ADTI-WP2 LEACHING COLUMN METHOD FOR OVERBURDEN ANALYSIS AND PREDICTION OF WEATHERING RATES

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Introduction and Background

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. 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 field results. Additional background information on the ADTI and the process of developing these standard kinetic test methods is found in Hornberger and Brady (1998), Geidel et al. (2000) and Hornberger et al. (2000).

The objectives of this current project are: (1) standardizing 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).

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 (Hornberger et al., 2003).

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. The three laboratories that participated in the study were Geochemical Testing and Mahaffey Laboratory, Ltd. of Grampian, PA and The Materials Research Institute at Penn State University (Hornberger et al., 2004; Brady et al., 2004).

For purpose of the case studies in this paper, only data from Mahaffey Labs were used for both simplicity, because of the total mass of data available, and because only they have conducted the testing on the noncoal bearing rocks discussed herein. 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.

Basic Description of ADTI-WP2 Leaching Column Method

The leaching columns were constructed from 6-inch diameter clear polycarbonate plastic tubing in accordance with the design specifications shown in Figure 1.

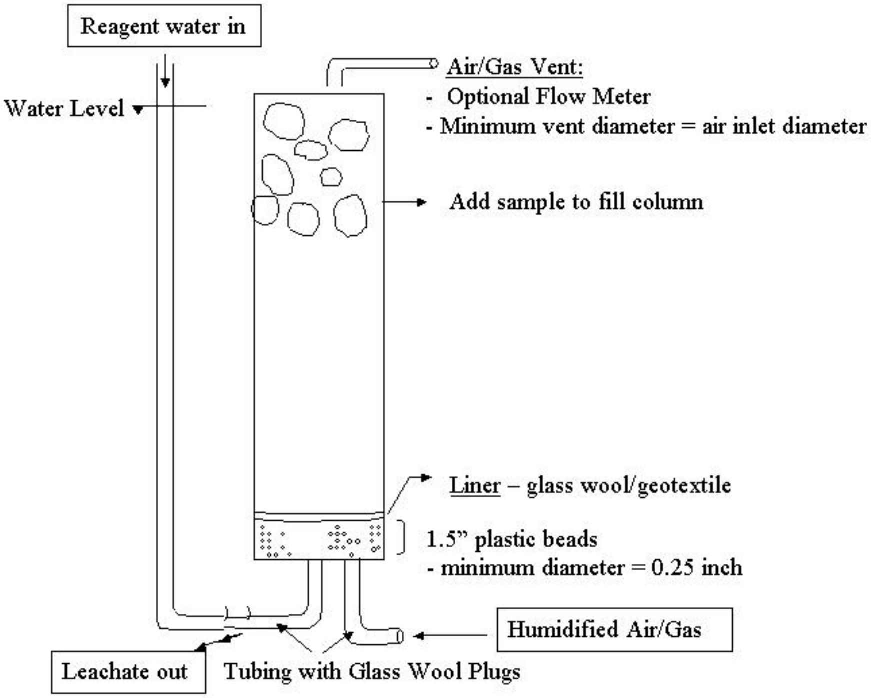

Figure 1. Leaching Column Schematic Drawing.

The rock samples were crushed to a nominal maximum size of 3/8" 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), #16 (1.19 mm), #35 (0.50 mm), and #60 (0.250 mm) sieve sizes) to yield 7 particle size classes (i.e. including >3/8" (9.52 mm) and <60 (0.250 mm) fines). The homogenized sample was then chemically analyzed for percent total sulfur and neutralization potential. The reconstruction of the particle size distribution following the crushing of each rock sample was included in the method 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. 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 1, would promote operational consistency of the weathering test procedures and facilitate better control in determining reaction kinetics. Regarding the determination of reaction kinetics, the importance of surface area to volume ratios is described in 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 1. 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

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-WP2 simulated weathering procedure consists of alternating cycles of saturation (i.e., water inundation) and unsaturation (drained) with circulated humidified, CO_2-enriched 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 inter-leach 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 (distilled, deionized) is introduced through the water inlet port at the bottom of the column (shown on Figure 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. Under unsaturated conditions, such as during the six days in which the humidified air is flowing through the unsaturated column, oxidization of pyrite to soluble sulfate minerals occurs (Cravotta, 1994; Hammarstrom, et al. 2004).

Following this first and each successive humidified air cycle, reagent water 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).

Surface Area Considerations

Protocols outlined in this paper establish a leaching procedure that includes sieving, and construction from specified sieve fractions of a common particle size distribution across laboratories for each rock type. Further, the surface area of the rock was determined both before and after the leaching cycle was completed. With these data, an effective surface area of materials that were leached could be calculated for each column removing the necessity that each laboratory identically pack each column, a nearly impossible requirement for any protocol.

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 measures the accessible surface of the rock to N_2 gas molecules. Additional discussion of the significance of surface area measurements, surface area to volume rations and their relationships to reaction kinetics is given by Pedersen et al. (1983), Scheetz et al. (1981), and White (1986).

Surface areas were measured on the composite sieve fractions and at the completion of the testing, the rock was again sieved and remeasured. The bulk surface areas of rock were determined by taking the individual masses of the sieve fractions, multiplying each mass by the surface area (SA), and combining their fractional percent of the total as a weighted linear average. The standardized particle size distribution is an integral part of the ADTI-WP2 method. The measurement of surface areas by BET techniques is not a required task in the ADTI-WP2 method, but was used in this study to gain additional significant information about the weathering process.

Description of rock samples used in this study.

The *Brush Creek shale* was selected because it has moderately high total sulfur and NP values classifying it as a "gray zone" type of sample. The samples were collected at the same site, an outcrop near Greensburg, PA, as USGS standard sample SBC-1. Thus, extensive geochemical and mineralogical characterization is available. Also, the site stratigraphy is well understood (Skema, 1995) 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 %. The NP ranges from 121 to 139 parts per thousand (ppt).

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 has one of the highest alkalinity concentrations in the state (>400 mg/L $CaCO_3$) (Hornberger and Brady, 1998; and Brady et al., 1998). The NP ranges from 256 to 282 ppt and the total sulfur is negligible (<0.02%).

Leechburg coal refuse samples were collected from refuse deposits associated with abandoned and active underground mines on the Lower Kittanning coal near Apollo in Armstrong County, PA. The 2002 weathering tests were conducted on samples collected from the abandoned coal refuse piles (sulfur 2.42 and 4.38%). The 2003 weathering tests were conducted on samples of fresh refuse from the active underground mine (total sulfur >6.5%).

Bald Eagle Sandstone. The deposit at Skytop, about 12 miles NW of the Pennsylvania State University, is located predominantly in the Bald Eagle sandstone with minor contributions in the Reedsville shale, the Juniata shale and the Tuscarora sandstone. The deposit is controlled by a linenament cross cutting the strike of the Bald Eagle Ridge with a width of approximately 300 meters. The deposit is in the form of a highly disseminated fracture fill. Estimates of the concentration of pyrite in this deposit of between 4 to 5% by weight of pyrite have been made by (Gold and Doden, 2005).

Table 2 shows the particle size distributions for the Brush Creek shale and Wadesville sandstone samples used in the 2002 weathering tests and the coal refuse sample. 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 1. 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. 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. This change is largely due to the reduction in surface area of the two finest size classes (Table 2). Two factors probably contributed to this reduction: (a) loss of fines during weekly sample collection and (b) weathering of fine-grained pyrite.

Table 2. 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
Wadesville 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
Bald Eagle Sandstone	#4	2.70	--	42.04	--		--
	#8	2.64	--	24.86	--		--
	#20	2.28	--	9.56	--		--
	#40	2.37	--	10.39	--		--
	#60	2.84	--	4.26	--		--
	<60	3.19	--	8.90	--		--
						2.66 m^2/g	--

Significance of Carbon Dioxide (PCO$_2$) on Carbonate Mineral Dissolution

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). Several experiments conducted at the laboratories involved in the method development process during 2002 and 2003 have demonstrated the importance of controlling the partial pressure of CO_2 in the leaching columns, as described below. Calculated PCO_2 values (Hornberger et al., 2003), showed 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.

A principal part of method development in 2002 was the evaluation of CO_2-enriched air versus atmospheric air on alkalinity generation. In Figure 2 for the shale leaching columns, 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. As a result of these findings method development in 2003 used only CO2-enriched air.

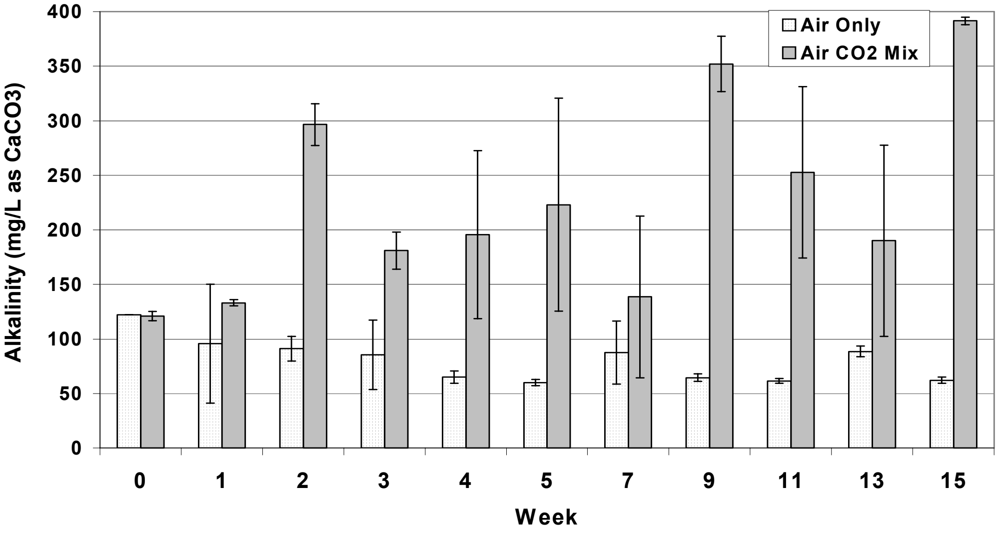

Figure 2. Graph illustrating the increase in alkalinity in shale leaching columns as result of enhanced concentrations of CO_2. Atmospheric air (Air Only) is about 0.03%. The "Air CO2 Mix" had a targeted 10% CO_2 enrichment. The histograms in Figure 2 depict the average or median values of alkalinity for each week, the bar diagrams in the top center of each histogram represent the range in alkalinity concentrations of the 2 duplicate samples

In the 2003 experiments, A comparison was made of the concentration of alkalinity for columns that had constant flow of CO_2-enriched air through the water saturated column, versus columns that had water saturated with CO_2 prior to being added to the column, but with no additional CO_2 added during the leaching cycle. Paired t-tests indicate that mean concentrations were significantly greater (at 99% confidence) for samples exposed to a constant CO_2 flow compared to those exposed to the CO_2-saturated water. The alkalinity concentrations produced by the constant CO_2-flow scenario generally were 50 to 100 mg/L higher than the CO_2-saturated water scenario.

The partial pressure of carbon dioxide in the leaching columns in 2002 was calculated through geochemical modeling using a spreadsheet developed by Dr. Charles A. Cravotta of USGS (personal communication). The equilibrium computations used 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. In general, the columns were supersaturated, or nearly saturated with respect to calcite. Box plots of these saturation indices are shown in Hornberger et al. (2003). Figure 3 is a comparison of calculated P_{CO_2} among the three labs for the columns with continuous air flow, which showed that the goal of maintaining 10% CO_2 was generally achieved at each lab. The values greater than 10% are probably due to the sample creating additional CO_2 from the acid from pyrite oxidation reacting with carbonate minerals.

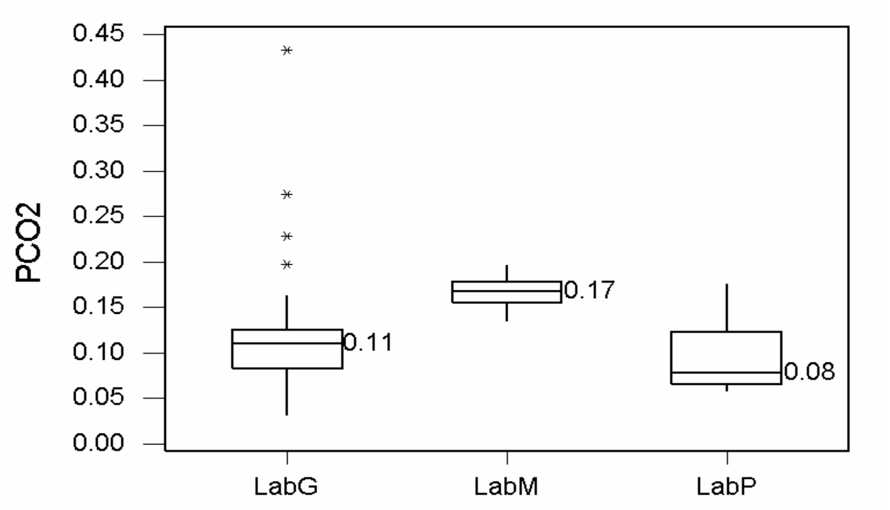

Figure 3. Comparison of P_{CO_2} among laboratories for the leaching columns that had continuous flow of 10% CO_2-enriched air. Horizontal lines within the "boxes" are medians and the values are plotted next to the box. The "boxes" extend from the 25th to 75 percentile of data and thus encompass the 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.

The time plots in Figure 4 show the highest alkalinity concentrations are produced in the two leaching columns with constant flow of CO_2–enriched air, followed by the two columns with CO_2–saturated influent water. For lab M the duplicates behave very consistently and represent excellent control of the gas-mixture throughout the entire test period.

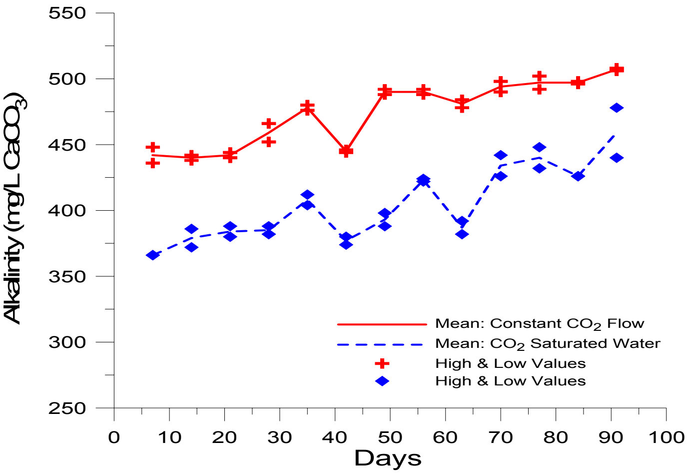

Figure 4. Alkalinity concentrations of Brush Creek shale leaching columns.

Case Study – Coal Mining Related Application : Pyrite and Calcite Leaching Rates of the Brush Creek Shale

Sulfate concentrations through time for the Brush Creek shale are shown in Figure 5. The data (Figure 5) show an initial increase in sulfate concentration followed by a decline, with an eventual leveling out of concentration at about 70 days.

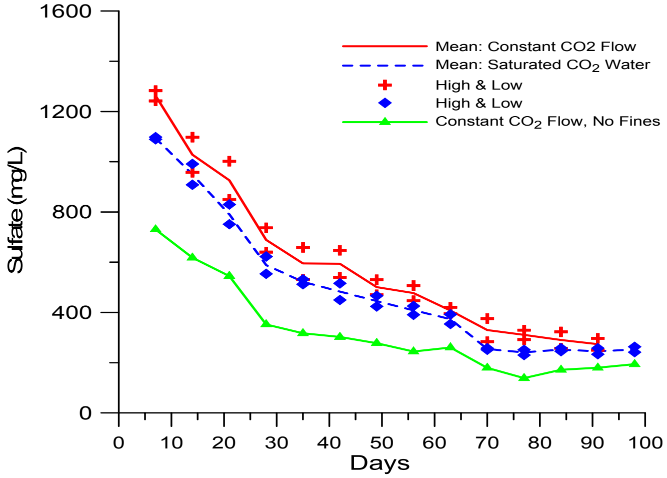

Figure 5. Sulfate concentrations of Brush Creek shale water that had (a) CO_2-enriched water continuously bubbled through the column, with 24 hours of water inundation (red line); (b) water that was initially saturated with CO_2, and water inundation for 24 hours (blue line); and water from a column with the fines removed, but subject to the same conditions as (a) (green line). .

Figure 6 shows a series of plots of the cumulative extracted sulfur as a function of the square root of time. The observed linear fit to the data means that the sulfur fraction, N_S, extracted from the columns can be described by an equation of the form

$$N_S \quad = \quad K t^{1/2} + F$$

In this equation, K is an empirical rate constant and F is a constant that takes account of the observation that the extracted sulfur does not become zero at time equals zero. The F-term is thus a measure of the "first flush" described above. Values for the coefficients K and F are listed in Brady et al. (2004, Table 3). The square root of time dependence in a rate equation usually implies a diffusion controlled mechanism. In the present experiments the oxidation of sulfides at the mineral/water interface, the effect of different particle sizes and surface reactivities, and the transport of dissolved species from the mineral surfaces to the bulk fluid are combined into a single empirical rate expression. This result suggests that chemical reactions at the surfaces of the grains are fast compared to the movement of dissolved species through the pore spaces between the grains.

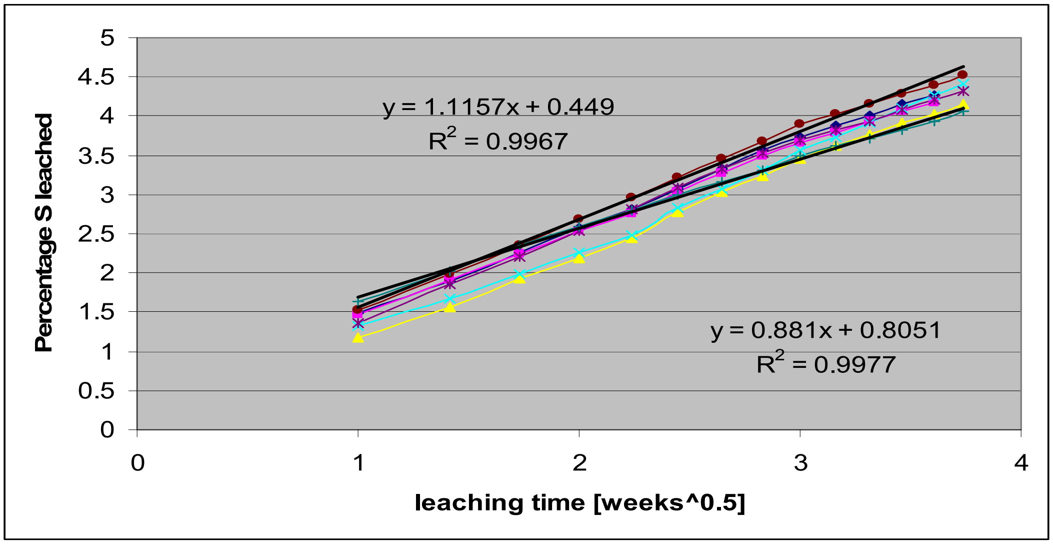

Figure 6. Cumulative % sulfur leached as a function of the square root of time. The two regression equations represent the maximum and minimum from the data sets, (see Brady et al., 2004)

The cumulative percentage of total sulfur and calcium carbonate depleted per week is plotted in Figure 7. Power functions were fitted to these data, and they produced higher coefficient of determination (R^2) values than exponential or linear functions. The total amount of $CaCO_3$ in the columns was determined based on neutralization potential data (ppt $CaCO_3$). The total amount of $CaCO_3$ leached per week was calculated as alkalinity, in mg/L $CaCO_3$, plus alkalinity that was neutralized by sulfide oxidation.

The total amount of sulfur in each column was calculated using the percent sulfur data. . The amount of sulfur oxidized per week was determined from sulfate. The total weight of $CaCO_3$ or S per week was divided by the total mass of $CaCO_3$ and S available in each column. This normalized the data and gave a percentage of the total mass of $CaCO_3$ or S per week. These weekly masses (in percent) were added to get a cumulative percent. In all instances, after 12 to 14 weeks, less than 2 percent of the calcium carbonate had weathered, but four to five percent of the sulfur had weathered. The weekly data were then plotted to determine the type of function (equation for a line) that best fit the data. For more detail on the methods see Brady et al., 2004. Figure 7 shows plots of these data. For both $CaCO_3$ and S the linear and power functions fit the data best.

The fitting of a function through the data allows prediction of results into the future. Figure 8 shows power function best-fit lines extended to six years. The leaching results are plotted to show how closely the data fit the projected line. The results suggest that if the sample were to be leached for 6 years the rate of pyrite oxidation would continue to be greater than that of carbonate dissolution. Considering the fact that the water remained alkaline throughout the test period, which had the highest rates of pyrite oxidation (steepest part of curve), this sample can be expected to produce alkaline drainage long into the future. In fact, the pyrite should be exhausted prior to calcite exhaustion. Presuming that the rates do not change, at the end of six years 16 to 18% of the pyrite would be consumed, whereas only 8 to 10% of the carbonate would be consumed.

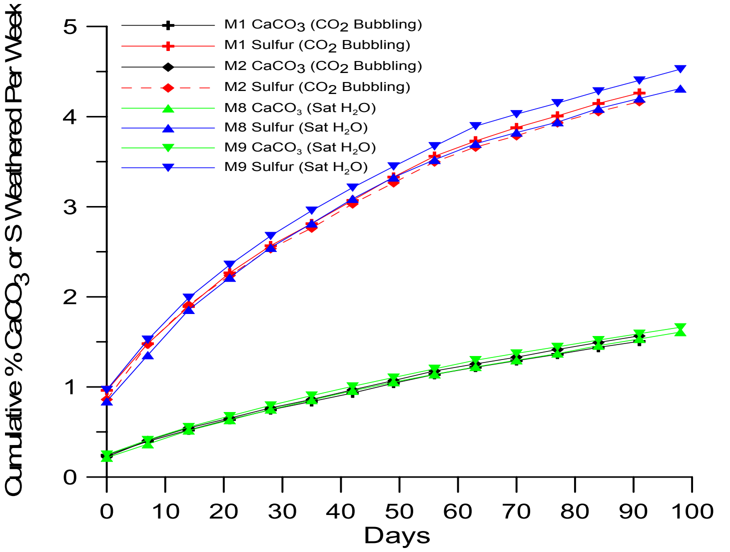

Figure 7. Cumulative percent sulfur and $CaCO_3$ leaching rates per week for all columns.

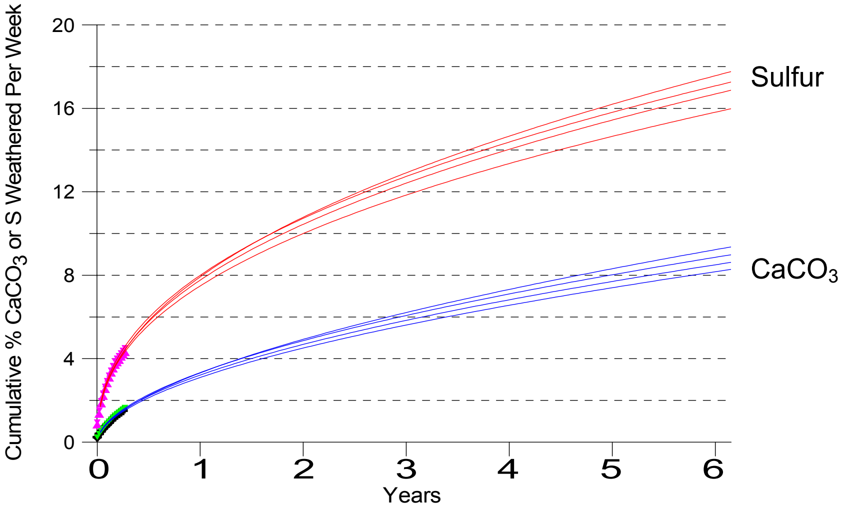

Figure 8. Power function best-fit lines for the cumulative percent $CaCO_3$ and S data for Lab M. Rates are predicted to 6 years.

In conclusion, the surface area of the Brush Creek shale was an order of magnitude greater than that for the sandstone and coal refuse, showing that the surface areas of different types of rocks can be quite different. The surface area after weathering was essentially the same for the sandstone, just slightly less for the shale and limestone, and about half for the refuse. The sandstone is strongly cemented and probably underwent little weathering. Due to the high pyrite content the refuse underwent the most weathering and had the greatest decrease in surface area. Both the limestone and the shale showed some decrease in surface area probably due to the effects of “rounding.” Sulfur weathering of the shale appeared to follow diffusion-controlled kinetics (White, 1986). Carbonate weathering was controlled by reaction with acid from pyrite oxidation products (neutralizing acid) and was limited by calcite saturation.

Case Study Non-Mining Application: Leaching of Hydrothermal Pyrite from the I-99 Corridor in Centre County, PA

During the construction of the final segment of I-99 that connects the PA Turnpike at Bedford with I-80 at Bellefonte to the northeast, a significant deposit of hydrothermal pyrite was unearthed and widely dispersed as sub-base fill in the construction. This material was subjected to the same leaching protocol as the coal-associated rocks that were leached previously. Significant localized environmental impact had occurred from the weathering of the exposed pyrite in fill and the wasted rock associated with a recent highway construction project. Weathering of the Bald Eagle sandstone in the field has produced drainage water with sulfate concentrations in the 10,000's of mg/L, iron and aluminum in the 1,000's of mg/L, zinc in the 100's of mg/L and a pH in the low 2's.

Examination of this very reactive material revealed that some of the pyrite was deposited as tabular crystals over a temperature range of 150 to 250°C (Detrie, et al., 2005) similar to forms described by Murowchick and Barnes (1987). In order to gain a quantitative understanding of the rate of alteration of this very reactive form of pyrite, PENNDOT commissioned a leach test, based on this column leach protocol, that was conducted at Mahaffey Labs. Mahaffey Lab was part of the second year program of the OSM sponsored method development program described above.

Sample preparation

A suite of eight columns were tested with two following the ADTI WP-2 protocol. One column followed the protocol exactly while the second column substituted a 3% hydrogen peroxide solution for water in an effort to evaluate the potential to accelerate the oxidization of the pyrite.

A sample of the Bald Eagle sandstone was collected from a 47,000 ton pile of processed rock that was going to be used for 2A base coarse aggregate. The sample was collected following ASTM D 75 protocol. The entire sample was homogenized by the laboratory in preparation of obtaining a sub-sample for the leach column testing and chemical analyses.

This sub-sample for the leaching columns was crushed and sieved according to protocol. The sieved components were then reassembled into the gradation as specified in the test protocol resulting in a BET measured surface area of $2.65m^2/g$.

The sandstone samples had a weathered appearance with a gray/green color. Significant amounts of a chlorite clay are present in the sandstone.

The sulfur content of the whole rock sample was 1.3 weight percent. All leachate samples were tested for acidity, alkalinity, specific conductance, pH upon collection. The leachates were analyzed for total metal and dissolved metal for the following elements: Al, As, Cd, Ca, Co, Cu, Fe, Mg, Mn, Ni, Se and Zn. Sulfate was the only anion tested, and the only one of consequence. All column leach testing was conducted in 6 inch diameter transparent columns

Results of the column leach tests

The 12 weeks leach testing has been completed. For the purposes of brevity, only sulfur will be discussed below. The leach data for the two test columns are presented in Figure 9. Column #1 followed the test protocol exactly while column #2 used a 3% hydrogen peroxide solution. These data are on non-replicated columns but appear to show that the peroxide is indeed strongly influencing the dissolution of the pyrite as anticipated. On average, the peroxide is removing 33% more sulfur.

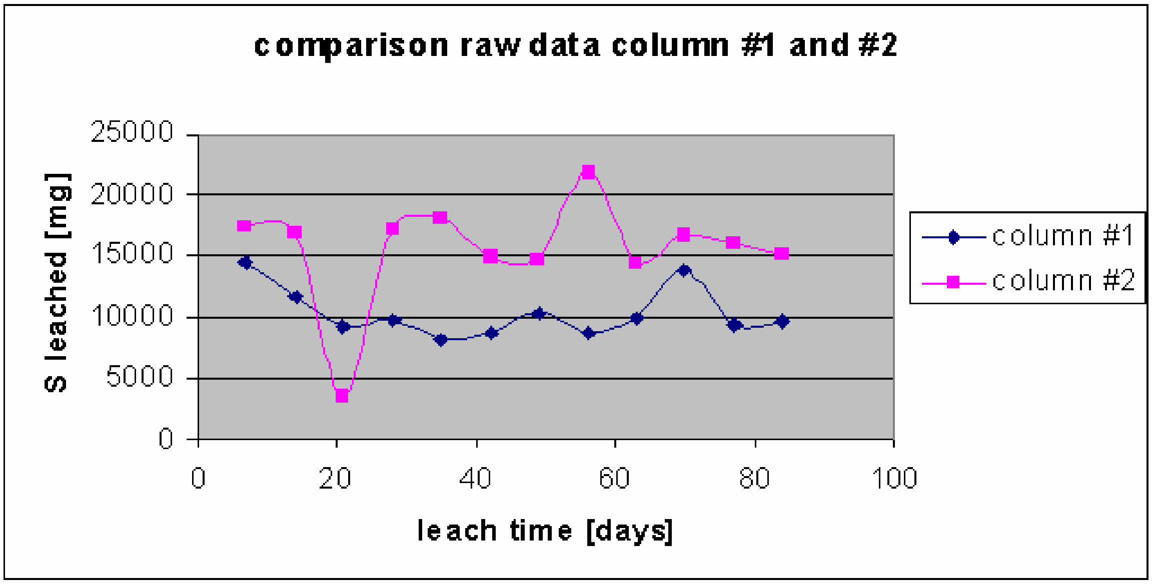

Figure 9. Weekly concentration of sulfur leached with and without 3% hydrogen peroxide following ADTI WP-2 protocol. Column #2 is with H_2O_2.

Examination of the specific conductance data, Figure 10, reveals a similar pattern where the peroxide column appears to be leaching at about 33% more than the column utilizing water. Integration of these data from columns #1 and #2 shows that the release of sulfur with time during this 12-week test follows a linear behavior, expressed in Figure 11. Table 3 summarized the statistics for these fits to these cumulative sulfur data sets.

Table 3. Dissolution rates and goodness of fit calculated for K_{gross}.

column	Fit equation	Rate [mg/day]	R^2
#1	y = 1398.6x + 14625	1399	0.9981
#2	y = 2370.1x - 11123	2370	0.9992

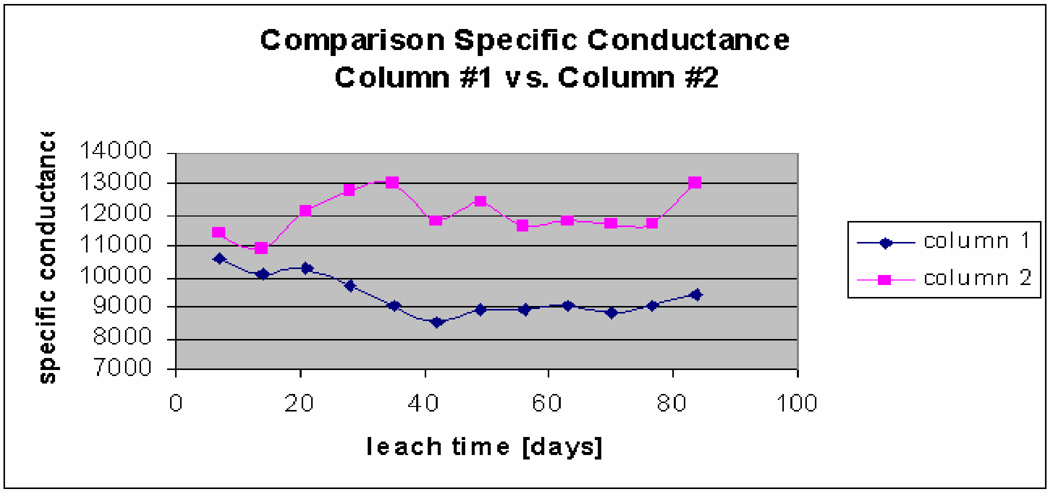

Figure 10. Week measurements of specific conductance for columns with and without 3% hydrogen peroxide leachant.

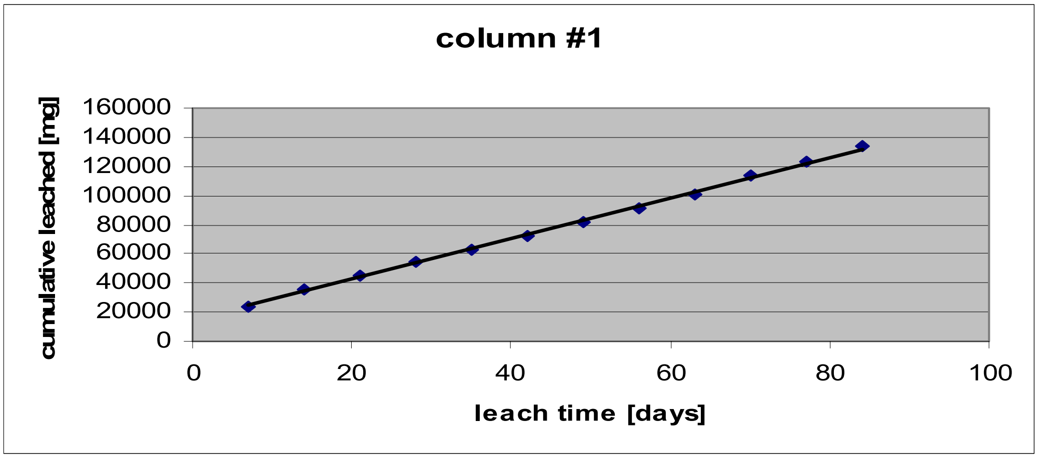

Figure 11. Cumulative leach results for S from I-99 pyrite following ADTI WP-2 leach protocol.

The rate of sulfur release can be described by a zeroth order rate equation of the form:

$$dC/dt = K_{gross}$$

where: C = concentration of sulfur
t = time [days]
K_{gross} = rate constant.

This rate constant can be refined to include a normalization of the leach rates to the surface area of the sandstone to the volume of leachant and to the inventory of sulfur that was leached from the stone. The form of this normalization is:

$$K_{gross} = [SA/V] \times [A/A_o] \times k = dC/dt$$

where: C = concentration of sulfur
t = time [days]
K_{gross} = rate constant.
SA = BET surface area of sandstone

V = volume of leachate
k = the normalized rate constant.
A = the amount of each element detected in solution
A_o = the total amount of element in the starting unleached solid.

When the data in Table 3 and Figure 11 are processed through this normalization procedure, the following dissolution rates result, Table 4:

Table 4. Comparison of K_{gross} and normalized dissolution rate constants for sulfur.

column	Rate [mg/day]	Normalized Rate [mol/m^2/sec]
#1	1399	3.45×10^{-10}
#2	2370	3.37×10^{-10}

These data sets clearly demonstrate the inaccuracies that accompany most leach testing which rely only on one or two test intervals and take no account of the surface area to volume ratio. On face value, the peroxide would appear to have a leach rate nearly twice that of the column using just deionized water. When the details that contribute to the leaching mechanism are taken into consideration, it is clear that the oxidization of the pyrite, in this example, is not the rate limiting step and the use of peroxide is ineffective as an accelerating step. As such column #2 is acting as a replicate for column #1.

The usefulness of this approach will allow a direct and quantitative comparison of sulfur release from different geo-media, the goal for the development of this test protocol in the first place. In testing under the OSM contract, a worst case coal refuse from Leechburg was subjected to the identical protocol as the I-99 sandstone. These data also exhibited a linear dissolution behavior for sulfur with time. Analysis of the coal refuse utilizing the same modeling procedure suggest that the worst case coal refuse that we could find leaches at about two orders of magnitude less than the hydrothermal pyrite from I-99, Figure 12.

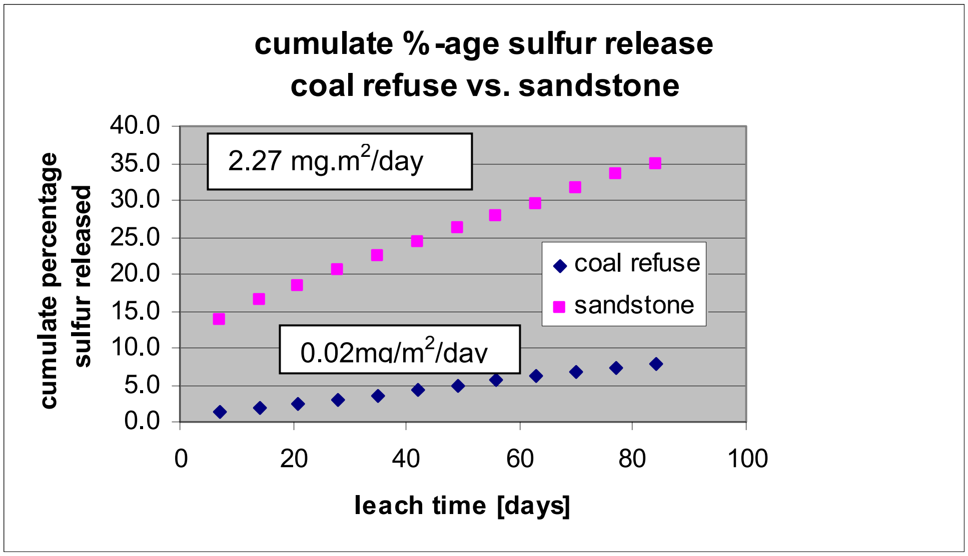

Figure 12. Comparison of leach rates between Leechburg coal refuse and I-99 sandstone.

Conclusions

1. The ADTI-WP2 leaching column method produces realistic concentrations of acidity, alkalinity, sulfates and metals that are directly comparable to the concentrations produced from rock weathering in the mine environment and the natural environment.

2. The laboratory performance data from the 2002 and 2003 method development work and the case studies described in this paper show good repeatability for results from duplicate samples in 6-inch and 2-inch diameter leaching columns.

3. To evaluate and compare weathering rates from different rock types, it is critically important to normalize the leaching data. As a step toward normalization a standardized particle size distribution was specified in the method, BET surface areas were measured, and surface area to volume ratios were calculated.

4. The evaluation of weathering data for the percent sulfur leached through time for the Brush Creek Shale, the Lower Kittanning coal refuse and the Bald Eagle Sandstone indicate some differences in the leaching processes for these pyritic samples. The sedimentary pyrite in the Brush Creek shale exhibits a square root of time dependence, which suggests a diffusion-controlled process. The abundant megascopic pyrite in the Lower Kittanning coal refuse (sedimentary pyrite) and on the joint faces of the Bald Eagle sandstone (hydrothermal pyrite) conform to a simple linear process apparently due to the readily available pyrite on the rock surfaces.

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