Chapter 2: First Phase of Weathering Tests (2002)

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Standard Method Development Process of EPA

EPA's cradle-to-grave analytical methods development process typically involves evaluation of existing documented techniques and development of procedures for an intended EPA application in a single laboratory. Single laboratory results and observations are used to prepare a draft method that is tested further in one or several multiple laboratory studies, including an interlaboratory study in which each laboratory evaluates identical unknown samples. Results of each study are used to revise the method, as appropriate, towards the goal of providing a method that can be sued for an intended purpose by a variety of laboratories. EPA methods that are intended to be required by EPA for use by industries monitoring compliance with regulations, are subjected to a federal rulemaking proposal process, and may be further revised prior to promulgation. In the case of the ADTI-WP2 Leaching Column Method, the method procedures were drafted based on published results of similar existing procedures, and the draft procedures were evaluated and further developed first in a single laboratory, followed by a multiple laboratory study, peer review, and finally, an interlaboratory study. Following each stage of method development, the draft method was revised as needed to address study results or reviewer comments.

Many EPA method development efforts include a built-in approach for providing performance-based criteria that can be used to (1) evaluate the validity of analytical results, and (2) allow the use of alternative equivalent procedures or equipment. This is consistent with the flexibility provided by EPA's Performance Based Measurement Systems (PBMS) approach to method development. Examples include study requirements for laboratories to analyze quality control samples to determine analytical precision and bias, such as statistical differences between results of replicate samples and recoveries of known spiked analyte concentrations. Statistical assessments of the results of these quality control samples are used to establish method performance criteria based on application of the procedures in multiple laboratories. Because of the complex nature of the samples and analytical components involved in the ADTI-WP2 method, it was not feasible to include an evaluation of bias in the method validation studies (i.e. the method is designed to evaluate the long-term effects of weathering, rather than the total amount of a contaminant that can be recovered in a singe analysis). The studies described in this report, for validation of the draft ADTI-WP2 method, included requirements for laboratories to evaluate duplicate samples throughout the weathering process. Results of these analyses were used to determine the precision that should be expected from laboratories analyzing replicate samples, and a requirement for analysis of replicate samples is built into the method as a means of evaluating data validity. Specifically, results of replicate samples were used to determine and establish the relative percent difference (RPD) in analytical results that can be expected between duplicate samples evaluated in a single laboratory and the relative standard deviation (RSD) that can be expected between more than two samples evaluated in a single laboratory. These criteria are based on the following equations:

Relative Percent Difference (RPD):

$$RPD = \frac{|C1 - C2|}{(C1 + C2)/2} * 100\%$$

Where: C1 and C2 are the concentrations of the original and duplicate results.

Relative Standard Deviation (RSD):

RSD = (Standard deviation / mean) x 100%

<u>Rock Samples Tested during Method Development</u>

Several rock samples were used during the initial development and testing of the humidity cell and leaching column kinetic test methods to determine how the procedures would perform using a variety of sample types that could be expected to encounter in overburden analysis. Neutralization Potential (NP) and total sulfur contents of these samples are provided in Table 2.1. The Brush Creek shale outcrop near Greensburg PA was selected as the primary rock sample for use in this project for several reasons: it has moderately high total sulfur and NP values classifying it as a "gray zone" type of sample; the sample site was selected in 1999 to be the first ADTI Coal Mining Sector standard reference material (thus, there is extensive geochemical characterization data available); the site stratigraphy has been confirmed and described by Skema (1995) in a published field guidebook; the sample site (Route 66 road cut) has long term accessibility for future sampling needs; and finally, the lithologic unit is known throughout Pennsylvania's Bituminous Coal Region to have sufficient NP to produce significant alkalinity in mine drainage discharges and pit waters (described in Brady et al., 1998). The range in total sulfur content of four splits of the Brush Creek shale is 0.90 to 0.93 % (see Table 2.1). The range of NP values is 133.39 to 138.28 parts per thousand (ppt), thus documenting the moderately high sulfur and NP characteristics of the sample (i.e. a gray zone sample) and the homogeneity of the sample splits.

The Wadesville sandstone was selected as the secondary rock sample for this project because it represents a hard lithologic unit, in distinct contrast to the more friable Brush Creek shale. For this reason, it was expected to allow evaluation of much different physical weathering characteristics. Wadesville sandstone samples were collected within the pit of a large anthracite open-pit surface mine in Schuylkill County, PA that has been operated by Reading Anthracite Co. since before 1950. This sandstone represents the only lithologic unit at the site containing appreciable carbonate minerals; yet the mine pool discharge is one of the most naturally high alkaline discharges in the state (i.e., alkalinity greater than 400 mg/L) as documented in Hornberger and Brady (1998) and Brady et al. (1998). X-ray diffraction on this sample determined the carbonate mineral to be ferrodolomite; with 2 or more percent additional iron content, this mineral could be properly classified as ankerite. The range of NP values for this sample is 255.84 to 281.96 ppt (see Table 2.1), and the total sulfur contents are negligible.

Table 2.1 Total Sulfur and Neutralization Potential Values of Rock Samples

Split Sample ID	Total% Sulfur	*Fizz	Neutralization Potential (ppt)
Brush Creek Shale			
#8	0.90	2	138.28
#16	0.92	2	135.58
#24	0.91	2	133.39
#32	0.93	2	135.83
Wadesville Sandstone			
#4	0.00	2	255.84
#8	0.00	2	274.24
#16	0.01	2	261.50
#24	0.00	2	281.96
Highwall "A"	0.01	2	225.62
Valentine Limestone			
"A"	0.00	3	928.99
"I"	0.00	3	926.68
"K"	0.00	3	931.82
"P"	0.02	3	928.35
Leechburg Coal Refuse			
S-1	1.68	0	0.91
S-2	3.03	0	-1.32
S-3	1.58	0	3.29
S-4	2.01	0	5.27
S-5	2.42	0	1.29
Ernest Coal Refuse			
1A	4.38	0	1.16
1B	4.03	0	1.65
2A	3.75	0	2.29
2B	4.19	0	1.36
3A	3.91	0	1.09
3B	3.45	0	1.02
4A	1.23	0	-0.37
4B	0.99	0	-0.21
5A	1.28	0	1.38
5B	1.39	0	1.13

The Valentine limestone and the Ernest and Leechburg coal refuse samples were not as rigorously tested as the primary and secondary samples described above (i.e., no duplicate samples were analyzed during kinetic test evaluation). However, results from these samples provide some useful additional information on the performance of the draft weathering methods as described in Hornberger, et al., (2003). The Valentine limestone is described in a PA Geologic Survey publication (O'Neill, 1964) and Brady et al., (1998, p. 8-46) as the purest limestone in Pennsylvania, typically having calcium carbonate content greater than 97%. The specific Valentine limestone sample used in this project was collected from a quarry and underground mine operated by Graymont (PA), Inc. in Centre County, PA. That Valentine Limestone sample was collected from a stock pile located at the mine site near the town of Pleasant Gap. The stock pile consists of high-calcite bench material known to have 98.5% $CaCO_3$ and essentially zero sulfur.

The Ernest coal refuse sample was collected from a large coal refuse pile associated with the abandoned underground coal mine at the town of Ernest in Indiana County, PA. The Leechburg coal refuse sample was collected from the large refuse deposit associated with the abandoned underground Leechburg coal mine near the town of Apollo in Armstrong County, PA. The Leechburg site produces some of the most acidic mine drainage in PA as described in Hornberger and Brady (1998, p. 7-7), wherein acidity concentrations greater than 16,000 mg/L are reported.

sample collection and preparation: Prediction of the effects of weathering is limited by the extent to which samples are representative of the overburden being evaluated. Samples were collected using standard procedures described in Sobek et al., 1978; Block et al., 2000; Griffiths, 1967; and Tarantino and Shaffer, 1998. Samples were collected by the Pennsylvania Department of Environmental Protection and were homogenized and split into sample aliquots by Geochemical Testing. The sampling team collected approximately 800 pounds each of Brush Creek Shale, Wadesville Sandstone, Valentine Limestone and the two coal refuse piles. Bulk sample volumes were crushed to approximately ½" maximum diameter, mixed, and homogenized using procedures described in ASTM C-702-98 and Noll, et al., 1988.

Samples were air dried overnight and crushed through a Marcy jaw crusher, with the opening set for approximately ½" top size. Once an entire sample was passed through the jaw crusher, the sample was spread evenly, mixed, and long piled. Finally, the sample was riffled through a bulk splitter with openings set at 1.5". The bulk sample was used to prepare a total of 32 sample aliquots weighting approximately 25 pounds each. Prior to exposure to the weathering conditions described in the draft methods, the sample aliquots were stored in clean 5-gallon opaque buckets. Sample aliquots were selected randomly for analysis of total sulfur, neutralization potential, maximum potential acidity, and fizz rating. Results of these analyses are presented in Table 2.1.

The particle size distribution of the crushed sample was determined using a series of sieves (#4 (4.76 mm), #10 (2.00 mm), #20 (0.84 mm), #40 (0.42 mm), #100 (0.149 mm) and #200 (0.74 mm) sieve sizes) to yield 8 particle size classes (i.e. including >3/8" (9.52 mm) and <200 (0.074 mm) fines). The homogenized samples were then chemically analyzed for percent total sulfur and neutralization potential as shown in Table 2.1.

Study Design and Laboratory Tasks

Toward the goal of developing standardized and effective test procedures, draft humidity cell (ADTI-WP1) and leaching column (ADTI-WP2) methods were developed for test application in two laboratories. The draft methods were designed to require low cost materials and minimal apparatus construction, maximize weathering efficiency, and produce reliable and verifiable data. The leaching columns were constructed from 6-inch diameter clear polycarbonate plastic tubing. The humidity cells were constructed from rectangular plastic food storage containers with airtight lids. Schematic diagrams describing the construction of the humidity cells, leaching columns, and humidified gas reservoir are presented in Figures 2.1a through 2.1c.

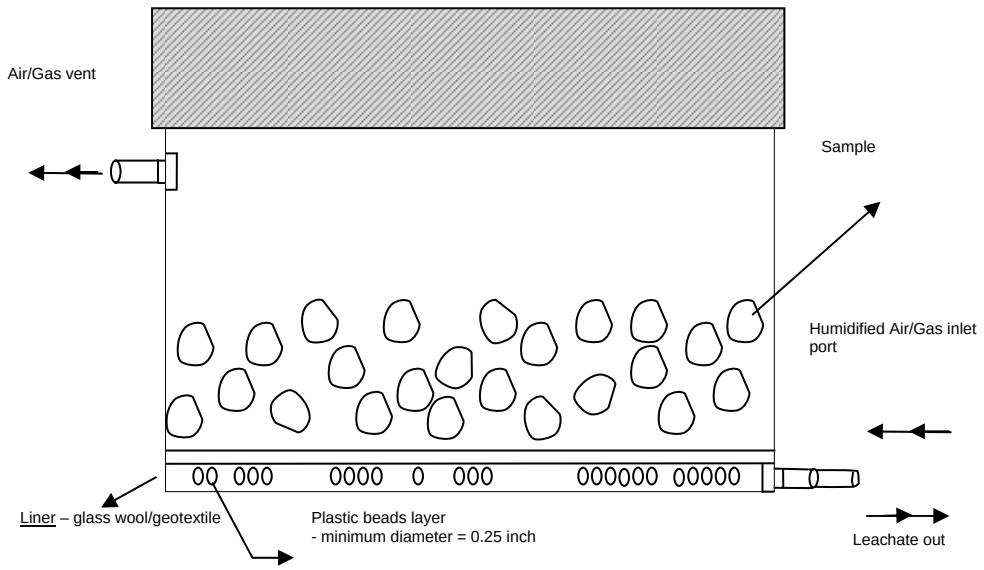

Figure 2.1a. Humidity Cell

To evaluate the performance of draft test methods and evaluate the effects of CO_2-enhanced air, the study involved two laboratories and the three sample types described above (shale, sandstone, and limestone). Laboratory 1 (Geochemcial Testing) was tasked with implementing both draft leaching column and humidity cell methods using duplicate samples exposed to two

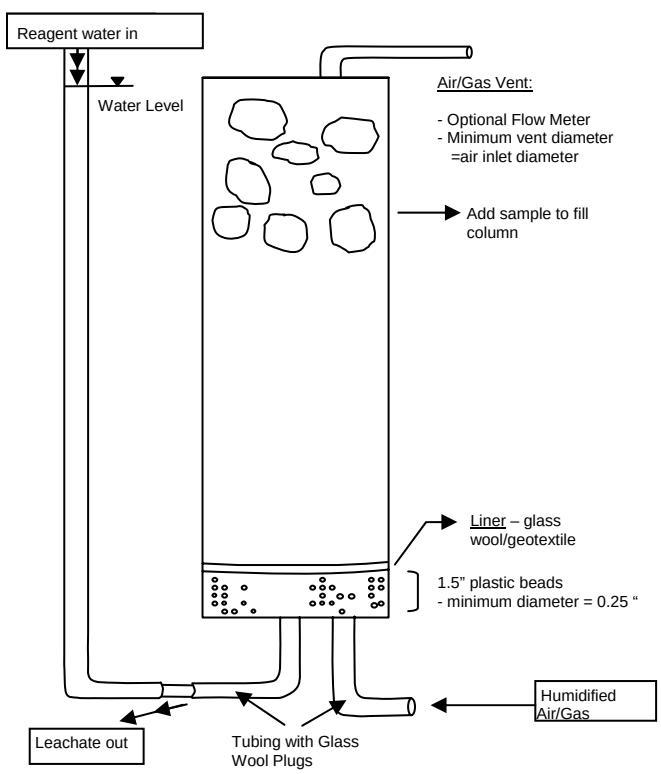

Figure 2.1b. Leaching Column

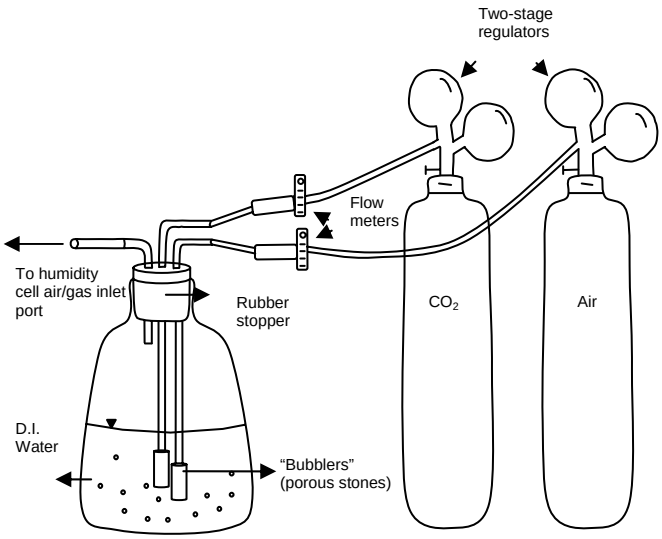

Figure 2.1c. Humidified Gas Mixture Schematic.

gas-mixture scenarios (i.e., air-only, and CO_2-enhanced air). Laboratory 2 (Materials Research Institute at Penn State University) was tasked with implementing the draft leaching column method using single samples exposed to CO_2-enhanced air. For a period of 15 weeks, each laboratory collected weekly samples from all columns and cells, and analyzed the samples for specific conductance and pH. Biweekly samples were filtered and analyzed for dissolved calcium, sulfate, acidity, alkalinity, iron, and manganese using EPA-approved methods. Data results of the analyses are included in Appendix C of this report.

Humidity cells were filled to 2/3 cell height; columns were filled to column height. Approximate weights of each sample added to the humidity cells were 1 kg and approximate weights added to the leaching columns was 13 kg. To provide an assessment of method precision, Laboratory 1 prepared duplicate samples for exposure to identical weathering conditions. Table 2.2 presents the weight of each sample added to each leaching column/humidity cell and exposed to either air only or CO_2-enhanced air.

Table 2.2.Sample Weights

		Column		Cell		
Lab	**Sample**	**Air**	**CO_2-Air**	**Air**	**CO_2-Air**	**Total # Samples**
1	Shale	12,722.6 g 12,749.7 g	12,825.8 g 12,650.1 g	1003.6 g 1003.2 g	1006.5 g 1001.3 g	8 (4 duplicate pairs)
	Sandstone	12,476.5 g 12,491.1 g	12,612.6 g 12,769.9 g	1002.1 g 1004.9 g	1005.9 g 1007.0 g	8 (4 duplicate pairs)
2	Shale	NA	13,284.0 g	NA	NA	1
	Sandstone	NA	13,227.5 g	NA	NA	1
	Limestone	NA	14,350.0 g	NA	NA	1

gas-mixing and handling procedures: Two alternative gas-mixing procedures were evaluated to attempt to achieve the target 10% CO_2 atmosphere in the weathering apparatus in a practical, cost-efficient manner. In the interest of economy, Laboratory 1 used one tank of CO_2 with a regulator, and mixed it with filtered house air (i.e. the compressed air piped throughout the lab) in the reagent water reservoir, prior to entry in the leaching columns and humidity cells. Precautions were taken to trap any drops of oil from the air compressor in the air lines prior to gas mixing, because any oil residue coating the rock samples would cause serious interferences in the weathering test. Laboratory 2 pursued a more rigorous mixing procedure, using separate tanks of CO_2 and compressed air, each equipped with regulators and mixing valves. A third alternative that was not evaluated would be to obtain an industrial grade gas mixture of 10% CO_2, 10% oxygen and 80% nitrogen in one tank, but it was determined that the cost of that prepared gas mixture was significantly higher than the other two alternatives.

water handling procedures/leaching cycles: The ADTI-WP1 & 2 simulated weathering procedures consist of alternating cycles of saturation and humidified air. A humidified gas mixture is introduced continuously through the gas inlet port of each leaching column and humidity cell during the periods of time between leaching episodes. These interleach periods of time are called "humidified air cycles" or "drying cycles". The leaching episodes are called "wetting cycles" or "saturation cycles". The gas mixture was also introduced into the leaching columns and humidity cells during periods of saturation (i.e. when the apparatus is filled with water).

In the ADTI-WP2 leaching column method once the leaching column has been filled with the rock sample and sealed, reagent water is introduced through the water inlet port at the bottom of the column (shown on Fig. 2.1a) until the column is full and all visible pore spaces are saturated. The first leaching episode is called the "initial flush", in which the reagent water was drained from the column after a 1-hour contact time. During this initial flush the column is filled and drained again until the conductivity of the flush water (leachate) stabilizes. This initial flush is intended to wash the rock samples of any oxidized materials that have accumulated during handling and storage.

The initial flush is followed by a one-week humidified air cycle. Following this first and each successive humidified air cycle, reagent water (distilled, deionized) was introduced through the water inlet port to just above the rock sample surface, and the saturation cycle begins. During this saturation cycle, the rock sample is in contact with the reagent water in the column for a 24-hour period. Following this 24-hour saturated condition, the column is drained and the leachate is tested for analytes of concern (e.g. acidity, alkalinity, Fe, Mn, Al, sulfate). Then the next one-week humidified air cycle commences, followed by the next 24-hour saturation cycle. This weekly pattern of alternating humidified air cycles and saturation cycles continues until method implementation is complete (e.g. 15 weeks).

The ADTI-WP1 humidity cell method includes alternating weekly wetting and drying cycles similar to the procedures described above for the leaching columns. The main difference between these two weathering procedures is that the humidity cells have a one-hour saturation period on the 7th, 14th, 21st day, etc. until method implementation is complete. The comparison of the effects of this one-hour contact time to the 24-hour contact time of the leaching columns is discussed below.

Results of Weathering Tests

The leaching column and humidity cell weathering procedures were conducted in 2002 for a period of 16 weeks in the two laboratories. Evaluations were made of: (a) the effect of the CO_2-enhanced gas mixture (i.e. 10% CO_2) as compared to normal atmospheric air conditions (i.e. 0.035% CO_2), (b) comparison of the leaching efficiency of the columns and cells, (c) comparison of calcite saturation indices and partial pressures of carbon dioxide within the columns and cells, (d) preliminary determination of the effects of the weathering procedure on particle size and surface area, (e) the abundance of iron-oxidizing bacteria related to rock type, and (f) the relative percent difference (RPD) of analyte concentrations produced between duplicate columns and cells, plus statistical comparison of gas mixtures.

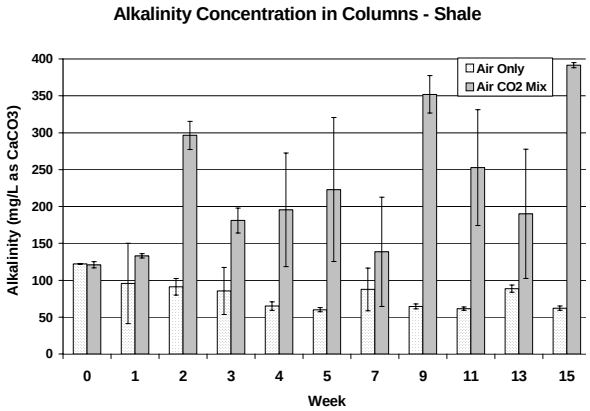

Figure 2.2a. Alkalinity concentrations from shale sample in leaching columns.

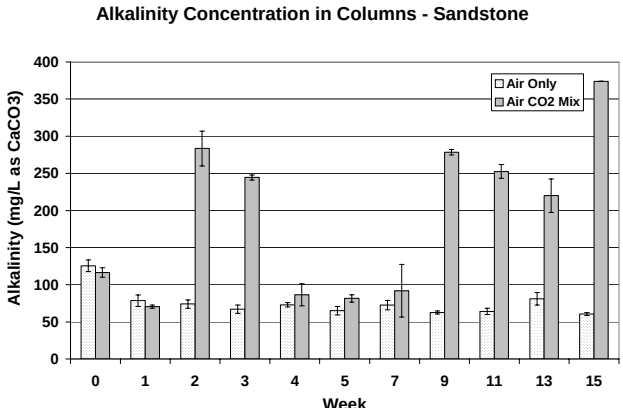

Figure 2.2b. Alkalinity concentrations from sandstone sample in leaching columns.

comparison of gas mixtures: Figures 2.2a and 2.2b were drawn from the alkalinity data set produced by Laboratory 1, but were developed specifically to facilitate the comparison of the air-only and CO_2-enhanced gas mixtures for the shale and sandstone samples using each of the draft methods (humidity cell and leaching column). In Figure 2.2a for the shale leaching columns, the highest alkalinity concentration for the air-only columns is 122 mg/L, while the highest alkalinity for the CO_2-enhanced columns is 394 mg/L; hence, the alkalinities were approximately three times greater in the columns with the additional CO_2 (in weeks 9 and 15 the alkalinities were 6 or 7 times greater). In the sandstone leaching column results shown in Figure 2.2b, the highest alkalinity concentration for the CO_2-enhanced gas mixture is 374 mg/L, while the highest alkalinity for the air-only columns is 120 mg/L; therefore the alkalinities are approximately three times greater with CO_2 addition, similar to that found with the shale columns. The histograms in Figures 2.2a and 2.2b depict the average or median values of alkalinity, and the bar diagrams in the top center of each histogram show the range in alkalinity concentrations of the duplicate samples.

Figures 2.2a and 2.2b show a lack of consistency in alkalinity concentrations with the CO_2-enhanced gas mixture from week to week, especially comparing the high values in weeks 2,

3 and 15 of the shale and sandstone humidity cells to the other weeks. That observation prompts further study of whether it is due to inconsistencies in the control of carbon dioxide partial pressures in the apparatus through time, or due to some geochemical factors in the weathering process.

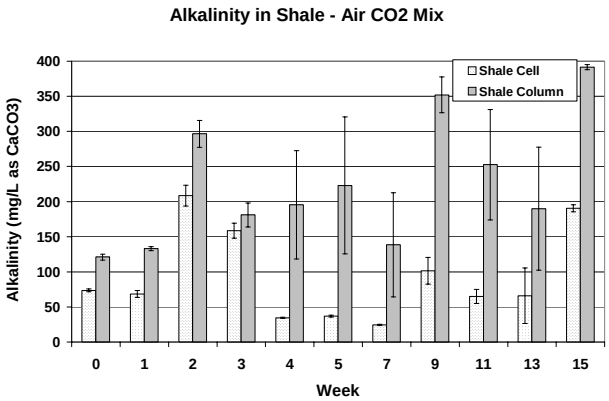

Figure 2.3a. Comparison of Humidity Cell and Leaching Column Performance on Alkalinity Production in Shale Sample Using CO_2 Enhanced Mixture

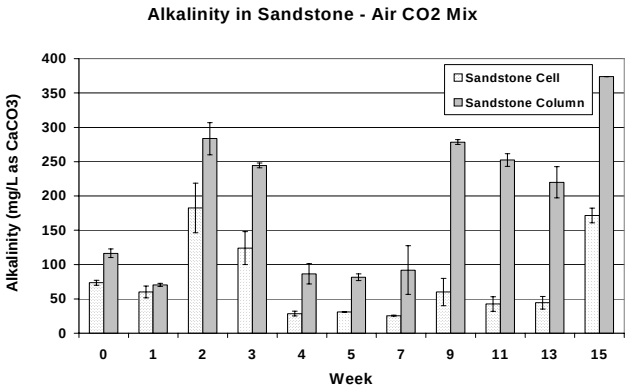

Figure 2.3b Comparison of Humidity Cell and Leaching Column Performance and Alkalinity Production in Sandstone Samples Using CO_2 Enhanced Gas.

<u>comparison of leaching efficiency of columns and humidity cells:</u> Figure 2.3 shows the comparison of humidity cell and leaching column performance on duplicate samples of shale and sandstone with air only and CO_2-enhanced gas mixtures. In comparing the performance of the humidity cells and leaching columns with the CO_2-enhanced gas mixture on the same shale sample, it is obvious that the alkalinities are much greater (i.e. often 2 to 6 times greater) in Figure 2.3a for the columns. The humidity cells in Figure 2.3a generally have alkalinities that are much lower than the leaching columns, and there is usually less variability between the duplicates and through time.

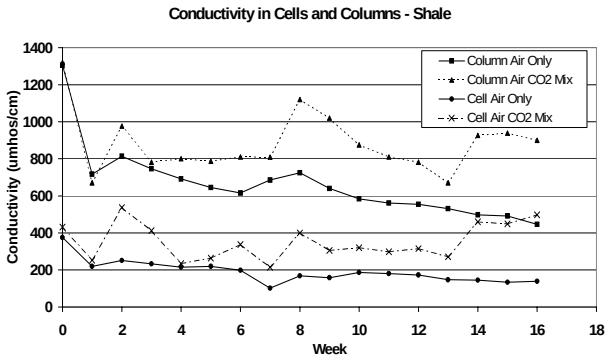

Figure 2.4a. Conductivity in Leachate from Shale in Humidity Cells and Leaching Columns

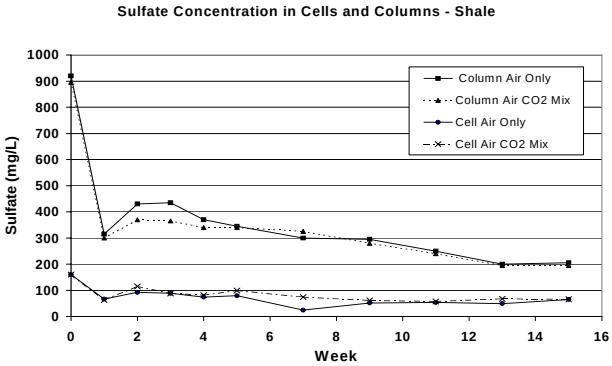

Figure 2.4b. Sulfate in Leachate from Shale in Humidity Cells and Leaching Columns

The leaching columns in Figure 2.3a exhibit alkalinity concentrations similar to alkaline mine drainage discharges from the Brush Creek shale interval in weeks 2, 9 and 15 (i.e. 300 to 400 mg/L), with relatively little difference between duplicates; but the variability from week to week and between duplicates is large in some of the 15 weeks shown. Figure 2.3b shows performance patterns for humidity cells and leaching columns on the Wadesville sandstone sample using the CO_2-enhanced gas mixture that are very similar to those described above for the shale in Figure 2.3a, except the variation in duplicate samples for the sandstone leaching columns is less than those for the shale.

Figures 2.4a and 2.4b depict variations in conductivity and sulfate concentrations throughout the 15-week weathering tests of the shale sample, using both draft test methods and both gas mixtures. These figures confirm that the humidity cells produce consistently lower conductivity values than the leaching columns, indicating lower total dissolved ionic species (i.e. total dissolved solids) and less aggressive weathering on these shale samples. Figure 2.4a shows the CO_2-enhanced gas mixture cells and columns have somewhat higher conductivity than their air-only companions, indicating that the influence of the additional CO_2 increases the dissolution of the carbonate minerals and adds calcium and magnesium cations and bicarbonate anions to the leachate.

Figure 2.4b shows that the CO_2-enhanced gas mixture has a negligible effect upon the sulfate concentrations, which follow a gradually declining trend after the initial flush. The leaching column sulfates are consistently higher than the humidity cell sulfates, and the response to the initial flush is much more dramatic in the columns; both observations being indications of more aggressive weathering conditions in the leaching columns. Finally, the apparently curious increase in conductivity in the last 3 weeks of the tests in both the columns and cells having the CO_2-enhanced gas mixtures has a rational explanation, because the authors decided to change the gas and water handling procedures at Laboratory 1 to determine the effect of using CO_2 saturated influent water rather than DI water (i.e. distilled, deionized) at that point, for possible future modifications in the draft procedures.

partial pressures of carbon dioxide (PCO_2) and calcite saturation indices: A goal of this project was to leach calcareous rock samples under conditions that are likely to be encountered in mine spoil, where O_2 concentrations tend to be diminished and CO_2 concentrations tend to be elevated relative to those in the ambient atmosphere. The concentration of CO_2 in the atmosphere is 0.03%, whereas in mine spoil it can exceed 10% (Cravotta et al., 1994; Lusardi and Erickson, 1985). Under subsurface conditions, where CO_2 is elevated, the weathering rate of calcareous materials can be accelerated and high concentrations of alkalinity can result (e.g. Cravotta et al., 1994). The target for CO_2-enriched leaching was equilibration with CO_2-enriched air containing 10% CO_2 (and 19% O_2 and 71% N_2).

A comparison of the water chemistry between the two laboratories showed significant differences in the leachate pH, alkalinity and corresponding computed values for PCO_2 and calcite saturation index. High pH and low PCO_2 values for many samples leached under high PCO_2 conditions indicated that leachate samples had evolved upon exposure to air outside the columns: CO_2 was degassed and, consequently, pH increased and calcite supersaturation was indicated. However, inside the columns, one would expect that calcite would have been

saturated or undersaturated in association with higher PCO_2 and lower pH. Therefore, we recalculated the pH for equilibrium with calcite and the corresponding PCO_2 assuming that Ca and alkalinity were conservative.

The partial pressure of carbon dioxide in the leaching columns and humidity cells was calculated through geochemical modeling using a spreadsheet developed by Dr. Charles A. Cravotta of USGS. The equilibrium computations were performed utilizing thermodynamic data from Ball and Nordstrom (1991) to estimate the PCO_2 and pH of solutions within the columns and cells, prior to equilibration with the atmosphere. The following chemical parameters were determined every other week: pH, alkalinity, acidity, iron, manganese, calcium, magnesium, and specific conductance. Additionally temperature was known. The spreadsheet estimates ionic strength from conductance using relationships explained in Hem (1985) and Langmuir (1997) and was well suited for limited chemical analyses resulting from the study. The activity coefficients were determined using the Debye-Huckel equation (see Hem, 1985). Temperature correction was by the van't Hoff equation (Hem, 1985) and the equilibrium pH was computed simply by subtracting the calcite saturation index from the reported pH of the leachate. Then, the PCO_2 at equilibrium with calcite was recalculated considering this equilibrium pH and the reported alkalinity.

Table 2.3. Partial pressure CO_2 as determined from geochemical modeling. "Calculated" values were determined for water that was saturated or oversaturated by assuming the saturation index for calcite was 0.0 (i.e., at saturation). Q1 and Q3 are the 25th and 75th percentiles respectively.

Description	N	Median %PCO_2 Unad-justed	Q1 %PCO_2 Unad-justed	Q3 %PCO_2 Unad-justed	Median %PCO_2 Calcul-ated	Q1 %PCO_2 Calcul-ated	Q3 %PCO_2 Calcul-ated	Median Saturation Index Calcite
Shale Air Column Lab 1	22	0.12	0.10	0.21	0.25	0.18	0.55	+0.290
Sandstone Air Column Lab 1	22	0.08	0.05	0.11				-0.236
Shale 10% CO_2 Column Lab 1	22	0.28	0.17	0.41	2.50	1.08	6.54	+0.963
Sandstone 10% CO_2 Column Lab 1	22	0.19	0.07	0.40	1.48	0.07	0.24	+0.494
Shale Air Humidity Cell Lab 1	22	1.48	0.07	0.12				-0.972
Sandstone Air Humidity Cell Lab 1	22	0.12	0.03	0.08				-1.044
Shale 10% CO_2 Humidity Cell Lab 1	22	0.90	0.10	1.06				-0.431
Sandstone 10% CO_2 Hum. Cell Lab 1	22	0.75	0.06	0.82				-0.822
Limestone 10% CO_2 Lab 2	12	10.45	9.09	11.36	14.97	12.25	16.79	+0.147
Sandstone 10% CO_2 Lab 2	13	10.05	9.07	11.31	9.71	6.61	13.18	-0.030
Shale 10% CO_2 Lab 2	14	12.55	9.27	16.19	30.19	21.27	32.79	+0.383

Table 2.3 shows the median and quartiles of PCO_2values for the columns and humidity cells, and recalculated PCO_2 assuming equilibrium with respect to calcite. The calculated PCO_2 values in Table 2.3 showed that the PCO_2 in humidity cells with and without the enhanced CO_2 gas mixture were nowhere near the 10% target CO_2 value; also leaching columns with carefully controlled CO_2 introduction usually met the target 10% value, while columns with less rigorous CO_2 introduction fell short of the target value.

The distribution of calculated saturation indices for leachate from the leaching columns and humidity cells is shown in a series of boxplots in Figure 2.5. Boxplots 5 through 8 are humidity cells, all others are columns. Stippled boxplots represent columns and cells that had air enriched with 10% CO_2 circulated through them. The boxplots that are not stippled represent apparatuses with atmospheric air only. Where duplicate columns were run, the data were combined (items 1 through 8 in Fig. 2.5). In general, the columns were supersaturated, or nearly saturated with respect to calcite. The humidity cells were almost always undersaturated with respect to calcite.

The gas handling procedures at Laboratory 2 differed from those of Laboratory 1, in that each of the three leaching columns had separate flow meter controls connected to the regulators of the tanks of compressed gas. Further evaluations of the kinetic test procedures demonstrated the importance of incorporating most of these Laboratory 2 gas handling procedures into the draft method, in order to maintain the target mixture within the leaching column (or humidity cell) apparatus throughout the weathering test. Laboratory 2 conducted leaching column tests on shale, sandstone and limestone samples for 16 weeks, using the ADTI-WP2 draft method. The rock samples were representative splits of the same Brush Creek shale and Wadesville sandstone samples used by Laboratory 1, plus a Valentine limestone sample. Figure 2.6 shows the alkalinity concentrations for the sandstone, shale and limestone samples for the 16 week weathering period.

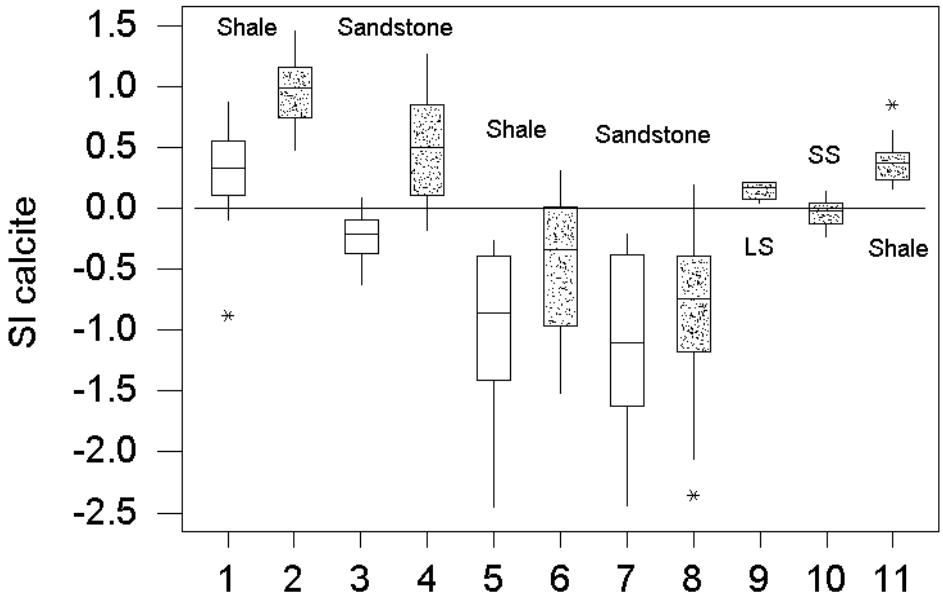

Figure 2.5. Boxplots showing the distribution of saturation indices for calcite for leaching apparatuses.

Three main observations are made from examining Figure 2.6 and comparing it to Figures 2.2a and 2.2b for the same shale and sandstone samples: (1) the alkalinity concentrations for the shale and sandstone samples are more consistent (i.e. exhibit less week to week variability) throughout the weathering test period than the weekly variations shown in Figures 2.2a and 2.2b, (2) the shale sample produced more alkalinity than the sandstone for each week of the test (and more than the limestone for each week except week 4), and (3) the alkalinity concentrations for the shale and sandstone samples in Figure 2.6 are significantly higher than shown for the same lithologic units in Figures 2.2a and 2.2b. The range of alkalinity concentrations for the sandstone sample in Figure 2.6 are 386 to 535 mg/L with a median alkalinity of 435.5 mg/L. The highest alkalinity concentration for the same sandstone sample in Figure 2.2b is 374 mg/L, which is much less than the median in Figure 2.6 and slightly less than the lowest alkalinity in Figure 2.6. The corresponding range of alkalinity concentrations for the shale sample in Figure 2.6 are 458 to 770 mg/L, with a median of 551.5 mg/L. The highest alkalinity concentration for the same shale sample in Figure 2.2a is 397 mg/L, which is considerably less than the median and the lowest alkalinity in Figure 2.6.

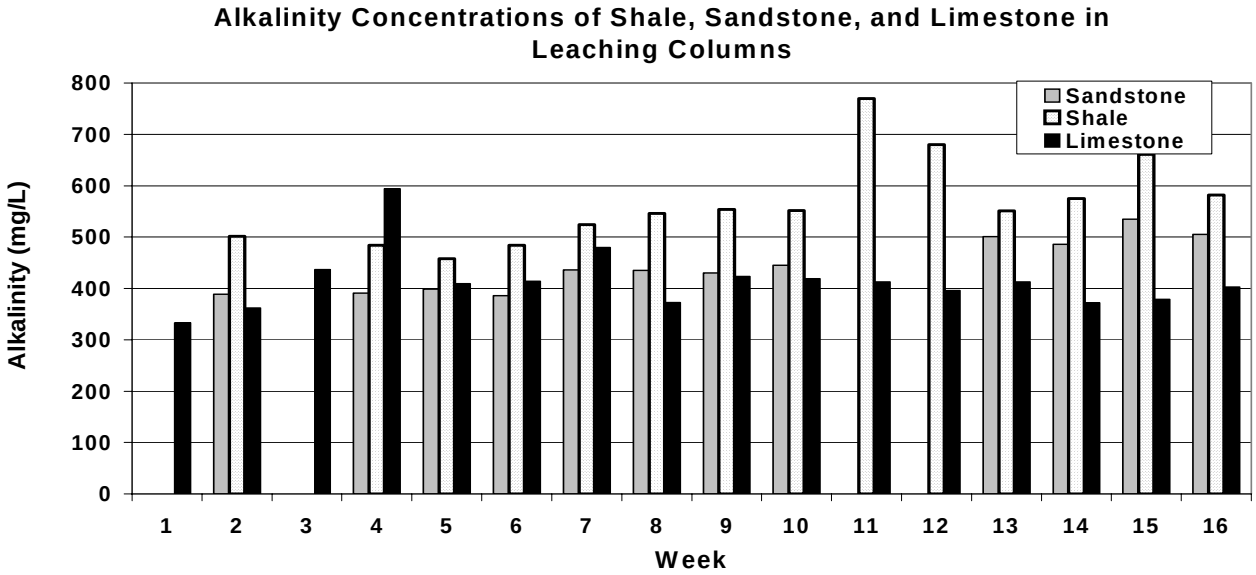

Figure 2.6. Alkalinity Concentrations of Shale, Sandstone, and Limestone Samples in Leaching Columns

preliminary study of particle size and surface area effects: The MRI researchers at Penn State University evaluated the differences in the sieve analyses of the shale and sandstone samples performed prior to the start of the weathering test and after the completion of the 16 week test in the leaching columns. The differences in the post-leaching particle size distributions were not as great as expected, but the shale sample did have a greater amount of fines in the 100 and 200 mesh size classes prior to weathering and had a greater percentage of loss in these size classes post-leaching, than the sandstone, as was expected.

The researchers at MRI also conducted some preliminary surface area measurements on the sandstone sample using BET equipment. The measurement of surface areas by the Brunauer,

Emmett and Teller (BET) Method was originally described in Brunauer et al. (1938) and more recently in Yates (1992). The MRI researchers found that sandstone sample from the #8 sieve had a surface area of 0.76 square meters per gram, while sandstone sample from the #20 sieve had a surface area of 1.33 square meters per gram. Additional work on surface area measurements was needed in order to obtain measurements on a greater range of particle sizes and different lithologic units. These measurements would lead to further work on surface area to volume ratios as discussed in Hornberger and Brady (1998, p. 7-15).

bacteria populations: The bacteria *Thiobacillus ferroxidans* catalyzes the formation of acid mine drainage (AMD) (Singer and Stumm, 1970 and Kleinmann et al., 1981). The most probable number (MPN) for iron-oxidizing bacteria (including *Thiobacillus*) was determined by the methods of Alexander (1982) and Greenberg et al., (1992). The abundance of iron-oxidizing bacteria in leachate drawn from humidity cells and leaching columns was determined in the fourth week and the last week of the 15 week weathering tests performed in Laboratory 1. The most probable number counts per 100 mL of sample ranged from <30 to 11,000 for shale and sandstone leaching columns and humidity cells. Both of these rock types produced alkaline leachate. The MPN values for the highly acidic coal refuse humidity cells ranged from 4.6 billion to >24 billion. These results demonstrate that these iron-oxidizing bacteria populations are suppressed under alkaline conditions, but can be superabundant under acidic conditions. The results also show that the humidity cells and leaching columns do not have to be inoculated with the bacteria to catalyze acid producing reactions, particularly in high sulfur samples.

Method Performance Data

statistical comparison of duplicate samples in Laboratory 1: Results from Laboratory 1 were used to evaluate method implementation, assess method precision (through comparison of duplicate results), and evaluate the effects of air vs. CO_2-enhanced air weathering conditions. Because the study was designed to assess the effect of CO_2-enhanced conditions on alkalinity production, this section presents an evaluation of the effects of the test methods on production of alkalinity, sulfate, calcium, and specific conductance. The precision of the draft leaching column and humidity cell test procedures was assessed using results of duplicate samples exposed to identical weathering procedures. Relative percent differences (RPD) were calculated for duplicate samples prior to implementation of method procedures (initial flush at week 0) and as pooled RPDs for all sample weeks beginning with week 1 (15-week RPD). Resulting RPDs are presented in Table 2.4. RPDs between duplicate samples were determined as RPD = [(2A - B2)/(A + B)] x 200. Fifteen week Pooled RPDs were determined as the square root of the average squared weekly (Weeks 1 - 15) RPDs for each parameter.

Pooled RPDs ranged between 0 and 58%. RPD results could be largely due to precision inherent to the analytical methods used to measure the parameters of interest. However, pooled RPDs were greater than the initial flush RPDs, indicating that the implementation of weathering procedures increased variability between duplicate samples. EPA methods often include RPD performance criteria of up to 30% for duplicate analyses. (e.g. EPA draft Method 200.7, May 2001, includes RPD criteria ranging from 0.5 to 20%. EPA draft Method 1630 includes an RPD criterion of 35%).

Table 2.4: Relative Percent Differences (RPD) of Duplicate Samples

Sample Type	Method	Gas Mix	Conductivity (RPD) umhos/cm	Calcium (RPD) mg/L	SO_4 (RPD) mg/L	Alkalinity (RPD) mg/L $CaCO_3$
Shale (Initial Flush)[1]	Column	Air	5.36	2.96	4.35	0
		Air-CO_2	6.06	6.83	10.06	4.96
	Cell	Air	1.60	1.94	0	4.44
		Air-CO_2	0.70	3.39	0	4.08
Shale (15-week pooled) [2]	Column	Air	7.77	10.77	17.47	33.25
		Air-CO_2	13.85	21.73	18.09	41.86
	Cell	Air	12.19	8.52	21.21	36.47
		Air-CO_2	17.62	17.36	16.45	28.20
Sandstone (Initial Flush)[1]	Column	Air	5.36	2.96	4.35	0
		Air-CO_2	6.06	6.83	10.06	4.96
	Cell	Air	1.60	1.94	0	4.44
		Air-CO_2	0.70	3.39	0	4.08
Sandstone (15-week pooled) [2]	Column	Air	12.55	10.66	13.78	10.54
		Air-CO_2	18.53	21.35	28.08	19.25
	Cell	Air	28.34	26.04	58.43	5.61
		Air-CO_2	21.11	25.08	25.93	24.60

[1] RPD between duplicate samples is determined as RPD = [(2A - B2)/(A + B)] x 200.

[2] 15-week Pooled RPDs are determined as the square root of the average squared weekly (Weeks 1 - 15) RPDs for each parameter

Out of thirty-two pooled RPD results, only four were above 28% (see shaded cells in Table 2.4). Pooled RPDs for alkalinity in duplicate shale samples ranged from 28.2 to 41.9%. Because alkalinity production is directly related to the presence of O_2 and CO_2, it is possible that the gas flows through the systems containing these duplicate shale samples were not identical.

statistical comparison of gas mixtures: Statistical comparisons between samples exposed to air-only and CO_2-enhanced gas mixtures were determined using paired t-tests. For each parameter, sample type, method type, and week, the difference was calculated between the mean of the two log transformed results for samples exposed to CO_2-enhanced air and the mean of the two log transformed results for samples exposed to air-only conditions. The mean of the weekly differences was then calculated for each parameter, sample and method type, and the paired t-tests were run to determine whether the mean of the differences was significantly greater or less than 0. A mean significantly greater than 0 suggests that the CO_2-enhanced gas type yields higher results than the air only gas type, while a mean significantly less than 0 suggests that the CO_2-enhanced gas type yielded significantly lower results than the air-only gas type.

With the exception of sulfate, the resulting mass and concentrations of all parameters were significantly greater in the samples exposed to CO_2-enhanced air during drying cycles. Because sulfate is the result of pyrite oxidation and is therefore influenced by the concentration of oxygen, it is not likely to be influenced by the addition of CO_2.

The results of these preliminary tests indicate that the introduction of 10% CO_2 does significantly increase alkalinity production. Most importantly, the alkalinity concentrations, particularly in samples taken from the leaching columns, are similar to the alkalinity concentrations found in mine drainage samples taken from these particular rock units in the natural environment.