Chapter 3: Second Phase of Weathering Tests (2003)

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Following evaluation of the 2002 weathering test results described in Chapter 2, the draft methods were revised for use in the 2003 weathering tests as follows: (a) the humidity cell apparatus was constructed identical to the cylindrical leaching column apparatus, (b) the diameter of most of the leaching columns and humidity cells was reduced to 2 inches (from 6 inches in 2002), (c) the rock samples were crushed to a nominal 3/8" diameter, and procedures for reconstructing rock samples according to specified particle size partitioning were included in each method, and (d) two options were provided for exposing rock samples to the CO_2-enhanced gas mixture during saturation periods. Those two options were the introduction of a continuous flow of CO_2-enhanced air into the columns during periods of saturation as well as drying periods, and exposure to influent water saturated with CO_2-enhanced air during periods of saturation.

Rock Samples Tested

The three rock samples used in the 2003 weathering tests were: (1) the Brush Creek shale sample used in the 2002 weathering tests (and described in more detail in Chapter 2), (2) the Vanport Limestone, and (3) a Lower Kittanning coal refuse sample.

Two limestone samples were selected to serve as high-alkalinity producing end members in the 2202 and 2003 weathering tests. The Valentine limestone is the purest limestone in Pennsylvania (O'Neill, 1964) and Brady et al. (1998, p. 8-46), typically having calcium carbonate content greater than 97%. The Valentine limestone sample used in the first phase of this project during 2002 was collected from a quarry and underground mine operated in Centre County, PA. The Valentine is a marine limestone of Ordovician Age. For the 2003 weathering tests, the Vanport limestone was selected because it is a Pennsylvanian Age limestone, stratigraphically positioned between the Clarion and Lower Kittanning coals. The Vanport limestone samples were collected in a quarry and coal mining operation in Butler County, PA. The range of NP values of this sample is 900 to 916 ppt as shown in Table 3.1, while the total sulfur content is negligible.

Two coal refuse samples were selected to serve as high-acidity producing end members in the weathering tests (i.e. Ernest and Leechburg abandoned coal refuse piles). The Leechburg coal refuse samples used in 2002 were collected from the large refuse deposit associated with the abandoned underground Leechburg coal mine, and the samples used in 2003 were from an active adjacent underground mine on the Lower Kittanning coal located near the town of Apollo in Armstrong County, PA. The abandoned mine refuse site at Leechburg 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. The 2002 weathering tests were conducted on samples collected from the abandoned coal refuse piles having sulfur contents between 2.42 and 4.38%. The 2003 weathering tests were conducted on samples of a fresh refuse pile at the end of a conveyor belt from the active underground mine, which have total sulfur contents greater than 6.5% as shown in Table 3.1.

Samples of a relatively inert sandstone, stratigraphically positioned between the Middle Kittanning and Upper Kittanning Coals, were collected from a quarry in Clearfield County, PA.

This lithologic unit was selected to serve as a "blank" in these weathering tests, but was not included in the 2003 weathering experiments due to financial constraints on the number of different rock types to be tested. The range in total sulfur contents of this sample is 0.03% to 0.08% as shown in Table 3.1, while the range of NP values is 14.3 to 20.9 ppt. This Middle Kittanning sandstone sample was stored in sealed containers and was used as the "blank" sample in the 2006 interlaboratory weathering tests described in Chapter 4.

Table 3.1: Sample Characterization

Description	Total Sulfur %	Fizz Rating	Neutralization Potential
SH Bucket #26 Shale PSU Brush Creek [1]	0.90	3	112.05
SH Bucket #28 Shale PSU Brush Creek [1]	0.90	3	121.42
SH Bucket #32 Shale PSU Brush Creek [1]	0.91	3	120.78
LRBT Bucket #4 Coal Refuse [2]	6.64	0	2.64
LRBT Bucket #9 Coal Refuse [2]	6.94	0	-0.39
LRBT Bucket #14 Coal Refuse [2]	7.67	0	-1.71
VLS Bucket #1 Limestone [3]	0.00	3	902.94
VLS Bucket #9 Limestone [3]	0.01	3	915.77
VLS Bucket #11 Limestone [3]	0.00	3	899.73
HSS Bucket #2 Sandstone [4]	0.08	0	20.87
HSS Bucket #8 Sandstone [4]	0.04	1	17.70
HSS Bucket #12 Sandstone [4]	0.03	1	14.29

[1] Brush Creek Shale from Route 66 road cut near Greensburg, PA

[2] Lower Kittanning Coal Refuse from Rosebud deep mine near Leechburg, PA

[3] Vanport Limestone from Allegheny Minerals mine in Butler County, PA

[4] (Not used in method evaluation) Middle Kittanning Sandstone - Hawbaker quarry in Clearfield County, PA

Study Design and Laboratory Tasks

To further evaluate performance of the draft methods, the 2003 study involved three laboratories and the three sample types described above (shale, limestone, and coal refuse). Laboratories 1 and 2 (Geochemical Testing and Mahaffey Laboratories) were tasked with evaluating (1) the two exposure scenarios (constant exposure to CO_2-enhanced air vs. exposure to water saturated with CO_2-enhanced air) and (2) the leaching column (24-hour saturation periods) vs. humidity cell (1-hour saturation periods) methods. Laboratory 3 (Materials Research Institute at Penn State University) was tasked with implementing the leaching column method using three sizes of cylindrical testing structures (i.e., 2-inch, 4-inch, and 6-inch diameter). Laboratory 3 (MRI) also performed surface area measurements, using BET methods, on each of 8 particle size classes, before and after the weathering tests, on selected lithologic units.

For a period of 15 weeks (12 weeks for Laboratory 3), each laboratory collected weekly water samples from all columns and cells, and analyzed the samples for pH, specific conductance,

alkalinity, acidity, and sulfate. Samples also 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 D of this report.

The original type of humidity cell apparatus, used in the 2002 weathering tests, was constructed from rectangular plastic food storage containers with airtight lids. This approach was consistent with the project goals of requiring low cost materials and minimal apparatus construction. However, the humidity cells yielded consistently lower concentrations of key analytes reflecting less aggressive weathering than the leaching columns. A reason for this difference between humidity cells and leaching columns, particularly for carbonate minerals, may be the large amount of air space above the rock sample in the rectangular cells. As some humidity cell tests reported in the literature use a cylindrical apparatus resembling a short leaching column (e.g. White et al., 1994), the shape and dimensions of the humidity cells used in the 2003 weathering tests were made equivalent to the leaching columns.

Standardized Particle Size Distribution and Surface Area Measurements

The reconstruction of the particle size distribution following the crushing of each rock sample was included in the methods because variations in particle size distribution of the same lithologic unit can occur due to differences in crushing equipment, and the particle size distribution may vary significantly by rock type as shown in Table 3.2.

Table 3.2. Particle size distribution (by percent total weight) of as prepared rock samples.

	Limestone				Shale					Coal Refuse				
Lab	**1**	**2**	Mean	SD	**1**	**2**	**3**	Mean	SD	**1**	**2**	**3**	Mean	SD
***Sieve Size**														
+3/8	0.1	0.0	0	0.1	0.0	0.0	0.0	0	0.0	0.0	0.0	0.0	0	0.0
3/8-#4	40.2	41.9	41	1.2	22.5	23.7	28.8	25	3.4	46.1	49.3	54.0	50	4.0
#4-#10	25.3	26.5	26	0.8	32.6	32.1	33.4	33	0.6	27.8	23.1	23.5	25	2.6
#10-#16	12.1	9.7	11	1.7	16.4	12.8	8.1	12	4.2	10.6	9.5	7.1	9	1.8
#16-#35	8.2	10.2	9	1.4	10.8	15.7	12.2	13	2.5	6.4	9.3	8.0	8	1.4
-30+#60							10.5					5.3		
#35-#60	5.1	3.8	5	0.9	6.8	4.9			1.3	3.7	3.2			0.3
-#60	9.1	8.0	8	0.8	10.8	10.9	7		2.2	5.3	5.7	2.2		1.9

*US sieve # or equivalent mesh size; SD represents standard deviation

Since the particle size distribution of the crushed rock sample is largely an artifact of the crushing process, rather than a natural systems process (like the particle size distribution of a soil or an unconsolidated sedimentary deposit), it was determined that the standardized particle size distribution, shown in Table 3.3 would promote operational consistency of the weathering test procedures and facilitate better control in determining reaction kinetics. Regarding operational consistency of the method, large amounts of fine particles within specific zones of the leaching columns were found to impede uniform fluid flow and/or gas flow in this study, and similar problems with fines are described in Bradham and Caruccio (1990, 1995) and Hornberger and

Brady (1998). Regarding the determination of reaction kinetics, the importance of surface area to volume ratios is described in Brady et al., 2004, and other references discussed in Chapter 1 and Chapter 6, and significant differences in crushed particle size distributions and effective surface areas were found among the lithologic units tested in this study. Standardizing the particle size distribution in each leaching column and humidity cell promotes control of that variable at the start of the weathering test, and facilitates the evaluation of surface area and related kinetic variables after weathering.

Table 3.3. Particle size distribution of reconstructed samples.

Sieve Size	Percent of Total Weight
+3/8 (9.52 mm)	-
3/8 - #4 (4.76 mm)	40
#4M - #10 (2.00 mm)	25
#10 - #16 (1.19 mm)	10
#16 - #35 (0.50 mm)	10
#35 - #60 (0.250 mm)	5
-#60 (0.250 mm)	10

<u>surface area effects on selected rock samples from 2002 and 2003 weathering tests:</u>
Laboratory 3 performed BET surface area measurements on three distinctly different lithologic units to evaluate the effects of weathering by particle size classes and by rock type characteristics. Table 3.4 shows the particle size distributions for the Brush Creek shale and Wadesville sandstone samples used in the 2002 weathering tests and the LRBT coal refuse sample used in the 2003 weathering tests at Laboratory 3.

For this study, the surface area of each fraction of sieved starting material was determined by BET (Brunauer et al., 1938; Yates, 1992) instrumentation using N_2 gas bulk adsorption. This method is a routine analytical approach to measure the accessible surface of the rock to gas molecules. Additional discussion of surface area measurements and their relationships to porosity and reaction kinetics are given by Brantley and Mellott (2002), Lasaga (1984, 1998) and Brady et al., (2004).

Surface areas were measured on the starting material sieve fractions, and at the completion of the testing, the resultant rock was again sieved and remeasured. The bulk surface areas for each column were determined for the post-leaching rock by taking the individual masses of the sieve fractions specified in the protocol above, multiplying each mass by the surface area (SA), and combining their fractional percent of the total as a weighted linear average.

$$A \times SA_{sieve1} + B \times SA_{sieve2} + C \times SA_{sieve3} = SA_{bulk}$$

Where: $A + B + C = 1$
A = fraction of total sieve 1 size
B = fraction of total sieve 2 size
C = fraction of total sieve 3 size

Table 3.4. Surface area measurements, sieve analysis, and calculations of effective surface areas before and after weathering tests.

	Sieve Size	Surface Area (BET) m^2/g		% retained on Sieve		Effective surface area	
		before	after	before	after	before	after
Shale	3/8	15.90	16.40	3.84	4.36	0.611	0.715
	#4	11.10	10.00	21.79	26.83	2.419	2.683
	#8	13.70	11.00	24.13	26.21	3.306	2.883
	#20	14.90	13.80	24.08	22.41	3.588	3.093
	#40	15.70	15.40	9.21	8.23	1.446	1.267
	#100	15.30	15.20	9.76	7.54	1.493	1.146
	#200	15.50	15.40	6.04	2.56	0.936	0.394
	pan	16.90	16.20	1.15	1.87	0.194	0.303
					Total	**13.993 m^2/g**	**12.484 m^2/g**
Sandstone	3/8	0.66	0.25	25.50	26.30	0.168	0.066
	#4	0.81	1.00	36.96	35.80	0.299	0.358
	#8	1.42	1.30	14.08	16.60	0.200	0.216
	#20	0.91	0.80	10.77	8.60	0.098	0.069
	#40	1.02	1.41	4.01	4.10	0.041	0.058
	#100	1.75	2.99	4.73	4.70	0.083	0.141
	#200	2.68	4.17	3.24	2.20	0.087	0.092
	pan	2.91	5.00	0.97	1.70	0.028	0.085
					Total	**1.004 m^2/g**	**1.083 m^2/g**
Coal Refuse	3/8	0.17	0.40	40.00	37.40	0.068	0.150
	#4	0.92	0.60	25.00	26.90	0.230	0.161
	#8	0.21	0.90	10.00	9.90	0.021	0.089
	#20	0.39	0.50	10.00	8.00	0.039	0.040
	#40	3.39	0.70	5.00	6.40	0.170	0.045
	#100	9.17	1.40	10.00	11.50	0.917	0.161
	#200						
	pan						
					Total	**1.445 m^2/g**	**0.646 m^2/g**

The before-weathering distributions for the shale and sandstone samples are exactly what resulted from crushing the samples; the particle size distribution for the coal refuse sample was reconstructed/adjusted to meet the specification of the revised method as shown in Table 3.3. The BET measurements of surface area for the shale are an order of magnitude greater than the sandstone and coal refuse surface areas for most size classes (except the 0.149 mm coal refuse pre-weathering). This is probably due to much greater intrinsic porosity in the shale laminae. The sandstone sample was from a very hard and well-cemented lithologic unit, thus there was little difference in the particle size distributions or surface area measurements after weathering. The coal refuse sample showed the greatest change in effective surface area of all samples tested at Laboratory 3 in the 2002 and 2003 weathering tests (Table 3.5). This change is largely due to the reduction in surface area of the two finest size classes (Table 3.4). Two factors that probably contributed to this reduction are (a) loss of fines during weekly sample collection and (b) weathering of fine-grained pyrite in these size classes.

Table 3.5. Summary of changes in surface areas after weathering.

Rock Type	Column Size	m^2/g before	m^2/g after	% change
Shale	6”	14.0	12.5	10.71
Shale	6”rpt	14.3	15.1	-5.59
Shale	4”	14.3	14.1	1.40
Shale	2”	14.3	15.5	-8.39
Limestone	6”	3.5	3.0	14.29
Sandstone	6”	1.0	1.1	-10.00
Coal Refuse	6”	1.4	0.6	57.14

calculation of SA/V ratio: The design of the column experiments allows a direct calculation of the surface area to volume ratio. The surface area for the reconstituted rock mass in the column is calculated as shown above. This quantity is then scaled to the total rock mass in the column. The volume is simply the volume of water drained from the column after each weekly 24-hour fill-and-drain cycle.

$$\frac{SA}{V} = \frac{1000\, m\, SA_{Bulk}}{V}$$

Where:
SA/V = surface area to volume ratio (meters $^{-1}$)
m = mass of solids in column (grams)
SA_{Bulk} = BET surface area of solids (meter-squared/gram)
V = volume of leachate from each drain cycle (liters)

The significance of the surface area to volume ratio in leaching processes is described in Machiels and Pescatore (1983), Pederson et al., (1983), White (1986) and Scheetz et al., (1981).

Method Preparation, Implementation and Results

The laboratories assembled leaching columns and humidity cells as described in Figure 3.1 from the draft leaching column method (see Appendix A of this report). Samples were reconstructed after sieving according to the particle size distributions presented in Table 3.3 above. To provide an assessment of method precision, Laboratories 1 and 2 prepared duplicate Shale and Coal Refuse samples for exposure to identical weathering conditions. Table 3.6 presents the weight of each sample added to each leaching column/humidity cell exposed to either constant flow of CO_2-enhanced air or CO_2-Air saturated water during wet weathering conditions.

The leaching column and humidity cell weathering procedures were conducted for a period of 15 weeks in the three laboratories. Evaluations were made of: (a) the two options for introducing the CO_2-enhanced gas mixture into the leaching columns, (b) laboratory performance on duplicate samples by calculation of relative percent differences (RPD’s) and relative standard

deviations (RSD's), (c) the leaching effectiveness of the column and humidity cell methods (d) the effect of removing the fines (i.e. 2 smallest particle size classes < #35 mesh), and (e) influence of different leaching column diameters (i.e. 2", 4" and 6"). The concentration data for leaching column and humidity cell effluent for the 3 rock types are presented in Appendix D.

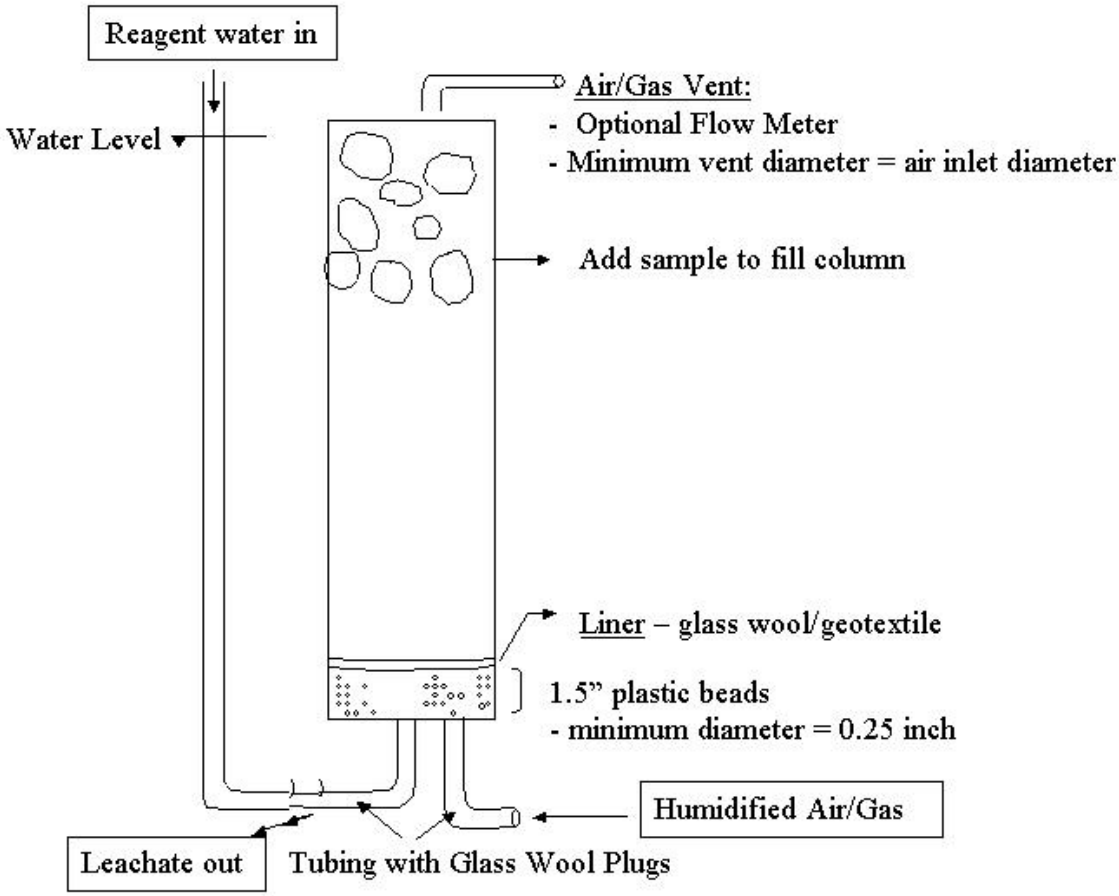

Figure 3.1. Revised Leaching Column Design.

comparison of the two gas mixture options: Statistical comparisons between samples exposed to a constant flow of CO_2-enhanced air and those exposed to reagent water saturated with Co_2-enhanced gas mixture during wet weathering were determined using paired t-tests. For each parameter, sample type, method type, and week, the difference was calculated between the mean of the results for duplicate samples exposed to constant CO_2-enhanced air and the mean of the results for duplicate samples exposed to saturated reagent water. The mean of the weekly differences was then calculated for each parameter, sample and method type, and paired t-tests were run to determine whether the mean of the differences was significantly greater or less than 0. Sample results were evaluated as (1) straight concentrations, and (2) "normalized" to account for the volume of sample collected and the weight of sample exposed to weathering. Sample results were normalized by multiplying concentration by the volume of sample collected, then dividing by the total weight of the sample to obtain mg/kg.

Table 3.6: Sample Weights (in grams)

		Column		Cell		
Lab	**Sample**	**CO_2-Air Constant Flow**	**CO_2-Air - Saturated H_2O**	**CO_2-Air Constant Flow**	**CO_2-Air - Saturated H_2O**	**Total # Samples**
1	Shale	1770.45 1765.24 1583.11 [1]	1764.77 1764.84	-	1764.97 1764.93	7 (3 duplicate pairs, one extra)
	Coal Refuse	-	1129.52 1129.48	-	1130.42 1129.51	4 (2 duplicate pairs)
	Limestone	1771.11	1765.52	-		2
2	Shale	2025.3 2025.4	1873.8 2025.5	-	2054.4 2054.1	6 (3 duplicate pairs)
	Coal Refuse	-	1278.1 1278.4	-	1278.4 1278.1	4 (2 duplicate pairs)
	Limestone	2008.6	2008.1	-	-	2
3	Shale [2]	1198 (2" column) 5430 (4" column) 12,608 (6" column)	-	-	-	1

[1] Lab 1 prepared an extra Shale sample small particle fractions removed (<35M sieve).
[2] Lab 3 evaluated Shale in three leaching columns of varying diameters (2-inch, 4-inch, and 6-inch)

Comparisons were made on alkalinity, sulfate, calcium and conductivity. Results of the paired t-tests indicate that for all four parameters, mean concentrations were significantly greater for samples exposed to a constant flow compared to those exposed to the saturated water (i.e. significant at the 99% confidence interval). A graph depicting the comparisons run on alkalinity results for the two gas mixture scenarios is shown in Figure 3.2.

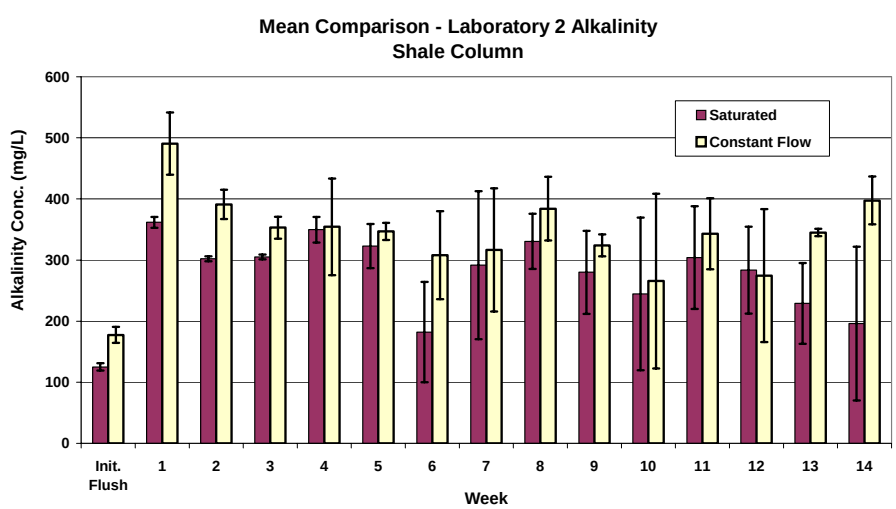

Figure 3.2. Alkalinity concentrations of two gas mixture scenarios.

In this Figure, the vertical lines extending symmetrically in each direction from the average concentration result (top of each column) represent the range of results from the duplicate samples. In Figure 3.2, the alkalinity concentrations produced by the constant-flow scenario generally appear to be 50 to 100 mg/L higher than those produced by the CO_2-saturated water scenario. Paired t-tests also were performed on normalized results, but there were no significant differences between samples exposed to constant flow and samples exposed to the saturated gas mixture for any of the four parameters in Laboratory 1. For Laboratory 2, however, normalized results were significantly higher for samples exposed to the CO_2-saturated water compared to those exposed to constant gas flow.

Figure 3.3 is a comparison of calculated PCO_2 among the three labs for the columns with continuous air flow. Horizontal lines within the "boxes" are medians and the values are plotted next to the box. The "boxes" extend from the 25th to 75 percentile of data and thus encompass the middle 50% of the data. "Whiskers" (the vertical lines) show the range of the data to 1.5 times the interquartile range. Asterisks indicated statistical outliers.

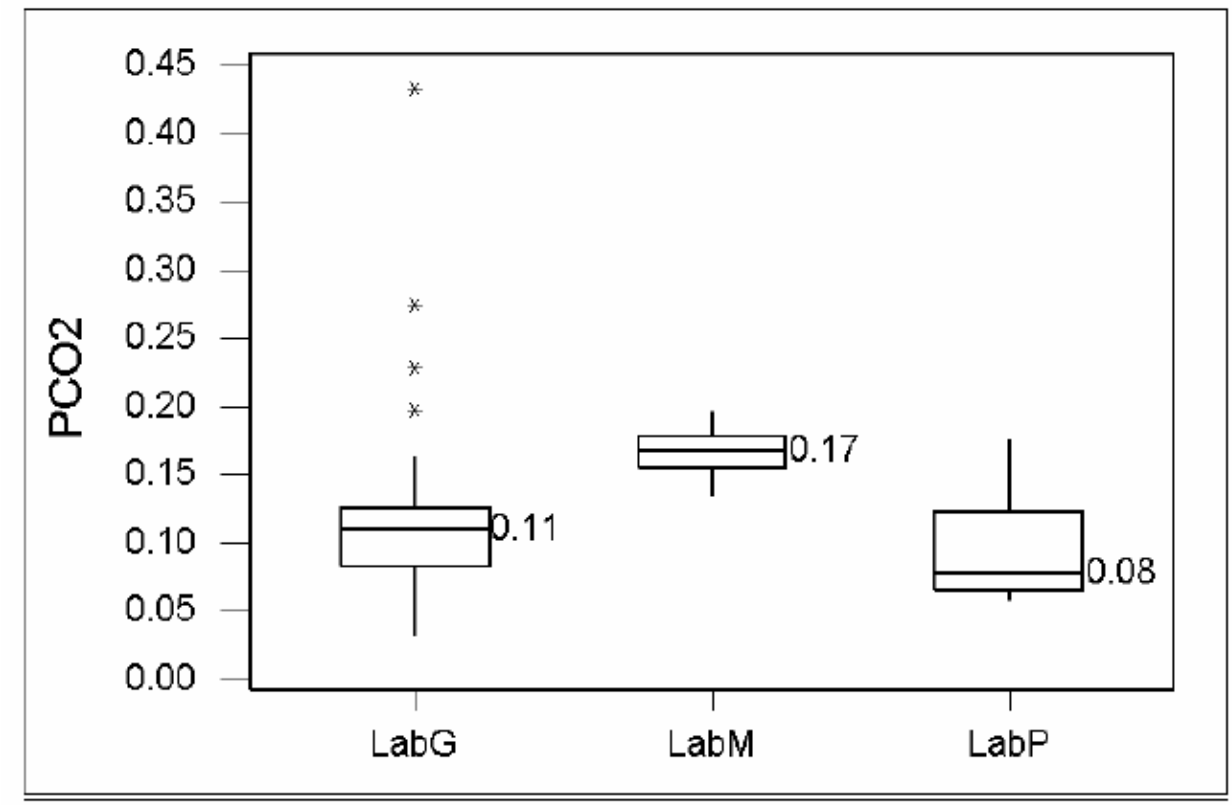

Figure 3.3. Comparison of PCO_2 among laboratories for the leaching columns that had continuous flows of 10% air.

<u>comparison of duplicate samples:</u> The precision of the methods was assessed using concentration results of duplicate samples exposed to identical weathering procedures. Relative percent differences (RPD) were calculated for results of 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 through week 14. Pooled RPDs were determined as the square

root of the average squared weekly (weeks 1 to 14) RPDs for each parameter. For Laboratory 1, pooled RPDs ranged between 3.3 and 41.5%. For Laboratory 2, pooled RPDs ranged between 6.5 and 50%. These ranges were based on concentrations of alkalinity, sulfate, calcium and conductivity measured in shale samples, and on concentrations of acidity, sulfate, conductivity, calcium, manganese and iron measured in coal refuse.

In addition to calculating RPDs between the measured concentrations of the duplicate samples, RPDs were also calculated using normalized results. Pooled RPDs based on normalized results ranged from 7.5 to 47% for Laboratory 1, and from 8.5 to 50.2% for Laboratory 2. Out of 96 pooled-RPD results from the two laboratories, 26 were above 30%. It is important to note that EPA methods often include RPD performance criteria of up to 30% for duplicate analyses.

comparison of leaching column and humidity cell methods: Results of samples exposed to humidity cell weathering procedures (exposure to 1-hour wet weathering) were compared to the results of samples exposed to leaching column weathering procedures (24-hour wet weathering) to determine if increased sample immersion in water produces significantly more of the target parameters. Based on results of this analysis, shale samples were affected by method type most significantly in terms of alkalinity and conductivity. Conductivity and alkalinity concentrations were significantly greater in leaching columns than humidity cells for both laboratories. Calcium concentrations from shale samples also were significantly greater in leaching columns evaluated in Laboratory 1 but not in Laboratory 2. The method type did not have a significant effect on sulfate for either laboratory. Normalization had little effect on the results of this analysis.

The type of weathering method had a lesser effect on coal refuse samples than on shale samples. In general, these results show that the leaching column weathering procedures are more aggressive than the humidity cell procedures.

effects of removal of small particle size fraction: In addition to the duplicate shale samples evaluated using leaching columns by Laboratory 1, a third sample was also analyzed. Unlike the duplicate pair, this third column did not include particles less than 35 mesh. Based on the results of the paired t-tests, removal of fine particles decreased the concentration of sulfate, calcium and conductivity significantly, but did not have a significant effect on alkalinity. These results did not change after data normalization.

Figure 3.4a displays the effect of fine particle removal on sulfate concentration. The difference in sulfate concentrations between the column without the fines and the columns with fines at week 1 (approximately 275 mg/L) showed that the concentration of sulfates in the column without fines decreases steadily until week 9, and in weeks 13 and 14 the difference is less than 50 mg/L. This may be due to a depletion of the fines in the other columns as a result of the weathering process. However, it is uncertain whether this convergence of sulfate plots in the last 5 weeks in Figure 3.4a is due to: (a) a reduction or consumption of fine particles by dissolution (e.g. carbonate minerals) or some other weathering process, (b) a reduction in the reactivity of remaining fine particles (e.g. sulfur/sulfate depletion) or (c) the loss of fine particles during weekly leachate collection procedures (leaving the columns as suspended solids in the leachate).

Figure 3.4b shows that the removal of fine particles from the third constant-flow leaching column had essentially no effect upon alkalinity concentrations produced by the Brush Creek shale samples. The time plots of the three constant-flow columns in Figure 3.4b are nearly identical, and represent consistently higher alkalinity concentrations than the pairs of columns and humidity cells with CO_2-saturared influent water. These findings support the principle that the major factors controlling alkalinity production from a rock sample with a high neutralization potential are the solubility of the carbonate minerals and the partial pressure of carbon dioxide in the system (i.e. in the pore spaces in the leaching column or in the spoil gas mixture in a mine environment). The concentration of alkalinity produced tends to be independent of particle size and surface area, if sufficient time is available to reach saturation. Saturation with respect to $CaCO_3$ was reached in all instances within the 24-hours that the sample was inundated with water. The ultimate alkalinity that can be produced under inundated conditions is a function of the PCO_2, whereas, the major factors controlling sulfate (and acidity) production from a rock sample with appreciable total sulfur content include particle size and surface area.

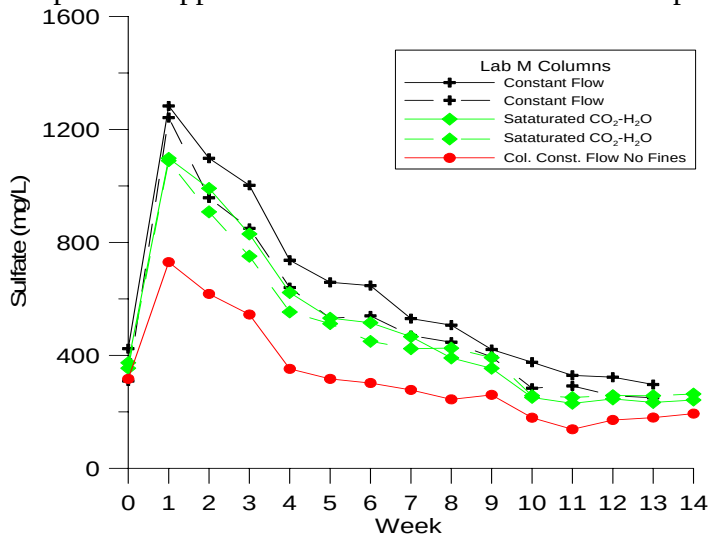

Figure 3.4a**.** Effects of fine particle fractions on sulfate production in shale.

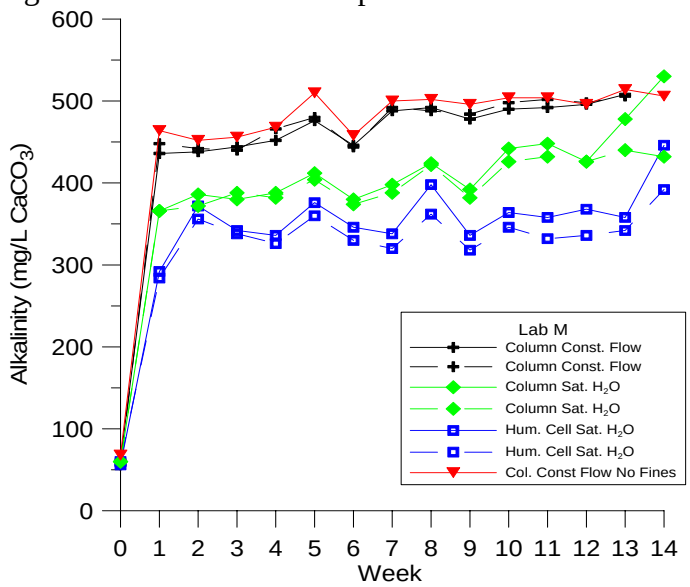

Figure 3.4b. Effects of fine particle fractions on alkalinity in shale**.**

effect of varying leaching column diameter: Comparison of Column Sizes (2-inch, 4-inch, and 6-inch diameters). Laboratory 3 evaluated the effects of the leaching column weathering procedures on samples of shale in three cylindrical column structures of identical height (24-inches) and different diameters (2-inch, 4-inch, and 6-inch). Results of this comparison are presented in Figures 3.5a and 3.5b. A comparison of the effect of leaching column sizes upon analyte concentrations showed that mean and maximum alkalinity concentrations produced from the shale sample in the 6 inch column were not greater than those corresponding to the smaller column diameters. Curiously, the calcium concentrations produced in the leachate from the 2 inch and 4 inch columns declined significantly through time, while that from the 6 inch column did not decline – resulting in a much higher median calcium concentration from the 6 inch column.

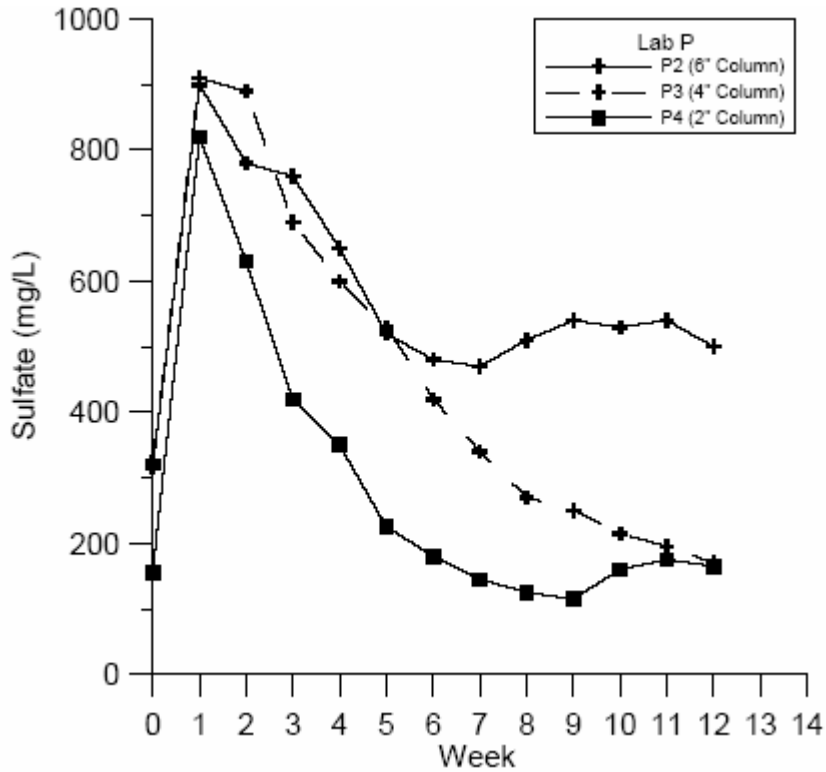

Figure 3.5a. Sulfate concentrations of Brush Creek shale using two inch, four inch, and six inch column diameter.

Figures 3.4 and 3.5 show concentrations of sulfate and alkalinity through time for the Brush Creek shale from various leaching columns. Sulfate concentrations from the three diameters of leaching columns at Lab 3 are plotted in Figure 3.5a. These plots resemble the classic leaching behavior shown in White (1986), with the steep initial slope, followed by supersaturation, and then a flattening (6-inch column) or decline (2-inch and 4-inch columns) in concentration through time for the remainder of the weathering test. Notice that these plots do not originate at zero, they extend to negative weeks time, indicating that weathering of the shale samples commenced prior to the start of the leaching column tests (i.e. prior to the initial flush).

Figure 3.5b is the time plot of alkalinity concentrations of the Brush Creek shale from leaching columns. The plots resemble the leaching behavior of a combination of the initial linear and latter diffusion-controlled mechanisms, shown in White (1986). Laboratory 3, which evaluated different diameter columns, had similar alkalinities in the three columns.

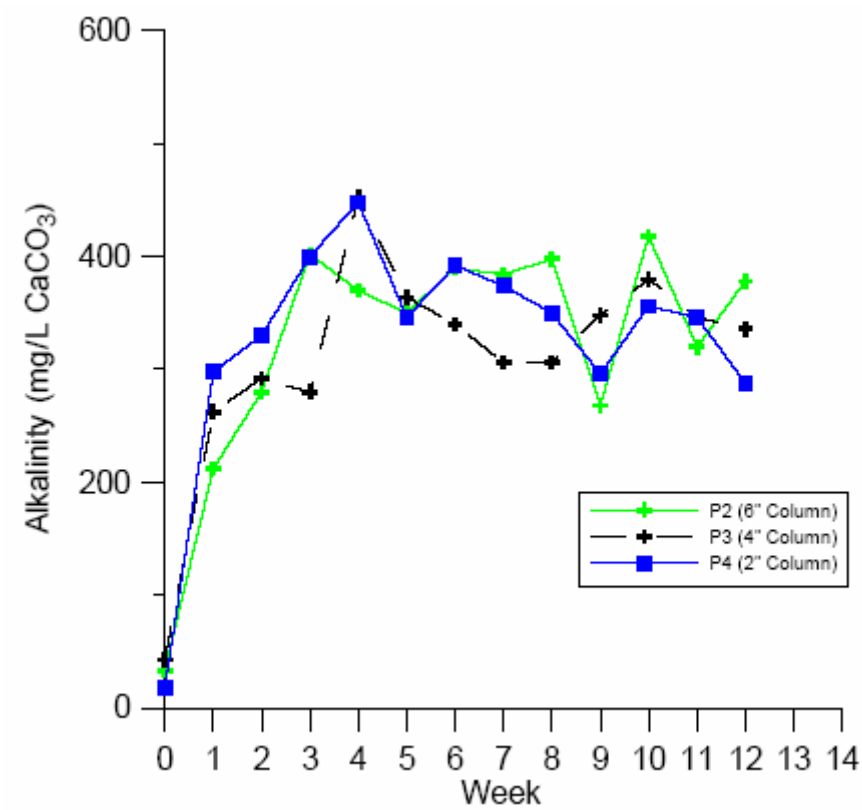

Figure 3.5b. Alkalinity concentrations of Brush Creek shale using two inch, four inch, and six inch column diameter.

Conclusions:

The results of this second phase of weathering tests indicate that the leaching columns are superior to the humidity cells in rock weathering performance, and the 2 inch diameter columns used in this second phase performed as well as the 6 inch diameter columns used in the first phase (2002) of weathering tests. The results also show that the continuous flow of CO_2-enhanced air was a superior gas handling method in comparison to the exposure of influent water saturated with CO_2-enhanced air. The standardized particle size distribution appears to be an improvement in the performance and the data interpretation of the method. The removal of fine (<35 mesh) particle components affected sulfate concentrations, but had essentially no effect upon alkalinity concentrations. The coal refuse sample exhibited the greatest change in effective surface area.