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REFINEMENT OF ADTI-WP2 STANDARD WEATHERING PROCEDURES, AND EVALUATION OF PARTICLE SIZE AND SURFACE AREA EFFECTS UPON LEACHING RATES: PART 1: LABORATORY EVALUATION OF METHOD PERFORMANCE [1]

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Abstract. The second year of method development work was conducted on the ADTI-WP1 (Humidity Cell) and the ADTI-WP2 (Leaching Column) standard test methods. The performance of the leaching column method was superior to the humidity cell method. In making improvements to the leaching column method, variations in column diameter and water-handling/gas-handling procedures were evaluated. Two commercial laboratories and a university research lab participated in the study. Relative percent differences between duplicate samples and relative standard deviations between laboratories were evaluated.

Surface area measurements, using BET methods, were conducted on each of 8 particle size classes, before and after weathering tests on 4 different lithologic samples. Observed alkalinity concentrations were consistent with the elevated PCO_2 and approached saturation with respect to calcite for calcareous rocks. The maximum concentrations of acidity (33,700 mg/L), sulfates (37,404 mg/L) and iron (9,120 mg/L) for the high-sulfur coal refuse sample were consistent with the maximum concentrations observed in the field. The measured surface areas of the shale samples were significantly higher than the sandstone, limestone and coal-refuse samples. However, the surface area measurements post-weathering were not significantly different from the pre-weathering measurements for most rock samples and most particle size classes.

Additional Key Words: kinetic test, leaching column, humidity cell

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Introduction

Two weathering procedures are being developed by the Acid Drainage Technology Initiative, Coal Mining Sector, (ADTI-CMS) in cooperation with federal agencies (OSM and EPA). Toward the goal of developing standardized and effective test procedures, draft humidity cell (ADTI-WP1) and leaching column (ADTI-WP2) methods were tested in three laboratories. The draft methods are designed to utilize low cost materials and minimal apparatus construction, maximize weathering efficiency, and produce reliable and verifiable data. The draft methods also are directed primarily toward the goal of characterizing water quality that will be produced from the effects of weathering on overburden samples, and include procedures that represent and/or enhance weathering conditions that may occur in the field.

The objectives of this project are: (1) standardizing humidity cell and leaching column procedures; (2) improving test methods by (a) maintaining a carbon dioxide-enriched environment to optimize carbonate mineral dissolution and (b) quantifying particle size variables to evaluate reaction kinetics; and (3) providing flexibility in test method implementation consistent with EPA guidelines for Performance-Based Measurement Systems (PBMS). The companion paper by Brady et al. (2004) addresses practical and theoretical aspects of leaching kinetics, including surface area to volume ratios.

Background

Leaching column tests have been used in mine drainage studies since prior to 1950 (e.g. Braley, 1949) and humidity cell tests have been in use since the early 1960's (e.g. Hanna and Brant, 1962). Although several of these humidity cell methods and numerous leaching column methods have been used to predict the quality of drainage from coal and metal mines, there currently are no standard methods that are widely used and accepted as accurate predictors of coal mine drainage quality by state and federal regulatory agencies or the coal mining industry. Even though a great deal of analytical information has been obtained using tests of these types, the utility of that information is limited by the lack of standardization and basis for comparing the information to other test results.

The Acid Drainage Technology Initiative (ADTI) was established in 1995 by federal agencies, the National Mining Association and the Interstate Mining Compact Commission to identify, evaluate, and develop cost-effective and practical acid drainage technologies. One of the major goals of ADTI is to resolve disagreements over the accuracy and precision of prediction methods for mine drainage quality by improving and developing consensus on these test methods. From 1995 through 1997 the Kinetic Tests Subgroup of the ADTI Prediction Workgroup worked to summarize the status of kinetic testing research and developments relevant to coal and metal mining and to promote the development of standard kinetic test methods. The concept of these standardized kinetic tests for mine drainage prediction, including provisions, to increase the carbon dioxide partial pressure in the apparatus, were described by Hornberger and Brady (1998). That study evaluated physical, chemical and biological factors in kinetic tests and reviewed the chronology of the development of various kinetic tests with more than 300 scientific references. In December 2000, the ADTI-CMS Prediction workgroup published a study titled "Prediction of Water Quality at Surface Coal Mines." (Kleinmann et al., 2000). Chapter 5 of that publication by Geidel et al., (2000) listed guidelines and recommendations for the use of kinetic tests.

The need for these standardized kinetic test methods is recognized by OSM and EPA to make improved predictions of coal mine drainage quality and overburden strata characterizations for use by state and federal regulatory agencies and the mining industry. Such predictions can be used in addressing the Probable Hydrologic Consequences (PHC) and Cumulative Hydrologic Impact Assessment (CHIA) requirements of the SMCRA, associated federal and state regulations, and surface mining permit applications. OSM is funding and administering this project and EPA is ensuring that the method development process meets their rigorous requirements to become an approved EPA method.

Rock samples tested with ADTI-WP 1 & 2 methods

Several rock samples were selected to provide a range of geochemical and physical lithologic characteristics for the testing of these weathering procedures. Approximately 500 to 1,000 pounds (200 to 400 kg) of each sample were collected at selected sample sites described below. Table 1 shows the total sulfur content and neutralization potential (NP) for each of the seven lithologic units. The rock samples were crushed and homogenized through a long- piling technique and riffle splitting. This process resulted in approximately 32 splits of each of the 7 lithologic units. Selected splits in the series were tested to confirm the homogeneity of the samples (see Table 1).

The range in geochemical characteristics of stratigraphic units for coal mine drainage prediction is usually expressed in terms of the possible combinations of low to high percent total sulfur (as an indicator or surrogate measure of maximum potential acidity, MPA) and low to high neutralization potential (NP as an indicator or surrogate measure of potential alkalinity). Geidel et al. (2000, p. 119 & Fig. 5.4) describe and depict a "gray zone" or "uncertain zone" for predictions based upon the results of acid-base accounting static tests, expressed as the "NP/MPA ratio," the "Neutralization Ratio," or the "Net NP." Lithologic units that fall into this gray zone typically have moderate to high total sulfur content and moderate to high NP values. Lithologic units and stratigraphic sequences in the gray zone have been described by Hornberger and Brady (1998, p.7-28), Kania (1998, p.18-2), Skousen et al. (2000, p.92), Geidel et al. (2000) and Perry (2000) as problematic for the use of acid-base accounting in coal mine drainage prediction, and therefore, represent the types of samples for which kinetic tests (like the ADTI-WP 1 & 2 weathering procedures) are needed to make better predictions.

Table 1. Total sulfur and neutralization potential of rock samples.

Lithology and Split Sample ID	**Total% Sulfur by weight**	**Fizz Rating**	**Neutralization Potential (ppt) (Ca CO_3)**
Brush Creek Shale			
#8	0.90	2	139
#16	0.92	2	136
#24	0.91	2	133
#32	0.93	2	136
#32 R	0.91	3	121
Wadesville Sandstone			
#4	0.00	2	256
#8	0.00	2	274
#16	0.01	2	262
#24	0.00	2	282
Middle Kittaning Sandstone			
HHS #2	0.08	0	20.9
HHS #8	0.04	1	17.7
HHS #12	0.03	1	14.3
Valentine Limestone			
"A"	0.00	3	929
"I"	0.00	3	927
"K"	0.00	3	932
"P"	0.02	3	928
Vanport Limestone			
VLS#1	0.00	3	903
VLS #9	0.01	3	916
VLS #11	0.00	3	900
Leechburg Coal Refuse			
LRBT #4	6.64	0	2.64
LRBT #9	6.94	0	-0.39
LRBT #14	7.67	0	-1.71
S-2	3.03	0	-1.32
S-5	2.42	0	1.29
Ernest Coal Refuse			
1A	4.38	0	1.16
1B	4.03	0	1.65
2B	4.19	0	1.36

The Brush Creek shale outcrop near Greensburg, PA was selected as the primary rock sample for use in this weathering procedures 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 also was selected by USGS and two of the authors (Brady and Hornberger) in 1999 to be the first ADTI-CMS standard reference material and thus, extensive geochemical and mineralogical characterization data is available; the site stratigraphy has been confirmed and described by Skema (1995) in a published field guidebook and the sample site (Route 66 road cut) has long-term accessibility for future sampling needs. The range in total sulfur content of four splits of the Brush Creek shale is 0.90 to 0.93 % (see Table 1). The range of NP values is 121 to 139 parts per thousand (ppt). Sample #32R in Table 1 was rehomogenized after 1 year storage.

Wadesville sandstone samples were collected within a large anthracite open-pit surface mine in Schuylkill County, PA. This indurated 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 reported as $CaCO_3$) as shown in Hornberger and Brady (1998) and Brady et al. (1998). The range of NP values for this sample is 256 to 282 ppt (see Table 1), and the total sulfur contents are negligible.

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 1, while the range of NP values is 14.3 to 20.9 ppt.

Two limestone samples were selected to serve as high-alkalinity producing end members in the 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 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 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. The Leechburg coal refuse samples were collected from the large refuse deposit associated with the abandoned underground Leechburg coal mine and an active 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 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 2002 weathering tests were conducted on samples collected from the abandoned coal refuse piles shown at the bottom of Table 1 (i.e. S-2, S-5, 1A, 1B, 2B), 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 1.

Study Design

In 2002, the ADTI-WP1 (Humidity Cell) and ADTI–WP2 (Leaching Column) draft weathering test methods were conducted in two laboratories for a period of 16 weeks in order to evaluate the performance of the methods and the effects of sample exposure to CO_2–enhanced gas mixtures. Geochemical Testing, a commercial laboratory in Somerset, PA, conducted comparative testing of humidity cells and leaching columns and comparative testing of gas mixtures (i.e., atmospheric air conditions, and 10% CO_2–enhanced air), using duplicates to provide information for evaluating method performance. The Materials Research Institute (MRI) of the Pennsylvania State University conducted leaching column tests on 3 of the rock samples (sandstone, limestone, and shale), using a gas mixture containing 10% CO_2-enhanced air, that was carefully metered and controlled for each of 3 leaching columns. MRI also performed particle size distribution (sieve analyses) and surface-area-to-volume-ratio measurements (using BET equipment) on the rock samples before and after exposure to method weathering conditions. The results of this first year of weathering tests are described in Hornberger, et al. (2003), which contains schematic drawings of both types of apparatus, plus numerous graphs of the weekly leachate data.

In 2003, the two weathering procedures were modified to reflect the results of the 2002 studies and the tests were conducted in three laboratories for a period of 15 weeks to evaluate the performance of the method refinements. Two commercial labs participated in the study, Geochemical Testing and Mahaffey Laboratory, Ltd. of Grampian, PA. These two laboratories conducted identical comparisons of the humidity cell and leaching column draft methods, and also compared two alternative procedures for introducing the CO_2-enhanced gas mixture into the leaching columns, using duplicates for both of these comparisons. The third lab, the Materials Research Institute (MRI) at the Pennsylvania State University, conducted a comparison of the effectiveness of leaching columns with 2-inch, 4-inch and 6-inch diameters. MRI also performed surface area measurements, using BET methods, on each of 8 particle size classes, before and after the weathering tests.

The original type of humidity cell apparatus, used in the 2002 weathering tests, was constructed from rectangular plastic 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. Therefore the major difference between the ADTI-WP 1 & 2 draft methods evaluated in 2003 involved the water handling and gas handling procedures (i.e. humidity cells were exposed to 1-hour periods of saturation vs. column exposure to 24-hour periods of saturation). Since the leaching column and humidity cell apparatus is essentially the same for the 2003 weathering tests, and the performance of the columns was again superior to the cells, most of the remainder of this paper is devoted to the refinement and interpretation of the leaching column method.

First Year (2002) Weathering Test Results

The first series of weathering tests were performed on representative splits of the Brush Creek Shale, Wadesville sandstone, Valentine limestone and coal refuse samples from the Ernest and Leechburg abandoned refuse piles. The leaching columns were constructed from 6-inch diameter clear polycarbonate plastic tubing in accordance with the design specifications shown in Fig. 1. The humidity cells were constructed from the rectangular plastic storage containers in accordance with the schematic drawings and specifications in Hornberger et al. (2003), which also contains the schematic drawing of the equipment used to prepare the humidified gas mixture.

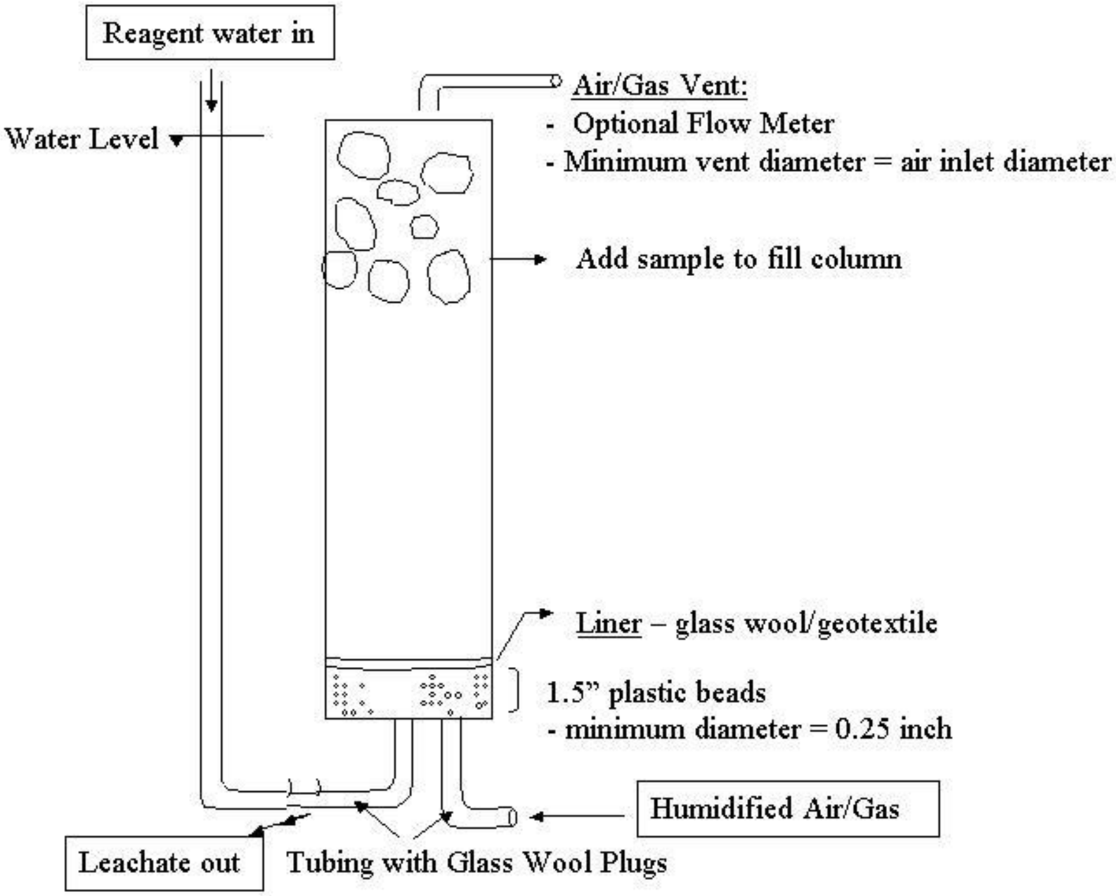


Figure 1. Leaching Column Schematic Drawing.

Sample preparation and characterization

The rock samples were crushed to a nominal ½" diameter using a jaw crusher, and then mixed and homogenized using a riffle splitter and procedures described in ASTM C-702-98 and Noll, et al., (1988). 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 (0.074 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 sample was then chemically analyzed for percent total sulfur and neutralization potential.

Gas-mixing & 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, the commercial lab 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. The university research lab 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.

The ADTI-WP1 & 2 simulated weathering procedures consist of alternating cycles of saturation and humidified air. The 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 is also introduced into the leaching columns and humidity cells during periods of saturation (i.e. when the apparatus is filled with water).

Water-handling procedures/leaching cycles. 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. 1) 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 is 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 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) is 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 (effluent water) 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, and 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.

Method Performance Data

The leaching column and humidity cell weathering procedures were conducted in 2002 for a period of 16 weeks in the two labs. Evaluations were made of: (a) the effect on weathering 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) the relative percent difference of analyte concentrations produced between duplicate columns and cells, (d) comparison of calcite saturation indices and partial pressures of carbon dioxide within the columns and cells, (e) preliminary determination of the effects of the weathering procedure on particle size and surface area, and (f) the abundance of iron-oxidizing bacteria related to rock type.

Comparison of the CO_2 enhanced gas mixture and air-only conditions. The alkalinity concentrations in leachate from the humidity cells and leaching columns of Brush Creek shale and Wadesville sandstone samples were plotted for CO_2-enhanced and air-only gas conditions, as shown in Fig. 2a. Generally, the alkalinity concentrations resulting from the CO_2-enhanced gas mixture were 3 to 4 times higher than those resulting from exposure to normal atmospheric air, for both the shale and sandstone samples. In Fig. 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. In weeks 9 and 15, the alkalinities were 6 times greater. The histograms in Fig. 2a depict the average or median values of alkalinity for each week, and the bar diagrams in the top center of each histogram represent the range in alkalinity concentrations of the 2 duplicate samples.

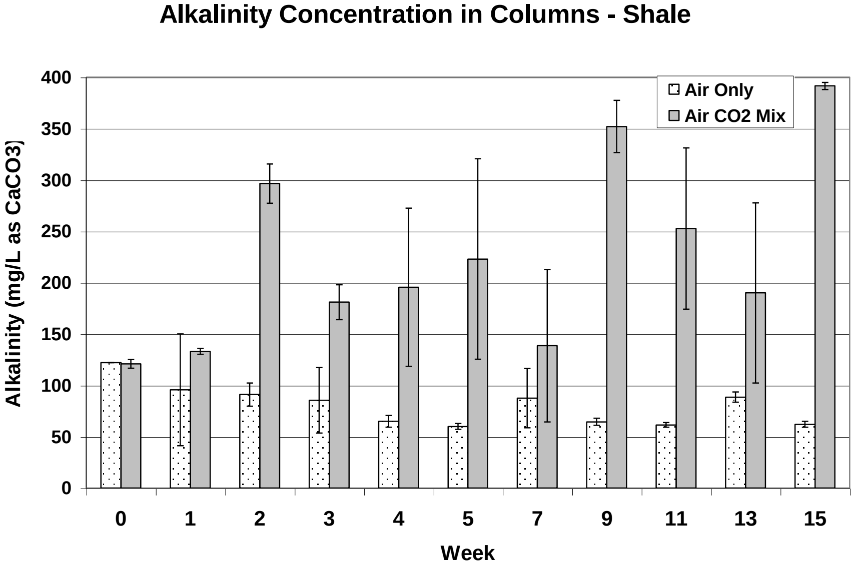


Figure 2a. Alkalinity concentrations from Brush Creek shale sample in leaching columns.

Comparison of Leaching Columns and Humidity Cells. The leaching effectiveness of the humidity cell and leaching column methods was compared in several ways as described in Hornberger, et al. (2003). Plots of concentration through time showed that the conductivity and sulfate concentrations were consistently higher in the leaching columns. Fig. 2b shows that the sulfates produced in the leaching columns are consistently higher than those produced in the humidity cells. This observation is an indication of more aggressive weathering conditions in the leaching columns. The longer residence time of influent water in the leaching column method (i.e. 24-hour saturation period vs. 1-hour in cells) is probably a large factor in these differences.

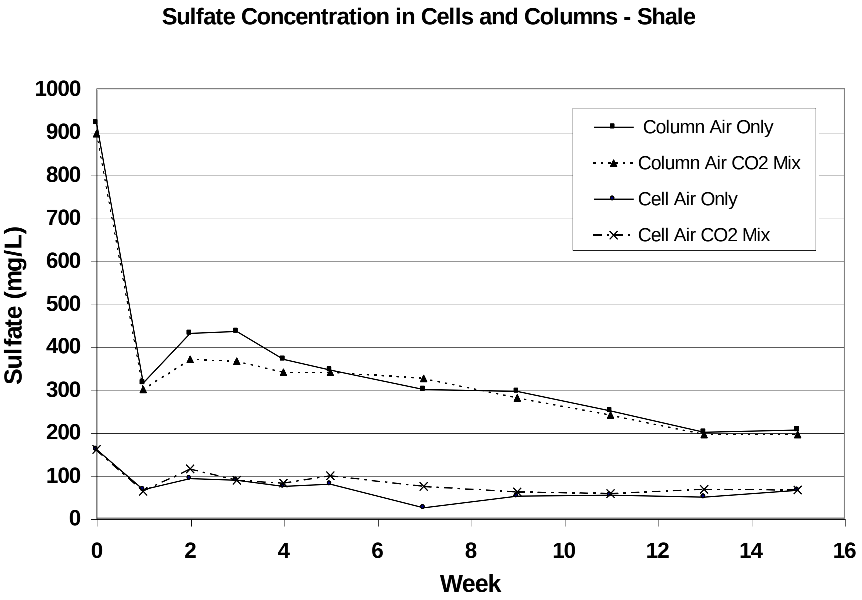


Figure 2b. Sulfate in leachate from shale in humidity cells and leaching columns.

Comparison of duplicate samples. The precision of the draft leaching column and humidity cell test procedures was assessed using results of duplicate samples exposed to identical weathering procedures in 2002. Relative percent differences (RPD) between concentrations of the analytes produced by the duplicate samples were calculated 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). A table of these RPD values is presented in Hornberger et al. (2003). Out of thirty-two pooled RPD results, only four were above 30% (three of these were alkalinity from shale). EPA methods often include RPD performance criteria of up to 30% for analyses of duplicate samples.

Calcite saturation indices and CO_2 partial pressures. 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 (personal communication). 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 distribution of calculated saturation indices for leachate from the leaching columns and humidity cells is shown in a series of boxplots in Fig. 3. 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 that had atmospheric air circulated through them. Where duplicate columns were run, the data were combined (items 1 through 8 in Fig. 3). In general, the columns were supersaturated, or nearly saturated with respect to calcite. The humidity cells were almost always undersaturated with respect to calcite.

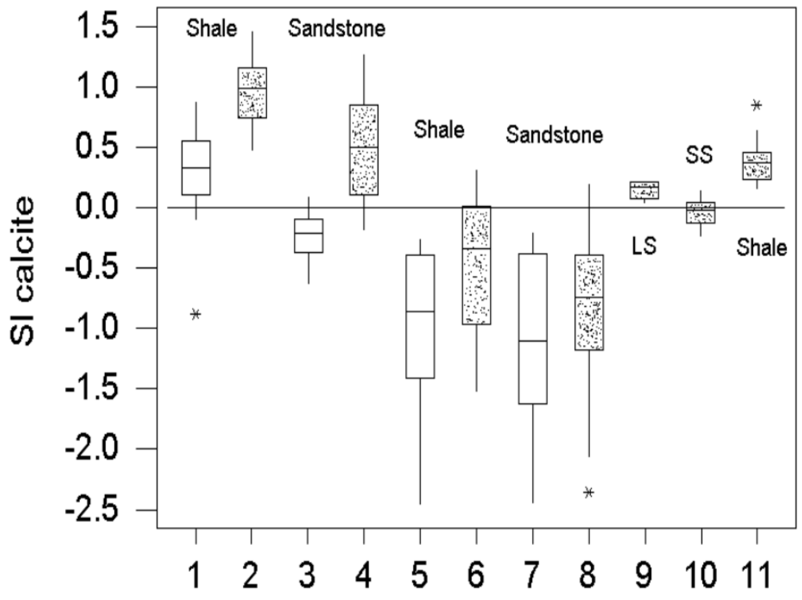


Figure 3. Boxplots of the distribution of saturation indices for calcite in various leaching apparatuses. (Stippled boxes represent apparatus with 10% CO_2-enriched air mixture; The first eight boxplots represent the results from Lab 1 and the last three boxplots represent results from Lab 2.)

A goal of this project was to leach calcareous rock samples under conditions likely to be encountered in coal mine spoil. 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 calculated PCO_2 values were arranged in a table in Hornberger et al. (2003), which 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.

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. 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 innoculated with the bacteria to catalyze acid producing reactions, particularly in high sulfur samples.

Second Year (2003) Weathering Test Results

Following evaluation of the 2002 weathering test results, the draft methods were revised 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 are 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. A comparison of the results of those options is discussed below.

Standardized Particle Size Distribution. 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 2.

Table 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, 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 Part II of this paper (Brady et al., 2004), 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 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. 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

Method Performance Data

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 A.

Comparison of gas mixture introduction 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.

Comparisons were made on alkalinity, sulfate, calcium and conductivity. Concentrations of manganese and iron in leachate from the shale samples were too low for accurate comparisons to be made. 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 of the 99% confidence interval). A graph depicting the comparisons run on alkalinity results for the two gas mixture scenarios is shown in Fig. 4.

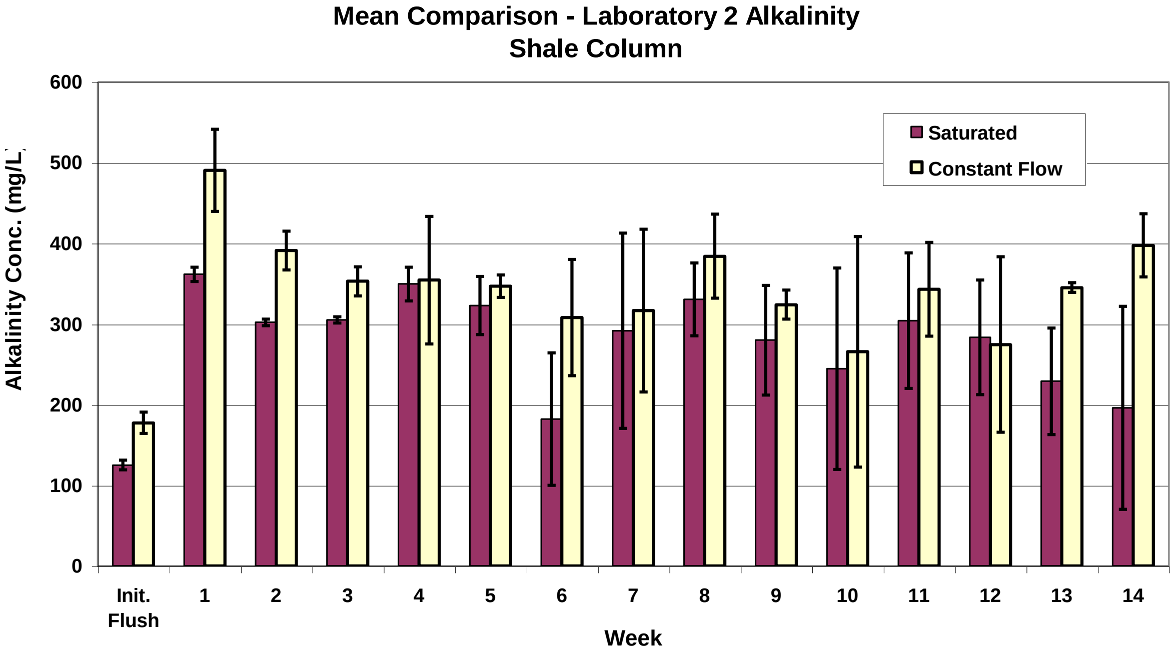


Figure 4. Alkalinity concentrations of two gas mixture scenarios in shale leaching columns at Laboratory 2.

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 Fig. 4, 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. Closer examination of Figure 4 shows that some larger differences exist. For example, in week 14, the range in constant flow duplicates is 378 to 417 mg/L with a median of 398, while the range in CO_2-saturated water is 133 to 259, with a median of 196 – the difference between medians being 202 mg/L. 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.

Comparison of Duplicate Samples. 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. It is important to note that RPD results include the variability that is inherent to the analytical methods that were used to measure the parameters of interest. However, pooled RPDs typically were greater than the initial flush RPDs, indicating that the implementation of weathering procedures had an effect on the results of duplicate samples.

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. The iron and manganese results measured in shale were detected at levels at or near the detection limit of the analytical methods used, therefore, the high RPDs resulting from these measurements are not considered in this discussion.

In addition to calculating RPDs between the measured concentrations of the duplicate samples, RPDs were also calculated using normalized results. Normalized results were determined by multiplying the concentration by the volume of sample collected and dividing by the total sample mass to get a result in mg/kg. 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.

Statistical analyses were performed comparing pooled RPDs between Laboratories 1 and 2 using an F-test (see Appendix B). Pooled RPDs were first converted to relative standard deviations (RSDs) by dividing by the square root of 2, and the F-test was run to assess whether the ratio of pooled squared RSDs was significantly greater than one. Results of this test are shown in Appendix B. In most cases, the direction and magnitude of differences between RPDs were consistent regardless of whether the concentrations were normalized prior to the RPD calculation. Laboratory 2 tended to have greater RPDs in shale, but lower RPDs in coal refuse. The largest differences between laboratories occurred for alkalinity.

<u>Comparison of Humidity Cell to Leaching Column Methods.</u> 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. Similar to comparisons of gas-mixture scenarios described in the previous section, analyses were performed using paired t-tests on both concentration and normalized results. Comparisons were run on iron and manganese for coal refuse samples only, because of the low concentrations measured for these parameters in shale.

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 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. All significant differences in concentration results from shale samples analyzed by Laboratory 1 were also observed in normalized concentrations. For Laboratory 2, however, normalized sulfate and calcium results are significantly greater in effluent samples collected from the leaching columns, but not significantly different for conductivity.

The type of weathering method had a lesser effect on coal refuse samples than on shale samples. Concentrations and normalized results of acidity, sulfate, iron and conductivity were significantly greater in leaching columns than humidity cells in samples analyzed by Laboratory 1. There were no significant differences for any parameters other than conductivity in samples analyzed by Laboratory 2. Of the 40 paired t-tests performed for leachate analysis of the shale and coal refuse samples, 20 t-tests showed no significant difference between columns and humidity cells (mostly for the coal refuse samples) and 20 were statistically significant. In all 20 cases where there was a significant difference, the levels of target parameters produced by the leaching columns were greater than those produced by the humidity cells. In general, these results show that the leaching column weathering procedures are more aggressive than the humidity cell procedures.

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. Comparisons of this extra sample and the duplicate pair were run using paired t-tests, by calculating the difference between the duplicate pair mean and the extra sample for each week, and then testing whether the mean of the differences over all weeks was significantly different from 0. A mean significantly greater than 0 suggests that the removal of small particles in the extra sample significantly decreases the concentration of the parameter, while a mean significantly less than 0 suggests that the removal significantly increases the concentration. Comparisons were run on alkalinity, sulfate, conductivity, and calcium only, because of the low concentrations of manganese and iron in leachate from the shale samples.

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. Fig. 5a 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) 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 Fig. 5a 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).

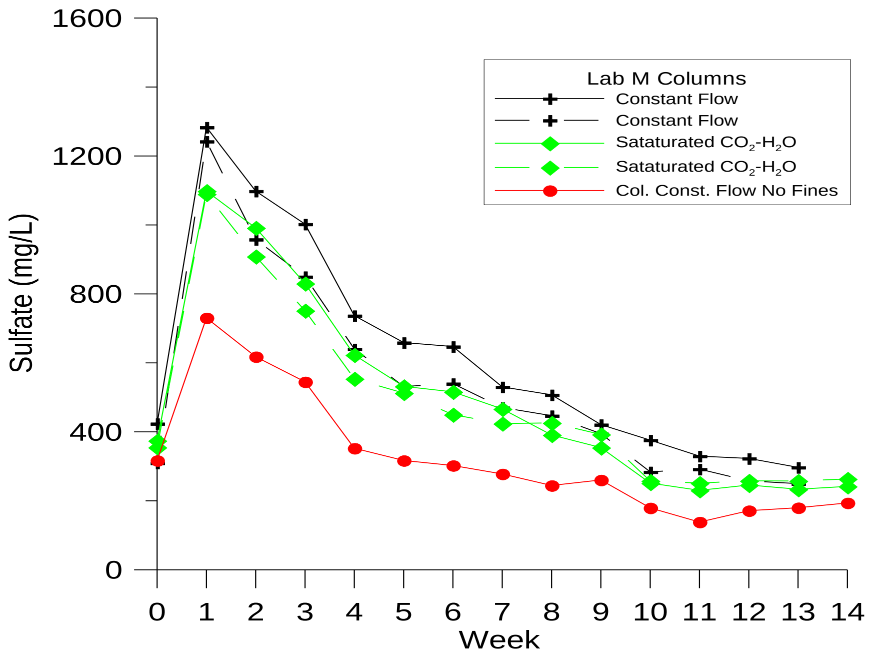


Figure 5a. Effects of fine particle fractions on sulfate production in shale.

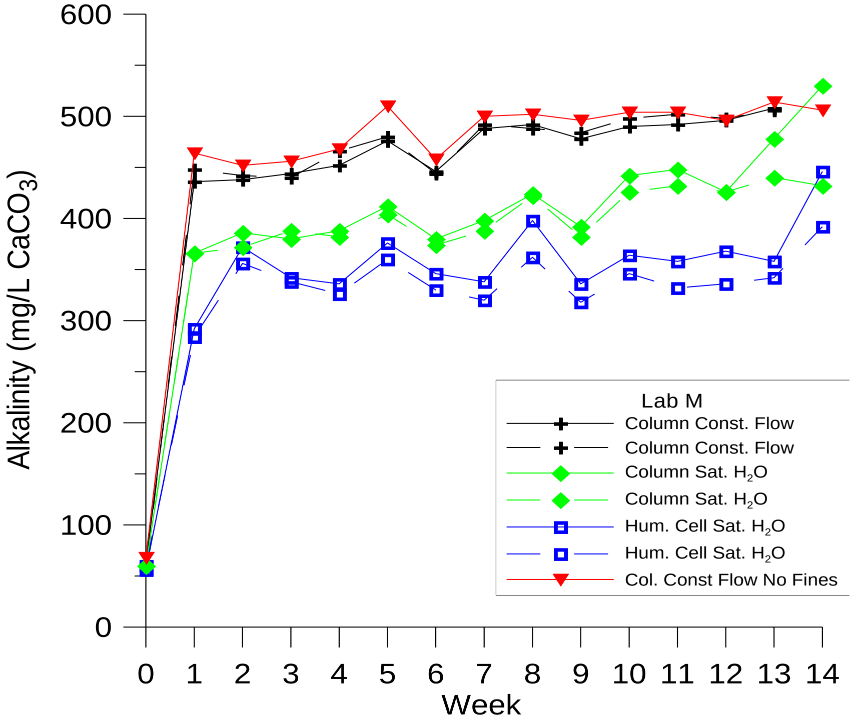
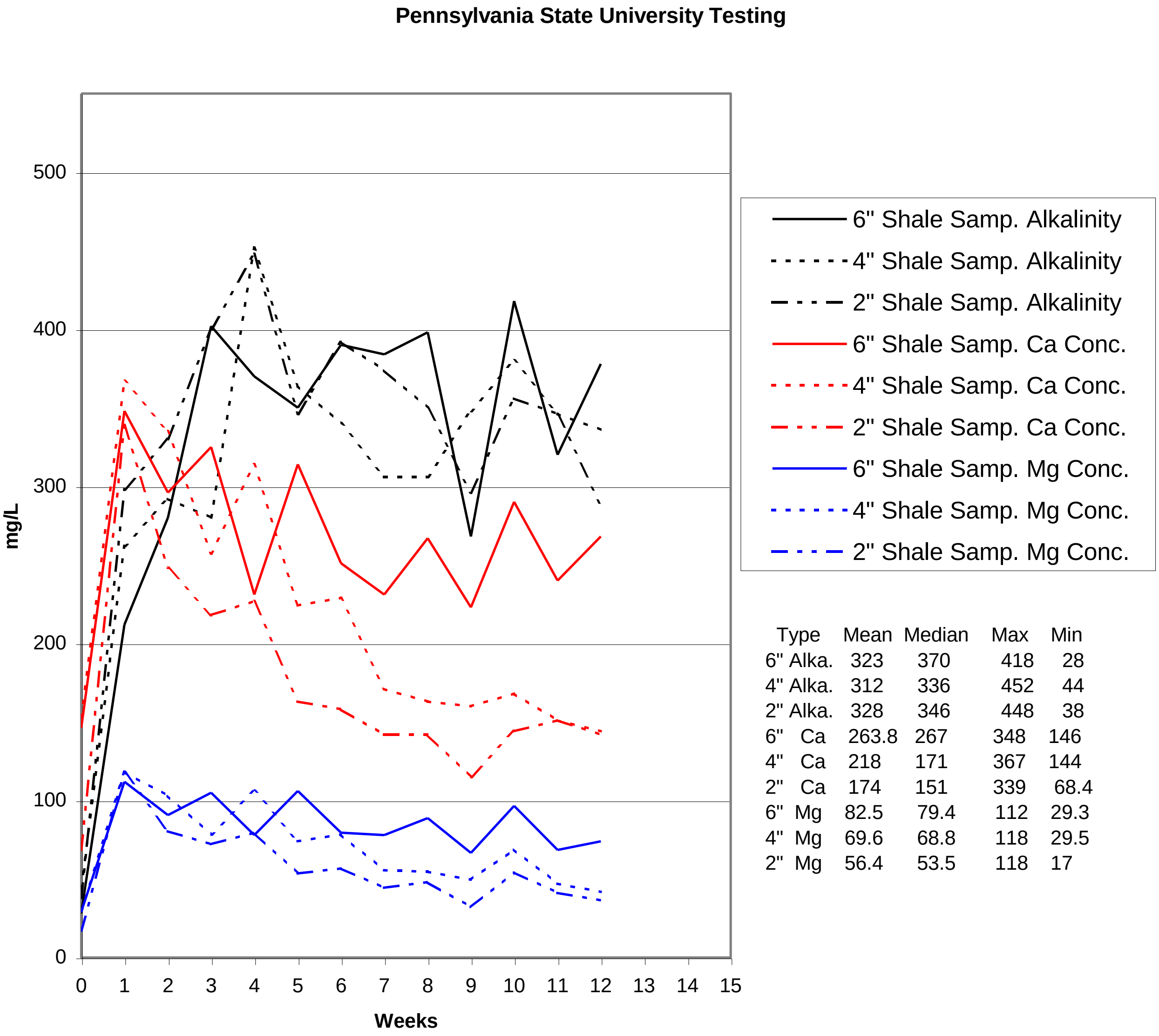


Figure 5b. Effects of fine particle fractions on alkalinity in shale.

Fig. 5b 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 Fig. 5b are nearly identical, and represent consistently higher alkalinity concentrations than the pairs of columns and humidity cells with CO_2-saturated 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. These relationships are discussed in more detail in Brady et al. (2004), Geidel (1979) and Hornberger and Brady (1998).

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 Fig. 6. 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.



Type	Mean	Median	Max	Min
6" Alka.	323	370	418	28
4" Alka.	312	336	452	44
2" Alka.	328	346	448	38
6" Ca	263.8	267	348	146
4" Ca	218	171	367	144
2" Ca	174	151	339	68.4
6" Mg	82.5	79.4	112	29.3
4" Mg	69.6	68.8	118	29.5
2" Mg	56.4	53.5	118	17

Figure 6: Comparison of Column Sizes Using Shale Samples (Laboratory 3)

Conclusions

The ideal kinetic test procedure will accurately represent the alkalinity and acidity producing system behavior of coal overburden strata and refuse. The procedure also would provide useful prediction data on metals and other analytes of interest. The following conclusions, based on two years of evaluation data, can be used to revise and improve method procedures toward this goal:

1. Evaluation of two years of data from the ADTI-WP1 and ADTI-WP2 methods development process indicate that the ADTI-WP2 leaching column method is superior to the ADTI-WP1 humidity cell method, particularly for rock samples with appreciable amounts of carbonate minerals (i.e. high NP, alkalinity-producing samples). Therefore it was determined that further methods development work would focus on refinement of the leaching column method.
2. The ADTI-WP1 humidity cell method includes a shorter period of saturation than the leaching column method (i.e. 1-hour period of inundation with reagent water per week vs. 24-hour inundation per week), and is intended to model intermittent periods of wetting and drying of coal overburden and coal refuse samples, rather than saturated conditions below the water table at a mine site. Therefore, this humidity cell method may be useful for predicting acidity, sulfate, and metals concentrations at coal refuse disposal sites and other mine environments where periodic rainfall events flush accumulated weathering products from the overburden or refuse materials in unsaturated ground-water flow conditions.
3. Evaluation of gas handling procedures and gas mixtures in the 2002 weathering tests clearly proved that increasing the carbon dioxide content in the gas mixture to approximate the P_{CO2} values found in soils, mine spoils and groundwater (i.e. approximately 10% CO_2) is the most important factor in developing a weathering test method that will produce alkalinity concentrations similar to those found in mine drainage discharges, receiving streams and groundwater. (see Figure 2a)
4. Further evaluation of gas handling procedures in the 2003 weathering tests involved comparisons between rock 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. The alkalinity concentrations from the leaching columns with the constant-flow scenario were generally higher (see Figure 4), and the results of paired t-tests indicate that mean concentrations of alkalinity, sulfate, calcium and conductivity were significantly greater for samples exposed to a constant flow compared to those exposed to the CO_2 saturated water. This indicates that the constant flow gas handling scenario produces superior results; however, the CO_2 saturated water scenario is also capable of producing meaningful alkalinity concentrations from high NP (neutralization potential)

rock samples. Regardless of which of these two gas handling procedures is selected in using the draft method or specified in the final method, precautions must be taken in gas handling to ensure consistency in alkalinity results within and between laboratories.

5. The water handling procedures of the leaching column method provide adequate residence time under saturated conditions (i.e. 24 hour saturation) to produce meaningful and realistic concentrations of alkalinity, acidity, sulfates, metals and other analytes of concern. (see Figures 2b, 3, 5a & 5b). For high sulfur samples without appreciable carbonate minerals (e.g. the coal refuse samples), the patterns of variation and concentration ranges for the CO_2 enhanced gas mixture humidity cells were generally similar to those of the air-only cells. This demonstrates that the CO_2 enhanced gas mixture in the apparatus, as necessary for significant carbonate dissolution, is not detrimental to weathering conditions for non-carbonate rock samples.
6. Relative percent differences (RPDs) between duplicate samples were calculated to evaluate differences within and between laboratories, and relative standard deviations (RSDs) were calculated to perform variance ratio (F-tests) of whether pooled RPDs between laboratories were statistically significant. Data were normalized to account for the differences in the volume of the leachate sample collected and the weight of the rock sample exposed to weathering. While conceptually meaningful, this normalization step did not uniformly improve the interpretation of the data.
7. An evaluation of the presence and abundance of iron-oxidizing (*Thiobacillus ferroxidans*) bacteria in the leachate drawn from the weathering test apparatuses during the 2002 tests demonstrated that it is not necessary to inoculate the rock samples with these bacteria in order to produce meaningful results, nor is it necessary to include the determination of the most probable number of bacteria present (MPN) in the method. These iron-oxidizing bacteria are ubiquitous in the mine environment and in rock samples with appreciable total sulfur contents.
8. It is believed that providing a standardized particle size distribution for samples exposed to weathering procedures is necessary to promote operational consistency of the test method, and facilitate evaluation of pollutant generation and reaction kinetics. Although such standardization may not be representative of actual field conditions, it is not practical to evaluate actual particle-size distributions found in the field. Because of the

physical limitations inherent to any humidity cell or leaching column procedure (i.e., laboratory, bench-scale test vs. field test), particle size distribution in the samples is largely an artifact of the crushing process that is necessary to produce samples that can be evaluated. The removal of the fine particle size fraction from one of the leaching columns caused a greater effect on sulfate production from the Brush Creek shale sample, than the effect on alkalinity production from the same shale sample (see Figure 5a and 5b).

Conclusions drawn from the data produced during the two studies discussed in this paper are being used, along with numerous valuable observations made by the laboratory analysts involved, to revise the draft leaching column method for further evaluation. The draft method also is currently undergoing review by experts from state and federal agencies, academia, and industry. These and other review comments are being evaluated and will be used to improve application of the method for use in providing a standardized tool for predicting the pollutant-producing behavior of coal mine overburden and refuse. The current version of the draft methods is included in the ADTI-CMS website http:/wvwri.nrcce.wvu.edu/ADTI.

It is anticipated that additional evaluation and development of this test procedure will be necessary. Further potential method evaluation includes: additional evaluation of the effects of particle size distribution and corresponding surface area on reaction kinetics; additional evaluation of the removal of particle fines to facilitate method implementation; further evaluation of effects of leaching column diameter and related factors (e.g. differences in rock sample mass and leachate volumes) upon analyte concentrations: and evaluation of method performance in an interlaboratory study involving multiple laboratories evaluating identical samples; and evaluation of the generation of additional pollutants.

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Appendix A.

Table 4a. Examples of leachate concentrations from weathering tests at Labs 1, 2, & 3.

Lab	Rock	App/Gas	Week	pH	Sp.Cond. *(uS/cm)*	Alk. *(mg/L)*	Acidity *(mg/L)*	SO4 *(mg/L)*	Fe *(mg/L)*	Mn *(mg/L)*	Al *(mg/L)*	Ca *(mg/L)*	Mg *(mg/L)*
1	SH	LCF	1	6.7	2570	436	0	1310	0.01	1.48	0.02	367	164
1	SH	LCF	13	6.8	1310	508	0	297	0.01	0.4	0.01	199	69
1	SH	LCS	1	6.8	2200	366	0	1102	0.27	1.09	0.02	324	142
1	SH	LCS	13	6.8	1120	478	0	230	0.77	0.41	0.02	198	60.3
1	SH	HC	1	6.8	1300	292	0	495	0.01	0.6	0.01	178	70.4
1	SH	HC	14	6.6	1140	446	0	333	0.01	0.07	0.01	154	59.5
1	SH	LXF	13	6.6	1100	514	0	203	0.01	0.64	0.01	171	54.3
2	SH	LCF	1	6.3	1120	516		830	0.16	0.57	<0.1	285	113
2	SH	LCF	1	6.4	1910	465		1000	0.06	1.48	<0.1	388	133
2	SH	LCS	4	6.6	1780	339		690	0.07	1.63	<0.1	257	85.3
2	SH	LCS	1	6.4	1610	366		760	<0.05	1.24	<0.1	292	94
2	SH	HC	8	6.5	1550	319		640	<0.05	1.46	<0.1	243	79.6
3	SH	LC6	3	6.55	1984	402		760	1.2	1.14	<0.2	325	105
3	SH	LC4	4	6.59	1726	452		500	0.1	1.32	<0.2	314	106
3	SH	LC2	4	6.62	1384	448		350	0.05	1.12	<0.2	227	79.4
1	LS	LCF	1	6.7	939	616	0	59	0.01	0.04	0.01	172	14.5
1	LS	LCF	14	6.5	920	498	0	34	0.01	0.01	0.01	151	4.62
1	LS	LCS	1	6.7	763	420	0	50	0.78	0.05	0.03	140	11.4
1	LS	LCS	14	6.7	809	394	0	38	0.21	0.02	0.01	137	6.89
2	LS	LCF	1	6.5	786	495		41	<0.05	1.31	<0.1	156	23.1
2	LS	LCS	4	6.6	2040	393		150	5.39	1.09	0.4	139	18.9
1	CR	LCS	12	1	81600	0	33700	37404	9120	17.4	109	58.2	46.4
1	CR	HC	1	2.8	2620	0	900	1487	342	3.04	15.1	178	41.2
1	CR	HC	2	1.8	21800	0	10300	11497	3181	11.3	67.3	265	82.1
1	CR	HC	11	1.3	66000	0	28000	28059	7771	18	124	117	60.3
2	CR	LCS	8	1.2	35300	<5	24999	21000	8390	51.2	128	46.7	51.2
2	CR	HC	1	2.3	4230	<5	2684	3100	969	3.87	25.1	118	33.6
2	CR	HC	9	1.3	24300	<5	27703	26000	9340	14.6	101	35.6	37.3
3	CR	LCF	0	2.73	470	0	247.8	427.7	171	2.84	10.7	121	34.5
3	CR	LCF	1	2.21	>1990	0	6208.6	5986.7	2090	9.44	79.1	378	108
3	CR	LCF	8	1.88	23930	0	26062	24516.9	9480	10.9	105	69.5	54.3

Appendix B.

Table 4b. Laboratory RPD comparison.

Sample Type	Method	Parameter	Result Type	Lab 1 RPD	Lab 2 RPD	Significant Difference?	p-value
Shale	Cell	Alkalinity	Concentration	6.4%	50.1%	Yes	<0.0001
			Normalized	9.0%	48.8%	Yes	<0.0001
		Sulfate	Concentration	23.8%	21.1%	No	0.3308
			Normalized	23.7%	26.0%	No	0.3640
		Calcium	Concentration	11.2%	17.9%	Yes	0.0451
			Normalized	14.2%	22.4%	Yes	0.0486
		Conductivity	Concentration	8.8%	15.3%	Yes	0.0248
			Normalized	14.4%	19.9%	No	0.1183
	Column (Saturated)	Alkalinity	Concentration	6.3%	31.2%	Yes	<0.0001
			Normalized	9.6%	20.2%	Yes	0.0045
		Sulfate	Concentration	9.1%	14.5%	Yes	0.0468
			Normalized	11.7%	41.3%	Yes	<0.0001
		Calcium	Concentration	9.1%	10.1%	No	0.3540
			Normalized	8.5%	36.5%	Yes	<0.0001
		Conductivity	Concentration	3.8%	6.5%	Yes	0.0265
			Normalized	7.5%	32.0%	Yes	<0.0001
	Column (Constant Flow)	Alkalinity	Concentration	3.3%	22.9%	Yes	<0.0001
			Normalized	16.3%	50.2%	Yes	<0.0001
		Sulfate	Concentration	18.9%	23.4%	No	0.2179
			Normalized	10.2%	31.6%	Yes	<0.0001
		Calcium	Concentration	9.4%	18.7%	Yes	0.0072
			Normalized	13.9%	40.0%	Yes	0.0002
		Conductivity	Concentration	5.6%	29.2%	Yes	<0.0001
			Normalized	10.9%	46.8%	Yes	<0.0001
Coal Refuse	Cell	Acidity	Concentration	41.5%	12.0%	Yes	<0.0001
			Normalized	47.0%	11.1%	Yes	<0.0001
		Sulfate	Concentration	37.8%	15.2%	Yes	0.0008
			Normalized	44.5%	14.1%	Yes	<0.0001
		Iron	Concentration	36.4%	11.8%	Yes	<0.0001
			Normalized	43.1%	11.0%	Yes	<0.0001
		Manganese	Concentration	34.4%	10.0%	Yes	<0.0001
			Normalized	40.5%	11.3%	Yes	<0.0001
		Calcium	Concentration	22.2%	21.1%	No	0.4278
			Normalized	32.6%	21.5%	No	0.0661
		Conductivity	Concentration	35.7%	7.0%	Yes	<0.0001
			Normalized	41.1%	8.5%	Yes	<0.0001
	Column	Acidity	Concentration	29.1%	25.4%	No	0.3072
			Normalized	22.6%	26.7%	No	0.2703
		Sulfate	Concentration	32.2%	31.6%	No	0.4735
			Normalized	22.7%	32.4%	No	0.0961
		Iron	Concentration	25.4%	37.4%	No	0.0795
			Normalized	20.9%	39.8%	Yes	0.0109
		Manganese	Concentration	19.8%	23.8%	No	0.2465
			Normalized	16.7%	19.4%	No	0.2912