Chapter 4: Results of Interlaboratory Study

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Background

In November 2001, a project team consisting of the U.S. Department of Interior's Office of Surface Mining (OSM), U.S. Environmental Protection Agency (EPA), Pennsylvania's Department of Environmental Protection (PADEP), and Computer Sciences Corporation (CSC, formerly DynCorp Systems and Solutions) drafted ADTI-WP1 (Humidity Cell) and ADTI-WP2 (Leaching Column) test methods for predicting the quality of mine drainage. The methods were based on weathering procedures already used by the mining industry and mine drainage researchers, and were designed to be cost efficient and practical.

During 2001 - 2003, the methods were tested in two studies, involving three laboratories, to evaluate the effects of weathering conditions on samples of shale, limestone, sandstone, and coal refuse. These studies and the resulting data are described in *Development of Test Methods for Prediction of Coal Mine Drainage Water Quality*, August 2002 and *Development of Test Methods for Prediction of Coal Mine Drainage Water Quality*, September 2003. Results of this testing demonstrated cylindrical (column) test structures (as opposed to rectangular humidity cells) and continuous exposure to humidified mixed gas facilitated uniform sample exposure to weathering conditions. The draft ADTI-WP2 Column Test Method was revised to reflect the results of these studies, and the revised method was distributed for expert review by representatives of the U.S. Bureau of Land Management, U.S. Department of Energy, Minnesota Department of Natural Resources, University of South Carolina, Pennsylvania State University, and the Western Research Institute.

Following test method review and evaluation of the 2001 - 2003 study results, the draft method was revised as follows:

- Relative percent differences (RPDs) between results of duplicate samples exposed to identical weathering conditions were included based on results of duplicate samples run in each of two laboratories that can be expected when implementing method procedures.
- Procedures for reconstructing samples according to particle size partitioning were included.
- Previous draft included two options for exposing samples to CO_2-enhanced air during saturation periods: (1) continuous flow of CO_2-enhanced air, and (2) exposure to water saturated with CO_2-enhanced air. The method was revised to specify use of Option 1 only.
- The diameter of the leaching columns was revised to 2 inches (from six inches).

- In order to assess the effects of the weathering conditions on overburden samples, it is important to remove residual target analytes from the samples prior to method implementation. Once samples were added to the leaching columns, the systems were flushed with reagent water until the reagent water demonstrated stable conductivity results (i.e., changes in conductivity ≤10%).

This report presents the results of an interlaboratory study designed to further evaluate the draft leaching column method across multiple laboratories, each evaluating the method procedures in replicate samples. Study results will be used to revise the draft method to include improved procedures and criteria for evaluating method performance in a single laboratory.

Study Description

Sample Collection and Characterization

The draft test method is intended for use in evaluating the effects of weathering on consolidated rock or mining overburden samples with geochemical characteristics that fall into a gray zone (e.g., containing moderate amounts of neutralization potential and sulfur) in cases where more information is needed than can be provided by acid/base accounting. For these sample types, acidity or alkalinity production is difficult to predict, and more information is needed than can be provided by typical leachate or acid base accounting tests. To represent this gray zone and at the same time include some geological diversity across study samples, aliquots of the following samples were provided to each of eight laboratories participating in the method validation study:

- **Brush Creek Shale (BCS3-PA):** Brush Creek Shale from Route 66 road cut near Greensburg, PA. Selected because it is well known and because of its high alkalinity and total sulfur content.
- **Kanawha Black Flint Shale (KBF-WV):** Kanawha Black Flint Shale. Selected with the assistance of West Virginia (WV) University National Research Center for Coal and Energy and the WV Department of Environmental Protection as a gray-zone shale sample from a terrain where selenium problems are believed to occur. [Note: Results of rock characterization performed concurrent with this interlaboratory study demonstrated that this sample contained low NP and sulfur.]
- **Lower Kittanning Shale (LKFC-PA):** Lower Kittanning Shale from the Redbank Creek watershed in Pennsylvania. Selected because coal and overburden in this watershed are known to produce alkaline drainage even though the neutralization potential (NP) is not high.
- **Houchin Creek Shale (HCS-IN):** Houchin Creek Shale from the Eastern Interior Coal Basin. Selected with input from OSM, as a gray zone sample containing high sulfur and low NP, but producing alkalinity.
- **Middle Kittanning Sandstone (MKSS-PA):** Middle Kittanning Sandstone from Hawbaker quarry in Clearfield County, PA. Selected for use as a blank study sample, because of its expected low production of target analytes (i.e., low sulfur and relatively low NP).

Laboratories evaluated duplicate columns of each of the four shale samples and a single column containing Middle Kittanning Sandstone.

Prior to exposure to the weathering conditions in the draft method, sample aliquots were selected randomly for analysis of neutralization potential. Results of these analyses are presented in Table 4.1.

Table 4.1: Sample Characterization

Sample	Neutralization Potential		
	Total Sulfur (%)	1978 [(1)] (ppt)	1997 [(2)] (ppt)
Brush Creek Shale (BCS3-PA) - 1	0.59	96.97	49.68
Brush Creek Shale (BCS3-PA) - 2	0.59	96.96	49.31
Brush Creek Shale (BCS3-PA) - 3	0.56	96.98	47.61
Brush Creek Shale (BCS3-PA) - 4	0.59	96.97	47.07
Kanawha Black Flint Shale (KBF-WV) - 1	0.35	15.17	13.17
Kanawha Black Flint Shale (KBF-WV) - 2	0.30	16.76	13.34
Kanawha Black Flint Shale (KBF-WV) - 3	0.21	17.17	13.65
Kanawha Black Flint Shale (KBF-WV) - 4	0.32	18.69	14.26
Lower Kittanning Shale (LKFC-PA) - 1	0.93	12.71	15.63
Lower Kittanning Shale (LKFC-PA) - 2	0.90	16.47	16.36
Lower Kittanning Shale (LKFC-PA) - 3	0.89	12.57	15.65
Lower Kittanning Shale (LKFC-PA) - 4	0.92	12.41	16.06
Houchin Creek Shale (HCS-IN) - 1	5.27	41.85	41.05
Houchin Creek Shale (HCS-IN) - 1	5.21	41.29	45.27
Houchin Creek Shale (HCS-IN) - 1	4.73	45.87	47.55
Houchin Creek Shale (HCS-IN) - 1	5.10	47.53	48.27
Middle Kittanning Sandstone (MKSS) - 1	0.08	20.9	-
Middle Kittanning Sandstone (MKSS) - 2	0.04	17.7	-
Middle Kittanning Sandstone (MKSS) - 3	0.03	14.3	-

[(1)] Results obtained using 1978 NP method (Sobek, et al., 1978).
[(2)] Modified neutralization potential method (Skousen, et al., 1997).

Laboratory Tasks

To evaluate method performance in multiple laboratories, and to ensure the generation of at least six useable datasets [1] the 2006 study involved seven participating laboratories implementing method procedures in 9 columns over a 15-week period and analyzing weekly column leachate samples for conductivity, pH, alkalinity, and net acidity. Each laboratory also shipped a filtered sample aliquot from each of its 9 weekly leachate samples (one from each column) to a metals laboratory for measurement of dissolved metals and sulfate. An eighth participating laboratory joined the study during the third week of the 15-week study period.

This laboratory was responsible for measuring conductivity, pH, alkalinity, net acidity, metals, and sulfate in all weekly leachate samples generated in that laboratory. All eight participating laboratories also recorded daily measurements of room temperature, gas flow into each column, and %CO_2 discharge from each column.

The analytes to be measured by laboratories and the analytical methods used are listed in Table 4.2. Data results of the analyses are included in Appendix E.

Table 4.2: 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% CO2 with a tolerance of +/- 2%
Weekly	pH	EPA 150.1; Standard Methods 4500-H; ASTM D1293; USGS I-1586
	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

Method Preparation

column construction: Column assemblies for all but two of the participating laboratories were constructed in a single laboratory familiar with implementation of method procedures from participation in the 2003 evaluation study. This laboratory constructed setups for Laboratories 2, 3, 4, 5, 6, 7 and 8, each setup consisting of nine columns, nine flow meters (one flow meter attached to each of nine columns) a carboy (for introduction of the humidified gas mixture), and all necessary tubing, clamps, and seals. An example of these assemblies is provided in Figure 4.1. Because Laboratory 1 initiated weathering procedures approximately 3 months prior to Laboratories 2 through 8, this laboratory was responsible for construction of their column assemblies.

column preparation: The size of the particles within each sample being evaluated is a contributing factor to the effects of exposure to weathering (i.e., the smaller the particle size, the greater the surface area exposed). For this reason, and because particle size distributions within the samples that will be evaluated using this method are largely the result of mechanical sample crushing, the method developers have determined that the method should include a procedure for reconstructing samples according to a standardized particle-size distribution. This standardized distribution can facilitate comparison of the effects of weathering on various sample types. Laboratories participating in this study were tasked with preparing samples for each column according to the particle-size distributions listed in Table 2 of the draft method and in Table 4.3 below.

Table 4.3: 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**

To provide an assessment of method precision, laboratories were tasked with preparing aliquots of each shale samples for exposure to identical weathering conditions in separate duplicate columns. Laboratories were also tasked with preparing a sandstone sample to evaluate weathering effects in a sample known to produce only small amounts of target analytes (i.e., contain low sulfur and relatively low NP).

Method Evaluation

Laboratories evaluated column test procedures as written and according to study requirements, with the following exceptions:

- **sample duplicates:** Laboratories were instructed to evaluate weathering procedures in duplicates of all four shale samples and in a single sandstone sample. Laboratory 8 evaluated procedures in duplicates of three of the four shale samples, in duplicates of the sandstone sample, and a single Kanawha Black Flint Shale sample.

- **study schedule:** Due to laboratory contracting schedules, not all laboratories were available to initiate study activities concurrently. Six of the eight participating laboratories initiated the test procedure on January 9, 2006. Laboratory 1 began the study approximately 12 weeks before these laboratories, using a slightly different column construction. Laboratory 8 began method activities approximately 4 weeks following study initiation, performing metals analysis in the laboratory rather than sending samples to the metals laboratory.

- **net acidity and alkalinity measurements:** Laboratories were instructed to measure net acidity and alkalinity in weekly leachate samples using methods listed in Table 4.2. Laboratory 6 did not measure net acidity and measured alkalinity in samples using indicator paper. For this reason, alkalinity and acidity results from this laboratory were not comparable to results generated in the other participating laboratories and were not used in determining method performance.
- **initial flush of samples:** Section 7.4.1 of the method describes procedures for performing an initial flush of the samples prior to exposing the samples to weathering procedures. This initial flush is intended to remove precipitates and salts that may have accumulated during sample storage. Laboratories flushed each column with reagent water, from three to four times during this initial flush period. With the exception of Laboratory 8, laboratories reported the volume of water added and removed from each column during the initial flush.
- **weekly saturation:** Columns in Laboratory 1 were exposed to a two-week period of saturation during Weeks 13 and 14. Laboratory 1 results submitted during these weeks are not comparable to results submitted by other laboratories, and were therefore eliminated from method performance evaluations.
- **metals measurements:** Analytical results for measurement of metals in samples from Laboratories 1 through 7 were reported in µg/L by the metals laboratory. Laboratory 8 reported analytical results for measurement of metals in mg/L. These results were not comparable to the results reported µg/L and therefore, were not included in determinations of interlaboratory RPD or relative standard deviation (RSD).

Figure 4.1 Leaching Column Assembly.

Data Results and Evaluation

The precision of this test method is dependent on numerous factors, including but not limited to:

- sample reconstruction and compaction,
- water volumes added and collected,
- total sample weight,
- column preparation,
- exposed surface areas,
- particle surface area to volume ratio,
- partial pressure of CO_2,
- mixed gas introduction, and
- results of water analyses (e.g., analytical precision for metals, acidity, alkalinity, sulfate, conductivity, pH).

Results of the interlaboratory study were used to evaluate and improve the test method, and to determine the precision that can be expected in a single laboratory implementing method procedures using duplicate samples. Single laboratory precision is determined as:

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

Where:
C1 = result in original sample
C2 = result in duplicate sample

Single laboratory RPDs, representing the community of laboratories that are expected to use this method, were determined by pooling the RPDs resulting from duplicate columns across all the interlaboratory results according to the following equation:

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

Where:
RPD_i = the RPD for laboratory *i*
m = the number of laboratories

To compensate for the effects of sample size and of the volume of water collected from each column, RPDs were determined in terms of both analyte concentration (weight of analyte per volume of water analyzed) and weighted results (analyte concentration multiplied by the volume of water collected and divided by total sample weight). RPD results are presented in a later section of this chapter.

Precision that can be expected in multiple laboratories testing replicate (more than two duplicate) samples also was evaluated in terms of RSD in both concentration and weighted results in replicate samples across laboratories. RSDs and pooled RSDs were determined using the following equations:

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

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)

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

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

The effect of the test method on the production of the analytes discussed in this report also was evaluated, but that evaluation is not the subject of this report. Detailed results of this study are presented in Appendix E.

Water Volumes

Laboratories reported the volume of water that was added to and collected from each column throughout the study, including during the initial flush. Volumes were used to evaluate data in terms of weighted results and to provide information regarding the amount of water remaining in the columns. Volumes also were used to assess the amount of water absorbed by samples during the initial flush, prior to sample weathering. Tables 4.4a through 4.4e present the volume (mL) of water remaining in each column throughout the study (determined by subtracting the volume collected from the volume added). Detailed Volume In / Volume Out measurements are provided in Appendix E. Volumes added to columns in Laboratory 8 were not reported, and therefore, are not included in this evaluation.

Fifty three of the fifty five columns run in Laboratories 1 through 7 retained significantly more water during the initial flush period than during any of the subsequent testing weeks. The exceptions were one HCS-IN column run in Laboratory 6 and one KBF-WV shale column run in Laboratory 3. Excluding these two columns, volumes of water added by laboratories during the initial flush ranged from 940 to 2406 mL; volumes collected ranged from 197 to 2177 mL. Volume differences indicate that columns retained from 85 to 1098 mL of water during the initial flush period, and that water volumes overall were retained in all columns. Columns in Laboratory 1 retained the most water (500 – 1098 mL) out of all other columns during the initial

flush and retained much of that water throughout the 15 weeks; with only one HCS-IN sample from Laboratory 3 coming close at 566 mL initially. The different column packing technique of Laboratory 1 could account for this water retention. Differences also indicate that collection of retained water volumes during a subsequent collection period (indicated by negative Volume Added – Volume Collected results) occurred across several laboratories through approximately Week 6, but most often through Week 3.

In evaluating the analytical results submitted during this study, it is assumed that the concentration of analytes measured is consistent throughout the aqueous phase within each column (i.e., the concentration of each analyte measured in the sample volume collected is representative of the concentration of the analyte in the water throughout the column). It is also assumed that analytes will continue to partition or dissolve into any water that is retained in the column. With these assumptions in mind, it is important to note that the amount of water that is added, collected, and retained in each column must be considered as a variable affecting sample discharges. This is true irrespective of the sample being evaluated. It is also important to note that evaluation of data in terms of weighted results (analyte concentration, multiplied by the volume of water collected and divided by total sample weight) will compensate for the volume of water collected and the sample weight, but will not compensate for the impact of water retained from a previous week or weeks.

Table 4.4a: Houchin Creek Shale Volume Differences

Sample ID: HCS-IN														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
Sample Weight (grams)														
	2000	*2000*	*1298*	*1589*	*1521*	*1489*	*1487*	*1515*	*1482*	*1521*	*1361*	*1410*	*1412*	*1487*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	1098	1024	230	390	475	566	220	300	267	252	85	245	310	315
1	25	-41	-15	-45	54	-55	25	20	125	75	90	115	90	180
2	35	16	25	-55	81	93	30	20	56	95	-65	-40	140	10
3	17	31	-10	5	17	-115	25	50	54	123	35	65	284	160
4	28	20	25	20	52	107	70	55	76	50	45	50	120	190
5	71	52	5	0	102	26	35	35	58	49	-10	15	182	120
6	40	38	-5	5	58	75	40	25	69	82	65	80	240	172
7	28	33	10	50	125	194	50	40	57	78	10	5	246	240
8	25	46	15	10	131	27	55	60	84	100	20	10	210	210
9	60	64	15	5	28	10	65	60	90	73	10	80	85	100
10	82	14	10	5	73	42	60	40	80	84	40	65	85	120
11	35	40	10	20	34	37	45	55	60	55	25	55	70	110
12	84	62	5	15	28	24	55	60	75	88	35	20	125	75
13	-	-	5	10	14	-8	80	55	103	115	40	75	130	80
14	56	7	0	5	19	10	60	50	59	43	5	0	200	200
Net	**1684**	**1406**	**325**	**440**	**1291**	**1033**	**915**	**925**	**1313**	**1362**	**430**	**840**	**2517**	**2282**

Table 4.4b: Kanawha Black Flint Shale Volume Differences

Sample ID: KBF-WV														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	Sample Weight (g)													
	2000	*2000*	*1653*	*1883*	*1819*	*1849*	*2055*	*2039*	*2079*	*2056*	*1999*	*2002*	*1862*	*1912*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	824	848	270	235	305	12	260	155	322	235	345	300	345	315
1	-87	-55	-35	-20	51	52	25	30	66	50	35	35	155	245
2	34	23	0	20	125	69	15	20	35	35	15	15	240	90
3	45	30	5	0	22	11	40	35	28	39	45	45	209	215
4	22	23	25	25	23	34	30	45	37	17	60	55	245	175
5	25	31	-5	0	79	58	50	35	81	65	25	35	200	170
6	36	60	0	0	38	46	40	30	63	71	55	65	190	170
7	29	46	0	25	49	38	40	30	74	68	35	-5	140	160
8	36	35	10	30	39	45	50	50	64	61	45	60	77	255
9	28	38	5	5	27	25	50	50	100	82	60	40	60	4
10	23	60	10	10	44	30	30	15	78	73	30	55	50	20
11	29	28	10	5	42	32	70	30	66	50	20	70	30	50
12	22	44	5	5	51	76	50	50	54	61	160	55	20	15
13	-	-	5	5	22	10	60	70	65	55	5	25	20	80
14	29	50	5	5	28	44	55	50	67	50	100	65	60	100
Net	**1095**	**1261**	**310**	**350**	**945**	**582**	**865**	**695**	**1200**	**1012**	**1035**	**915**	**2041**	**2064**

Table 4.4c: Brush Creek Shale Volume Differences

Sample ID: BCS3-PA														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	Sample Weight (grams)													
	2000	*2000*	*1802*	*1807*	*1691*	*1828*	*1850*	*1922*	*1879*	*1904*	*1833*	*1859*	*1900*	*1836*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	918	1061	217	215	229	415	195	260	206	228	295	300	225	350
1	105	96	-40	-10	70	82	3	30	86	79	70	75	70	175
2	0	27	10	10	95	51	20	25	-10	15	5	-5	100	100
3	72	68	10	10	18	34	25	15	49	70	35	35	55	45
4	34	16	35	20	66	69	35	30	25	31	80	65	160	50
5	31	88	10	5	81	61	40	45	100	66	5	15	175	50
6	67	36	5	15	91	86	40	40	56	72	65	95	180	180
7	64	55	20	10	95	69	35	35	70	66	50	0	40	110
8	65	29	10	0	17	30	55	45	86	85	35	55	125	170
9	62	30	5	15	10	16	60	60	63	81	50	65	65	75
10	67	19	20	15	61	51	25	40	80	81	35	25	85	95
11	57	33	10	15	60	57	65	60	64	63	15	20	80	80
12	54	44	5	5	53	25	75	60	60	57	35	45	50	70
13	-	-	5	5	1	53	80	90	81	63	20	30	50	60
14	78	37	0	5	3	40	50	55	80	78	15	0	140	120
Net	**1674**	**1639**	**322**	**335**	**950**	**1139**	**803**	**890**	**1096**	**1135**	**810**	**820**	**1600**	**1730**

Table 4.4d: Lower Kittanning Shale Volume Differences

Sample ID: LKFC-PA														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
Sample Weight (grams)														
	2000	*2000*	*1896*	*1842*	*2011*	*1884*	*2078*	*2038*	*2014*	*2002*	*1971*	*1934*	*1970*	*2010*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	755	500	335	215	319	284	225	305	212	240	285	270	445	360
1	0	28	-5	-10	42	111	25	30	45	60	85	75	125	135
2	21	13	0	20	67	68	30	30	57	80	-55	20	220	100
3	28	26	-5	5	19	24	30	35	68	51	30	20	194	146
4	24	29	20	15	45	42	65	50	76	70	65	55	135	110
5	27	35	0	0	102	68	30	40	63	70	15	5	130	120
6	33	27	0	5	39	19	25	40	61	66	60	40	210	174
7	40	19	30	10	64	62	40	40	71	52	30	55	180	230
8	15	21	5	10	60	48	55	60	61	66	60	25	190	210
9	27	38	15	10	28	15	65	60	99	80	50	35	135	80
10	24	24	15	5	39	23	35	40	74	78	35	30	95	180
11	27	35	10	30	46	60	40	65	55	60	35	20	80	190
12	26	39	0	5	20	14	60	65	90	60	20	35	90	120
13	-	-	10	0	37	19	60	60	88	74	35	25	140	180
14	22	32	0	0	16	21	45	60	53	78	5	-10	110	200
Net	**1069**	**866**	**430**	**320**	**943**	**878**	**830**	**980**	**1173**	**1185**	**755**	**700**	**2479**	**2535**

Table 4.4e: Middle Kittanning Sandstone Volume Differences

Sample ID: MKSS - PA							
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7
Sample Weight (g)							
Week	*2000*	*1684*	*1751*	*1964*	*1896*	*1905*	*1790*
Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)							
Initial Flush	883	440	233	285	200	485	245
Week 1	41	45	83	30	73	-15	95
Week 2	57	35	74	15	67	-35	70
Week 3	15	55	13	35	45	35	160
Week 4	49	55	52	45	86	95	95
Week 5	60	30	56	5	60	15	115
Week 6	52	30	42	35	69	90	145
Week 7	53	35	62	50	59	-35	150
Week 8	49	5	49	65	95	80	155
Week 9	42	5	11	50	111	40	85
Week 10	60	5	52	40	93	40	110
Week 11	46	10	30	50	40	40	90
Week 12	43	5	40	55	78	90	70
Week 13	-	15	25	75	65	15	130
Week 14	54	15	44	45	105	10	140
Net	**1504**	**1325**	**866**	**880**	**1246**	**950**	**1855**

Sample Weights

As described previously, laboratories reconstructed samples according to the particle size distribution in Table 4.2. All laboratories, with the exception of Laboratory 8, prepared duplicates of four shale samples and a single sandstone sample. Laboratory 8 prepared a single Kanawha Black Flint Shale sample and duplicates of all other samples, including sandstone. Weights of reconstructed samples added to columns in each laboratory are presented in Table 4.5.

Table 4.5: Sample Types and Weights (in grams)

Lab	Brush Creek Shale (BCS3-PA)	Kanawha Black Flint Shale (KBF-WV)	Lower Kittanning Shale (LKFC-PA)	Houchin Creek Shale (HCS-IN)	Middle Kittanning Sandstone (MKSS)
1	2000	2000	2000	2000	2000
	2000	2000	2000	2000	-
2	1801	1653	1895	1298	1684
	1807	1883	1841	1589	-
3	1691	1819	2011	1521	1751
	1828	1849	1884	1489	-
4	1850	2055	2078	1487	1964
	1922	2039	2038	1515	-
5	1880	2079	2014	1482	1896
	1904	2056	2001	1521	-
6	1833	1999	1971	1361	1905
	1859	2002	1933	1410	-
7	1900	1862	1970	1412	1790
	1836	1912	2010	1487	-
8	1900	1800	2000	1800	2000
	1900	-	2000	1800	2000

Columns in Laboratory 1 were prepared in accordance with initial method instructions to add approximately 2 kg sample to each column. The remaining laboratories initiated study activities approximately three months later, following revised instructions to fill columns to approximately 4 inches below the top of the column, using little to no packing. Discussions with Laboratory 1 indicated that sample compaction was needed to add 2000g to each HCS-IN column. All other laboratories added from 1361 to a maximum of 1800g to HCS-IN columns. Recorded water volumes indicate that sample compaction could have affected the amount of water added to and collected from samples, particularly the HCS-IN samples.

Method Performance

Method performance, in terms of the precision that can be expected to be achieved in a single laboratory, was evaluated in terms of the RPD in unweighted (concentration) results and weighted (concentration multiplied by water volume collected over the total weight of the sample) results between duplicate samples. Precision that can be expected in multiple laboratories testing replicate (more than two) samples was evaluated in terms of the RSD in concentration and weighted results in replicate samples across laboratories.

analytical precision and recovery: In addition to the effects of water volumes and total sample weight, the RPDs between duplicate samples are due in part to the variability and accuracy that is inherent to the analytical methods that were used to measure the analytes of interest.[1] For example, EPA methods often include RPD performance criteria of up to 35% for duplicate analyses. EPA draft Method 200.7 (which was used to measure the concentration of metals during this study) includes RPD criteria ranging from 0.5 to 20%. In this study, analytical RPDs between duplicate analytical QC samples for dissolved metals and sulfate measurements that were above the laboratory's minimum detection limit (MDL) ranged from 0 to 109%, with 4.5 percent falling outside method prescribed analytical RPD of 20%. The highest RPDs were observed for datasets that included a majority of results that were below or near laboratory detection level, as indicated by the percentage of sample pairs with results falling below the laboratory MDL (see Table 4.6). Analytical recoveries in spiked samples run by the metals laboratory, ranged from 62 to 134%.

For each analyte measured by the metals laboratory, Table 4.6 lists (1) the percent of total sample pairs with results below the laboratory MDL, (2) the range of RPDs across analytical duplicate QC samples, (3) the pooled RPD across all analytical QC duplicates, and (4) the range of percent recovery in analytical spikes. To isolate the results of weathering as much as possible from the variability introduced by sample analysis, data results for the analytes listed in Table 6 and associated with quality control samples (i.e., analytical duplicates or analytical spikes) that fall above an RPD of 20 or outside a % recovery range of 75 to 125, were eliminated from the assessment presented in this report. The percentage of results eliminated based on analytical quality control also are included in Table 4.6.

Table 4.6: Relative Percent Differences (RPD) Between Analytical QC Duplicates

Analyte	%Total Pairs with results <MDL	Analytical RPDs (excluding results < MDL)	Pooled Analytical RPD	% Recovery Range	% of Column Results Eliminated based on analytical QC Failures
Fe	41	0 – 109	29	78 – 122	1.7
Mn	0	0 – 30.1	5.4	80 – 130	0.2
Al	80	0 – 30.3	10.3	81 – 112	0.2
Ca	0	0 – 7.5	2.2	65 – 128	0.4
Mg	0	0 – 7.9	2.3	80 – 133	0.2
Se	16	0 – 75.7	24.6	62 – 134	2.2
Zn	8	0 – 20.1	4.6	78 – 112	0.1
Na	0	0 – 37.8	7.8	75 – 115	0.4
K	0	0 – 15.4	4.8	80 – 110	0
SO_4	0	0 – 4.8	1.2	90 – 125	0

Only a subset of the laboratories measuring acidity, alkalinity, pH and conductivity reported laboratory detection limits and/or results of analytical quality control (QC) samples. All QC results reported for these analytes passed method-specified criteria; therefore, none of these data were eliminated based on association with failed QC results.

[1] EPA methods often include RPD performance criteria of up to 30% for duplicate analyses. EPA draft Method 200.7 (May 2001) includes RPD criteria ranging from 0.5 to 20%. EPA draft Method 1630 for measurement of methylmercury includes an RPD criterion of 35%.

comparison of duplicate weathering samples: Method precision was assessed using unweighted and weighted results from duplicate samples exposed to identical weathering procedures. Relative percent differences (RPD) were calculated for analytical results prior to weathering (initial flush at Week 0) and as pooled RPDs for all sample weeks beginning with Week 1 and continuing through Week 14 (14-week RPD). The following results were eliminated from RPD calculations:

- Results associated with analytical QC failures
- Results reported at less than the laboratory MDL
- Results identified as outliers using Grubbs Test for outlying results (Grubbs, 1972)
- Laboratory 6 did not submit acidity results. This laboratory also submitted alkalinity results obtained using indicator paper; these results were not comparable to results submitted by other laboratories.
- Laboratory 1 did not include a saturation period during Week 13. Results submitted by this laboratory during Weeks 13 and 14 were not comparable to results submitted by other laboratories
- Analytical results for measurement of metals in samples from Laboratories 1 through 7 were reported in µg/L by the metals laboratory. Because Laboratory 8 joined the study several weeks following the study's initiation, it was responsible for measurement of all study analytes, including metals, in samples collected. Laboratory 8 reported analytical results for measurement of metals in mg/L. These results were not comparable to the results of the metals laboratory (reported as µg/L) and therefore, were not included in interlaboratory RPD or RSD determinations.

Pooled RPDs calculated based on unweighted and weighted results for each sample type are presented in Tables 4.7a and 4.7b. Pooled RPDs calculated using unweighted and weighted results for all samples are presented in Table 4.7c. Because pH measurements are not reported in units of concentration, comparative pH results are presented as the mean absolute difference.

Table 4.7a: Pooled RPDs based on analyte concentrations in duplicate sample pairs
(Note: Highlighted cells contain RPDs >50.)

	BCS3-PA				LKFC-PA			
	Unweighted		Weighted		Unweighted		Weighted	
Analyte	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		

Table 4.7b: Pooled RPDs based on analyte concentrations in duplicate sample pairs
(Note: Highlighted cells contain RPDs >50.)

	HCS-IN				KBF-WV			
	Unweighted		Weighted		Unweighted		Weighted	
Analyte	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		

Table 4.7c: Overall RPDs based on analyte
(Note: Highlighted cells contain RPDs >50.)

	Initial Flush		14-week period		
Analyte	Unweighted	Weighted	Unweighted	Weighted	Analytical (from Table 6)
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
SO_4	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		

The largest pooled RPD in all weathered samples resulted between measurements of iron, aluminum, manganese, and acidity; for the metals, this corresponds to the analytes with the greatest number of results falling below the laboratory MDL (see Table 4.6). The lowest variability between duplicates occurred with magnesium, sodium, potassium, and sulfate. With the exception of sulfate, these analytes were measured in mg/L or g/L ranges in water samples collected from the test columns (compared with µg/L levels for iron, aluminum, and manganese).

For most analytes, the RPDs between duplicate samples during the 14-week weathering period were similar to or decreased from the RPDs between duplicate samples during the initial flush, indicating that the method 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.

RPDs for the following analytes increased significantly during the 14-week weathering period (see Table 4.7c):

- **Iron (Fe)** − Unweighted and weighted pooled RPDs are 44.8 and 50.9 during the initial flush period, compared to 91.5 and 90.4 during the 14-week weathering.

- **Aluminum (Al)** − Unweighted and weighted pooled RPDs are 37.0 and 38.6 during the initial flush, compared to 76.9 and 72.5 during the 14.week weathering period.

- **Selenium (Se)** − Unweighted and weighted pooled RPDs are 23.5 and 26.2 during the initial flush period, compared to 44.2 and 42.9 during the 14-week weathering.

- **Acidity** − Unweighted and weighted pooled RPDs are 20.0 and 27.0 during the initial flush period, compared to 106 and 99.9 during the 14-week weathering.

comparison of replicate weathering samples: Method precision across laboratories was assessed using weighted results from replicate samples exposed to weathering procedures in multiple laboratories. Weighted results (analyte concentration multiplied by the volume of water collected and divided by total sample weight) were used to mitigate the effects of the weight of individual samples and the volume of water collected when comparing results. Relative standard deviations (RSD) were calculated for replicate sample results prior to weathering (initial flush at Week 0) and as pooled RSDs for all sample weeks beginning with Week 1 and continuing through Week 14 (14-week). 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.

The following results were eliminated from RSD calculations:

- Results associated with analytical QC failures
- Results reported at less than the laboratory MDL
- Results identified as outliers using Grubbs Test for outlying results
- Laboratory 6 did not submit acidity results, and submitted alkalinity results obtained using indicator paper; these results were not comparable to results submitted by other laboratories.
- Laboratory 1 did not include a saturation period during Week 13; results submitted during Weeks 13 and 14 were not comparable to results submitted by other laboratories
- Laboratory 8 reported analytical results for measurement of metals in mg/L. These results were not comparable to the results of the metals laboratory (reported as µg/L) and therefore, were not included in interlaboratory RPD or RSD determinations.
- Analytical results for measurement of alkalinity and acidity in Laboratories 2, 4, 5, 7 and 8, were reported to a laboratory-specific censoring level. For example, Laboratories 2, 4, 7 and 8 reported results of acidity to <10, "negative," <1, and 0, respectively. Laboratories 2, 4, 5 and 7 reported results of alkalinity to <20, <5, 0, and<1, respectively. Although these data were used to determine within laboratory precision (as RPD), the data are not comparable to data results from other laboratories and were not used for evaluations of method performance across laboratories (i.e., pooled RSDs).

Pooled RSDs from replicate samples across laboratories are presented for each analyte in each sample in Table 4.8a; analyte-specific RSDs are presented in Table 4.8b.

Table 4.8a: Pooled interlaboratory RSDs based on analyte concentrations in replicate samples *(Note: Highlighted cells contain RSDs >50.)*

	BCS3-PA		HCS-IN		LKFC-PA		KBF-WV		MKSS-PA	
Analyte	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
SO_4	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

Table 4.8b: Overall pooled RSDs based on analyte
(Note: Highlighted cells contain RSDs >50.)

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
SO_4	43.4	37.2
Conductivity	26.0	39.6
	Standard Deviation	
pH	0.6	0.7

Resulting pooled RSDs across laboratories are consistent with results of the pooled RPDs between duplicate samples. RSDs are largest for iron, zinc, aluminum, and manganese 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 calcium, magnesium, sodium, potassium, and sulfate.

Conclusions Regarding Method Performance

Results of this interlaboratory study are consistent with both ASTM and U.S. EPA guidelines, using at least six datasets generated by laboratories representing the community of potential users of the method. Results of the study represent the variability and accuracy that would be expected across laboratories and support the method's use as a standard method for predicting mine drainage, particularly in samples representing gray zone areas that would be expected to need additional evaluation by the method.

The interlaboratory study presented in this report is one of several studies that have been completed to support development of a standardized and effective test procedure for predicting the quality of mine drainage in mining areas that are otherwise difficult to characterize, and combines the efforts of the U.S. Department of the Interior's Office of Surface Mining, the U.S. Environmental Protection Agency, the Pennsylvania Department of Environmental Protection, several private laboratories, universities, and consultants. Results of this study will be used to revise the existing draft leaching column method (ADTI-WP2) and to provide performance criteria regarding the RPDs and RSDs that should be expected by laboratories using the method (see Tables 4.9 and 4.10).

RPD results included in Table 4.9 reflect the pooled results of the interlaboratory study, using datasets from seven laboratories evaluating the effects of weathering on samples of Brush Creek shale, Kanawha Black Flint shale, Lower Kittanning shale, Houchin Creek shale, and Middle Kittanning sandstone. These results will be included in the draft test method as precision criteria that can be expected from duplicate samples run in a single laboratory.

Table 4.9: Expected method precision (as RPDs) based on Interlaboratory Study Results

Analyte	14-week RPD	Initial Flush RPD	Weathering Test RPD (Difference between 14-week and initial flush RPD)
Fe	90.4	50.9	**39.5**
Mn	52.5	44.1	**8.4**
Al	72.5	38.6	**33.9**
Ca	21.9	38.8	**(16.9)**
Mg	21.4	16.4	**5.0**
Se	42.9	26.2	**16.7**
Zn	60.2	52.0	**8.2**
Na	25.1	21.1	**4.0**
K	23.7	21.5	**2.2**
SO_4	27.5	20.4	**7.1**
Alkalinity	28.7	35.2	**(6.5)**
Acidity	99.9	27.0	**72.0**
Conductivity	13.2	11.1	**2.1**
	Mean absolute difference		
pH	0.2	0.2	**0**

RSD results included in Table 4.10 reflect the pooled results of the interlaboratory study, using datasets from seven laboratories evaluating the effects of weathering on samples of Brush Creek shale, Kanawha Black Flint shale, Lower Kittanning shale, Houchin Creek shale, and Middle Kittanning sandstone.

Table 4.10: Overall pooled RSDs based on Analyte

Analyte	14-week	Initial Flush	Weathering Test RSD (Difference between 14-week and initial flush RSD)
Fe	114	109.4	**4.6**
Mn	78.0	65.4	**12.6**
Al	86.0	78.8	**7.2**
Ca	34.1	41.6	**(7.5)**
Mg	33.5	52.7	**(19.2)**
Se	48.8	47.4	**1.4**
Zn	85.0	97.6	**(12.6)**
Na	40.5	49.3	**(8.8)**
K	36.5	46.6	**(10.1)**
SO_4	37.2	43.4	**(6.2)**
Conductivity	39.6	26.0	**13.6**
	Standard Deviation		
pH	0.7	0.6	**0.1**

Based on results of the study, several general patterns also are apparent as to the effectiveness of the draft weathering procedures in producing valid and verifiable results for prediction of mine drainage water quality.

- The variability between duplicate samples during the initial flush period can provide an indication of variability that will occur during weathering. The lower the variability (as RPD) during the initial flush, the more likely the samples being evaluated are indeed duplicates. All precautions should be taken during sample construction, to ensure duplicate samples are identical as possible (e.g., identical column construction; identical sample weight and particle-size distribution, and the addition and collection of identical volumes of water).

- In terms of the results of dissolved metals, overall variability in all four shale samples and the single sandstone sample, was greatest in results of iron, aluminum, manganese, and zinc and lowest in calcium, magnesium, sodium and potassium. These results are consistent with the concentration levels of these analytes in the water samples (i.e., variability is high across low-level samples and low across high-level samples).

- Variability was greatest in iron and acidity results, and this variability increased with weathering.

- Much of the variability (measured as RPD and RSD) between within-laboratory duplicate samples and inter-laboratory replicate samples can be attributed to the differences in the sample masses used and the water volumes collected from each sample. Because attempts to normalize results to compensate for sample masses and leachate volumes did not significantly affect RPD results, it is likely that additional factors (e.g., sample density, column construction, gas and water introduction) affected sample exposure to weathering conditions.

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