

STANDARD WEATHERING PROCEDURE FOR COAL OVERBURDEN, INTER-LABORATORY STUDY OF LEACHATE COMPOSITION¹

Eric F. Perry², Joan Cuddeback, Keith B. C. Brady and Roger J. Hornberger

Abstract. Simulated weathering tests are used to estimate leachate quality from rocks containing varying concentrations of pyrite and carbonates at mines. Five rock samples of coal overburden materials were subjected to a standardized column leaching test at eight commercial, university and government laboratories. Splits from sized, homogenized bulk samples were loaded in duplicate columns, incubated under humid air containing 10% CO₂, and leached every 7 days for a 14 week period. Leachates were analyzed for mine drainage parameters including acidity, alkalinity, metals, sulfate and selected trace elements.

Relative percent difference (RPD) and relative standard deviation (RSD) statistics show the variation within individual labs and among the group of labs. Fe, Al, Se, Zn and Acidity exhibited the greatest variability in results across all rock samples and labs. RPD's usually exceeded 30% for these parameters. The variation in Fe and Acidity increased with weathering duration. Ca, Mg, Na, SO₄, and specific conductance were the most consistent parameters. Mass weighting the chemical concentrations to account for differences in sample mass and leachate volumes did not noticeably improve the RPD and RSD statistics. Cumulative quantities leached were, however, consistent among labs for most parameters.

About 2 to 6 % of the total sulfur present in the rocks was leached during the test. One rock sample was near saturation for gypsum, and some sulfate may have been retained in the column. Acid neutralizing capacity was depleted at a faster rate than acid producing potential. Carbonate dissolution varied, with 3 of 5 rocks producing solutions that were saturated for calcite, while two rocks produced under-saturated solutions. Four of five rocks had less than 5 % of total Ca and Mg leached, with similar or smaller leaching fractions for other elements. More than 90% of the iron mobilized by pyrite weathering was retained in the column for all samples. One acid forming sample leached elements more aggressively than the rocks producing neutral leachates.

The inter-lab results show that the standard column test can yield consistent estimates of mine water composition, and differentiate the behavior of various rock and mineral assemblages.

¹Paper was presented at the 2008 National Meeting of the American Society for Surface and Reclamation, Richmond VA, *New Opportunities to Apply Our Science* June 14-19, 2008.

R.I. Barnhisel (Ed). Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

² Eric F. Perry, Hydrologist, Office of Surface Mining, 3 Parkway Center, Pittsburgh, PA, 15220; Joan Cuddeback, Senior Project Manager, Chemistry Studies, Computer Sciences Corporation, Alexandria VA 22304; Keith B.C. Brady, Geologist, Chief, Surface Mining Section, Pennsylvania Dept. of Environmental Protection, Harrisburg, PA 17105; Roger J. Hornberger, District Mining Manager (retired), Pennsylvania Dept. of Environmental Protection, Pottsville, PA, 17901.

Proceedings American Society of Mining and Reclamation, 2008 pp 807-836

DOI: 10.21000/JASMR08010807

<http://dx.doi.org/10.21000/JASMR08010807>

Introduction

Simulated weathering tests are used to estimate leachate quality of rocks containing varying concentrations of pyrite and carbonates at mines. This study reports the inter-laboratory results from the third phase of a three part effort to develop a standardized, reproducible simulated weathering test for coal mine overburden. Initial development in phases I and II included evaluation of different test apparatus, effects of particle size, gas composition, leaching frequency and other variables. Phases I and II results are reported by Brady et al (2004) and Hornberger et al (2004). In Phase III, a standard column leaching protocol was used by eight commercial, government and university labs to test five rocks of different lithology, pyrite and carbonate content.

Ideally, a simulated weathering test should have three characteristics to be useful in mine drainage studies. These include the capability to produce repeatable results, accuracy in simulating field conditions, and a concise test protocol of weeks to a few months.

Simulated weathering, or kinetic testing, produces an effluent that simulates mine drainage composition. This can be beneficial for predicting mine drainage quality in comparison to whole rock analyses. The effluent may be tested for the same water quality parameters as the drainage produced during mining, such as pH, acidity, alkalinity, SO_4^{2-} , Fe, Mn, Al or other parameters. If the physical, chemical, and biological conditions of the kinetic tests are representative of those found in the mine environment, leachate composition may be used to estimate the water quality parameter concentrations produced during mining.

Hornberger and Brady (1998), and Geidel et al (2000), compiled comprehensive chapters on kinetic tests for mine drainage prediction. These sources included: (1) a chronology and synopsis of scientific literature on these kinetic tests as they have developed over approximately 50 years, (2) discussion of the influence of physical, chemical, and biological processes, and (3) general guidelines for test procedures, data interpretation, and recommendations for further research to develop standard methods. Most of the kinetic test methods in use today were substantially developed and applied more than 40 or 50 years ago, including leaching columns (Braley, 1949), humidity cells (Hanna and Brant, 1962), Soxhlet reactors (Pedro, 1961), and field scale tests (Glover and Kenyon, 1962).

The most commonly used kinetic tests for mine drainage prediction are leaching columns and humidity cells. While these kinetic test methods and others have been used in hundreds of mine-

drainage studies as shown in Hornberger and Brady (1998) and other references (e.g. Sorini, 1997), they have rarely been used in coal mine permitting by either regulatory agencies or the mining industry. The major impediment to routine use of kinetic test methods is the variation in the design and operation of these kinetic tests, and lack of a standardized, accepted (e.g. by EPA or ASTM) test method. Interpretation and data comparison from different studies can be difficult.

Methods

Five rocks of varying lithology, mineralogy, carbonate and pyrite content were collected in bulk from Pennsylvanian age coal measures in Pennsylvania, West Virginia and Indiana. Mineralogical composition of the samples was characterized in detail by Hammerstrom et al (in press) using optical, X-ray diffraction, scanning electron microscopy and electron microprobe methods. Acid-Base Accounting (Sobek et al 1978; Skousen et al, 1997, Kania, 1998) was performed on bulk samples for % total sulfur (%S) as a measure of pyrite and potential acid generation, and Neutralization Potential (NP) as an index of carbonate content. A modified NP test, following the procedure suggested by Skousen et al, 1997 was also conducted for four of the five samples. The modified NP test accounts for initial acid consumption, Fe oxidation, and subsequent Fe hydrolysis by the iron carbonate mineral siderite. Siderite, even though it is a carbonate gives zero net alkalinity. Lithologic, Acid Base Accounting and general mineral composition data for the five rocks are shown in Table 1. Whole rock elemental analysis for major and trace elements was conducted on a sub-sample of each rock type.

One laboratory was contracted to mix, homogenize, and size the bulk samples and prepare sub-samples for all the participating labs. Splits were sent to eight labs, and each organization was provided a detailed set of instructions for column assembly and leaching procedure. The protocol was developed based on results from phases 1 and 2 of this study. The principal features of the column assembly are: a specific composition of particle size by weight (Table 2), weekly leaching cycles, and incubation under humidified air containing 10% CO₂. Figure 1 shows the column construction. 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, the standardized particle size distribution, shown in Table 2, promotes operational consistency of the weathering test procedure, and provides better control over reaction kinetics. Large amounts of fine particles

within specific zones of the leaching columns have been found to impede uniform fluid flow and/or gas flow (Hornberger and Brady, 1998). Regarding reaction kinetics, the importance of surface area to volume ratios has been described in a previous phase of this study (Brady et al., 2004), and significant differences in crushed particle size distributions and effective surface areas were found among the lithologic units. Standardizing the particle size distribution in each leaching column promotes control of surface area at the start of the weathering test, the distribution of minerals such as pyrite, and the evaluation of kinetic variables after weathering.

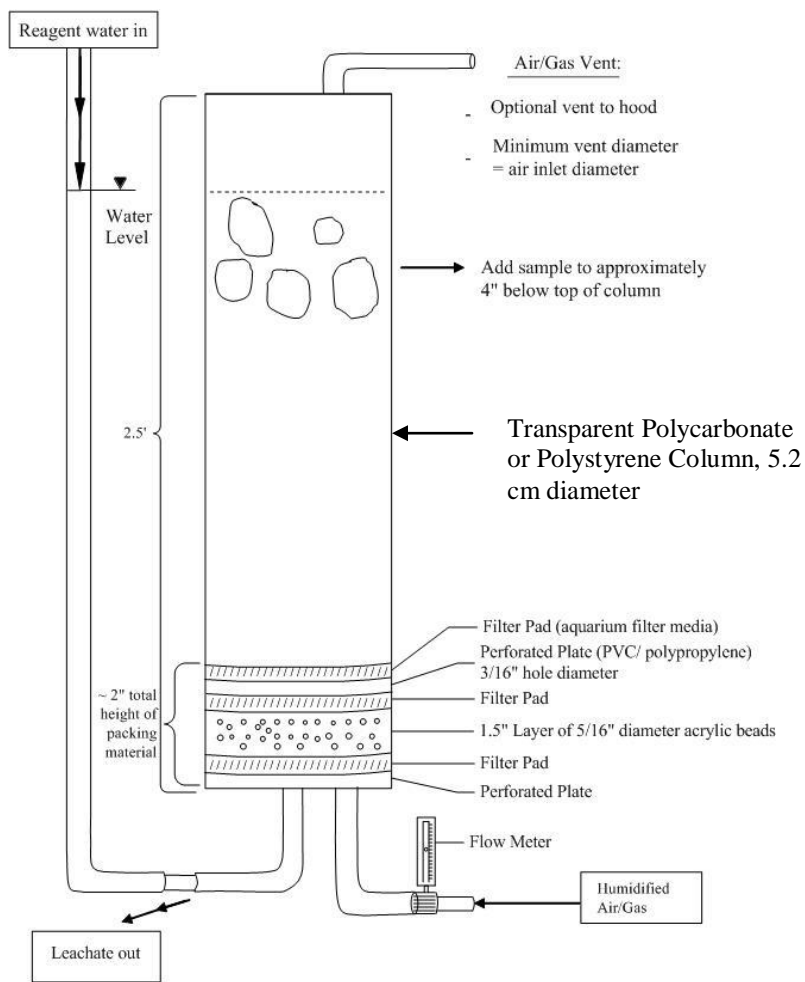


Figure 1. Leaching Column Setup.

Table 1.
Summary Lithologic, Acid-Base Accounting and Mineralogical Data for Five Rocks

Sample ID (Locale)	Lithology (Stratigraphy)	% Sulfur ⁽¹⁾	Neutralization ⁽¹⁾ Potential	Modified ⁽¹⁾ Neutralization Potential	Quartz ⁽²⁾	Micas/clays ⁽²⁾	Feldspars ⁽²⁾	Carbonates ⁽²⁾	Chlorite ⁽²⁾	Pyrite ⁽²⁾
BCS3-PA (Pennsylvania)	Shale (Conemaugh)	0.59	96.97	48.46	34%	37%	2%	10%	11%	3%
KBF-WV (West Virginia)	Shale (Pottsville)	0.31	16.97	13.49	42%	34%	11%	4%	6%	<1%
LKFC-PA (Pennsylvania)	Shale (Allegheny)	0.91	12.64	15.64	37%	34%	3%	5%	10%	8%
HCS-IN (Indiana)	Shale (Carbondale)	5.15	43.58	46.41	32%	26%	6%	3%	5%	17%
MKSS-PA (Pennsylvania)	Sandstone (Allegheny)	0.04	17.7	-	65%	18%	2%	8%	4%	<1%

(1) Median of 4 replicates, three replicates on sample MKSS-PA. No modified neutralization potential analysis was conducted on sample MKSS-PA. Neutralization Potential data in ppt. Analyses on whole rock samples.

(2) Estimated percentage mineral composition from Hammerstrom et al (in press), based on X-ray diffraction analysis of the crystalline fraction of the rock sample only.

Table 2.

Particle size distribution of reconstructed samples	
U.S. Sieve # (or equivalent mesh size)	Percent of Sample (by weight)
3/8" to 4	40
4 – 10	25
10 – 16	15
16 – 35	10
35 – 60	5
Less than 60	5
Total	100

Each lab prepared duplicate 5.1 cm diameter columns containing between about 1.5 and 2 kg of reconstructed sample. The sandstone served as a “blank” and a single column was run by each lab for this sample. Each column was initially saturated and drained up to four times in a 24 hour period until specific conductance values stabilized. After the initial flush, humidified air containing 10% CO₂ was passed continuously through the column for six days at a rate of about 1 liter per minute. On the seventh day, the column was water saturated for 24 hours. The column was then drained, and a leachate sample collected for analysis. Each lab measured pH, specific conductance, alkalinity and acidity, leachate volume, and sent a filtered sample to one central lab on a weekly basis. The central lab conducted all analyses for metals, nonmetals and selected trace elements using EPA and ASTM methods. Table 3 lists the analytical methods used. The eight participating labs also recorded temperature, gas inlet flow rate, and % CO₂ in the discharge air on a daily basis. The air-leach cycle was repeated for a total of 14 weeks. Further details are provided in Hornberger et al (2004). The addition of a CO₂ enriched atmosphere is a major departure from many other simulated weathering test methods. It was prompted in part by the many mine water analyses we have observed with alkalinity concentration well above amounts that can be accounted for by carbonate dissolution under normal atmospheric conditions. A major outcome of the Phase I and II evaluations was the decision to use a controlled atmosphere, and attempt to simulate subsurface conditions in spoil piles and underground mines. Equilibrium calculations based on measured alkalinity and pH values in mine water, and field measurements show that elevated pCO₂ exist in minespoil and underground mines (Cravotta et al, 1994).

Table 3 Analytes Measured and Analytical Methods Used

Frequency	Analyte	Analytical Method
Daily	Room temperature	EPA Method 150.1; Standard Methods 4500-H; ASTM D1293; USGS I-1586
	Gas inlet flow rate	Rotameter attached between humidified gas source and column
	% Carbon dioxide (CO ₂) discharge	Portable meter capable of measuring 10% CO ₂ with a tolerance of +/- 2%
	pH	EPA 150.1; Standard Methods 4500-H; ASTM D1293; USGS I-1586
Weekly	Conductivity	EPA 120.1; Standard Methods 2510B; ASTM D1125; USGS I-1780
	Net acidity	EPA 305.1; Standard Methods 2310; ASTM D1067
	Alkalinity	EPA 310.1, 310.2; Standard Methods 2320B; ASTM D1067; USGS I-1030, I-2030
	Dissolved metals (Al, Ca, Fe, K, Mg, Mn, Se, Zn)	EPA Method 200.7
	Dissolved sulfate (SO ₄)	EPA Method 300.0

Results and Discussion

Four of the five rock samples produced circumneutral drainage with generally low concentrations of metals, and varying amounts of alkalinity and SO₄²⁻. Sample HCS-IN initially produced neutral leachate, but ultimately produced acidic drainage with high concentrations of metals and sulfate before the 14 week cycle was completed. Sample weights and leachate volumes varied between duplicate samples and among all samples and labs. The leachate data was therefore analyzed on both a concentration and flux basis to evaluate effects of varying leachate volume. One sample, HCS-IN, exhibited significant physical weathering during the test, and impeded the movement of gases and fluid through the column.

Whole Rock Characteristics

The five rocks provide a geologic and geographic mix of coal overburden rocks whose drainage characteristics under field conditions are known. The samples are from middle to upper Pennsylvanian stratigraphy (Table 1), including the Allegheny, Conemaugh, Carbondale and Pottsville Groups. Sample BCS3-PA, for example, contains moderate amounts of S and carbonate, and typically produces alkaline drainage with elevated SO_4^{2-} concentration when exposed at Pennsylvania mines (Brady et al, 1998). Sample HCS-IN contains about 5% total S (Table 1), much of it in pyritic form (Hammerstrom et al, in press). The overall column leaching results were in agreement with drainage quality predictions made from Acid-Base Accounting. Sample MKSS-PA has very low amounts of total S and is not expected to produce acidic drainage. It was in fact included in the study to serve as a “blank” because of its very low pyrite and carbonate content, and abundance of non-reactive minerals.

The NP and modified NP data in Table 1 show that sample BCS3-PA results are strongly affected by NP test method. The lower modified NP values imply that much of the carbonate present in this sample is siderite or related minerals. Siderite produces zero net alkalinity, because Fe(III) hydrolysis produces acidity equivalent to the initial neutralization by carbonate dissolution (Skousen et al, 1997; Perry,1998). Samples KBF-WV and HCS-IN show little difference in NP methods, implying that carbonates other than siderite, such as calcite, are present as acid neutralizers. The mineralogical data from Hammerstrom et al (in press) shows that a mixture of carbonates is typically present in these rocks, including impure phases and solid solution series.

The four shale samples contain 32 to 42% percent quartz in the crystalline fraction (Table 1), 26 to 37% micas/clays and 2 to 11 % feldspars. Sample KBF-WV has the highest feldspar content, and is the most sodic of the rocks, containing identifiable albite (Hammerstrom et al, in press). All the rocks contained less than 10 % carbonates, and except for HCS-IN, the rocks also contain between <1 to about 8% pyrite in the crystalline fraction. The X-ray diffraction percentages differ from the ABA values, because the mineral data is based on the crystalline fraction only. The ABA data are whole rock analyses including both crystalline and amorphous materials. The mineral fractions of carbonates and pyrite, which control leachate chemistry in the columns, are a small portion of the rock. Most of the columns consist of inert minerals like quartz, or other minerals that weather slowly.

Method Performance and Reproducibility Within Lab Performance

Method performance, in terms of the precision achieved in a single laboratory, was evaluated in terms of the relative percent difference (RPD, equation 1) in unweighted (concentration) results and weighted or flux data (concentration multiplied by water volume collected, divided by total weight of the sample) results between duplicate samples.

$$RPD = (|C1 - C2| / ((C1 + C2)/2)) * 100 \quad (1)$$

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

RPD's were calculated for duplicate samples at initial flush (Week 0), and as pooled RPDs for all sample weeks beginning with Week 1 and continuing through Week 14 (14-week RPD). Pooled RPDs are presented for unweighted and weighted results for each analyte in each sample in tables 4a and 4b. Analyte-specific pooled RPDs are presented in table 4c.

Pooled RPD's, combining results across labs, were determined from duplicate columns using equation 2:

$$RPD_{pool} = \sqrt{\frac{1}{m} \sum_{i=1}^m RPD_i^2} \quad (2)$$

Where:

RPD_i = the RPD for laboratory *i*

m = the number of laboratories

EPA methods often include RPD performance criteria of up to 30% for duplicate analyses. The shaded cells in tables 4a, 4b and 4c are analytes that exceed 30%.

The highest RPD's are associated with analytes that frequently occurred at or near detection levels, or exhibit complex geochemical behavior in response to redox conditions. Iron and Mn, for example, were frequently measured near detection levels in four of the five samples which produced circumneutral drainage, and both are redox sensitive elements. Acidity, which is determined in part by Fe and Mn concentrations, also has high RPD's. The lowest variability between duplicates occurred with Mg, Na, K, and SO₄²⁻. These analytes were usually present in

mg/L range in water samples collected from the test columns, compared with typical µg/L levels for Fe, Al, and Mn.

Table 4a.⁽¹⁾ Pooled RPDs based on analyte concentrations in duplicate sample pairs

Analyte	BCS3-PA				LKFC-PA			
	Unweighted		Weighted		Unweighted		Weighted	
	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week
Fe	19.1	85.5	17.0	86.6	13.2	79.7	24.5	75.9
Mn	10.6	53.5	24.0	53.7	18.4	18.5	11.3	22.7
Al	–	9.6	–	13.2	50.8	79.8	50.4	54.5
Ca	17.7	16.6	29.5	16.3	18.7	20.2	11.5	22.2
Mg	14.0	18.1	14.2	16.3	12.4	18.0	12.8	22.1
Se	17.2	38.5	28.6	38.2	13.7	24.8	10.0	19.8
Zn	66.4	74.7	54.6	73.1	14.2	33.0	8.7	32.8
Na	13.2	23.3	28.0	19.2	18.6	18.2	14.9	24.5
K	8.5	11.9	28.8	17.9	13.7	14.6	12.7	21.4
SO ₄	18.6	34.6	28.9	26.0	17.6	20.0	13.1	22.9
Alkalinity	17.5	20.9	28.4	30.3	12.5	24.3	37.8	29.8
Acidity	18.9	40.9	36.8	43.5	40.6	176	20.5	158
Conductivity	14.4	15.4	-	-	9.36	9.21	-	-
	Mean absolute difference				Mean absolute difference			
pH	0.15	0.18			0.18	0.22		

(1) Shaded cells indicate RPD's exceeding 30%. Unweighted is concentration data, weighted is flux data.

Table 4b.⁽¹⁾ Pooled RPDs based on analyte concentrations in duplicate sample pairs.

Analyte	HCS-IN				KBF-WV			
	Unweighted		Weighted		Unweighted		Weighted	
	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week
Fe	65.7	104.7	74.3	103.6	36.7	77.1	36.1	79.7
Mn	18.8	34.0	20.7	36.3	86.2	82.9	86.2	82.2
Al	20.1	76.6	25.6	74.1	–	–	–	–
Ca	19.4	7.7	72.4	25.1	4.1	17.5	11.0	23.2
Mg	20.4	21.9	25.0	24.4	4.8	17.1	10.6	21.8
Se	20.8	61.1	21.7	59.3	33.3	38.8	36.9	45.0
Zn	15.2	46.8	22.5	49.7	102.3	83.6	104.6	80.3
Na	14.5	34.2	24.6	29.9	6.9	23.5	13.1	25.5
K	18.0	23.2	27.9	32.9	3.5	13.5	9.2	20.5
SO ₄	15.2	28.2	23.4	34.2	7.3	21.2	10.9	25.5
Alkalinity	53.1	28.7	53.4	34.4	7.9	15.4	19.6	20.9
Acidity	23.8	65.7	28.2	78.5	17.8	35.6	28.0	36.4
Cond.	13.0	12.7			5.6	14.6		
	Mean absolute difference				Mean absolute difference			
pH	0.3	0.4			0.1	0.1		

(1) Shaded cells indicate RPD's exceeding 30%. Unweighted is concentration data, weighted is flux data.

Table 4c⁽¹⁾ Overall RPDs based on analyte

Analyte	Initial Flush		14-week period		Analytical (from Table 6)
	Unweighted	Weighted	Unweighted	Weighted	
Fe	44.8	50.9	91.5	90.4	29.0
Mn	43.1	44.1	52.1	52.5	5.4
Al	37.0	38.6	76.9	72.5	10.3
Ca	36.0	38.8	16.1	21.9	2.2
Mg	15.6	16.4	18.9	21.4	2.3
Se	23.5	26.2	44.2	42.9	24.6
Zn	54.5	52.0	61.4	60.2	4.6
Na	14.5	21.1	25.6	25.1	7.8
K	12.2	21.5	16.3	23.7	4.8
SO₄	15.3	20.4	26.8	27.5	1.2
Alkalinity	32.2	35.2	22.1	28.7	
Acidity	20.0	27.0	106	99.9	
Conductivity	11.1		13.2		
	Mean absolute difference				
pH	0.2		0.2		

(1)Unweighted is concentration data, weighted is flux data.

For most analytes, the RPDs during the 14-week weathering period were similar to or decreased from the RPDs during the initial flush, indicating that the weathering procedures do not impose a notable increase in variability between duplicate samples. RPDs for both calcium and alkalinity improved during the 14-week weathering period.

Four parameters showed an increase in RPD during the 14 week weathering compared to the initial flush. Acidity, Fe, Al, and Se RPD's all increased as the test progressed. Iron, Se and Al were typically measured in the µg/L for four of the five rocks, and the first two elements are redox sensitive.

High RPD's indicate variation in duplicate samples. However, the absolute differences are small for many of the analytes at low concentrations.

Method Performance and Reproducibility Multiple Lab Performance

Precision in multiple laboratories testing replicate samples was evaluated in terms of the relative standard deviation (RSD) in weighted or flux results in replicate samples across laboratories. Relative standard deviations (RSD) were calculated for results of replicate samples at initial flush (Week 0) and as pooled RSDs for all sample weeks beginning with Week 1 and

continuing through Week 14 (14-week). RSD's were determined as :

$$RSD = \frac{StDev(C_1, \dots, C_n)}{Mean(C_1, \dots, C_n)} * 100\% \quad (3)$$

Where:

C_1 = The original sample result from Laboratory 1

C_2 = The duplicate sample result from Laboratory 1 (or the original sample result from Laboratory 2 if no duplication)

C_n = The duplicate sample result from Laboratory 7 (or the original sample result from Laboratory 7 if no duplication)

Because the differences in water volumes collected and total sample weights used can increase variability greatly across laboratories, RSDs are presented based on weighted results only. Pooled RSDs from replicate samples across laboratories are presented for each analyte in each sample in Table 5a; analyte-specific RSDs are presented in Table 5b. Pooled RSD's were determined in equation 4 as:

$$RSD_{pool} = \sqrt{\frac{1}{n_T - m} \sum_{i=1}^m (n_i - 1) * RSD_i^2} \quad (4)$$

Where:

RSD_i = the RSD for laboratory i

m = the number of laboratories

n_i = the number of measurements for laboratory i

n_T = the total number of measurements over all laboratories

Resulting pooled RSDs across laboratories are consistent with results of the pooled RPDs between duplicate samples. RSDs are largest for Fe, Zn, Al, and Mn, and show only a slight increase during weathering from the variability across initial flush results. Pooled RSD results show a slight decrease in variability during weathering for production of Ca, Mg, Na, K, and sulfate.

Much of the variability (measured as RPD and RSD) between within-laboratory duplicate samples and inter-laboratory replicate samples appears to result from differences in the sample

mass used and the leachate volumes collected for each sample. Attempts to normalize concentration results to compensate for sample mass (as well as volume of leachate collected) did not significantly affect RPD results, it is likely that additional factors (e.g., sample density, column construction, gas and water introduction) had an impact on sample exposure to weathering conditions.

Table 5a. ⁽¹⁾ Pooled interlaboratory RSD's based on analyte concentrations in replicate

Analyte	BCS3-PA		HCS-IN		LKFC-PA		KBF-WV		MKSS-PA	
	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week
Fe	130	110	118	150	84.7	80.0	130	86.8	44.3	44.6
Mn	46.0	112	67.5	45.1	36.7	29.3	101	1.4	50.3	59.2
Al	4.3	39.1	87.1	97.6	69.5	37.5	131	–	–	–
Ca	35.5	30.5	56.7	29.0	25.5	30.8	43.8	41.4	39.9	40.8
Mg	31.7	30.9	61.4	35.6	44.4	30.2	45.7	37.4	86.6	31.9
Se	43.4	40.8	47.9	63.0	33.3	27.2	62.6	63.4	41.4	45.9
Zn	131	98.3	85.5	84.7	33.6	63.2	135	85.8	89.9	97.2
Na	39.2	30.2	47.6	39.8	52.9	38.9	53.6	41.9	55.1	59.0
K	40.9	24.1	53.8	57.8	41.0	26.0	53.5	31.7	35.5	30.0
SO₄	35.1	26.0	55.8	51.4	32.1	26.2	45.5	25.8	45.2	56.9
Cond.	25.1	15.0	22.5	48.9	28.6	40.6	20.0	11.3	36.0	11.8
Standard Deviation										
pH	0.3	0.4	1.0	1.8	0.4	0.5	0.3	0.5	0.3	0.3

(1) Shaded cells indicated RSD's greater than 50%.

Table 5b. ⁽¹⁾ Overall pooled RSD's based on analyte

Analyte	Initial Flush	14-week
Fe	109.4	114
Mn	65.4	78.0
Al	78.8	86.0
Ca	41.6	34.1
Mg	52.7	33.5
Se	47.4	48.8
Zn	97.6	85.0
Na	49.3	40.5
K	46.6	36.5
SO₄	43.4	37.2
Conductivity	26.0	39.6
Standard Deviation		
pH	0.6	0.7

(1) Shaded cells indicated RSD's greater than 50%.

Chemical Leaching Behavior

All samples across all laboratories produced an initial flush of soluble weathering products, followed by a generally consistent leaching rate for the remainder of the test. Data from the initial saturation and flushing were not included in the overall analysis, since this leach cycle does not represent the weathering process.

Specific conductance values, used as a surrogate for dissolved solids content, were typically greatest during the first 3 to 4 weeks of leaching cycles and declined slowly thereafter. Figure 2 shows median specific conductance values for all labs and samples. Only sample HCS-IN, which generated acidic leachate in the late stages of the test, showed increasing specific conductance with time. Specific Conductance values are in general agreement with predictions made from ABA and mineralogy data. The sandstone “blank” sample MKSS-PA, which contains very low concentrations of pyrite and carbonates, and a large fraction of quartz, produced dilute leachate. The high sulfur HCS-IN sample weathered aggressively and produced leachate 3 times or more conductive than any other rock. Rocks with sulfur and carbonate content in between the extreme values produced leachates with intermediate conductance and dissolved solids content.

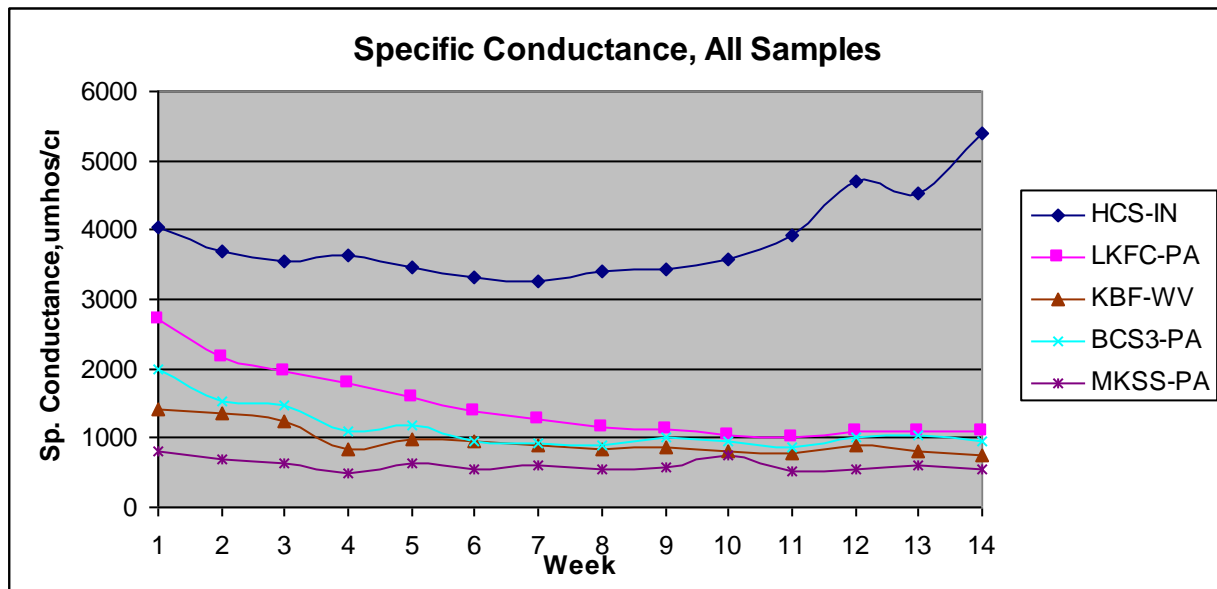


Figure 2. Specific Conductance vs. Time. Data are median values of all labs.

Elevated specific conductance values in the early phase of the test, followed by gradual decline, are similar to the time dependent behavior described for field scale mine discharges.

Younger (1997) describes an early flush of stored weathering products from flooded mines in the U.K., followed by a decline in pollutant concentrations. After 10 to 20 years, the curves become asymptotic or nearly so. Similar behavior has been described for coal mines in Appalachia (Perry and Rauch, 2006). The column test conductivity data mimic this behavior for 4 of the 5 rocks.

The fraction of major and selected minor and trace elements leached from the column during the test was compiled from flux data and total element content. Leaching fraction data and total element content are shown in Table 6. These data represent only the elemental fraction removed completely from the column. It does not account for materials that weathered and were retained in the column by the formation of other minerals, adsorption or exchange reactions.

Table 6. Total Elemental Content of the Rock and Fraction Leached⁽¹⁾

Sample Element	BCS3-PA		HCS-IN		KBF-WV		LKFC-PA		MKSS-PA	
	Total ⁽²⁾ (%)	% ⁽³⁾ Leached	Total (%)	% ⁽³⁾ Leached	Total (%)	% ⁽³⁾ Leached	Total (%)	% ⁽³⁾ Leached	Total (%)	% ⁽³⁾ Leached
Fe	6.66	< 0.001	6.36	0.15	6.14	< 0.001	7.74	0.001	2.25	<0.001
Mn	0.10	0.0009	0.04	18	0.10	0.01	0.18	7	0.05	0.6
Al	10.83	< 0.001	6.66	0.03	8.49	0.1	9.41	0.009	5.89	0.003
Ca	1.61	3.3	1.61	8.9	0.74	2.7	0.62	5.2	1.29	2.3
Mg	1.45	1.8	0.97	11	1.09	1.5	1.13	1.8	0.54	0.8
Na	0.18	1.2	0.37	3.2	0.55	0.09	0.16	0.08	0.10	0.3
K	2.91	0.07	2.28	0.12	2.85	0.1	3.05	0.09	1.99	0.1
S	0.53	3.5	5.54	4.5	0.20	2.4	0.81	4.3	0.09	2.1
Se	<3	2.1	81	11	<3	0.4	<3	6.8	<3	2
Zn	171	5.5	456	8.8	126	0.06	151	0.7	86	2
pH Week 1	7.12		6.61		7.19		5.45		7.20	
pH Week 14	7.14		3.24		7.18		6.27		7.16	

(1) Median values of all columns, all labs.

(2) Se and Zn total concentrations are in ppm.

(3) Leached fraction calculated as cumulative total mass of element in leachate / total mass of element in sample.

Four of five rocks leached about 0.001% or less of the Fe and Al present. Only the acidic leachate from sample HCS-IN contained appreciable quantities of Fe and Al. Less than 1% of total Mn was leached, except in sample HCS-IN where nearly 18% of Mn was removed. Between about 3 to almost 9% of total Ca was removed during the test and about 1 to 2 % of Mg was leached. Calcium and Mg leaching percentage was greatest in sample HCS-IN and least in sample MKSS-PA. Sodium leaching followed a similar pattern among the 5 samples. Potassium leaching was less than 1% for all rocks, suggesting either limited weathering of K bearing minerals, incorporation of K into secondary minerals, or retention in the column by adsorption/exchange. For sulfur, initially present mostly as sulfides, about 2 to 4.5 % of total sulfur was removed during leaching, with the highest leaching fraction in sample HCS-IN, followed by KFFC-PA, BCS3-PA, KBF-WV and MKSS-PA. The trace element Se is in low concentrations (<3 ppm) in four of the five rocks, and less than one to about 11% of the total was removed during the test. The acidic HCS-IN sample which had the highest elemental Se content, also leached the greatest fraction.

Three of samples had essentially constant pH conditions through the test (table 6). Sample LKFC produced mildly acidic leachate (pH 5.45) in the first week, but pH increased to about 6.3 by end of the test period. Sample HCS-IN pH declined over 3 units by end of the test.

The acid forming shale HCS-IN leached the greatest elemental fraction for each parameter in table 6. The samples rank for overall weathering intensity and element leaching as follows:

HCS-IN > LKFC-PA > BCS3-PA > KBF-WV > MKSS-PA.

The ordering is in general agreement with interpretation of mineralogical characterization reported by Hammerstrom et al (in press) and the ABA data. The high sulfur sample HCS-IN weathered most aggressively, and the low sulfur, low carbonate “blank” sandstone MKSS-PA produced the least alteration. The rocks with intermediate properties lie between the end members.

The elemental fractions leached range from less than 0.001% to a maximum of about 18% in Table 6. The extremely low leaching fractions of Al are attributable to the limited solubility of Al oxy-hydroxide minerals at circumneutral pH. Table 6 shows that week 1 and final pH was circumneutral for all samples except HCS-IN.

Over 90 % of the Fe potentially mobilized by pyrite oxidation did not exit the columns. The small fractions of Fe leached during the test were much less than expected based on SO_4^{2-} concentrations and the stoichiometry of pyrite composition and oxidation. One mole of Fe is liberated for every two moles of SO_4^{2-} produced during pyrite oxidation. Assuming mostly conservative SO_4^{2-} behavior in solution, Fe to SO_4^{2-} mole ratios should be about 1:2. Computed mole ratios were much less than the theoretical value.

Iron oxy-hydroxides are a common sink for Fe in soils, sediments and rocks undergoing low temperature weathering processes (Langmuir, 1997). One laboratory measured solution Eh weekly at the time a leachate sample was collected, although it was not required by the test protocol. Equilibrium calculations were performed using PHREEQC (Parkhurst and Appelo, 1999), and the solution compositions to estimate mineral saturation indices. The waters were over-saturated for even the most soluble Fe oxy-hydroxide minerals like poorly crystalline $\text{Fe}(\text{OH})_3$, with saturation indices generally greater than about + 0.5, and much higher indices for minerals such as goethite. The strongly oxidizing column environment was therefore conducive to the formation of Fe oxy-hydroxide minerals, and could account at least in part for the retention of Fe in the column. The leachates were 4 to 5 orders of magnitude under-saturated for K-jarosite for four of five rocks, showing that mineral is unlikely to control Fe activity in these samples. Only the acidic leachates from sample HCS-IN approach saturation for K-jarosite.

We also examined saturation indices for calcite, dolomite, siderite, gypsum, chlorite and other minerals in all samples and labs. Three of five samples, including BCS3-PA, KBF-WV and MKSS-PA were saturated or super-saturated for calcite, imposing solubility constraints on solution alkalinity. Figure 3, showing calcite saturation indices for sample BCS3-PA, typifies the behavior of 3 of the 5 rocks. There is some variation among individual labs and through the course of the test, but with few exceptions, the leachates remain at or above calcite saturation. Calcite solubility and pCO_2 control alkalinity, and indirectly, the in-situ acid neutralization capability of these rocks. Sample HCS-IN and LKFC-PA were under-saturated for calcite, indicating that alkalinity production from these rocks is more limited or it was being consumed.

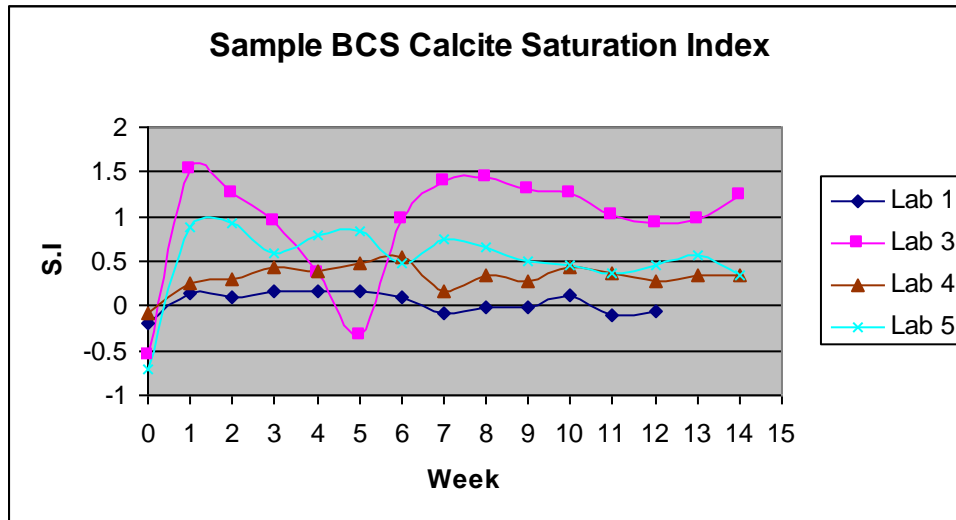


Figure 3. Calcite Saturation, sample BCS3-PA

Four of the five rocks were under-saturated for gypsum. Figure 4, gypsum saturation indices for sample KBF-WV, typifies the behavior of these samples. The solutions are consistent among all labs for the duration of the test. Sample HCS-IN, however was at or near gypsum saturation for most labs throughout the test. Mineralogical characterization by Hammerstrom et al (in press) identified gypsum as present in this sample before leaching. For this rock, both Ca and SO_4^{2-} solution activity are constrained by gypsum solubility.

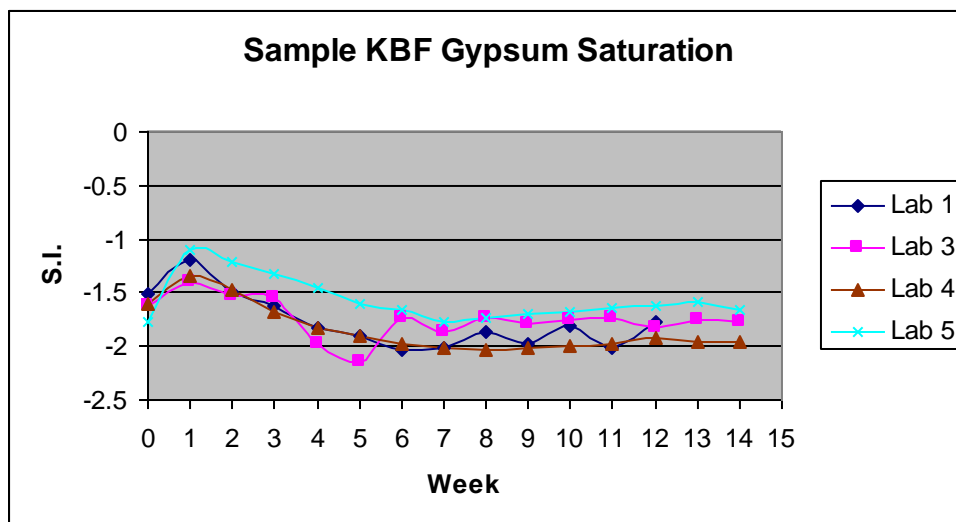


Figure 4. Gypsum Saturation Index, Sample KBF-WV

Mineral saturation indices discussed in this section are calculated based on pure mineral phases. The carbonates in fact occur as impure phases, solid solution series, or minerals with trace inclusions (Hammerstrom et al, in press) whose solubility properties may differ some from the pure crystalline mineral.

Cumulative leaching rates of Ca and Mg were approximately linear for 4 of 5 samples after the initial flush, and differed among the rocks. A natural log function provided the best fit for Ca leaching from LKFC-PA. Figure 5 shows cumulative Ca leaching for the five rocks. Sample HCS-IN, which was under-saturated for calcite and also contained gypsum, leached Ca 3 to 6 times faster than the other rocks. Calcium leaching rates were within a factor of 2 for the other four rocks. The linear plots for BCS3-PA, MKSS-PA and KBF-WV are consistent with calcite solubility and $p\text{CO}_2$ constraints controlling Ca leaching, and with the computed calcite indices. The natural log function for LKFC-PA leaching suggests the rock cannot dissolve calcite at a consistent rate and carbonate alkalinity will decrease with time. Magnesium also exhibited more or less linear leaching behavior over time for all samples. Sample HCS-IN leached Mg 5 to 16 times faster than the other rocks, while the sandstone MKSS-PA had the slowest Mg leaching rate.

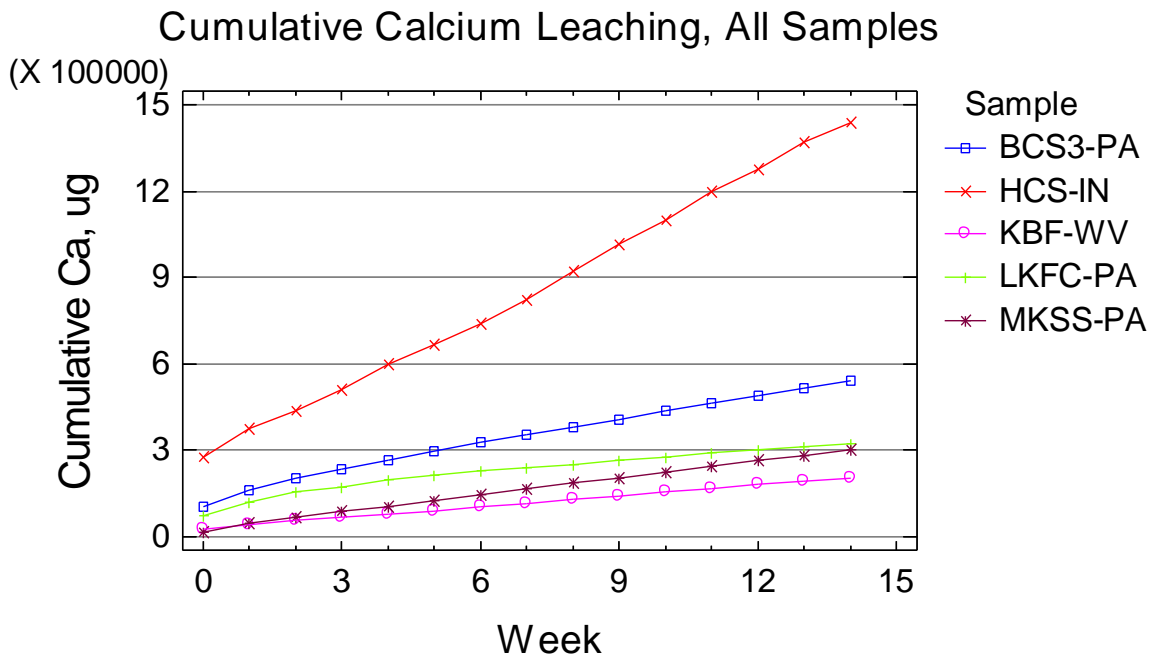


Figure 5. Cumulative Calcium Leaching All Samples. Data are median values of all labs.

Leaching behavior of SO_4^{2-} , and other major and trace elements were best described by exponential functions. Figure 6 shows cumulative Se leaching for all samples on a log scale plot. As with other parameters, Se was leached most aggressively from sample HCS-IN, while the sandstone MKSS-PA and KBF-WV shale were the least active. Sample HCS-IN also contained the highest initial concentration of Se at 81 ppm, whole rock basis (Table 5). There was no obvious relationship between Se whole rock content and leaching behavior for the other 4 rocks, however. Selenium is sometimes found as a trace inclusion in pyrite (Yudovich and Ketris, 2006), and MKSS-PA and KBF-WV had the lowest S contents of the five samples. Selenium has also been found to be mostly closely associated with coal and carbon rich shales in parts of the Kanawha formation in West Virginia (Vesper and Roy, 2006). Interestingly, sample KBF-WV, which was collected from the Kanawha formation, had negligible quantities of Se leached. Sample HCS-IN was the most carbon and pyrite rich sample tested in this study. Se leaching behavior is related in part to pyrite content and oxidation. Redox conditions and speciation of Se(IV) and Se(VI) also influence Se mobility.

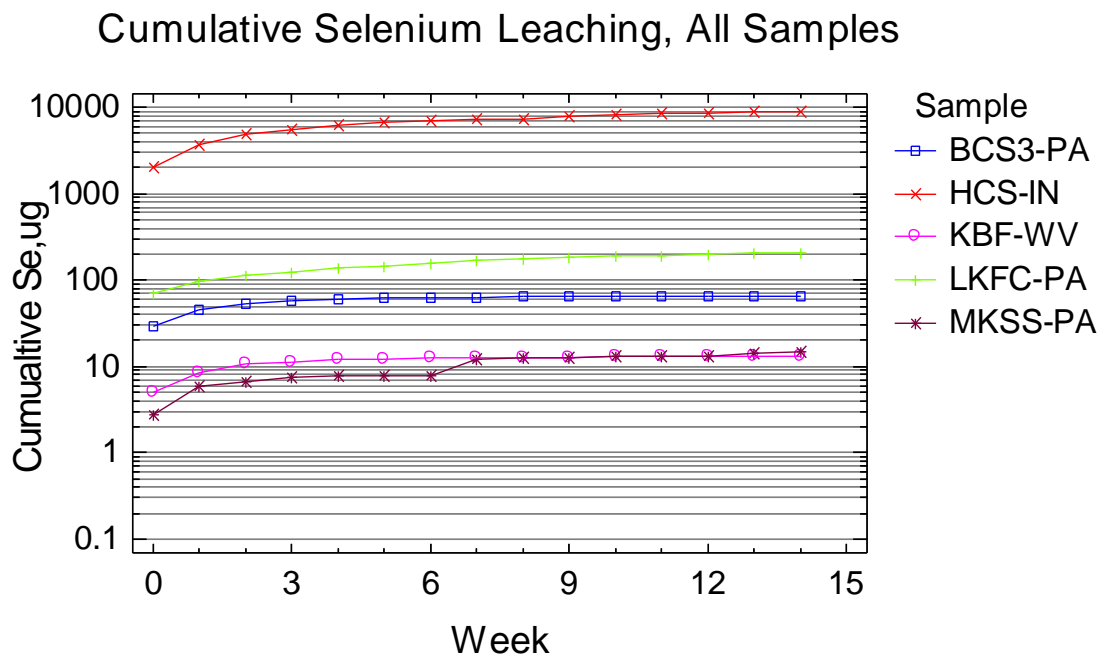


Figure 6. Cumulative Selenium Leaching, All Samples. Data are median values of all Labs.

Cumulative SO_4^{2-} leaching for all samples is shown in Fig. 7. Four samples were undersaturated for gypsum and K-jarosite, and SO_4^{2-} was assumed to behave conservatively in the columns. The amount of SO_4^{2-} leached was taken as representing the quantity of pyrite oxidized. Four rocks leached between about 2 and 6 % of the total S during the 14 week test. The fifth sample, HCS-IN, leached nearly 10% of the total S. The rate accelerated near the end of the test (Fig. 7) and coincides with a decline in pH. Although we did not analyze the microbial population, accelerated oxidation is characteristic of microbial catalysis of ferrous iron oxidation in the overall pyrite oxidation process at low pH (Nordstrom, 1982). Excluding the initial flush (week zero), cumulative sulfide weathering fit an exponential function of the form:

$$\ln(\%S) = \text{constant} + b \cdot \ln(\text{Time}) \quad (5)$$

About two thirds of sulfate leaching results have power exponents (b in equation 5) between 0.4 and 0.6. All but one of the power exponents fell between 0.35 and 0.7. Encouragingly, the results from the labs studied were very consistent among each other. The fact that a power function fits the data well provides predictive capabilities for estimating sulfide weathering beyond the 14 week test period. The similarity in plots and fitted equations shows that the test is capable of reproducing weathering processes across a wide range of S content, from < 0.1 to > 5%.

Leachates from sample HCS-IN were saturated for gypsum and possibly K-jarosite after the sample began producing acid drainage, based on equilibrium solubility calculations. For this sample and other similar rocks, SO_4^{2-} flux out of the column may not represent the total amount of pyrite oxidized. The depletion of nearly 10% of the total S in Fig. 7 may actually under-represent oxidation taking place, if SO_4^{2-} minerals are precipitating in the column. Mineral solubility constraints should be considered when interpreting column leach data.

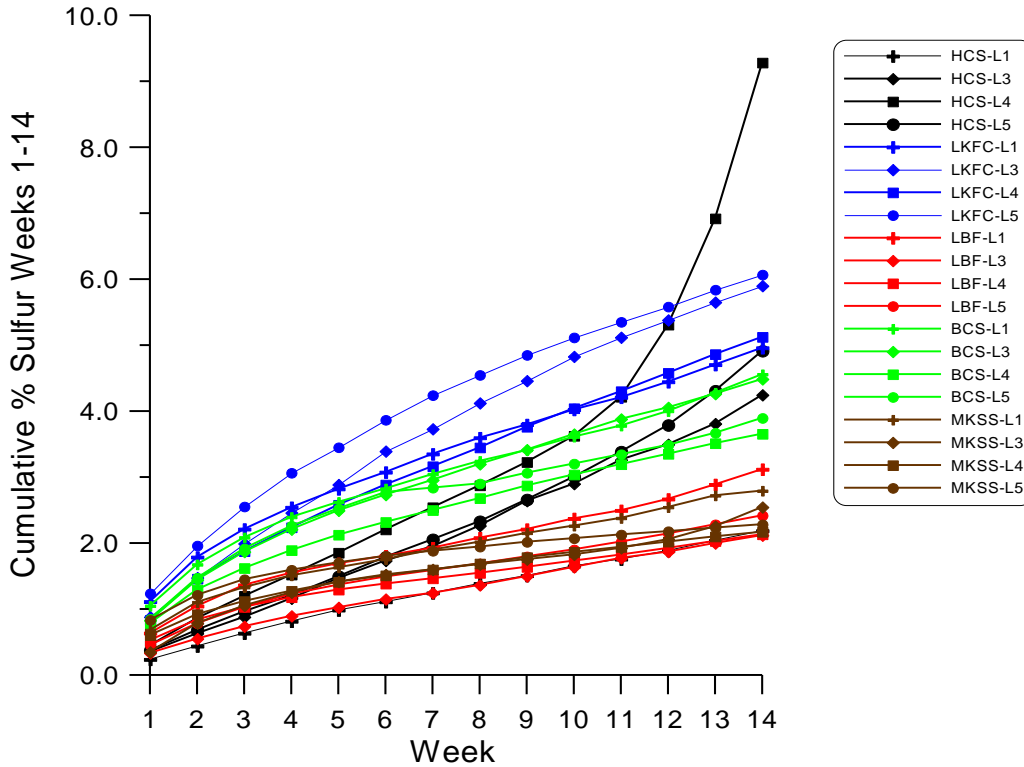


Figure 7. Cumulative Sulfur weathering, All Samples.

Consumption of acid neutralizing capacity was estimated from two components; leachate alkalinity, and alkalinity consumed in-situ in the column. Leachate alkalinity was measured directly in the drainage. In-situ neutralization was estimated from sulfate content of the leachate, on the basis of two moles of acidity produced and neutralized per mole of SO_4^{2-} . Solution alkalinity and estimated in situ neutralization were summed on a flux basis, and compared to Neutralization Potential (NP) data for the rock. The average cumulative fraction of NP consumed as alkalinity and in-situ neutralization is shown in Fig. 8. The estimated acid neutralizing capacity did not include any contributions from alumino-silicate weathering, because the reaction rates are usually orders of magnitude less than carbonate dissolution (Kowaleski and Rimstidt, 2003).

Acid neutralizing capacity of the rocks was consumed from about 1 to 6 times more rapidly than acid producing potential. The greatest disparity in consumption (compare Fig. 7 and 8) was with samples HCS-IN and KBF-WV, while the mostly closely matched rates were in sample BCS3-PA. In Phase II, which included both column and humidity cell weathering, sample BCS3-PA leached carbonates more slowly, and was expected to produce alkaline drainage long-term

(Brady et al 2004). An initial comparison of data from this study suggests carbonates and other neutralizers may be exhausted before acid generating capacity is depleted.

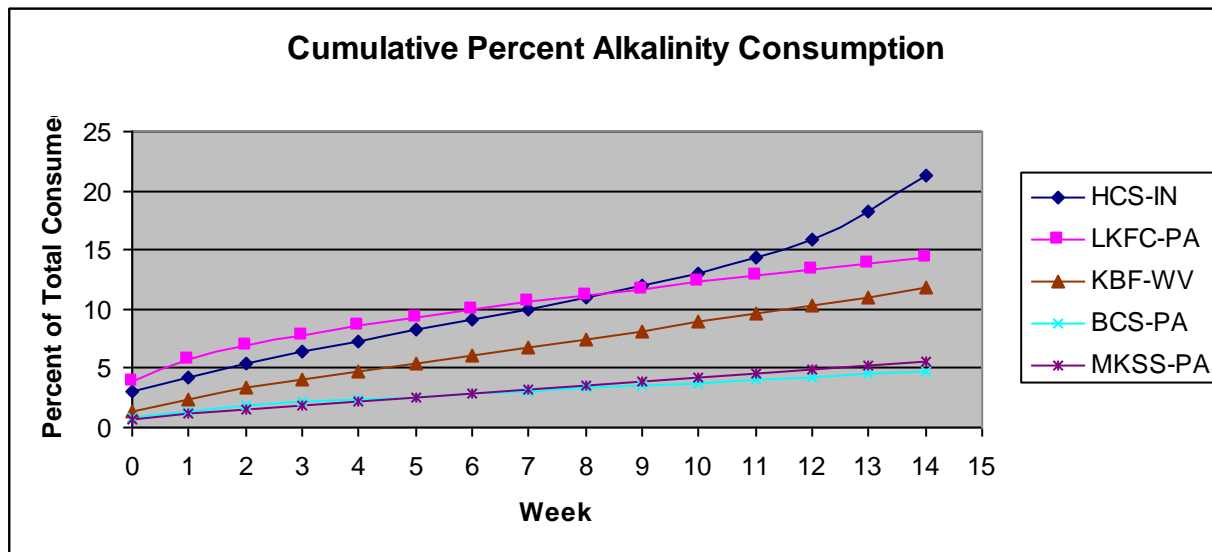


Figure 8. Cumulative Consumption of Acid Neutralizing Capacity. Data are median values of all labs.

Sulfide consumption follows an exponential trend, with decreasing acid production over time. Consumption of carbonates and other acid neutralizers is more linear for three samples, except sample HCS-IN which actually increased, and LKFC-PA which fits an exponential function. It's uncertain whether the disparity in process rates would continue over the long term, or if consumption of acid neutralizing capacity would decrease. Field behavior of these rocks generally has been to produce alkaline water, suggesting that neutralizers are not rapidly depleted. One sample produced acidic drainage in the 14 week test, while the other four leached net alkaline water. Lapakko et al (2006) have noted a lag in leachate acidification depending on the relative exposed surface area of acid forming and neutralizing minerals. Their study suggests the fraction of reacted carbonates and particle size influences solution pH.

The amounts of acid production and acid neutralization consumed show that the test is vigorous enough to establish the weathering characteristics of the rock, and distinguish the behavior of different rocks.

Figure 9 shows average alkalinity concentrations for all labs and samples. Two samples MKSS-PA and KBF-WV, produced alkalinities higher than might be expected based on the

Neutralization Potential (NP) data in Table 1. MKSS-PA had an NP of about 18 ppt, but consistently produced leachate alkalinity greater than 200 mg/L. Sample KBF-WV has an NP of about 17 ppt, but produced leachate alkalinity between 350 and 400 mg/L or more. These alkalinities are unusually high for the amount of reported NP. Brady et al (1994) and Perry and Brady (1995) compared post-mining water quality data and ABA properties of the rocks on about 40 surface mines. For sites having measurable alkalinity, the observed ratio of alkalinity (mg/L) to NP (ppt) averaged about 5:1, with most values falling between 2 and 7. Samples KBF-WV and MKSS-PA have ratios of about 23:1 and 13:1 respectively. We are uncertain why two of the five samples tested here produce alkalinities greater than expected based on ABA and other data. The relatively rigorous test condition of including 10% CO₂, and specified particle size distribution may partly account for the elevated alkalinity concentrations. The lab alkalinities were determined on non-filtered samples. If any suspended carbonate particles were present and dissolved during titration, the reported alkalinity would increase. The other three rocks have average alkalinity to NP ratios ranging from about 1.7 to 4.2, similar to that observed in the field scale study.

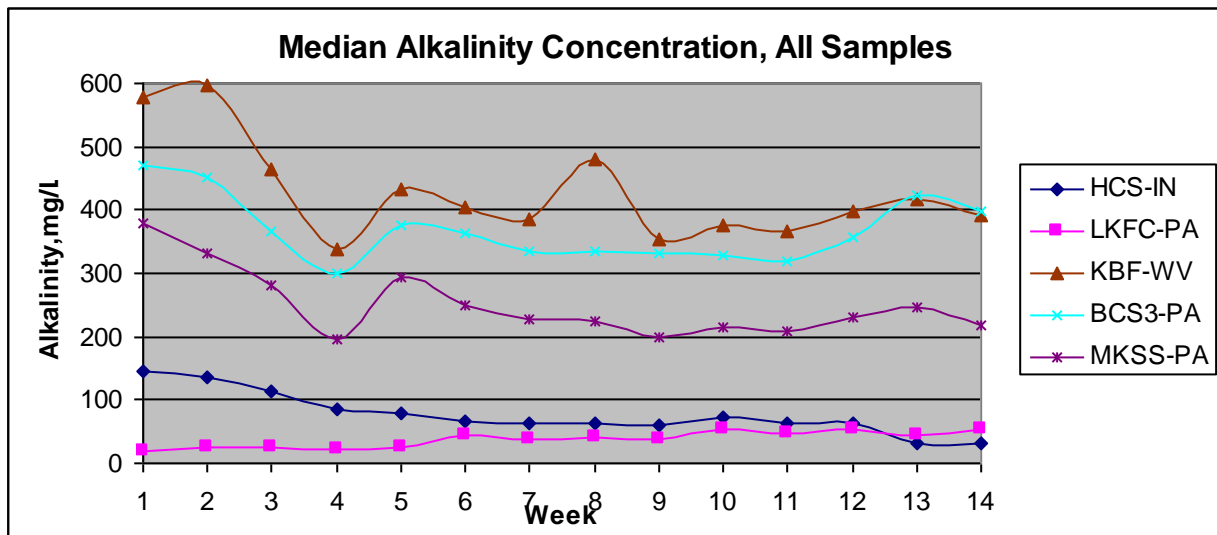


Figure 9. Alkalinity Concentration, mg/L. Data are median values of all labs.

Summary and Conclusions

Five rock samples of coal overburden materials were subjected to a standardized column leaching test at eight commercial, university and government laboratories. At each lab, splits

from sized, homogenized bulk samples were loaded in duplicate columns, incubated under humid air containing 10% CO₂, and leached every 7 days for a 14 week period.

Relative percent difference (RPD) and Relative Standard Deviation (RSD) were used to evaluate reproducibility of the test method within and among labs. Calcium, Mg, Na, K, sulfate and specific conductance were the most consistent parameters. The five elements were present in mg/L range of concentration. Iron, Al, Mn, Se, Zn and acidity were the parameters with greatest variation in results. These five elements were present in ug/L concentrations for most samples, and in many instances the absolute differences were small. The behavior of Fe, Mn and Se also depends on their redox sensitive solubility and mobility, and more complex mineralogical controls.

Weathering intensity was evaluated from fractions leached of major and minor elements, alkalinity and acidity, and specific conductance data. Leaching intensity is relatively consistent across all parameters. The high S shale sample HCS-IN has the highest elemental fractions leached, while the sandstone MKSS-PA and the shale KBF-WV were the least chemically active rocks. The behavior was consistent with the ABA measurements of S content and the detailed mineralogical characterization provide by Hammerstrom et al (in press).

Mineral solubility constraints can influence the composition of the leachate. Carbonate solubility was strongly influenced by the use of a 10 % CO₂ atmosphere in the test column. Three samples were saturated or super-saturated for calcite throughout the test. Leachates from one acidic sample were at or near saturation for gypsum and possibly K-jarosite. Solution activity of Ca, SO₄²⁻, and possibly Fe was constrained by mineral phases in these columns. Control of solution activities by mineral phases complicates the interpretation of leachate composition.

Most of the Fe liberated by sulfide oxidation never leached from the columns. The Eh and pH measurements, combined with solubility calculations, showed that even the most soluble forms of Fe oxy-hydroxides could precipitate in the column. Four of the five samples produced leachates with circumneutral pH which limited Al solubility and mobility.

Most elemental leaching could be described by a power function, which is useful for estimating weathering behavior. Most elemental leaching declined with time, which is consistent with observed field behavior. Sample HCS-IN was exceptional, and displayed increased elemental leaching after pH declined and the columns underwent acid leaching. Results were

relatively consistent across labs and samples, showing that the test can simulate weathering across S contents ranging from < 0.1 to > 5%. Cumulative Ca and Mg leaching, however, followed a more linear trend for most samples, as might be expected for carbonate dissolution under specified pCO₂.

Consumption of acid neutralizing capacity, estimated from SO₄²⁻ and alkalinity data, exceeded the rate of sulfide oxidation. Between about 2 and 6% of the total S was leached during the test, while about 4 to 20% of the estimated acid neutralizing capacity was consumed. The 14-week leaching data suggest that neutralizers may be depleted before pyrite is exhausted. Field behavior of most of these rocks, however, is to produce alkaline water. We are uncertain whether the disparity in process rates would continue over the long term, or if consumption of acid neutralizing capacity would decrease. The estimated acid neutralizing capacity did not include any contributions from alumino-silicate weathering, because the reaction rates are much slower than carbonate dissolution.

Two samples produced alkalinity concentrations greater than expected, based on ABA interpretation. The unexpectedly high alkalinity concentrations may be a function of the 10% partial pressure of CO₂ used to aerate the columns, or other mineralogical controls. The other three samples had alkalinity and NP relationships similar to that observed in field studies.

Acid production, acid neutralization consumed and elemental leaching show that the test is vigorous enough to simulate weathering characteristics of the rocks, and distinguish the behavior of different rocks. Overall, leachate compositions were similar to that observed at field scale. The standardized leaching test is a useful technique for estimating long-term mine-water quality.

Acknowledgements

We thank the labs who participated in this study including the US Geological Survey, Benchmark Analytical, Consol Energy, Geochemical Testing, Mahaffey Laboratory, Ltd., Pennsylvania State University, ProChem Analytical, Sturm Environmental Services, and West Virginia University. Support for this work was provided by the US Environmental Protection Agency (US EPA) and the US Office of Surface Mining. Thanks to William A. Telliard (US EPA, retired) for his support and championing this work. Finally, thanks to the anonymous reviewers whose comments improved the manuscript.

Literature Cited

- Brady, K., Perry, E., Beam, R., Bisko, D., Gardner, M., and J. Tarantino. 1994. Evaluation of Acid Base Accounting to Predict the Quality of Drainage at Surface Coal Mines in Pennsylvania, U.S.A. In Proceedings International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage. US Bureau of Mines Special Publication SP 06A-94, Vol 1 pps 138-147.
<https://doi.org/10.21000/JASMR94010138>
- Brady, K., Hornberger, R. and G Fleeger. 1998. Influence of Geology on Post Mining Water Quality: Northern Appalachian Basin. In Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, Harrisburg PA.
- Brady, K. B. C., R. J. Hornberger, B. E. Scheetz, and C. M. Loop. 2004. Refinement of ADTI-WP2 Standard Weathering Procedures, and Evaluation of Particle Size and Surface Area Effects Upon Leaching Rates. Part 2: Practical and Theoretical Aspects of Leaching Kinetics. Proceedings America Society of Mining and Reclamation, 2004 pp 174-200.
<http://dx.doi.org/10.21000/JASMR04010174>.
- Braley, S. A., 1949. Annual Summary Report of Commonwealth of Pennsylvania, Dept. of Health Industrial Fellowship No. B-3. Pittsburgh: Mellon Institute of Industrial Research.
- Cravotta, C. A., D. L. Dugas, K. B. C. Brady and T. E. Kavulchuk, 1994. Effects of Selective Handling of Pyritic, Acid-Forming Materials On The Chemistry of Pore Gas and Ground Water At A Reclaimed Surface Coal Mine, Clarion County, PA, USA. *In* Proceedings International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage. US Bureau of Mines Special Publication SP 06A-94, Vol 1 pps 365-374.
<https://doi.org/10.21000/JASMR94010365>
- Geidel, G., Carrucio, F., Hornberger, R. and K Brady, 2000, Chapter 5 Guidelines and Recommendations For the Use of Kinetic Test For Coal Mining (AMD) Prediction In the Eastern U.S. *In*: Prediction of Water Quality At Surface Mines, prepared by members of the Prediction Workgroup, Acid Drainage Technology Initiative. National Mined Land Reclamation Center, West Virginia University, Morgantown, WV.
- Glover, H. G. and W. G. Kenyon, 1962. Mineral Weathering Tests. National Coal Board, Mine Drainage Investigation Serial No. 85, Manchester, England, 8 p.

- Hammerstrom, J., Cravotta C., Galeone D., Brady K., Jackson J., and F. Dulong, (in press) Characterization of rock samples and mineralogical controls on leachates, Chapter in Kinetic Test Procedure for the Prediction of Coal Mine Drainage Quality, prepared for US Office of Surface Mining, Washington D.C.
- Hanna, G. P., Jr. and R. A. Brant, 1962. Stratigraphic Relations to Acid Mine Water Production. Purdue University Engineering Experiment Series No. 112, pp. 476 - 492.
- Hornberger, R., and K. Brady. 1998 Kinetic (Leaching) Tests for the Prediction of Mine Drainage Quality. In Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, Harrisburg PA.
- Hornberger, R. J., K. B. C. Brady, W. B. White, B. E. Scheetz, J. E. Cuddeback, W. A. Telliard, S. C. Parsons, C. M. Loop, T. W. Bergstresser, C. R. McCracken, Jr., and D. Wood. 2004. 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. Proceedings America Society of Mining and Reclamation, 2004 pp 916-947. <http://dx.doi.org/10.21000/JASMR04010916>.
- Kania, T. 1998. Laboratory Methods for Acid-Base Accounting: an Update. In Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, Harrisburg PA.
- Kowaleski, M., and J. Rimstidt. 2003. Average Lifetime and Age Spectra of Detrital Grains: Toward A Unifying Theory of Sedimentary Particles. The Journal Of Geology, Vol III, p 427-439. <http://dx.doi.org/10.1086/375284>.
- Langmuir, D.1997. Aqueous Environmental Geochemistry. Prentice Hall, 600 pps.
- Kim A. Lapakko, Jennifer N. Engstrom, and David A. Antonson 2006, Effects of Particle Size on Drainage Quality From Three Lithologies, Proceedings America Society of Mining and Reclamation, 2006 pp 1026-1051. <http://dx.doi.org/10.21000/JASMR06021026>
- Nordstrom, D. K. 1982. Aqueous Pyrite Formation and the Consequent Formation of Secondary Iron Minerals. In: Acid Sulfate Weathering, pp37-56. SSSA Special Publication No 10, Soil Science Society of America. Madison WI.

- Parkhurst, D. L. , and C. A. J Appelo., 1999. User's Guide to PHREEQC (Version 2)- A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. US Geological Survey Water Resources Investigation Report 99-4259.
- Pedro, G., 1961. An experimental study on the geochemical weathering of crystalline rocks by water. Clay Mineral Bull., v. 4, pp. 266 - 281.
<http://dx.doi.org/10.1180/claymin.1961.004.26.02>.
- Perry, E and K. Brady, 1995. Influence of Neutralization Potential on Surface Mine Drainage in Pennsylvania. In Proceedings 16th Annual West Virginia Surface Mine Drainage Task Force, Morgantown WV.
- Perry, E. 1998. Interpretation of Acid Base Accounting. In Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, Harrisburg PA.
- Perry, E. and H. Rauch, 2006, Water Quality Evolution In Flooded and Unflooded Coal Mine Pools, 7th International Conference on Acid Rock Drainage, 2006 pp 1564-1581.
<http://dx.doi.org/10.21000/jasmr06021565>.
- Skousen, J., J. Renton, H. Brown, P. Evans, B. Leavitt, K. B. C. Brady, L. Cohen, and P. Ziemkiewicz, 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, Vol. 26, pp. 673-681.
<http://dx.doi.org/10.2134/jeq1997.00472425002600030012x>.
- Sobek, A. A., W. A. Schuller, J. R. Freeman and R. M. Smith, 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils. , EPA-600/2-78-054, Cincinnati, Ohio: U. S. Environmental Protection Agency, 203 p.
- Sorini, S., 1997. A Summary of Leaching Methods. American Coal Ash Assoc. Inc. Alexandria, VA
- Vesper D. and M. Roy, 2006. Selenium Location and Mode of Occurrence in the Kanawha Formation Rocks in West Virginia. In Proceedings of the 27th Annual West Virginia Surface Mine Drainage Task Force, Morgantown WV.

Younger, P. L.,1997, The Longevity of Minewater Pollution: A Basis for Decision Making, The Science of the Total Environment, 194 195, pp. 457-466.
[http://dx.doi.org/10.1016/S0048-9697\(96\)05383-1](http://dx.doi.org/10.1016/S0048-9697(96)05383-1).

Yudovich, Y., and M. Ketris, 2006. Selenium in Coal: A review, International Journal of Coal Geology, 67, pp 112-126.
<http://dx.doi.org/10.1016/j.coal.2005.09.003>.