Evaluation of Humidity Cell Test Precision from an Ongoing Geochemical Characterization Program

Stephanie Theriault[1], Tamara Diedrich[1] and Stephen Day[2]

1. *Barr Engineering Company, USA*
2. *SRK Consulting, Canada*

ABSTRACT

Data from humidity cell tests (HCTs) are often used during mine development to design appropriate rock management plans and engineered systems, and can provide critical source terms in the predictive modelling of mine-impacted water quality. Information on reproducibility and repeatability of HCTs, in general, can be useful in providing a basis of reference during both the design of the HCT programs, and in the review of the quality of data used for making decisions, or forming inputs to the predictive models. Lapakko and White (2013) conducted repeatability and reproducibility analyses of duplicate HCTs on several rock types, including gabbro from the Duluth Complex with sulfur content ranging from 0.56% to 1.39%. An ongoing geochemical characterization program for a project in development to mine Duluth Complex rock presents an opportunity to augment this previous study with additional data from HCTs. As part of a characterization program, seven duplicate humidity cell tests (representing 14 individual tests) were conducted on Duluth Complex rock with total sulfur content from 0.04% to 3.79%, following the ASTM standard method D 5744-96 (Reapproved 2001) (ASTM, 2001). Results from this study indicate that for duplicate HCTs, maximum difference from the mean for pH varies between 0.05 and 0.18 units, while average difference from the mean for constituent release rates for sulfate, calcium, and magnesium were mostly within 15%. Variability in release rates for copper and nickel were greater, with average difference from the mean ranging from approximately 15-29%.

Keywords: Humidity cell tests (HCT), repeatability, precision, Duluth Complex

INTRODUCTION

Data from humidity cell tests (HCTs) are routinely used to estimate the rates by which constituents will be released during subaerial weathering of waste rock. These estimates may then be used as inputs to predictive geochemical models that serve as the technical bases for making decisions related to environmental assessment, mine design, and financing for mining projects. The U.S. Environmental Protection Agency Guidance for Quality Assurance Project Plans (USEPA, 2012), a guidance on quality assurance for environmental data, including data produced from models, recommends that a systematic planning process is used to establish criteria for the "Data Quality Indicators" (DQIs) that are consistent with the overall "Data Quality Objectives" (DQOs) for the project. DQIs for environmental data include properties such as precision, bias, representativeness, completeness, and sensitivity. Following from the above, characterizing the precision of HCTs may be a key component in evaluating whether geochemical model outcomes meet the DQOs for the overall project. In addition, knowledge of the precision of HCTs is required to assess representativeness and accuracy of the dataset. For the purpose of this paper, precision is defined as "an evaluation of agreement among replicate measurements of the same property under similar conditions; also referred to as random error or measured variability" (USEPA, 2012) whereas accuracy is defined as "a measure of the closeness of an individual measurement to a known or reference value" (USEPA, 2012) and is measured through both precision and bias. There is currently a limited amount of published data on repeatability and reproducibility of HCTs, factors that are used to quantify the overall precision. The current study aims to augment this existing body of information by opportunistic evaluation of the HCTs conducted for the quality assurance/quality control component of the ongoing geochemical chemical characterization program for a potential future mining project located in Duluth, north-eastern Minnesota.

Lapakko and White (2013) conducted repeatability and reproducibility analyses of duplicate HCTs on several rock types, including Duluth Complex gabbro (sulfur content ranging from 0.56% to 1.39%). The results of this study were used as a basis for the precision parameters in the present ASTM standard (method D 5744-96). Consistent with ASTM protocols (ASTM, 2011), repeatability refers to precision under conditions where the same test is performed by the same operator in the same lab within short periods of time, whereas reproducibility reflects precision when the test is performed by different operators at different labs. The majority of the repeatability HCTs analyzed by Lapakko and White (2013) were conducted over 59 weeks with a few extending up to 265 weeks. Comparisons were based on pH and release rates for sulfate, calcium, and magnesium. The maximum difference of the mean was used to compare drainage pH values whereas the percent difference from the mean was used for sulfate, calcium, and magnesium rate comparisons. The equations for both values are listed below:

(1) Maximum Difference of the Mean pH = maximum value for $|pH - pH_{ave}|$ where $pH_{ave} = -\log[(10^{-pH_1} + 10^{-pH_2})/2]$
(2) Percent Difference from the Mean = $100 * |rate - rate_{ave}|/rate_{ave}$

The percent difference from the mean was calculated for each individual rinse cycle and the mean and standard deviation of the percent difference was reported.

ASTM method D5744-96 includes two protocol options (Options A and B). Option A involves weekly cycles of three days of dry air followed by three days of water-saturated air pumped through the sample, with a water leach on the last day. Alternatively, Option B has six days of controlled and constant temperature and humidity and oxygen is supplied via diffusion (and possibly advection), not pumping, followed by a water leach occurring on the last day (ASTM, 2011). Lapakko and White (2013) evaluated both of these options. For Option A, both leaching alternatives were evaluated (drip and flood) for repeatability and reproducibility analyses whereas for Option B the drip and flood leach alternatives were only evaluated for the repeatability analysis (Lapakko and White, 2013).

Lapakko and White (2013) found that for the Option A drip alternative gabbro samples, repeatability of each laboratory was satisfactory. Two-thirds of the duplicate samples had a pH within 0.10 units of the mean. Similarly, sulfate, calcium, and magnesium rates were within 10% of the mean for over three-quarters of the samples. Deviations from the mean increased the longer the HCT was conducted. Reproducibility of the drip alternative for Option A were similar to that of the repeatability analysis during the first 125 weeks and as the length of testing increased, the percent difference from the mean increased as well. The increases were ultimately attributed to elevated temperature of the reaction environment resulting in an increase in sulfate release and lower drainage pH. Seasonal temperature changes resulted in differences in sulfate rates, most notably with increased rates in the summer months; increased oxidation rates also resulted in a lower pH. Similar trends were observed in the Option A flood alternative samples, as well as slightly lower pH values. One gabbro sample was run using each Option B method (drip and flood); initial results were similar between the leach alternatives and did not deviate with increasing time, presumably resultant to the stable temperature reaction environment (Lapakko and White, 2013).

The HCTs evaluated for the present study also contain rock from the Duluth Complex which enabled a direct comparison to Lapakko and White (2013). However, an expanded range in sulfur content was considered (duplicate HCT's use samples with sulfur content of 0.04-3.79%).

METHODOLOGY

An ongoing geochemical characterization program for a project in development to mine Duluth Complex rock presents an opportunity to augment this previous study with additional data from humidity cell tests on similar rock. This program was designed in cooperation with the Minnesota Department of Natural Resources Lands and Minerals Division and included seven duplicate HCTs (fourteen total) conducted on samples with a sulfur content ranging from 0.04% to 3.79% (Table 1) for 198 weeks. All humidity cells were analyzed by a single laboratory, allowing for the evaluation of the repeatability of the data only. Lithological designations for the Duluth Complex rocks are based on modal percentages of plagioclase, olivine, and pyroxene minerals present, using the classification scheme created by Phinney (1972). Humidity cell tests used in this study were conducted in accordance with ASTM standard method D 5744-96, Option A, flood leach. Sulfur content was determined using a LECO furnace. Aqueous metal concentrations were analyzed using ICP-MS and ICP-OES (alternating) bi-weekly. The ICP-OES was conducted to evaluate trends in major elements and provided trace metal concentrations, but at higher detection limits than the ICP-MS. pH was collected weekly. Results were recorded as mg/L and all non-detect data were recorded at the detection limit. For the purpose of this paper, only calcium, copper, magnesium, nickel, sulfate, and pH were evaluated.

Table 1 Duplicate HCT details

Sulfur Content	Lithology
0.04%	Anorthositic
0.04%	Troctolitic
0.06%	Ultramafic
0.09%	Anorthositic
0.25%	Troctolitic
1.68%	Troctolitic
3.79%	Virginia/Graywacke

Repeatability of the HCT samples is evaluated in a manner consistent with Lapakko and White (2013), as follows:

- pH: the difference from the mean (negative logarithm of the average hydrogen ion concentration) is determined by calculating an average pH between the duplicate HCTs (or group of non-duplicate, similar sulfur HCTs) for each weekly test cycle and the difference between the pH of individual HCT and the average. The maximum and average difference from the mean were determined and reported for each duplicate and similar sulfur content, non-duplicate groups.
- Release rates: the percent difference from the mean is determined by first converting concentration of ions to a release rate (μmol/kg/wk). Then, an average release rate is calculated for each test cycle and the difference between individual HCT analyses and the cycle average is calculated. The average of these differences for each test cycle is expressed as a percentage of the mean release rate for each cycle ("the percent difference from the mean"). The average percent difference from the mean is reported here for each duplicate set and similar sulfur content, non-duplicate groups.

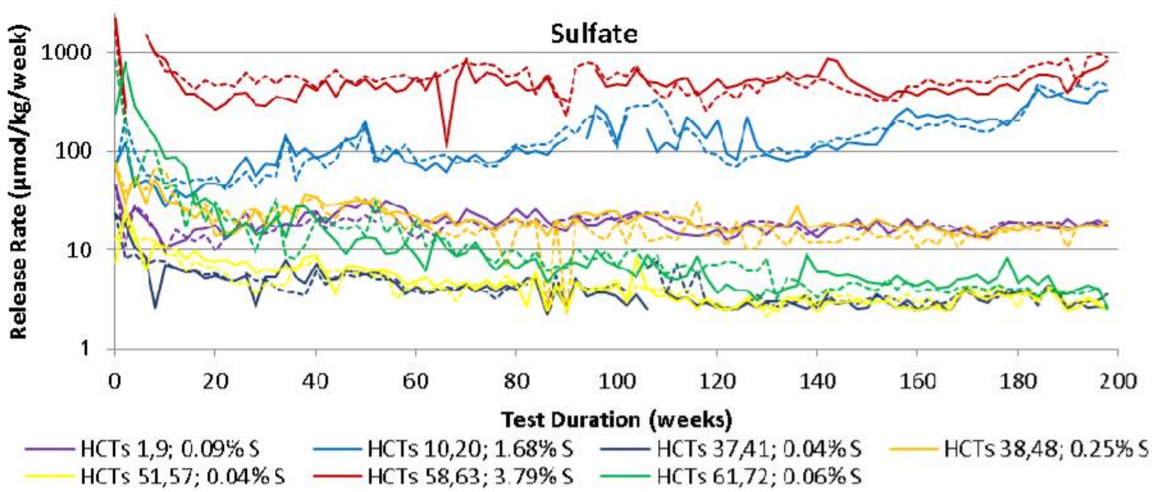
The method of calculation conducted by Lapakko and White (2013) assumes a normal distribution. Additional analyses were conducted on sulfate and pH to determine to actual distribution as well as the upper confidence limit (UCL) of the mean concentration based on that distribution. The statistical software program ProUCL 5.1.00 was used to determine the data distribution and UCL mean concentrations (Singh et al., 2013). The non-detect values are easily identifiable in ProUCL and are input at the detection limit.

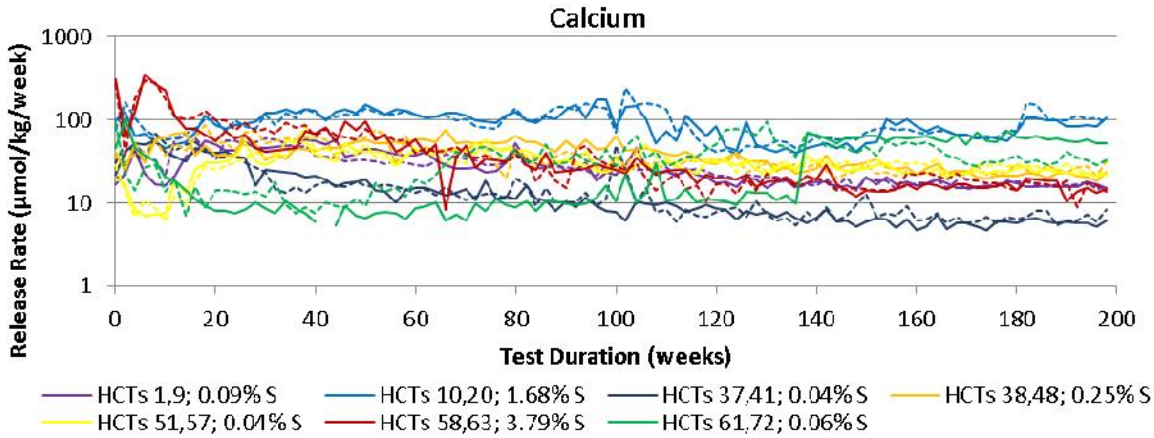
RESULTS AND DISCUSSION

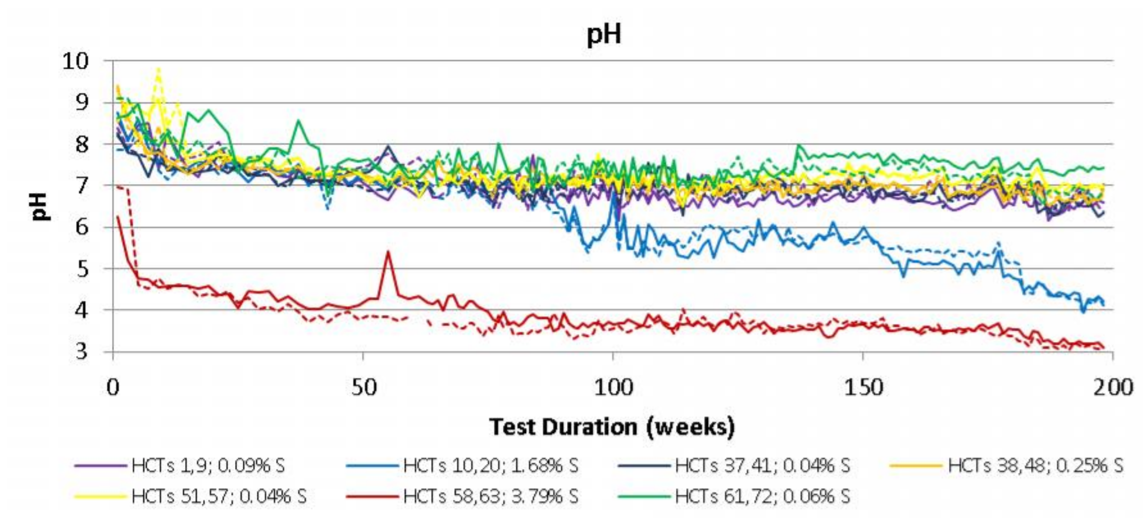
Results of the repeatability analysis of the duplicate HCTs are shown in Table 2. For sulfate, calcium, and magnesium, the average percent difference from the mean for release rates was less than 15%, except for the duplicate samples run on ultramafic material. For pH, the maximum difference from the mean was found to be between 0.05 and 0.18. These results are slightly higher, yet consistent, with findings reported in Lapakko and White (2013) Duplicate HCTs with less than 0.10% S are closer to the findings of Lapakko and White (2013) than those with more than 0.25% S, except in the case of ultramafic samples. Figures 1-3 portray the time sequence of release rates for duplicate HCTs for sulfate, calcium (trends for magnesium release rates are similar to calcium) and pH. For individual pairs of duplicate HCTs, there are no obvious trends in the difference from the mean, either in terms of test duration (i.e., the difference from the mean did not consistently increase or decrease as the HCT progressed) or relationship to the analytical detection limit (analyses closer to the detection limit did not show consistently greater differences than those far away).

Table 2 Repeatability of duplicate HCTs: maximum difference from the mean (pH) and average percent difference from the mean (SO_4, Ca, Mg release rates)

HCT IDs	Sulfur Content	Lithology	pH	SO4	Ca	Mg
37, 41	0.04%	Anorthositic	0.12	7.9%	11.2%	10.0%
51, 57	0.04%	Troctolitic	0.05	8.7%	8.9%	9.6%
61, 72	0.06%	Ultramafic	0.18	17.1%	35.0%	34.1%
1, 9	0.09%	Anorthositic	0.17	7.5%	8.7%	8.3%
38, 48	0.25%	Troctolitic	0.08	13.4%	12.6%	8.4%
10, 20	1.68%	Troctolitic	0.12	12.1%	8.9%	9.2%
58, 63	3.79%	Graywacke	0.12	12.8%	12.3%	14.0%







Figures 1-3 Sulfate and calcium release rates and pH for duplicate HCTs (shown by solid and dashed lines of the same color) throughout the 198 weeks of testing

Two different analytical methods, ICP-OES and ICP-MS, were used to measure constituent concentrations in HCT rinseate. The ICP-OES analyses, with detection limits up to two order of magnitude greater than the ICP-MS, were often dominated by analyses less than the detection limit for copper and nickel; therefore, only the ICP-MS data were used in the evaluation of copper and nickel repeatability. Repeatability of copper and nickel release rates using ICP-MS data are shown below in Table 3. The average percent difference from the means for all duplicate pairs are approximately 15% or greater for both copper and nickel release rates. For the duplicate HCTs, there does not appear to be a direct relationship between percent difference from the mean and closeness to the analytical detection limit. While repeatability was weaker for these trace metals than the major ions, trends in metal release was the same for duplicate pairs and distinctive differences between tests were maintained.

Table 3 Duplicate HCT repeatability analysis results: average percent difference from the mean for copper and nickel release rates

HCT IDs	Sulphur Content	Lithology	Cu	Ni
37, 41	0.04%	Anorthositic	22.2%	14.7%
51, 57	0.04%	Troctolitic	22.6%	16.3%
61, 72	0.06%	Ultramafic	26.2%	25.1%
1, 9	0.09%	Anorthositic	18.2%	18.2%
38, 48	0.25%	Troctolitic	21.2%	18.7%
10, 20	1.68%	Troctolitic	17.5%	21.5%
58, 63	3.79%	Virginia/Graywacke	29.4%	16.8%

The distribution of sulfate release rates and pH values for the duplicate humidity cells were conducted on results after the first 52 weeks of study using ProUCL. Significant variability occurred within the first 52 weeks and may not be indicative of long-term conditions encountered. Additionally, as previously mentioned, the Lapakko and White (2013) study based their analysis on the data being normally distributed, however, further analysis indicated that only 36% and 57% of the humidity cells sulfate release rates and pH values, respectively, were characterized as being normally distributed. The 95% UCL of the mean for each humidity cell was determined based on distribution criteria outlined in Singh et al. (2013).

Table 4 Repeatability of duplicate HCTs based on statistically determined distribution: maximum difference from the mean (pH) and average percent difference from the mean (SO_4 release rates)

HCT IDs	Sulfur Content	Lithology	pH		Sulfate	
			95% UCL	Max. Diff.	95% UCL	Ave. Percent Diff.
37 41	0.04%	Anorthositic	6.9 7.0	0.06	3.9 3.5	5.7%
51 57	0.04%	Troctolitic	7.2 7.2	0.01	3.8 3.8	0.7%
61 72	0.06%	Ultramafic	7.3 7.5	0.07	7.5 6.6	6.3%
1 9	0.09%	Anorthositic	7.0 6.7	0.13	19.0 19.3	0.8%
38 48	0.25%	Troctolitic	7.0 7.0	0.01	19.4 15.8	10.1%
10 20	1.68%	Troctolitic	5.9 5.8	0.01	200.8 217.8	4.1%
58 63	3.79%	Graywacke	3.6 3.7	0.07	582.9 529.8	4.8%

The recalculated maximum difference from the mean pH value was approximately one-half of those assuming normal distribution for all the samples. Similarly, the recalculated average percent difference from the mean sulfate release rates were 2 to 10% lower than those previously determined. Therefore, it is possible that with more rigorous statistical analyses, with particular attention on the distribution of the data as well as long-term stability of the dataset, the repeatability of the HCT improves.

CONCLUSION

Humidity cell test data is key input for predictive modelling of the quality of mine-impacted water. Understanding the repeatability of that data is necessary for accessing the quality of data being used for these models. Results from this study indicate that for duplicate HCTs, pH varies between 0.05 and 0.18 units from the mean, while constituent release rates for sulfate, calcium, and magnesium were within 15% of the mean, except for the ultramafic duplicate samples. This is consistent, although slightly higher, than precision parameters published in the ASTM method. Duplicate HCTs with less than 0.10% S are more consistent with the findings of Lapakko and White (2013) than those with more than 0.25% S, except in the case of ultramafic samples. The average difference from the mean for copper and nickel was greater than that of the major ions. Trends were not observed between either test duration or closeness to the detection limit and precision. Statistical analyses of the distribution of pH and sulfate release rates for data collected after the first 52 weeks of testing resulted in lower differences from the mean and therefore increased apparent repeatability of the humidity cell testing.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge permission from the mining company to publish these results. Interpretation of the test work results have benefitted from numerous discussions with individuals at both MDNR-LAM and the company. The authors would also like to acknowledge the contribution of two anonymous reviewers whose comments resulted in a much improved manuscript.

NOMENCLATURE

HCT humidity cell test

REFERENCES

ASTM Standard D5744-96 (2001). Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell. ASTM International, West Conshohocken, PA, 2001.DOI: 10.1520/D5744-96, www.astm.org.

Lapakko, K.A. and White, W.W. (2013). Interlaboratory Study to Establish Precision Statement for ASTM D5744-2013, Test Method for Laboratory Weathering of Solid Materials Using a Humidity Cell. Research Report: D34-1019. Committee D34 on Waste Management, Subcommittee D34.01.04 on Waste-Leaching Techniques, ASTM International.

Phinney, W.C. (1972) Duluth Complex, history and nomenclature, *in* Sims, P.K. and Morey, G.B., eds., Geology of Minnesota: A centennial volume: Minnesota Geologic Survey, p. 333-334.

Singh, A. and Singh, A.K. (2013). ProUCL Version 5.0.00 Technical Guide, Prepared for the US EPA. EPA/600/R-07-041. September 2013.

SRK Consulting (2007). RS53/RS42 – Waste Rock Characteristics/Waste Water Quality Modeling - Waste Rock and Lean Ore – NorthMet Project - DRAFT. [RS53/RS42 Draft-01]. SRK Project 1UP005.001. July 2007.

USEPA (2001). Data Quality Objectives Decision Error Feasibility Trials Software (DEFT)-USER'S GUIDE, EPA 240-B-01-007. September, 2001.

USEPA (2012). U.S. Environmental Protection Agency Guidance for Quality Assurance Project Plans, CIO 2106-G-05 QAPP. Final Draft, 17 January, 2012.