acid Base Accounting (ABA) for the confirmation of a materials acid generating potential. In a standard NAG test, a 2.5g portion of pulverized sample is leached in 250mL of 15% hydrogen peroxide (H_2O_2) solution. The NAG test intends to fully oxidize the sulfide minerals contained within the sample, generating acidity, releasing sulfide-associated elements into solution and reacting with fast-reacting acid buffering carbonate minerals. As well as providing information on acid generating characteristics, multi-element analysis of the generated NAG solution can reveal significant information on potential release of metals, metalloids and salts from the sample after complete sulfide weathering.

The NAG procedure has been sequentially developed by a number of researchers over the past 40 years; Smith et al. (1974), Sobek et al. (1978), O'Shay et al, (1990), Stewart et al (2006) and references therein; but so far, the use of NAG test data in the preliminary prediction of water quality for mine sites has not been addressed. The most likely reason for this is that analysis of NAG solution chemistry is not widely practiced and a reliable empirical database comparing standard kinetic (HCT) release rates and mass release from standard NAG test data is not readily available.

The purpose of this paper is to make comparison between multi-element assay of the NAG solution and the HCT results from the perspective of using NAG data to make a preliminary prediction of water quality suitable for use in mining development studies as a complementary methodology to (rather than a substitution for) standard kinetic testing methods.

The potential benefits of using such static tests for early water quality predictions would be to allow for better costing of engineering designs early on in a feasibility study program to mitigate the potential impact of ARDML to the environment without inclusion of excessively cautious designs approaches.

Prediction of water quality through scaling of kinetic data

Although it can be argued that the use of HCT data for the prediction of mine site water quality is less than ideal (i.e. Sunkavalli, 2014), it is not the intention of this paper to examine this. Therefore in this study, kinetic testing refers to standard ASTM D-5744 HCT and the resulting solute release rates. However, the author acknowledges that elemental release rates can be obtained from a large variety of kinetic tests, some of which are arguably superior to HCT more closely simulating field conditions in terms of fluid flow, temperature or liquid to solid ratio.

In order to convert laboratory derived solute release rate (R*lab)* into field water quality predictions, it is necessary to upscale R*lab*, to take into account such factors as oxygen availability, particle size distribution, and field temperature variation to give a primary field release rate (R*field*). Once R*field* has been calculated, it is then possible to estimate a concentration in pore water by taking into account the difference between laboratory and field liquid to solid ratio. The solute concentrations calculated using this method then need to be equilibrated using a thermodynamic equilibrium code (such as PHREEQC, Parkhurst and Appelo, 2013) to take into account such things as mineral saturation and adsorption to mineral surfaces. The resulting solutions 'source term' concentration can then be incorporated into site wide water quality predictions and / or assessed against relevant water quality guidelines, and used to develop suitable mitigation controls in the design and cost estimates prior to mine development.

Alternative methods of water quality prediction may also be undertaken such as deriving water quality from primary mineral weathering rates (effectively from first principals i.e. Linklater et al (2005) and references therein). However, these methods are complex and require data that is usually difficult to obtain during a mine development study. In addition, the first principal method of modeling commonly does not take into account all of the contaminants released from a deposit which would be included if scaling of kinetic test data is included. It is also possible to make a preliminary prediction of water quality from empirical relationships and analogue sites. This is often a very useful first approach (MEND, 2009) but again, does not take into account intricacies and variations that can be obtained through the scaling of leaching test data.

Potential for substitution of kinetic "rates" with static test release data

It is plausible that R*lab* obtained from kinetic testing can be substituted for an alternative rate derived from static testing methods. However, static tests generate only a mass release (usually referred to in mg/kg) and thus a release rate has to be assigned - for example, by assuming that all of the sulfide-S content of a sample is released as sulfate equally over a given time period. Furthermore, in the case of water leaching tests such as EN12457 or MWMP tests, the mass released often represents only the dissolution of soluble salts that are rinsed from the sample surface and do not take into account the release of solutes due to the oxidative dissolution of sulfides, and associated acidity driven dissolution.

The NAG test has the benefit of being able to determine (i) the solute release attributed to sulfide oxidation though the reaction of hydrogen peroxide (H_2O_2), and (ii) the solubility of the solutes at the pH of the final NAG solution. Therefore this method shows the most promise for use in rapid prediction of long-term weathering water quality. However, due to the very rapid reaction of H_2O_2 with the sulfide minerals within a mine waste sample, complete oxidation is commonly achieved within a matter of hours. Although attempts have been made to measure NAG release rates (Kinetic NAG), the exothermic breakdown of H_2O_2 during the test often results in very high temperatures which make measurement of a sulfide oxidation rate difficult.

Any rate used to substitution for R*lab* (HCT) must be derived in some way from the total mass release. The NAG tests simply gives a bulk release of sulfide-associated elements, an average for the entire humidity cell release if it were to be run to sulfide exhaustion. Additionally, NAG tests suffer many additional complications. For instance, incomplete oxidation of sulfides is often observed in samples due to the decomposition of H_2O_2 during the test. This is promoted by increasing pH and by the presence of catalytic metal ion, such as Mn, Fe and Cu or, in alkaline solution, by the presence of the carbonate ion (Liochev and Fridovich, 2004 and references there in) and in some cases simply by the method employed for the analysis (Charles et al, 2015). Despite these drawbacks, NAG tests may represent one of the most favorable static tests for rapid determination of water quality impacts.

Comparison of NAG data with HCT data

Eight samples of moderate to high sulfur waste rock materials were subjected to long term (greater than 160 weeks) ongoing HCT testing, details of the ARD characteristics of the samples are given in **TABLE 1.** The deposit utilized for the testing is a magnetite resource within an Iron Oxide Copper Gold (IOCG) style of mineralization. The deposit is characterized by a moderately elevated coarse grained sulfide (pyrite / pyrrhotite / chalcopyrite) content hosted in quartz veins within amphibolites, diorites and schists lithologies. Total sulfur (almost all present as sulfide sulfur) is in the range of 0.1 to 5 wt.%. In addition to sulfides, the deposit also has a relatively uniform but low magnitude carbonate mineral assemblage with inorganic carbon consistently between 0.05 - 0.5 wt.% and averaging 0.08 wt.%. All the static testing undertaken on the samples demonstrated them to be acid generating and all NAG tests produced pH conditions below pH 4.5.

Comparisons are made of data between times at which the HCTs were at circum-neutral pH and them later at acidic pH. It is important to note that within ARD systems, as pH decreases to < 4, dissolved Fe(III) becomes increasingly soluble and more important than O_2 as the (direct) sulfide oxidant. Laboratory data indicate that sulfide oxidation rates are circa one order of magnitude higher under acidic conditions than rates under neutral (O_2 dominated) pH conditions (cf.

McKibben and Barnes (1986); Olson (1991) and Rimstidt et al (1994). Observation made by the authors from previous kinetic testing have shown that, the ratio between sulfide oxidation rates at neutral pH and peak (maximum) sulfide oxidation rates under acidic condition may reach the factor of 10 and in some cases exceed this. However, this was generally only observed for a short duration (<10 weeks) and was not representative of average sulfide oxidation rates under acidic conditions. When the long term neutral and long term acidic sulfate release rates were compared, the ratio between neutral and acidic rates decreased significantly with a median ratio value of 4.87 and ranges between 1.8 and 8 (see inset graph in **FIGURE 1)**

Table 1 Summary of geochemical characteristics of waste material used in humidity cell testing

Sample No.	Material Type	Acid Base Accounting							NAG pH	Ave. week 151 – 160 HCT pH
		TIC	Total Sulfur	AP	NP from TIC	NP from Titr.	NNP Titr.	NPR Titr.		
		%	%	kg CaCO3 eq/t						
1	Skarn	0.10	3.25	93.31	8.33	11.00	-82.31	0.118	2.7	4.75
2	Schist	0.68	2.92	87.81	56.64	35.50	-52.31	0.404	2.8	4.27
3	Amphibolite	0.07	1.98	58.75	5.83	7.25	-51.50	0.123	3.3	5.97
4	Amphibolite	0.04	3.07	86.75	3.33	3.75	-83.00	0.043	2.8	*3.81*
5	Amphibolite	0.04	0.76	22.02	3.33	4.75	-17.27	0.216	3.7	4.92
6	Diorite	0.10	2.18	61.25	8.33	5.50	-55.75	0.090	3.2	5.60
7	Diorite	0.05	1.74	52.18	4.17	4.00	-48.18	0.077	3.3	6.35
8	Diorite	0.04	0.53	14.51	3.33	4.50	-10.01	0.310	4.2	6.80

NP	Neutralizing Potential	AP	Acid Generating Potential
NNP	Net Neutralizing Potential (NP-AP)	TIC	Total Inorganic Carbon
NPR	Neutralizing Potential Ratio (NP/AP)		

The main plot in **FIGURE 1** compares the rate of sulfate release at different periods within the HCT to the total sulfate mass release from the corresponding NAG tests. The red points represent early stage weathering (weeks 21 to 40) during which time pH of all HCT leach solutions was above pH 7 whilst ensuring that the early stage flushing of soluble sulfate salts had occurred. The second period is between weeks 151 and 160 which is the most recent data available and represents the cells at their lowest recorded pH and highest sulfate release (blue points). In both cases, a reasonable correlation can be drawn between the NAG release and HCT release rates with R^2 of 0.72 for weeks 21 to 40 and 0.93 for weeks 151 to 160, for linear best fit and zero intercepts. The slope of the correlation for weeks 21 to 40 is 0.0012 (1/776), whilst this is roughly double for weeks 151 to 160 at 0.0025 (1/391). This demonstrates the following:

1) That the rate of release in the HCT is proportional to the NAG sulfate release and likewise the total sulfur content of the samples. This is logical for samples such as these where sulfides (and their exposed surface area) are distributed uniformly through the sample.
2) That this proportionality between HCT S release rate and NAG S release is maintained at later stages of the HCT when pH is lower, albeit with higher HCT sulfate release rates.

3) That as with other literature, sulfide oxidation rates within the HCT increase as pH conditions become more acidic. In the example given here, the sulfate release rate has doubled between neutral and mildly acidic pH conditions of the test.

The upper orange line in **FIGURE 1** represents a 4.87 increase in the neutral oxidation rate as discussed above. Applying a factor of 4.87 to the week 21 to 40 rate slope of 1/776 gives a predicted sulfate release rate (under acidic conditions) / NAG sulfate release slope equal to 0.00635 (1/157.5) x the total NAG S. Or restated for clarity, after 157.5 weeks, the total sulfur content of the sample would be released at a fixed rate to exhaustion.

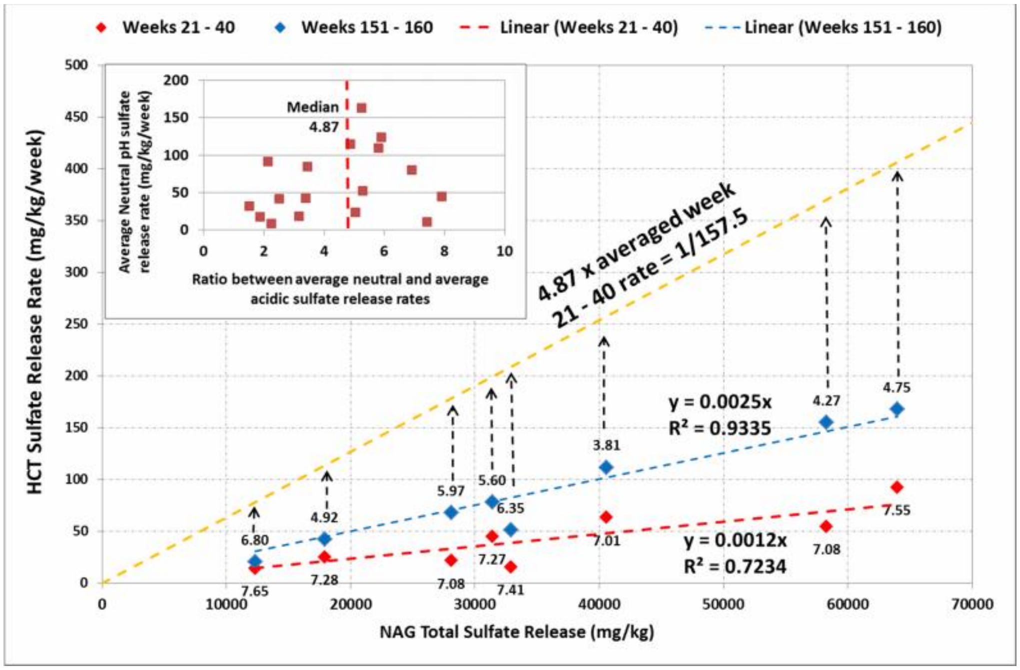

Figure 1 Variation between NAG release (mg/kg) and HCT sulfate release rate (mg/kg/week) for weeks 21 to 40 and weeks 151 to 160 HCT data respectively. Data point labels correspond to the average HCT pH for the period. The orange dashed line corresponds to 4.87 times multiplication of the weeks 21 to 40 slope rate resulting in a slope of 1/157.5. The inset graph shows the range of ratios between sulfate release rates under neutral and acidic conditions from previous HCT data.

Logically, for sulfide-bound metals, the rate at which sulfide is oxidizes and sulfate is released should correspond to the rate at which other sulfide-associated elements are released – except where solubility limits constraint this. The plots in **FIGURE 2** compare HCT release rates for Cu, Co, Ni and Zn with the corresponding calculated metals release rates using NAG test data divided by a factor of 157.5 (i.e. assuming that under acidic conditions within the HCT, that the total NAG metals are released linearly over 157.5 week period). Also shown is the line of unity between HCT and calculated NAG release rates. Measured HCT release rates are shown for both the average week 21 to 40 data and the 141 to 150 data.

It is clear that measured releases are significantly higher in the 141 to 150 period compared with the 21 to 40 period. In fact, during the early weeks of testing, both Cu and Co concentrations were consistently below the analytical detection limit (ADL) within the tests which accounts for the flat trend observed. Ni and Zn were both above ADL during the week 21 to 40 period with Ni showing a good linear correlation with calculated NAG Ni release rates.

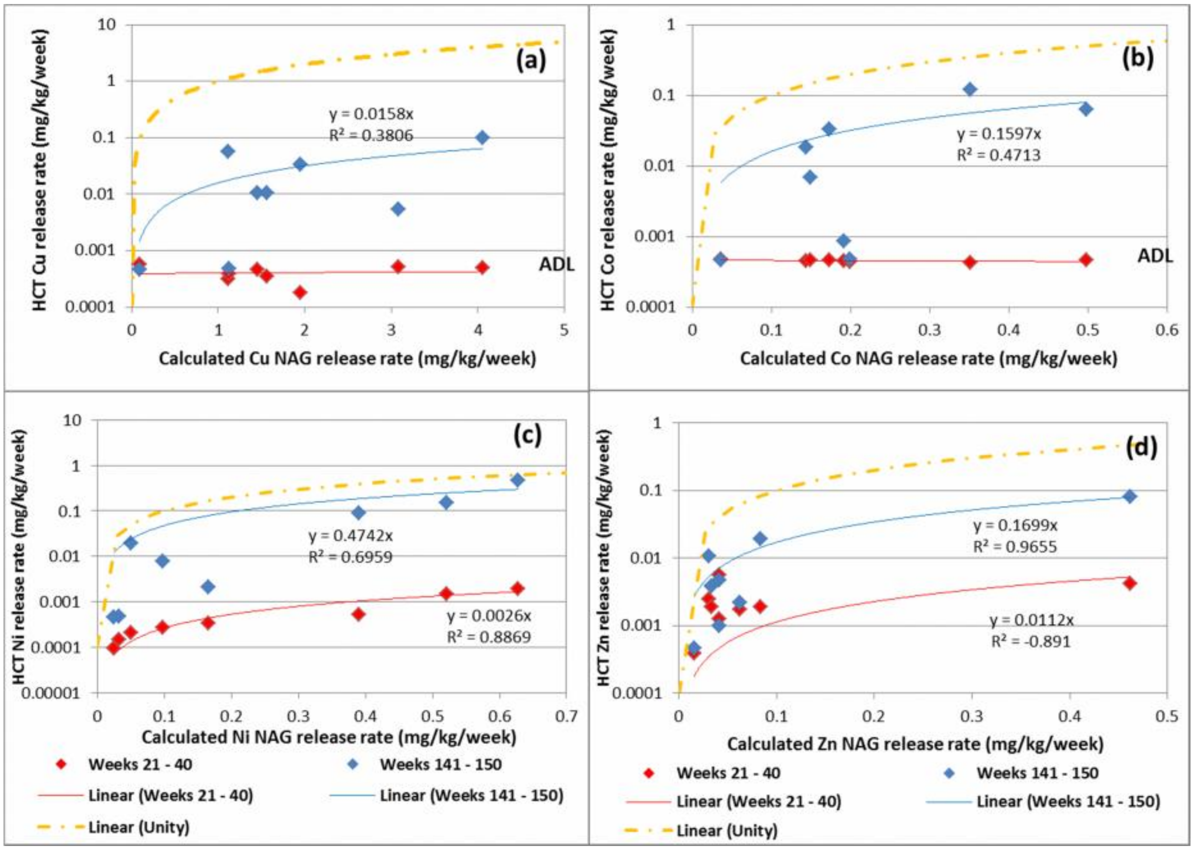

Figure 2 Comparison between measured HCT metals release rate (mg/kg/week) and calculated NAG release rate using the factor of 157.5 correction (as mg/kg/week equivalent) for a) Cu b) Co c) Ni and d) Zn. Comparison is made for HCT weeks 21 to 40 data and HCT weeks 141 to 150 data. The orange dashed shows 1:1 ratio between measured HCT release rates and calculated NAG release rates.

Metals release rates from the HCT increase significantly for Co, Cu, Ni and Zn, in most samples, between early stage and late stage leaching. However, it can be demonstrated that this increase in metals release is largely a result of the increasingly acidic pH as opposed to purely an increase in the rate of sulfide oxidation and primary release. For example, where the rate of sulfate release between early stage and late stage HCT weathering increases by a factor of about 2, in most cases, metals release increases by about 2 orders of magnitude for Co, Cu and Ni, and 1 order of magnitude for Zn. Therefore, the increasing sulfide oxidation rate cannot directly account for the increasing metals release. In order to further clarify this, a plot comparing metals release rate from the early stage and late stage HCT for Co, Cu, Ni and Zn against pH was produced (see **FIGURE 3**). This shows the clear log linear correlation between metals release rate and pH, behavior typical for transition metals cations due to retention through adsorption to iron oxides (Dzombak and Morel, 1999). The strong pH control of transition metal cations makes decoupling of the two processes of (i) primary release from sulfide minerals and (ii) actual release from the HCT column extremely difficult from HCT that have not reached acidic pH (pH << 4) due to the high proportion of metals being retained within the column. Due to the HCT metals release rate being compounded by sulfide oxidation rate and metals retention, it is difficult to use immature HCT release data to predict future release rates under acidic conditions without allowing the tests to run until such time as acidic pH conditions are reached. Because of the low final NAG pH, the calculated NAG metals release rates are not anticipated to be significantly moderated by sorption (in this example) and therefore, use of the calculated NAG release rate allows a better indication of long term release rates than could be achieved through scaling of premature HCT test data alone. This is where NAG test data can prove highly beneficial, to demonstrate this, the calculated NAG metals release rate plotted against the NAG test solution pH has also been included in **FIGURE 3**.

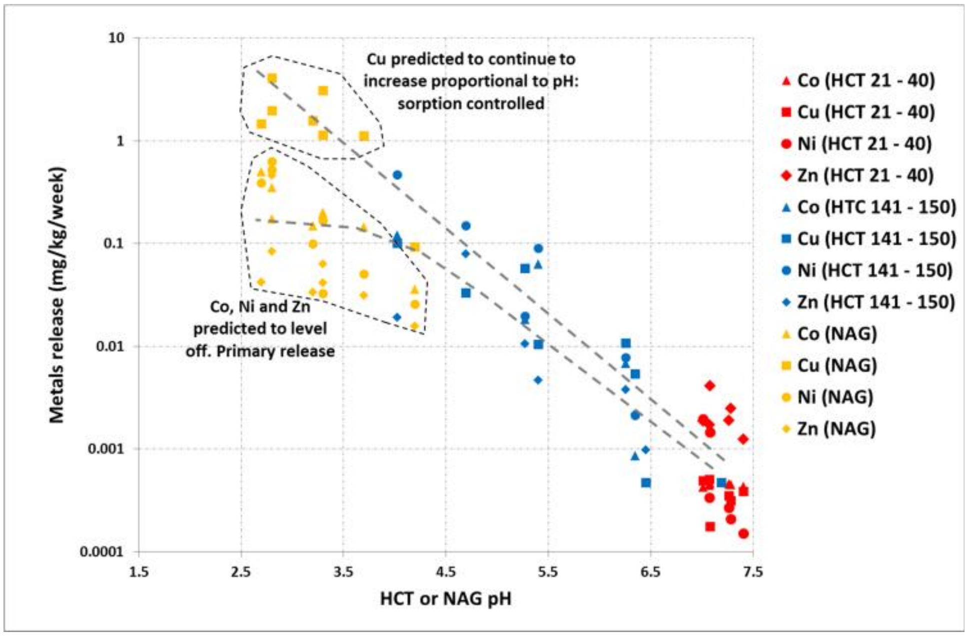

Figure 3 HCT metals release rates (mg/kg/week) verses pH for weeks 141 to 150 data. Also shown are predicted metals releases corresponding to NAG release rate (mg/kg) divided by a factor of 157.5.

The difference between measured and actual metals release rate are most apparent with the behavior of Cu. This is due to its high affinity for adsorption to iron oxides and the low adsorption edge relative to Co, Ni and Zn (Dzombak and Morel, 1999). The lower pH adsorption edge of Cu means that even at week 141 – 150, where most cells are generating mildly acidic pH solutions, a significant proportion of the Cu released through sulfide oxidation is likely to be retained within the cell through adsorption to iron oxides. It is only when the pH within the HCT drops significantly below 4 (assuming that this will occur) that the Cu release are predicted to increase to levels reflect by the proportion relationship with the NAG test data. Once the pH within the HCT solutions have declined below the adsorption edge of a particular metal, then the concentration of the metal within the solution should correlate with the sulfate release rate as the metal will no longer be retained within the cell. This can only be fully clarified by continuing the HCT tests until stable acidic pH are reached.

CONCLUSION

- For the particular samples and deposit type described in this paper, a good correlation was identified between HCT sulfate release rates and NAG test total sulfate release. This reflects the total available sulfur content within the sample which for these samples is correlated to the exposed sulfide mineral surface area.

- For samples that are expected to become acidic, the sulfide oxidation rate (in line with observations and literature) is expected to increase. It is possible that the initial sulfate release rate can be extrapolated to the final acidic pH release rate.
- The scaling of release rates under neutral condition to those under acidic conditions although logical for sulfate release, may not be applied to metals release so readily due to retention of metals by adsorption within the column. NAG test data shows promise for supplementing HCT prediction data by giving an indication of the maximum sulfide-associated metals release that can be expected under acidic conditions.

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