EVALUATION OF HUMIDITY CELL PARAMETERS THEIR EFFECT ON PRECISION AND REPEATABILITY [1]

D. L. Pool and R. M. Balderrama[2]

Abstract: The prediction of acid rock drainage (ARD) from mineral processing tailings is an inexact procedure, and variations in results are common. The U.S. Bureau of Mines has evaluated the major parameters associated with humidity cell tests to determine their effect on the test's precision and repeatability. A set of 44-week tests on 50-yr-old tailings was performed with temperature control and changes in effluent volume and airflow. The temperature was maintained at 30°±1° C. The airflow across the sample surface during the dry and wet air portions of the cycle was set at either 250 or 500 mL/min. The leach solution volume was varied to recover an effluent equivalent to up to 50% of the sample mass. The responses monitored were moisture removed during air addition, effluent volume, and acid in effluent (the amount of base required to titrate to pH 6), and total soluble sulfur. Changes in airflow and effluent volume affected the amounts of sulfate and acid reporting to effluent. Increased airflow resulted in more moisture removal and increased acid generation. As the effluent volume was varied, a maximum for acid generation was observed at 100 mL/325 g of sample. The data indicate that consistency in airflow and ratio of effluent volume to sample mass may improve the precision of the humidity cell test data. In addition, titration of the effluent provided a better measure of the acid content of the effluent than did pH monitoring. Precise and repeatable data should make the comparison of humidity cell data and ARD prediction between samples and testing facilities more reliable.

Additional Key Words: Humidity cell tests, acid mine drainage, AMD, acid rock drainage, ARD, tailings, fines.

Introduction

The U.S. Bureau of Mines is charged with ensuring the availability of metals to the economy with an acceptable impact on the environment. Research is underway at Reno Research Center to minimize the impact on the environment of mineral processing tailings from metal sulfide operations through source control for the prevention of acidic rock drainage (ARD). Samples of impounded tailings were collected and evaluated by static and kinetic leaching tests to determine their potential to generate ARD. Four replicate tests, to determine repeatability of modified humidity cell test results, were conducted using portions split from a well-blended head sample. During the performance of the kinetic humidity cell tests, parameters whose variation during testing could affect the consistency and magnitude of the results were identified. The parameters considered were airflow, leachant volume, air humidity, effluent volume, temperature, and percentage of water removed from a leached sample by aeration. The effects of two of these parameters, airflow rate and effluent volume, are presented in this paper.

Procedures for static ARD prediction tests are well defined, and the data from these tests are usually repeatable and comparable between laboratories. The static tests are used to make preliminary assessments of ARD generation potential and are based on acid-base accounting techniques (U.S. EPA 1978). Kinetic or accelerated weathering tests, however, are less well defined and are usually not conducted under closely controlled conditions. The authors look at these kinetic tests as a means of exposing the sample to conditions that are most likely to promote acid generation.

---

[1] Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994.

[2] Danny L. Pool, Senior Researcher, Robert M. Balderrama, Senior Researcher, U.S. Bureau of Mines, Reno Research Center, Reno, NV, USA.

Proceedings America Society of Mining and Reclamation, 1994 pp 326-333
DOI: 10.21000/JASMR94020326

https://doi.org/10.21000/JASMR94020326

Kinetic tests are usually conducted in modified humidity cells and consist of wet-dry cycles to speed up acid-generating chemical or biological reactions. The general procedure for humidity cell tests was established by Carruccio (1967) and is listed by the Environmental Protection Agency (U.S. EPA 1978) as an acceptable method for ARD prediction. The configuration of the cells has been modified by others (Lawrence 1990), but the 7-day cycle of 1 day leach, 3 days dry air, and 3 days wet air is still used. The duration of the test is usually 22 to 30 weeks (Nevada Department of Conservation & Natural Resources 1993). The responses commonly monitored are volume, concentration of sulfate (mg/L), pH, and conductivity of the effluent along with the cumulative amount of sulfate (g SO_4^{2-}/kg sample) leached.

Some of the conditions that may vary during kinetic testing include temperature, airflow, and leach solution volume and composition. Tests are usually conducted at "room" temperature, which may vary as much as 10° C owing to seasonal and locality changes. Changes in application rate and quality of air and water introduced to the cells are also conditions which are loosely regulated under common methodologies. These variations have potential to impact results of the predictive tests for ARD. Data reported and analyzed in this paper are the results of screening experiments to determine the effects of variations in procedure and technique on acid generation as measured in humidity cells.

Apparatus and Materials

The apparatus used in this research consisted of an enclosed cabinet which was kept at 30°±1° C using a thermostat, with a proportional controller which regulated power to two heat tapes. Air was circulated within the chamber by a 4-in caged fan. The cells used (fig. 1) in this testing program have been accepted by the Nevada Department of Conservation & Natural Resources, Division of Environmental Protection (1993), for use on either tailings or crushed rock and are similar to those recommended by MEND and CANMET (Lawrence 1990) which are acceptable to the EPA. The cells made of acrylic plastic had an 88-mm ID with a 160-mm-high sample compartment. An air inlet port was placed at 84 mm from the bottom. The depth of the sample bed was 40 mm. The leachant was added from the top through a gas dispersion tube, which was placed 0.5 cm from the sample surface to minimize erosion and produce turbulence in the airflow. The sample was supported by a perforated plate covered with a filter cloth and sealed to the side 30 mm from the bottom of the cell. The lid was sealed with silicon tape to prevent air loss from the system. Ambient air was pumped from the room into the system using a diaphragm pump. The air picked up heat as it passed through the tubing and apparatus inside the chamber, and was then dried or humidified and distributed through the appropriate manifold. Airflow to each cell was controlled by a needle valve-flowmeter assembly. The air exiting the cells was collected in a third manifold and guided to the exterior of the cabinet. Air was dried by passing ambient air through columns of calcium sulfate (Drierite). The relative humidity (RH) was decreased to less than 0.2%. The air was humidified by passing warmed ambient

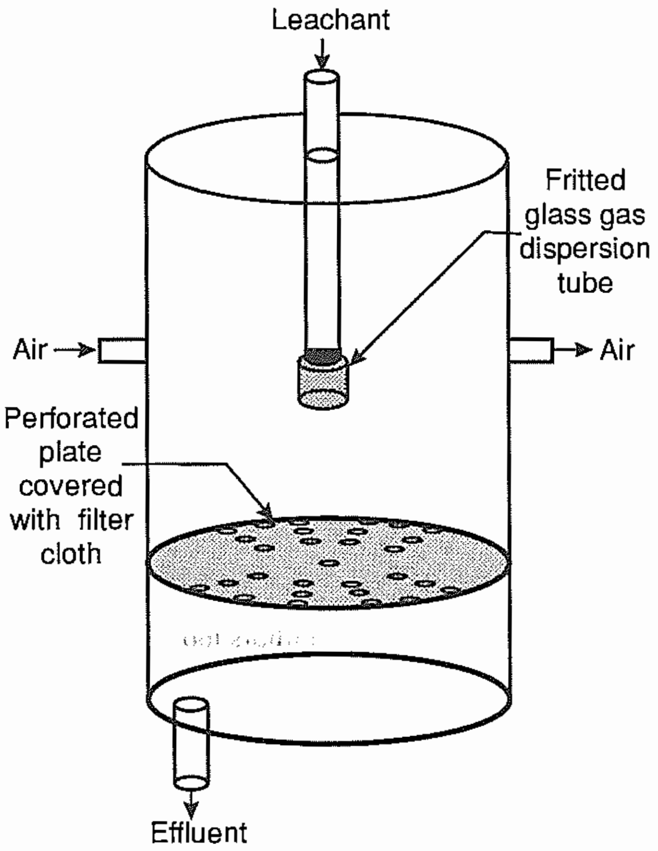

Figure 1. Schematic drawing of humidity cell used for the tests reported.

Table 1. Analyses of sample before and after 44-week humidity cell tests, percent.

Sample	Sulfur, total	Sulfur as sulfate	Sulfur as sulfide	Iron	Copper	Zinc	Lead
Head	[1] 2.40	0.28	[2] 2.12±0.05	4.0	0.080	0.080	0.01
Cell 1 tails	[1] 2.28	.14	[2] 2.14±.02	4.0	.027	.055	<.005
Cell 2 tails	[1] 2.25	.14	[2] 2.11±.01	3.8	.030	.039	.008
Cell 3 tails	[1] 2.26	.15	[2] 2.11±.07	3.8	.026	.050	.020
Cell 4 tails	[1] 2.29	.14	[2] 2.15±.11	3.8	.027	.046	<.005
Average tails	2.27	.14	2.13	3.8	.028	.048	.009

[1] Average of 2 assays. [2] Average of 2 assays with indicated variation.

air through two gas dispersion tubes submerged 250 mm in 35° C water which had been purified by a reverse osmosis (RO) process. The RH of the wet air was maintained above 90% and condensate was always present in the distribution system. The RH of the air streams was monitored to ±0.1% using a portable in-line relative humidity probe (Visala model HMI31). The RH was measured frequently during the first 20 weeks of the tests, then often enough to ensure consistency.

Water purified by RO was used to leach the samples. The water was characterized by measuring three parameters: the conductance, which ranged from 0.005 to 0.06 mS; the pH, which ranged from 4.17 to 4.87; and the oxidation reduction potential versus Ag-AgCl reference, which ranged from 273 to 391 mV. A container filled with this "characterized" leachant was placed inside the controlled temperature chamber at least 24 h before it was to be used.

The titration was conducted using a Mettler model DL25, which was capable of printing out volume added and the pH of a solution after each 0.1 mL of titrant was added. Using these data, the volume of titrant required to raise the pH to each selected pH was determined. The procedure was to place a 5- or 10-mL sample in the titrator cup and dilute to 40 mL using RO water, measure pH, and procede with the titration. A sample of RO water was titrated and a "blank" adjustment was made.

Solutions were analyzed for sulfur, copper, lead, calcium, and other metals by inductively coupled plasma (ICP), and for sulfate using ion chromatography (IC). Solids were analyzed for metals using ICP, and for total sulfur by combustion. Sulfate sulfur was determined by acid digestion in an inert atmosphere, followed by sulfur determination by ICP. Particle size distribution of the head sample was determined using a laser and white-light-based, computer-controlled particle size analyzer.

The material studied was a 30-lb sample collected from the 0-5 ft depth of a 50-yr-old copper-lead-zinc tailings impoundment. The particles in the head sample were 100% minus 150 μm, 75% minus 100 μm, and 50% minus 65 μm. The chemical analysis of this sample is listed on the first line in table 1. The main sulfidic mineral was pyrite, with minor quantities of galena, sphalerite, and chalcopyrite. The yellowish color of the tailings indicated that the tailings had been partially oxidized, and the presence of sulfate indicated that not all of the oxidized sulfur had been washed away during weathering.

Experimental Procedure

Four 325-g splits of the tailings were placed into 4 cells. The sample size was chosen to obtain a bed depth of 40 mm in each cell, which allowed the sample to be flooded during leaching without overflowing into the air lines. The cell plus sample was weighed at the start of the test, at the end of each leach step, after the dry air portion of each cycle, and again after the wet air portion of each cycle. The first cycle consisted of 1 day of leach followed by 3 days of dry air and was used to remove part of the soluble sulfate load from the samples.

All subsequent cycles were 7 days in length using the normal 1 day of leach, 3 days of dry air, and 3 days of wet air. The leach was conducted by weighing the required quantity of "characterized" leachant for each cell into individual wash bottles that could be emptied by squeezing. The leachant was introduced into each cell through the gas dispersion tube. The surface of the sample was flooded, and leachant was allowed to percolate through the sample bed. The remaining leachant was added during the next 4 to 6 h. The effluent was collected in a wide-mouth Erlenmeyer flask, which was vented to the cabinet. The volume, conductivity, oxidation potential, and metal content of each effluent was determined and recorded. Airflow was started late in the afternoon of the day of the leach.

The acid generated during the tests was monitored using three separate techniques:

1. pH Measurement: The pH of the effluent was considered to be the effect of sulfuric acid only. The concentration of acid was calculated from pH by using the definition that pH is the negative log of the H^+ activity. If it is assumed that activity and concentration are the same under the test conditions, then a solution with pH 3.2 has a H^+ concentration of $10^{-3.2}$ or 0.000631 g/L H^+. This is equivalent to (0.000631 x 49) = 0.031 g sulfuric acid per L.

2. Titration: A 5- or 10-mL aliquot of each effluent was transferred to a titration vessel, diluted to 40 mL, and then titrated using 0.01N or 0.1N sodium hydroxide in the automatic titrator. The amount of base required to adjust the pH of a sample of effluent to five different pH values was determined. The pH values selected, 3.5, 4.0, 6.0, 7.0, and 8.3, were considered as endpoints in different static tests (Lawrence 1990). During this test no attempt was made to remove the soluble CO_2 as recommended by Carruccio (1967). This simplified the procedure and accounted for all of the acidity in the solution, not just the sulfate acidity.

3. Sulfate Concentration: The sulfate content of the effluent was determined by analyzing for total sulfur in solution and assuming it was all sulfate. This assumption was confirmed on random samples by analyzing for sulfate. The acidity was calculated by assuming that all of the sulfate was from sulfuric acid.

Results and Discussion

Effect of Airflow

The percentage weight loss plotted in fig. 2 is the total for both dry and wet air portions of each cycle. The percentage was calculated based on the weight of the water contained in the sample after leaching and the weight loss during airflow. When the airflow was 250 mL/min, the wet air continued to remove moisture in spite of the condensation which occured in the system. The RH was measured in and out of the cell and usually increased about 2%, from 95% to 97%. Small changes in the pressure as the air flowed through the manifold and distribution system altered the moisture-carrying capacity of the air. After the airflow was increased to 500 mL/min, the weight loss during the wet air portion of the cycle was less than 10% of the total weight loss. The data in fig. 2 show that the average weight loss from the four replicate tests was dependent on the airflow into the cells, which affected the velocity of the air across the surface of the sample. An airflow rate of 250 mL/min over an 88-mm-diameter sample surface evaporated 36% to 58% of the water in the 40-mm-deep bed of tailings. An airflow of 500 mL/min evaporated 68% to 82% of the water.

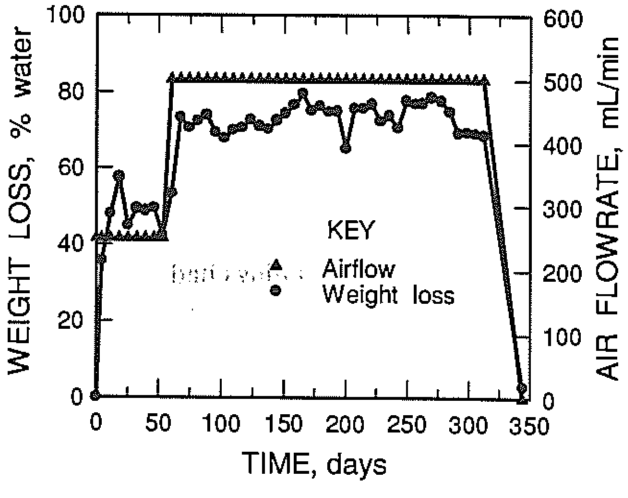

Figure 2. Effect of airflow across cell on weight loss of contained water over time.

During the last 32 days of the test, no air was pumped through the cells and the samples remained wet between leachings. In the absence of airflow, evaporation was nearly zero.

Effects of the Leachant Volume

The volume of the effluent is the difference between the amount of leachant added and the amount of liquid retained by the sample to replace evaporation. Thus, to recover a consistent volume of effluent, the airflow and the leachant volume must both be constant. The leachant removes the soluble salts and acid, thus changing the chemical and biological environment in which oxidation may occur. The data in table 2 and fig. 3 show these relationships for cell 1. Table 2 contains a description of the changes in the controlled variable and the accompanying measured responses. The values for effluent volumes and acid in solution, by titration, are averages for the days stated. The acid generation response from day 313 to day 342 shows that it is necessary to aerate the sample to generate acid. Part of the decrease in acid generation might be attributed to a depletion of sulfides in the tailings, but this is not supported by the data here and in fig. 3 since the acid generation rate increased with a decrease in leachant volume from day 208 to day 263. These data indicate that the degree of drying and the amount of effluent recovered from these tailings affected the amount of acid generated. The most acid was generated in this cell when 186 mL of leachant was added and 100 mL of effluent was recovered.

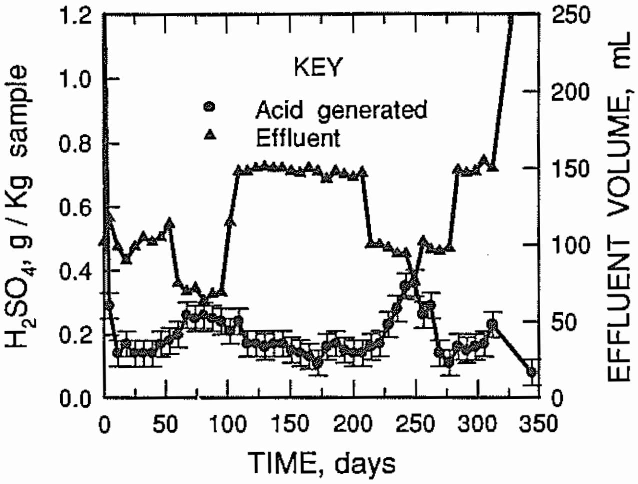

Figure 3. Effect of effluent volume on acid production, as determined by titration, over time--Cell 1.

Table 2. Data for cell 1--Timing of changes in controlled variables and the changes in two responses (effluent volume and acid generation).

Cycle No.	Segment, days		Controlled variable		Response measured		Variable changed	Cum. H_2SO_4, g/kg sample
	Start	Stop	Airflow rate, mL/min	Leachant vol, mL (ave/cycle)	Effluent vol, mL (ave/cycle)	[1]Ave H_2SO_4, g/kg sample per cycle		
0	0	4	250	150	100	0.92	Start	0.92
1-7	5	53	250	150	100	.15	None	1.97
8-13	54	95	500	150	75	.24	Air	3.41
14-15	96	109	500	190	115	.22	Leachant	3.85
16-29	110	207	500	230	150	.15	Leachant	5.95
30-38	208	263	500	186	100	.32	Leachant	8.83
39-45	264	312	500	230	150	.16	Leachant	9.95
46	313	342	0	300	340	.08	Air and leachant	[2]10.03

[1] By titration to pH 6.

[2] This value is equivalent to 0.33% S in the starting sample, which is 13.6% of the starting concentration of 2.40% total S. An extrapolation shows that if this reaction rate holds constant, a 6.8 year-long test may remove all of the sulfur. In practice it would take much longer because the rate would decrease as the amount of sulfur remaining in the sample became the controlling factor.

The optimum amount of leachant, to generate the most acid, is dependent on the amount required to replace evaporation and control the chemical and biological environment. For these tailings to produce the most acid, approximately half the weight of the sample was added as leachant with a subsequent recovery of only a third of the sample weight as effluent. The amount of water retained by the tailings at the start of the tests was 105 mL. If this is considered a "bed volume", then the data can be interpreted to show that the maximum acid was generated by almost complete drying of the sample, with an application of 1.8 bed volumes of leachant and a recovery of almost 1.0 bed volume as effluent.

Acid generation was the main response of interest. The endpoint of pH 6.0 was selected after titrating effluent samples for the first 20 weeks to pH 3.5, 4.0, 6.0, 7.0, and 8.3. The acid generation values for 6, 7, and 8.3 were almost identical while, as expected, the values for 3.5 and 4.0 were both lower than the upper group. According to the Code of Federal Regulations (1986), drainage with pH value of 6 or below is termed "acidic." A value of pH 6.0 was chosen as the endpoint for subsequent titrations because, it is the upper limit in the definition of acid drainage, and represents the value at which most of the acidity had been neutralized.

To determine if there was any difference in the values obtained by the three techniques used to measure acid generation, and to establish which values represented real or significant changes, the average data from all four cells were compared in figs. 4 to 6. The average acid generated by the four replicates between day 110 and day 207 was considered as baseline data because this was the longest period of time in which the controlled variables were held constant. The average acid generation during the baseline period was 0.15, 0.28 and 0.13 g H_2SO_4 per kilogram sample per cycle, for titration, pH, and soluble sulfate, respectively. Twice the standard deviation was calculated and added to and subtracted from the average. This estimated the random error in the system; therefore, any data outside these limits are considered to be significant, or probably the result of a change in a controlled variable. The standard deviations for the respective calculation methods were 0.02, 0.05, and 0.03 g H_2SO_4 per kilogram sample per cycle. These data show that titration and soluble sulfate have similar averages, and titration has the best precision

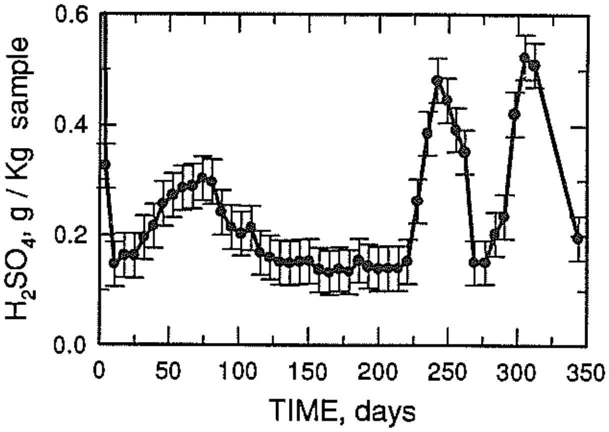

Figure 4. Acid generation, average of four cells, as determined by titration to pH 6.

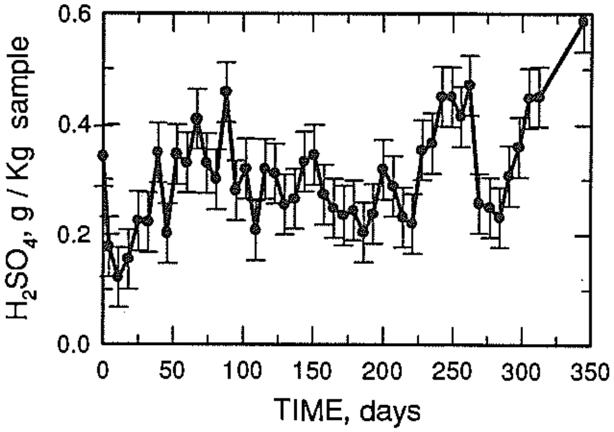

Figure 5. Acid generation, average of four cells, as determined by pH measurement.

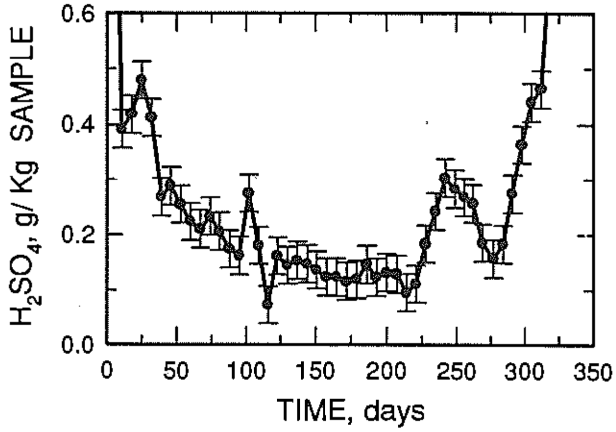

Figure 6. Acid generation, average of four cells, as determined by soluble sulfate in effluent.

during the baseline period, while pH may give a false high acid generation value because of random errors. The random errors were manifested in variations in pH meter measurements in tests conducted under the same conditions. The pH of the effluents ranged from 2.3 to 3.1 during the term of the tests, but only from 2.59 to 2.95 during the baseline period. The precision of the data from the titration method is better than that for the other methods, and any real changes in the response are more detectable if the samples are titrated to determine acidity.

Analyses for the solid material before and after the humidity tests are shown in table 1. These data show the reproducibility of the analysis of these rather high-sulfur tailings. Sulfur standards obtained from CANMET were also assayed and the results obtained were within the established limits (±0.15%) of variation (Smith and Bowman 1990). The same procedures were followed when assaying the tailing samples. The data in table 1 show that the total sulfur decreased an averaged of 0.13%, which is only 5.4 pct of the total sulfur, as determined by head and tails sulfur analysis, during more than 44 weeks of testing. These data indicate that most if not all of the sulfur collected in the effluent was from the sulfate, and that the sulfide sulfur did not change during this kinetic test. The data in tables 1 and 2 indicate that more sulfur was recovered in solution than was removed from the tailings; this is attributed to sampling and analytical variations.

Summary

Data presented in this paper are from observed trends in humidity cell tests that were conducted to measure acid rock drainage potential from a mineral processing tailings sample. The tests were conducted in a set of four in order to establish the repeatability of humidity cell tests using tailings. These data were not compared with the results in other laboratories using the same or standard samples. However, the authors feel that the responses noted should lead to further investigation on the degree of control required for each variable while conducting humidity cell tests. How to handle samples with a high sulfate load, and how this loading may affect any measurement of acid generation should be addressed in detail.

The important parameters that affect the acid production in the constant temperature humidity cell apparatus were the percent water removed and the amount of effluent recovered. The percent water removed was controlled by airflow through the cell and across the sample surface, and the amount of effluent recovered was dependent on the amount of leachant used and the airflow. The conditions at which the most acid was generated were as follows: When more than 75% of the contained moisture was removed during the 3 days of dry air and the moisture was maintained at that level for 3 days with wet air, the acid and dissolved salts were recovered by leaching with enough water to make up for the evaporative loss and recover one-third of the sample weight, which in this case was 1 bed volume. The measurement of the acid generated is best done by titrating an aliquot of the effluent as originally recommended by Carruccio (1967).

The authors' recommendation for humidity cell tests on tailings is to conduct the tests under the most consistent conditions possible and document them so others can perform comparable tests. This will make the results of these expensive long-term tests more usable in predictions of possible ARD.

Literature Cited

Carruccio, Frank T. 1967. An evaluation of factors influencing acid mine drainage production from various strata of the Allegheny group and the ground water interactions in selected areas of western Pennsylvania. Ph.D. Thesis, The Pennsylvania State Univ., University Park, PA, 213 p.

Code of Federal Regulations. 1986. 413 p. In U.S. Bureau of Mines Information Circular 9183, Mine drainage and surface mining reclamation and enforcement.

Lawrence, R. W. 1990. Acid rock drainage prediction manual, a manual of chemical evaluation procedures for the prediction of acid generation from mine wastes. Prepared for CANMET - MSL Division, Department of Energy, Mines and Resources, Ottawa, Ontario, Canada, November 30, 1990, 140 p.

Nevada Department of Conservation & Natural Resources, Division of Environmental Protection. 1993. Reno, NV, personal communication with D. Zimmerman.

Sobeck, A. A., and W. Schuller. 1978. Field and laboratory methods applicable to overburdens and minesoils. U.S. Environmental Protection Agency, EPA-600/2-78-054 (PB-280 495), 203 p.

Smith, C. W., and W. S. Bowman. 1990. RTS-1, RTS-2, RTS-3, RTS-4: Sulfide ore mill tailings reference materials. CANMET, Energy, Mines and Resources, 555 Booth St., Ottawa, Ontario, Canada, 91 p.