Chapter 7. Column Leaching Tests: The Underlying Physical Chemistry

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Introduction

The ADTI-WP2 column leaching tests are intended to produce empirical results of practical value in a reproducible manner. If the designated protocols are followed, any laboratory should be able to estimate the acid-producing properties of any rock or waste material. Underlying the practical leach test, however, is the basic physical chemistry of the dissolution process. The chapter that follows is an attempt to extract as much of the underlying science as possible.

Conceptual Models for Dissolution Kinetics

The dissolution of mineral matter involves the transfer of chemical elements from the solid surface to the surrounding fluid. The rate at which the transfer process occurs depends on the surface area exposed to the solution, on the rates of chemical reactions on the mineral surface, on transfer rates across the static boundary layer of fluid on the mineral surface, and on any diffusion barriers that build up on the surface during the course of reaction. Reaction rates are usually sensitive to the effects of other ions in solution which can act as either catalysts or inhibitors. All of these are potentially important which measuring reaction kinetics in such heterogeneous materials as crushed rock or coal waste samples. For a comprehensive discussion of chemical kinetics in geochemistry see Lasaga (1998).

As background for discussion of the column experiments, it is useful to consider various possible cases and the dependence of dissolution rate on time that might be expected. For earlier related discussions see White (1986; 1992).

There are several experimental approaches to the determination of dissolution kinetics. The most direct is to place a known mass of material with a known surface area in a known volume of solvent and then monitor the uptake of dissolved elements in solution (Fig. 7.1). In Case 1, the material has a low solubility and dissolves congruently. The concentration in solution will at first rise rapidly until concentrations reach values where back reactions become important. The rate then slows and the concentration gradually approaches the saturation concentration determined by thermodynamic equilibrium. The dissolution process can often be described by a rate equation of the form

$$\frac{dC}{dt} = \frac{S}{V}\left(1 - \frac{C}{C_S}\right)^n \qquad (7.1)$$

In this equation, C is the instantaneous concentration, C_S is the saturation concentration, S is the surface area, V is the volume of solution and n is the reaction order. If the equilibrium solubility is low, the surface area can be treated as a constant. In contrast, Case 2 (Fig. 7.2) describes the dissolution of a more soluble material of limited mass. Dissolution takes place rapidly and continues until the material is entirely dissolved. In Case 2, the surface area does not remain constant so the rate equation (7.1) must be modified to take account of the (generally unknown) time dependence of the surface area, S(t). When the soluble material is completely dissolved, of course, the accumulated concentration in solution becomes constant and the rate drops to zero. With respect to minerals that might be expected in spoil materials, calcite would behave as Case 1; gypsum as Case 2.

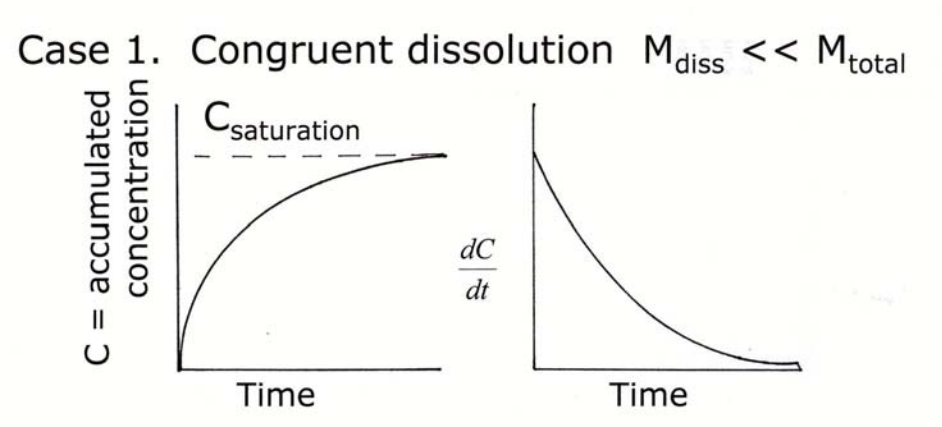


Figure 7.1. Schematic dissolution curve for a congruently dissolving solid of low equilibrium solubility.

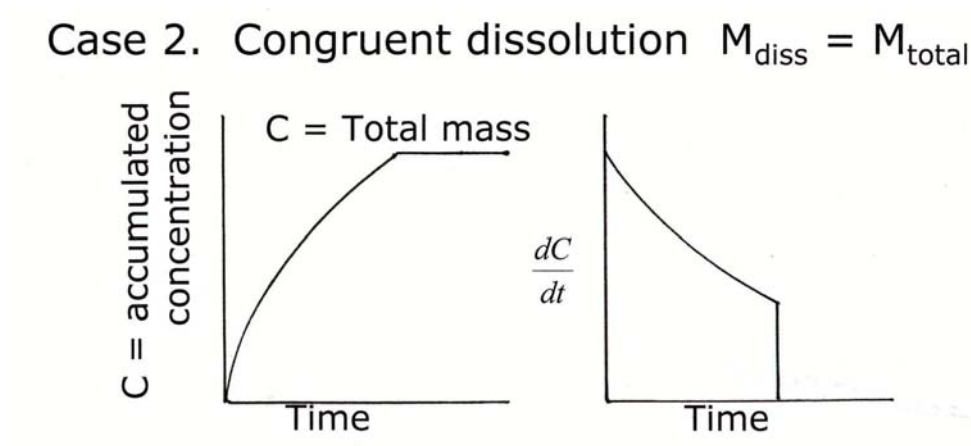


Figure 7.2. Schematic dissolution curve for a congruently dissolving solid of high solubility and limited mass.

Most minerals, however, do not dissolve by simple congruent dissociation into component ions but instead dissolve by chemical reaction with water or hydrogen ions as illustrated in

Case 3. The result will be that some components of the mineral will be taken into solution leaving other components as a solid reaction product. If the solid reaction products form a barrier layer, the rate of reaction will be controlled by diffusion of reactants through the barrier layer. Control by the rate of chemical reaction at the mineral surface will usually produce a linear dependence of concentration on time if the reaction is first order (n = 1 in equation 7.1). Control by diffusion typically produces a square root of time dependence (Fig. 7.3).

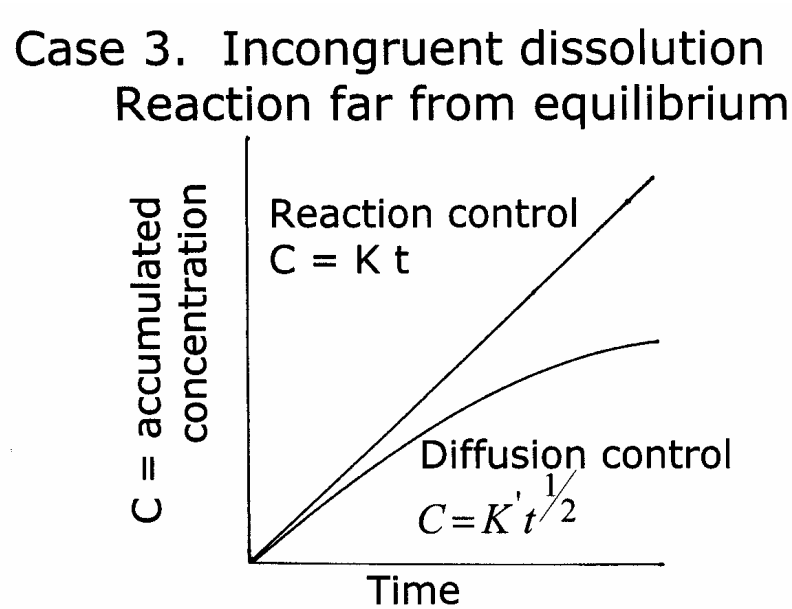


Figure 7.3 Schematic dissolution curves for materials dissolving by chemical reaction with the solvent.

Either of these mechanisms describes the dissolution of a single phase. In a heterogeneous material such a rock or mine spoil, there may be multiple phases, each releasing the same element but dissolving at different rates. The bulk rate curves for heterogeneous mineral assemblages does not lend themselves to easy mathematical analysis.

Alternative approaches to geochemical kinetics are various forms of flow-through experiments. These may be designed so that the material to be dissolved is continuously bathed in fresh solution. In flow-through experiments, the dissolving mineral never reaches equilibrium with the solution. The rate is given by the initial slope of the concentration/time curve and thus is usually the fastest rate. Instead of a continuous flow of solvent, the reaction vessels can be drained at periodic intervals and replaced with fresh solution. The column experiments are a variant of this experimental arrangement.

The materials in ADTI-WP2 leach columns, following an initial flush, undergo a 6-day weathering period as wet rock in contact with a flowing, CO_2-containing atmosphere. This is followed by a 1-day soak period in deionized water after which the water is rapidly drained for analysis and a subsequent weathering period begins. The release of leach elements from the test column is, therefore, episodic.

Each flush begins with fresh water so that the initial concentration is supposed to be zero. However, considerable water remains on mineral surfaces so that there is some, unknown, initial concentration. Concentrations rise rapidly as the weathering products accumulated from the previous six-day weathering cycle are dissolved and extracted (Fig. 7.4). Only the final concentrations, obtained when the columns are drained, were analyzed so the shapes of the curves in Figure 7.4 are completely schematic.

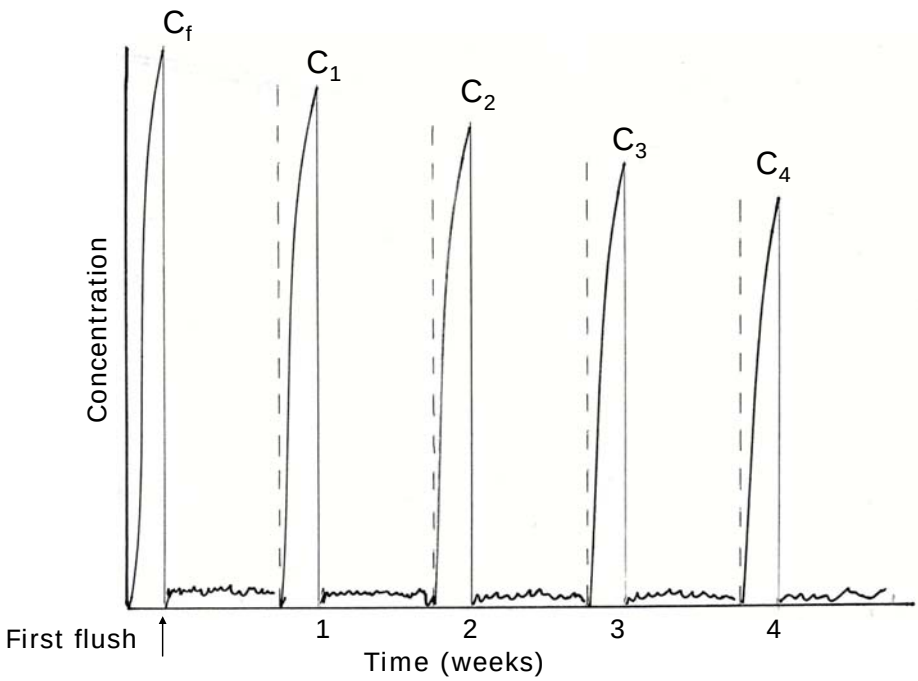


Figure 7.4. Schematic drawing of expected leaching curves from the experimental columns. The peak values, C_f to C_4 would be the instantaneous weekly concentrations which would be added to construct the cumulative curves.

Overview of Column Leach Analytical Data

The input for further analysis is the collected analytical data from the participating laboratories for the five rock types. This section examines several aspects of variations in the leaching column data from the 9 leaching columns in each of the eight participating laboratories, wherein 5 different rock sample types were tested for fourteen parameters of leachate chemistry on a weekly basis for 14 weeks. The chemical parameters are: pH, specific conductance, acidity, alkalinity, sulfate and nine metals: iron (Fe), manganese (Mn), aluminum (Al), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), selenium (Se)and zinc (Zn). Each of the eight labs conducted weekly chemical analyses of pH, conductivity, alkalinity and acidity, and were instructed to maintain daily records of room temperature, rate of gas flow through the columns, and carbon dioxide content of the gas exiting from the leaching columns. The chemical analyses of the 9 metals and sulfate for 7 of the labs were conducted by Prochem Analytical, an EPA contractor, on leachate aliquots sent to Prochem by each of the 7 labs.

The metals data from Lab 8 were not comparable to data from the other 7 labs, hence the raw data concentration plots of metals in this section do not include data from Lab 8.

Many factors control the leaching behavior of rock samples in leaching column tests as described in Geidel et al., (2000), Hornberger and Brady (1998), Bradham and Carruccio (1995) and numerous other references. The method specifications for this interlaboratory study required maintaining a constant temperature of 25° C, a CO_2 content of 10% in the gas mixture within the columns and an airflow rate of 1.0 liters per minute through the columns. The eight participating labs were not consistent in their adherence to these specifications. The records for Lab 1 and Lab 8 were incomplete; the other six labs maintained the daily log sheet provided for these records. The log sheets were developed to facilitate daily checks of the leaching environment for every day of the month, except weekends and holidays.

The monthly median temperatures and ranges of temperature are shown in Table 7.1. Lab 3 exhibited the best temperature control of the participating labs. Most of the labs were a few degrees cooler than the 25° C target value and most exhibited a few degrees of variation throughout each month. Lab 4 reported the temperatures in Fahrenheit and had the greatest variations in temperature, as shown in Table 7.1; in a three day period in March the temperature in the lab varied by 19° (i.e. March 8= 61° F, March 9= 70° F, March 10= 80° F).

Table 7.1. Median monthly temperatures and differences.

		Lab 2	Lab 3	* Lab 4	Lab 5	Lab 6	Lab 7
Jan	Median	22.3	25.0	68.0	23.4	21.0	20.0
	Difference	3.0	0.1	10.0	3.0	4.0	0.0
Feb	Median	22.2	25.0	65.0	23.9	21.0	19.0
	Difference	2.6	2.0	13.0	2.8	4.0	3.0
March	Median	23.3	25.8	70.0	23.3	22.0	20.0
	Difference	4.0	1.0	19.0	4.9	3.0	3.0
April	Median	23.0	26.0	72.5	23.1	22.5	21.0
	Difference	3.6	3.5	10.0	4.9	2.0	3.0

* Note: Lab 4 reported temperatures in Fahrenheit all others in Centigrade.

The carbon dioxide content or partial pressure of CO_2 in the leaching columns is a very important factor in how much alkalinity is generated from carbonate mineral dissolution as shown in Figure 1.1 (from White, 1988). The amount of carbon dioxide in the gas exiting the leaching columns was measured by a portable CO_2 meter, and the monthly median CO_2 values for Labs 2 through 7 are shown in Table 7.2.

Lab 5 did the best job of consistently maintaining the 10.0% CO_2 in the leaching columns for all 5 rock types as shown in Table 7.2. Labs 2, 4, 6 and 7 usually measured CO_2 amounts far less than the 10% target value as shown by the monthly median values in Table 7.2. Lab 3 frequently exceeded the 10% CO_2 target gas mixture, which could result in higher alkalinity concentrations in laboratory leaching than the actual mine environment. Labs 2 and 7 occasionally met the 10% CO_2 target.

Table 7.2. Median CO_2 content in leaching columns (percent).

		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
		C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2
HCS-IN	Jan.	7.5	8.5	11.7	13.8	5.3	5.8	10.5	10.5	-	-	7.0	7.0
	Feb.	4.0	4.0	12.0	12.0	5.0	5.0	10.5	10.5	2.5	2.0	7.0	6.5
	Mar.	5.5	4.0	6.0	10.0	5.0	5.0	10.3	10.6	2.5	2.3	6.0	6.0
	Apr.	4.0	4.0	9.0	8.0	5.3	5.0	10.5	10.3	2.8	3.0	5.5	5.3
LKFC-PA	Jan.	7.5	5.3	12.9	14.1	6.0	5.75	10.5	10.5	-	-	7.0	7.0
	Feb.	3.5	3.0	11.0	11.0	5.5	5.0	10.5	10.3	2.0	2.0	7.5	6.5
	Mar.	3.0	3.5	10.0	10.0	5.0	5.0	10.0	10.0	1.8	2.0	6.0	6.5
	Apr.	3.0	2.5	9.0	9.3	5.3	5.3	10.3	10.0	2.8	3.0	5.5	5.5
KBF-WV	Jan.	7.5	7.5	16.2	13.7	6.0	5.8	9.5	8.0	-	-	7.0	7.0
	Feb.	5.0	4.0	11.5	12.5	5.0	5.0	10.5	9.0	3.0	3.5	7.0	7.8
	Mar.	3.5	3.5	10.0	10.0	5.0	5.0	10.3	8.5	1.5	1.0	5.0	5.5
	Apr.	3.0	3.0	9.0	10.0	5.0	5.0	10.2	9.5	2.5	1.5	5.0	5.5
BCS_3-PA	Jan.	8.3	8.0	8.3	12.2	5.5	5.5	8.5	7.0	-	-	6.0	6.5
	Feb.	5.0	3.5	11.0	12.0	5.0	5.0	9.8	7.5	3.5	3.5	6.0	6.5
	Mar.	4.0	3.5	10.0	10.0	5.0	5.0	9.5	8.0	2.5	2.3	6.0	6.0
	Apr.	3.0	3.5	9.0	10.0	5.0	5.0	9.8	8.5	3.3	3.0	6.0	6.0
MKSS-PA	Jan.	6.0		12.3		4.8		9.0		-		7.5	
	Feb.	4.0		12.0		4.0		9.5		2.5		7.0	
	Mar.	3.0		10.0		4.0		9.0		2.5		5.5	
	Apr.	4.0		10.0		4.3		9.0		4.0		5.5	

The variations in CO_2 values within and between labs are shown in boxplots in Figure 7.5. The boxplots show that Labs 3 and 5 did the best job of controlling the CO_2 near to the 10% target value. Lab 3 had a median CO_2 content of 10.0%, but the spread from the median to the upper quartile is from 10 to 12%, and there are a few CO_2 values greater than 12%. Lab 5 had a median of 9%, and the interquartile range is smaller than Lab 3, with fewer values exceeding the target of 10%.

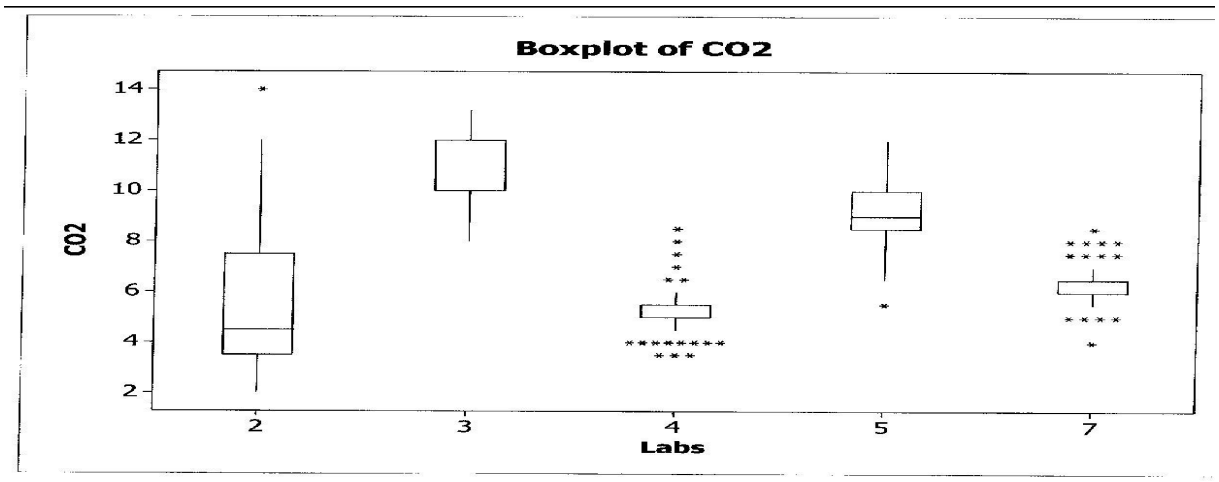


Figure 7.5. Range in CO_2 content of leach column atmosphere between laboratories. CO_2 concentration given in percent by volume.

A plot of CO_2 versus alkalinity is shown in Figure 7.6. This plot shows no distinct linear relationship with alkalinity in leaching column effluent as the dependent variable, and carbon dioxide content (i.e. CO_2%, partial pressure) as the independent variable. Theoretically, alkalinity produced from weathering this calcareous shale sample should increase in proportion to increasing CO_2 content within the leaching column (see Figure 1.1), but that relationship is not evident in this data set. However, several patterns of variation are evident in this bivariate plot. Lab 2 exhibited the greatest scatter of points, having the largest range in CO_2 and alkalinity. Labs 4 and 5 showed the least scatter of data points. Curiously, the range in alkalinity concentrations for Lab 5 is between 500 and 600 mg/l over a CO_2 range of 6.2 to 11%; for Lab 4 the range in alkalinity is 400 to 500 mg/l over a CO_2 range of 3.8 to 7.8%. This implies that relatively high alkalinity concentrations can be produced in leaching columns having far less than the 10% target value. The most unusual bivariate relationship is in the data from Lab 3 where there is a cluster of data points with relatively high alkalinity concentrations and a second cluster of four data points where relatively low (i.e. 50 to 100 mg/l) alkalinity is produced over a CO_2 range of 8.5 to 13 percent.

The gas flow rate of the gas mixture entering the leaching columns was controlled by Rotometers, which were intended to promote consistency in meeting the target 10% CO_2 value in each of the 9 leaching columns in each lab. Labs 4 and 5 very consistently maintained a gas flow rate of 1.0 liters per minute (lpm). Lab 2 typically reported gas flow rates of 0.2 to 0.35 lpm; Lab 3 was consistently at 0.35 or 0.45 lpm; while Labs 6 and 7 were typically higher than 1.0 lpm, with median values of 1.9 lpm in numerous cases. The gas flow rate is probably not independent of the method of gas mixing employed in the leaching test and the partial pressure of CO_2 in the columns. The three methods that may be used are: (1) a single tank of gas containing 10% CO_2, 10% oxygen and 80% nitrogen, (2) a tank of CO_2 mixed with a second tank of compressed air, or (3) a tank of CO_2 mixed with the "house air" line in the laboratory.

Lab 1 is the only lab which used the single tank mixture, which ensured attaining the 10% CO_2 target. Most other labs used the "house air" option, of which it appears that Labs 4 and 5 did the best job of controlling the rate of gas flow.

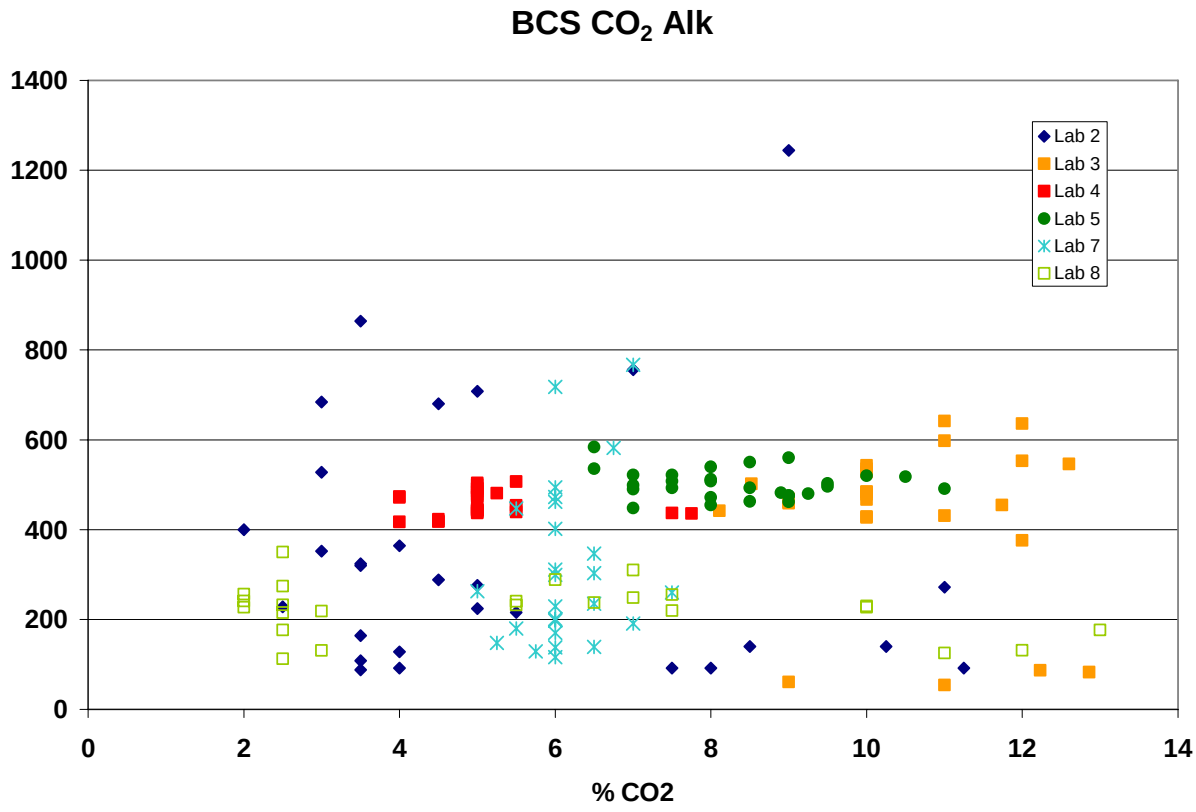


Figure 7.6. Alkalinity vs Carbon Dioxide for BCS shale in mg/L.

The volume of leachate drained out of the leaching columns on a weekly basis is summarized by lab and rock type in Table 7.3, which contains the minimum and maximum values, the range differences and the median for each leaching column. The volume of leachate drained out of a leaching column should be related to the amount of pore spaces within the column, the porosity of the particles of the lithologic unit, the surface area and the degree of packing of the rock particles. The difference in the water volume of duplicate columns within labs is much less than the differences in volume among labs in Table 7.3, which may be related to differences in the packing and volume of rock samples used between labs. There also appears to be subtle differences between the volume of leachate drained and lithology, with the sandstone sample columns having greater intergranular porosity. In cases where the differences in the volume of leachate are great, it may be necessary to normalize the data before attempting to interpret and analyze the results.

Table 7.3. Volume of leachate drained out of columns in mL.

Rock Type		Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7		Lab 8	
		C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2
HCS	min	304	338	190	200	171	166	350	340	225	170	315	270	196	220	164	124
-IN	max	323	360	380	365	362	443	440	420	259	305	430	385	365	420	274	280
	range	19	22	190	165	191	277	90	80	34	135	115	115	169	200	110	156
	med	315	351	285	295	246	254	370	363	245	261	373	313	268	250	200	198
LKFC	min	443	440	200	285	244	242	350	350	235	238	160	285	120	140	118	117
-PA	max	459	457	375	405	367	401	395	410	300	314	305	350	245	340	220	245
	range	16	17	175	120	123	159	45	60	65	76	145	65	125	200	102	128
	med	453	449	283	325	314	316	365	355	267	252	240	310	190	210	171	199
KBF	min	387	409	235	245	267	262	330	345	227	244	90	135	085	120		
-WV	max	408	422	385	370	370	370	405	410	249	269	295	275	155	155	230	
	range	21	13	150	125	103	108	75	65	22	25	205	140	155	70	110	
	med	402	420	300	300	305	326	340	360	239	260	228	178	96	140	195	
BCS3	min	516	462	325	315	313	245	385	340	260	265	240	240	350	260	116	161
-PA	max	565	559	490	500	420	412	460	440	340	315	330	385	530	430	274	250
	range	49	97	65	185	107	167	75	100	80	50	90	145	180	170	158	89
	med	523	522	398	385	347	312	410	350	282	299	283	308	400	288	193	208
MKSS	min	515		355		302		330		277		165		145		156	148
-PA	max	544		485		370		450		353		345		520		236	261
	range	29		130		68		60		76		180		105		80	113
	med	536		413		330		430		324		260		450		200	191

The first step in evaluating the leaching column data, especially for rock samples in the "gray zone", should be to examine the acidity and alkalinity data, and related mine drainage indicator parameters of pH, conductivity and sulfates. These data should be compared to the acid-base accounting data for these rock samples. The primary goal of the leaching test is to determine or predict whether the mine drainage is likely to be acidic or alkaline, and to what degree. The secondary goal is to determine whether the metals concentration data are indicative of the weathering of these rock samples in the mine environment and the resultant metals concentrations in mine drainage discharges. A simple plot of a water quality parameter (e.g. sulfate) through time, using the raw data (i.e. not weighted, not transformed), is often useful to explore patterns of variation or trends, and get a feel for the data prior to more complex analyses of the data. In this study, 14 water quality analytes were determined for 5 rock types which yields more than 70 plots if all of the analytes are plotted for each rock type and additional plots are delineated to compare rock types. This section includes some examples of these time plots. In these data plots week 1 is the "initial flush" and weeks 2 through 15 are the 14 weekly leaching episodes.

pH, Conductivity and Sulfate

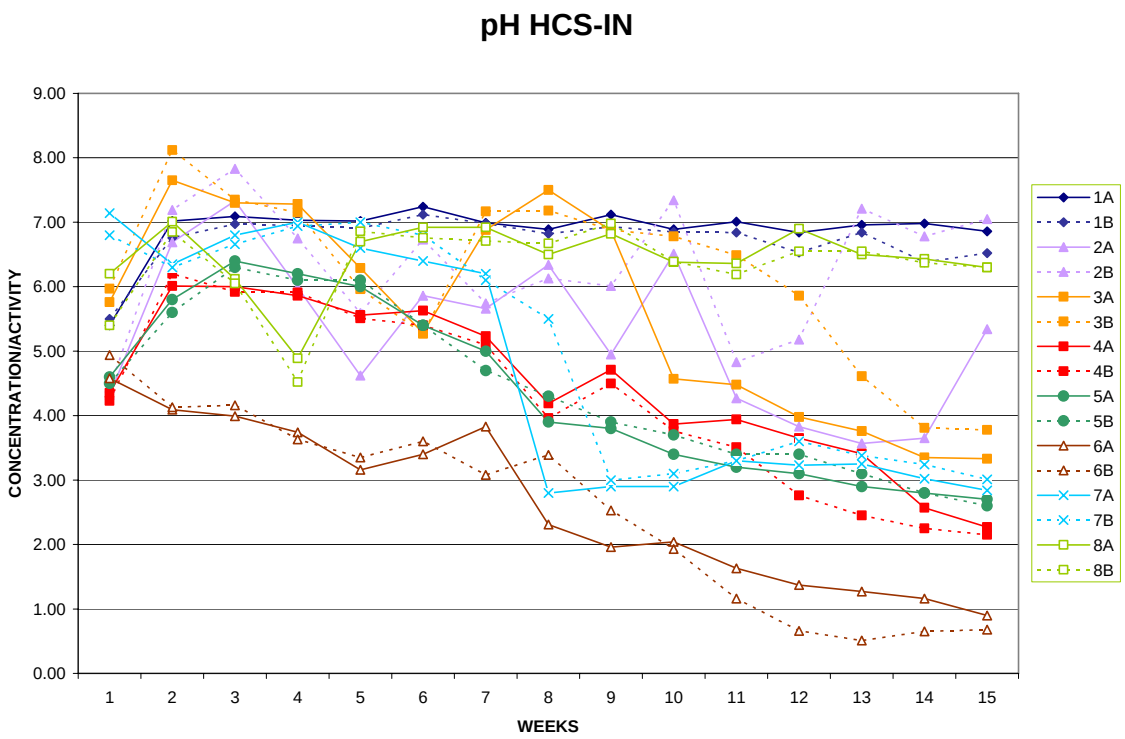


Figure 7.7. pH variations of the Houchin Creek Shale leachate.

The pH of leachate from the leaching columns containing the Houchin Creek shale from Indiana is shown in Figure 7.7. The median pH of the sixteen leaching columns ranged from 2.18 to 7.00. Figure 7.5a shows considerable variation in pH behavior among labs. The pH in Lab 1 remained constantly near 7.0 throughout the 14 week leaching period and there is a close alignment of the duplicate columns. Lab 8 exhibited pH behavior in a manner similar to Lab 1. In Lab 6 there was a steady decline in pH from pH 5 at the start of the weathering test, to a pH below 1.0 in both duplicates by week 14. Labs 2, 3, 4 and 5 also showed a decline in pH throughout the test period, but generally were above pH 5.0 for the first seven weeks of the test period, and then declined to the pH 2 to pH 3 range by the end of the weathering test. Extremely high acidity values of 16,000 mg/l and 12,000 mg/l were produced in week 14 in Lab 4, and corresponding sulfate values of 8,130 and 5,630 mg/l in Lab 4, and 20,600 mg/l in Lab 6, week 14.

The plot of sulfate in Figure 7.8 gives the appearance that some carbonate minerals were present in the leaching column for the first seven weeks of the weathering test, but became overwhelmed by acidity production from the high sulfur content and took off for the remainder of the weathering period in three of the labs (Labs 4, 5 & 6).

It appears that there were microenvironments favorable to acidity production in the columns of these labs, that were absent from Lab 1 and some of the other labs as shown on Figure 7.7 and 7.8.

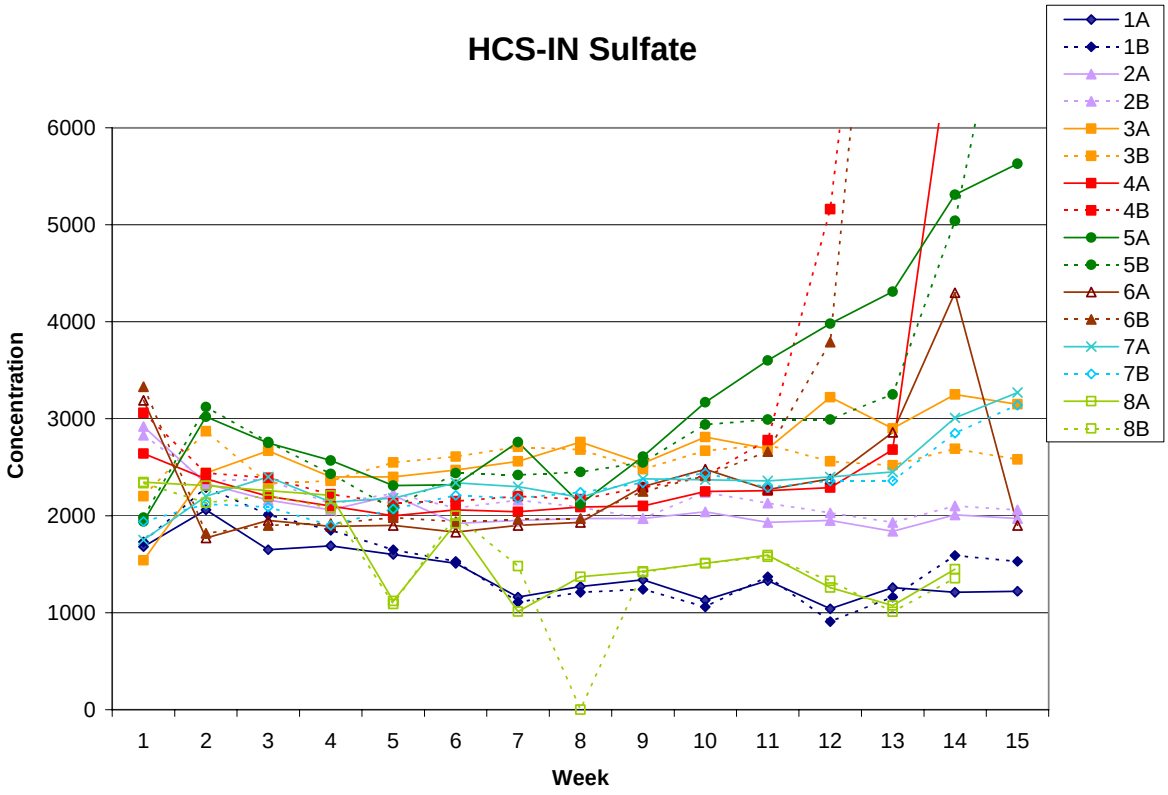


Figure 7.8. Sulfate in effluent from duplicate columns of Houchin Creek Shale.

The conductivity of the leachate is an excellent indicator of the amount of dissolved ionic species in the leaching column effluent. Figure 7.9 shows the conductivity of the 8 labs for the LKFC-PA sample. Week 1 consistently had the highest conductivity of the series after which the values gradually decreased through the 14 week period. Lab 7 had much higher conductivity values than the other seven labs. The pattern of variation for these seven labs is very similar, and the duplicate samples of each of the labs are close together. The pattern of variation for sulfate shown in Figure 7.10 is very similar to that described for conductivity above. A large part of the reasons for that similarity in conductivity and sulfate from the LKFC-PA rock sample is that sulfate is the dominant anion in the leachate.

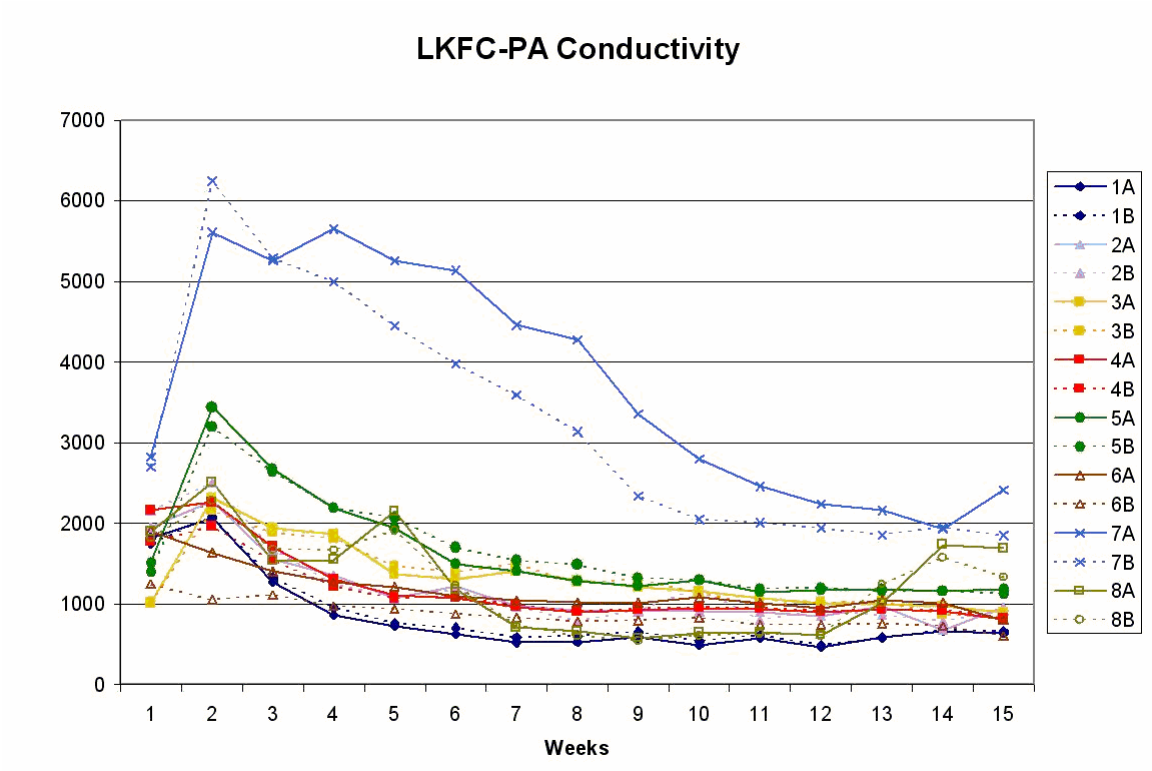


Figure 7.9. Patterns of variation of conductivity (microsiemens) from duplicate columns.

Alkalinity

The Brush Creek Shale produced significant alkalinity concentrations in Phase 1 (see Hornberger et al., 2003) and Phase 2 (see Brady et al., 2004) of this method development project. Most labs reported alkalinity values of several hundred mg/L throughout the 14 week leaching period for the Brush Creek Shale, but there was some scattering of values as shown on Figure 7.11. When the data are plotted for Labs 4 and 5 only, the scatter disappears and the duplicate samples are very consistent, as shown on Figure 7.12. The configuration of this plot is indicative of attaining calcite solubility control as described in Brady et al., (2004).

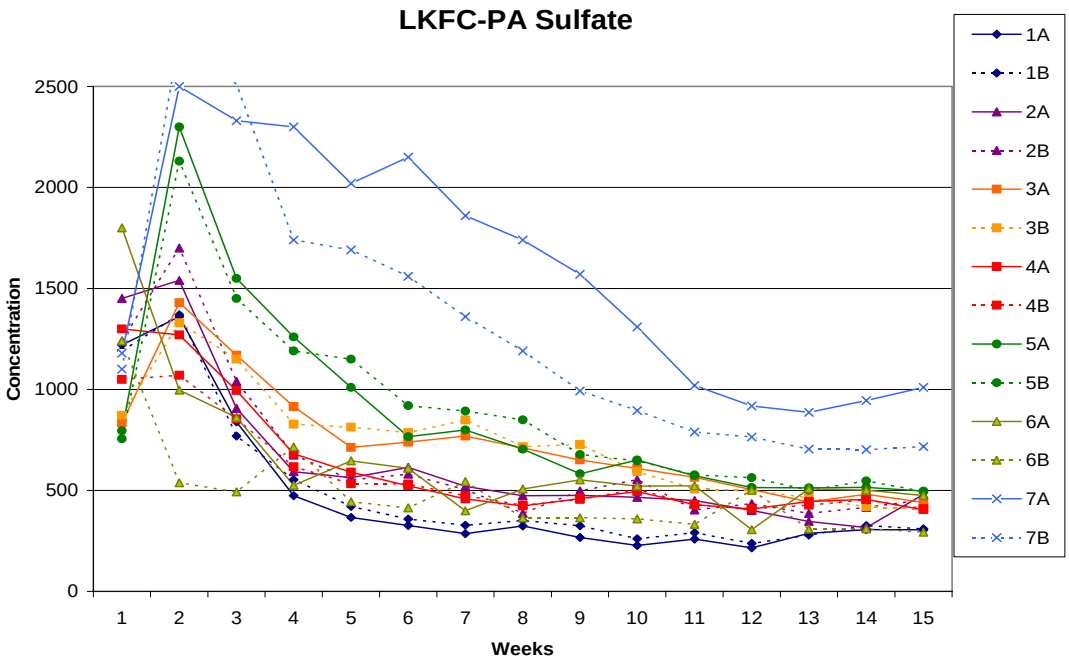


Figure 7.10. Patterns of variation of sulfate concentration in mg/L.

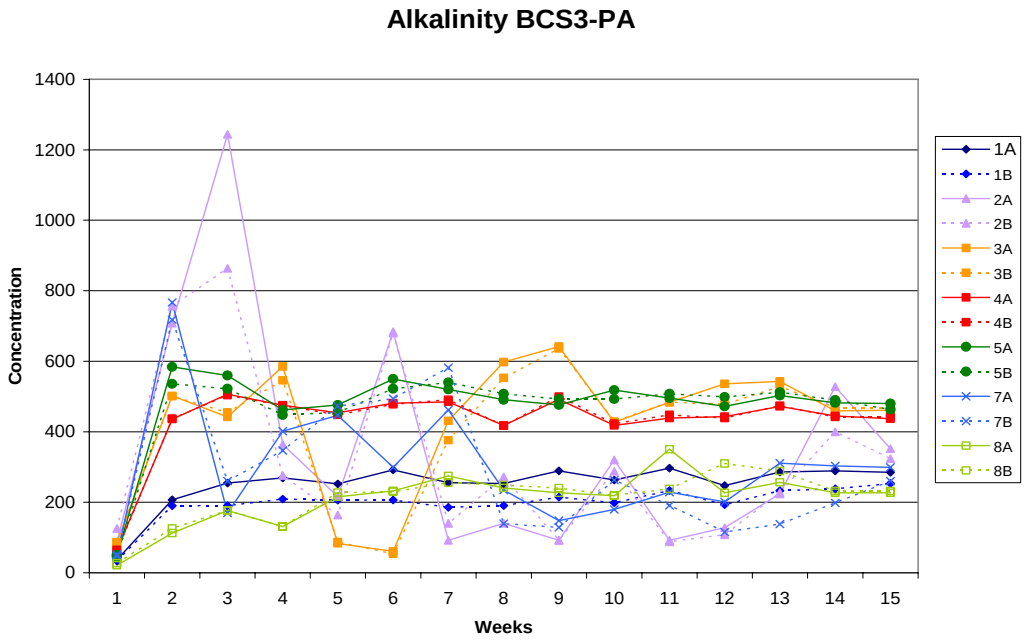


Figure 7.11. Alkalinity variations (mg/L) in duplicate leaching columns.

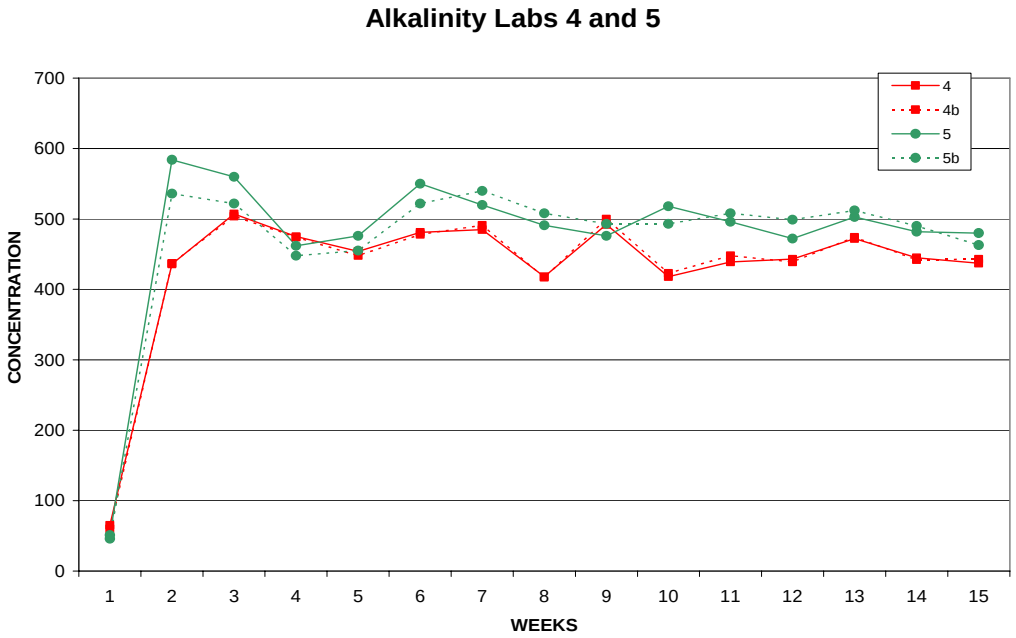


Figure 7.12. Alkalinity concentrations (mg/L) for duplicate Brush Creek Shale columns in Labs 4 and 5.

The relatively low NP values of the Lower Kittanning Falls Creek Shale do not make it a typical "gray zone" sample (NP 12.41 to 16.47), but its leaching behavior is remarkable in terms of alkalinity production. The alkalinity plot for seven of the labs exhibits considerable scattering of the data, as shown in Figure 7.13, but when the data from only Labs 3, 4 and 5 are plotted in Figure 7.14, there is a trend of increasing alkalinity through time.

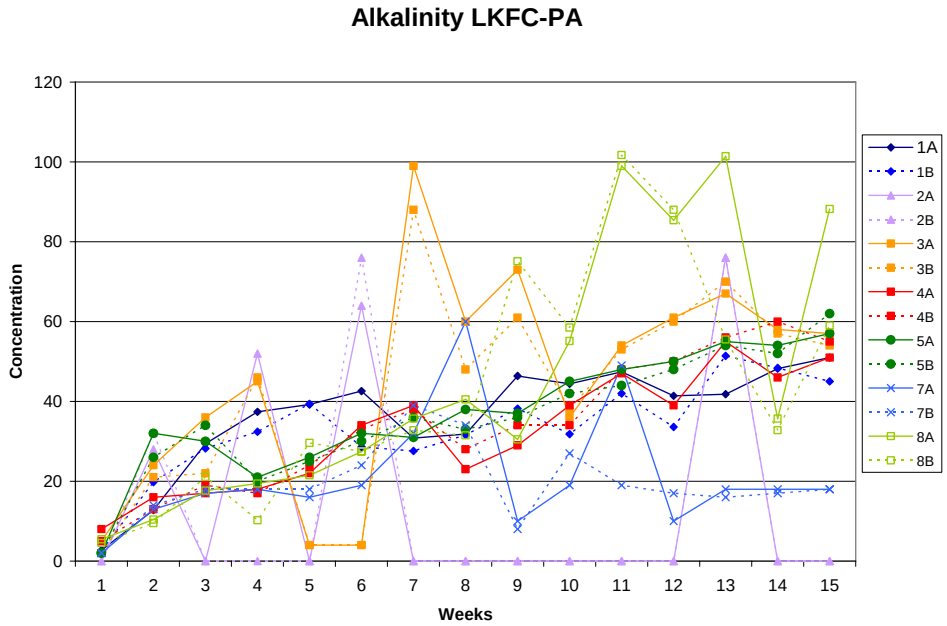


Figure 7.13. Alkalinity concentrations (mg/L) of Lower Kittanning Shale duplicate columns.

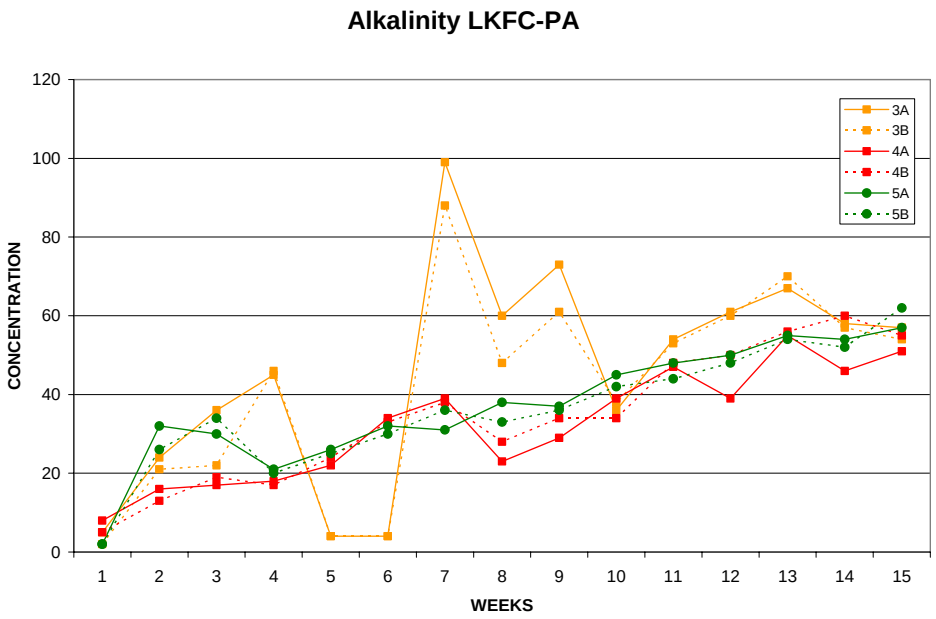


Figure 7.14. Increase in alkalinity concentrations (mg/l) in duplicate at Labs 3, 4, and 5.

Detection and Quantification Limits

The raw data tables from the arrays of leaching columns of the 8 participating labs that are discussed in this section of the report, are contained in Tables 2A through 2N of Appendix E. The "less than" values (e.g. <20) in Tables 2N and 2M on acidity and alkalinity, respectively, are related to detection limits. To report acidity values as <20, for example, is to indicate that the detection limit used in the laboratory titration for acidity is 20 mg/L and any values less than that are not significantly different than zero, and should be interpreted as negligible. In the following discussion of iron and other metals, the use of Method Detection Limits (MDL) and Minimum Levels (ML) will be reported in the data tables and used in the interpretation of the data. The MDL is defined as the lowest value of a determinative signal that shows a constituent of interest to be greater than zero. The ML is defined as the lowest value on a calibration curve, or the lowest point of quantification. (A MDL of 0.1 and a ML and 1.0 were used in the determination and quantification of sulfate values but all of the sulfate values for all five rock types were greater than 1.0 mg/L) The MDL's and ML's will become more meaningful in the following discussion of iron and other metals. In the data tables in Appendix E, analytical results below the ML but above the MDL are shaded in light gray and analytical results below the MDL are shaded in dark gray.

The metals analytical results are expressed in micrograms per liter (parts per billion) as is typically done with mine drainage, surface-water and ground-water data because some of the water quality parameters of interest, such as selenium, are present at very low levels. Some very high concentrations of iron are present in the leachate from the HCS-IN shale samples in Labs 4 and 6, which initially appeared to be unlikely or impossible values.

However, if these results are expressed as parts per million or parts per thousand they become more plausible. For example the HCS-IN sample in Lab 6, Column 6, week 14 produced 6,700,000 parts per billion, which equals 6,700 parts per million, or 6.7 parts per thousand or 0.67 percent.

The rationale for obtaining very high concentration results can also be explained in terms of laboratory instrumentation and operational procedures. Sample results that are significantly higher than the documented calibration range of the method and instrument used to analyze samples are typically obtained using sample dilution or a decreased sample volume. If a sample contains an analyte concentration that is outside (higher than) the calibration range of the analytical method or instrument, the analyst can dilute the sample, analyze the diluted sample, and multiply the result by the dilution factor. Alternatively, the analyst can use a decreased sample size, analyze the decreased volume, and multiply the result to compensate for the decreased volume.

Iron (Fe)

The overall range in reported iron concentrations for all five rock types is 0 µg/L to 6,700,000 µg/L (HCS-IN). The MDL for iron is 9.9 µg/L, so all 0 values were replaced with half of the MDL (4.95) for plotting purposes. (The ML is 50 µg/L.) The extreme range of the iron data makes meaningful plotting of the data very difficult, as there are many low values mixed with extreme peaks. Figure 7.15 shows the iron data plotted in a logarithmic scale, which makes the individual data points discernable, but there is considerable scatter among the data points. On Figure 7.15 for the HCS-IN shale, a trend of increasing iron concentrations is evident for the last seven weeks of the weathering period, especially in Labs 4, 5 and 6. This trend is consistent with the great increase in conductivity and sulfates discussed previously for the HCS-IN shale.

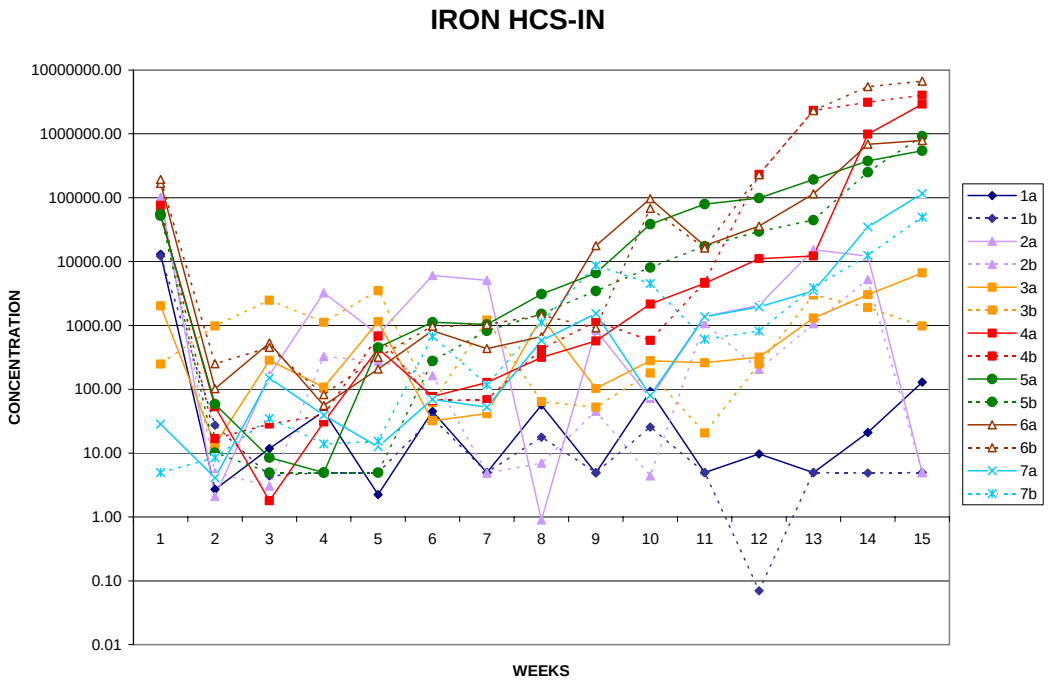


Figure 7.15. Range of iron concentrations (ug/l) of Houchin Creek Shale on a log scale.

Manganese (Mn)

The concentrations of manganese in the leachate for the LKFC-PA shale follow a consistent pattern on Figure 7.16, wherein the highest Mn values are consistently the first week after the initial flush, followed by a steady decline throughout the 14 week weathering period. The duplicate columns exhibited very similar behavior in all 7 labs. The manganese concentrations from the HCS-IN sample (shown in Figure 7.17) exhibit a very different pattern wherein after week 7 the concentrations in all labs except Lab 1 increase, often dramatically, for the remaining 7 weeks of the leaching test. The MDL for manganese is 0.12 µg/L and the ML is 2 µg/L.

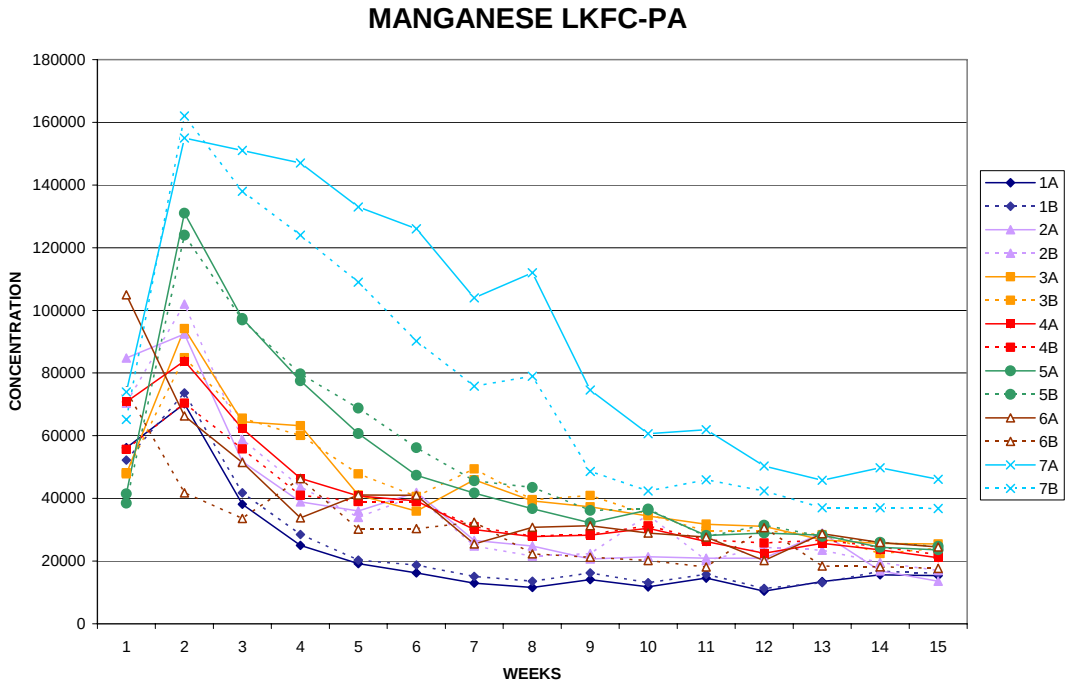


Figure 7.16. Pattern of variation of manganese concentration (ug/l) for Lower Kittanning Shale.

Calcium (Ca)

The plot of the calcium concentrations of the BCS3-PA shale shown in Figure 7.18 exhibits wide variations for Labs 2 and 7; whereas there is close agreement between duplicates and less variation for Labs 1, 4, 5 and 6. When the data are plotted for Labs 4, 5 and 6 only (Figure 7.19), there are some typical peaks in the first weeks of leaching followed by a gradual decline until week 7, after which the data from all three labs are stable at approximately 150 micrograms of calcium for the remaining seven weeks. This trend corresponds with attaining saturation with respect to calcite solubility. The MDL for calcium is 11.8 µg/L and the ML is 50 µg/L.

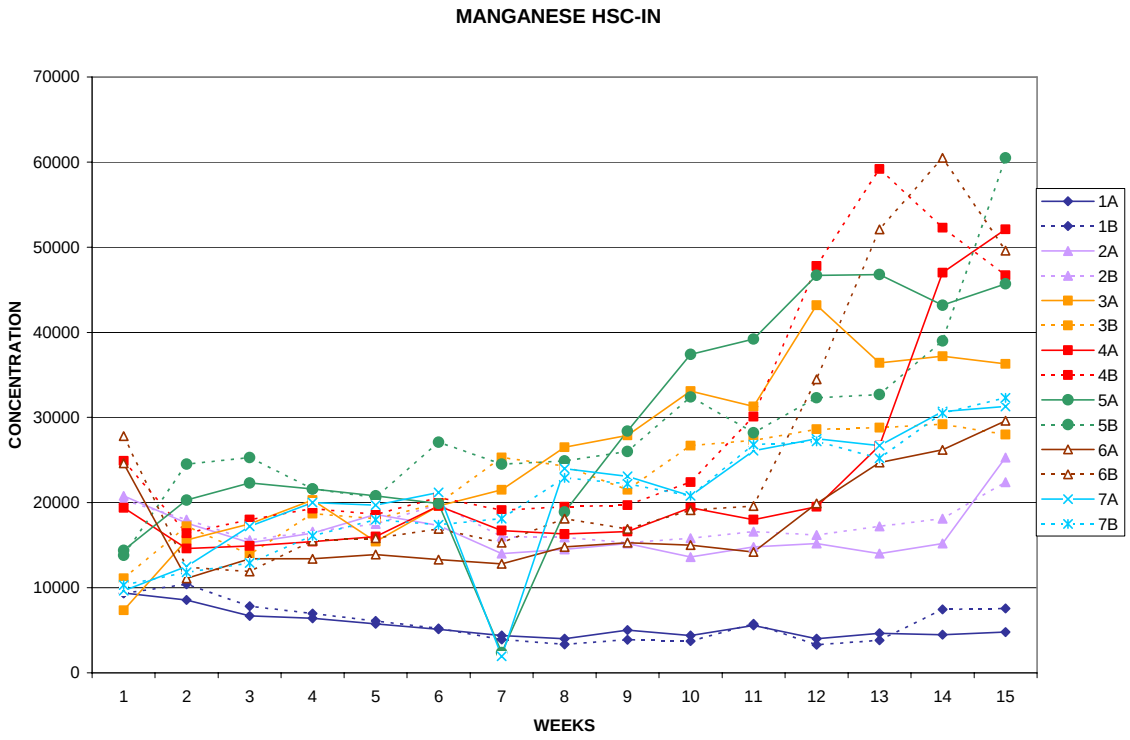


Figure 7.17. Range of manganese concentrations (µg/L) of Houchin Creek Shale .

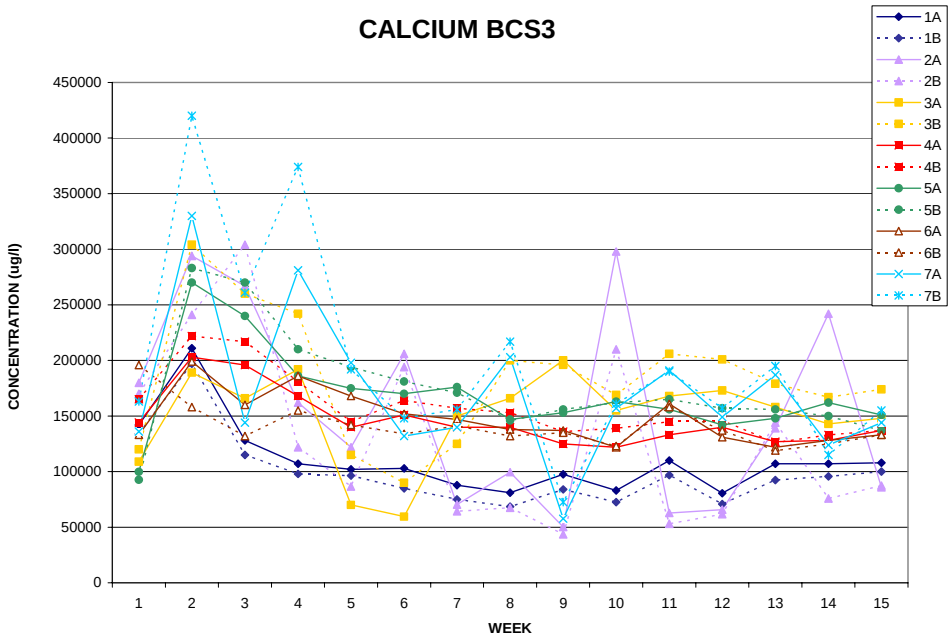


Figure 7.18. Calcium concentrations (µg/L) of Brush Creek Shale duplicate columns.

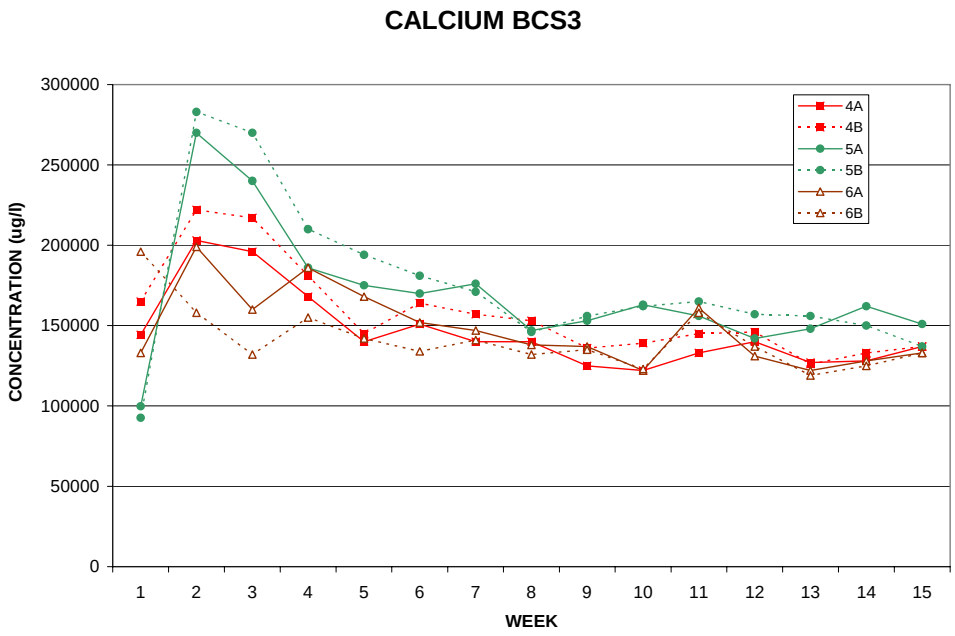


Figure 7.19. Similarity of variations of calcium concentrations (ug/l) in leachate at Labs 4, 5, and 6.

Variations in Leaching Behavior Between All Rock Types

The sulfate leached from all five rock types is shown on Figure 7.20 using data only from Lab 5. This data set shows very close agreement of duplicate columns for the four rock types having duplicate leaching columns. When the sulfate data are plotted on a log scale in Figure 7.20, the five rock types are neatly arranged in the increasing order of sulfate (and acidity) production that would be expected from the acid/base accounting data with the MKSS-PA sandstone the lowest to the HCS-IN shale the highest sulfate.

The alkalinity data shown in Figure 7.21 contains numerous findings that were not evident from the acid/base accounting data, and therefore illustrates the value of the leaching column method for mine drainage prediction. The Brush Creek shale produces 500 to 600 mg/L alkalinity throughout the weathering period as seen in Phase 1 and Phase 2 of the project, and as expected herein. However, the KBF-WV shale and the MKSS-PA sandstone both produce far greater alkalinity than expected from the relatively low NP values. Also, two more subtle types of weathering behavior are seen in Figure 7.21. First, the HSC-IN shale has appreciable alkalinity for the first few weeks of the weathering period, and then declines and is depleted by week 8. The second subtle pattern of weathering in Figure 7.21 is the LKFC-PA shale which starts with the lowest alkalinity of the five rock types, but gradually increases to an appreciable amount by the end of the weathering period. These two types of weathering behavior were not found in Phases 1 and 2 of this study. The succeeding sections of this chapter contain discussion that the leaching column effluents from the BCS3-PA shale, the KBF-WV shale and the MKSS-PA sandstone are saturated with respect to calcite.

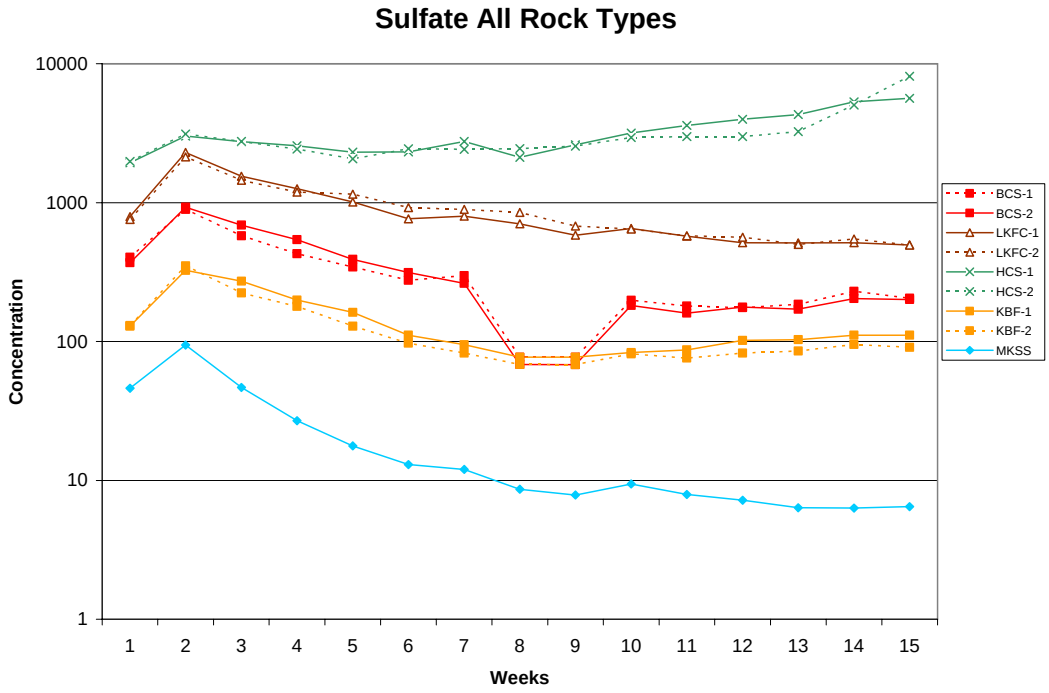


Figure 7.20. Sulfate concentrations (mg/L) in effluent from leaching columns of all rock types.

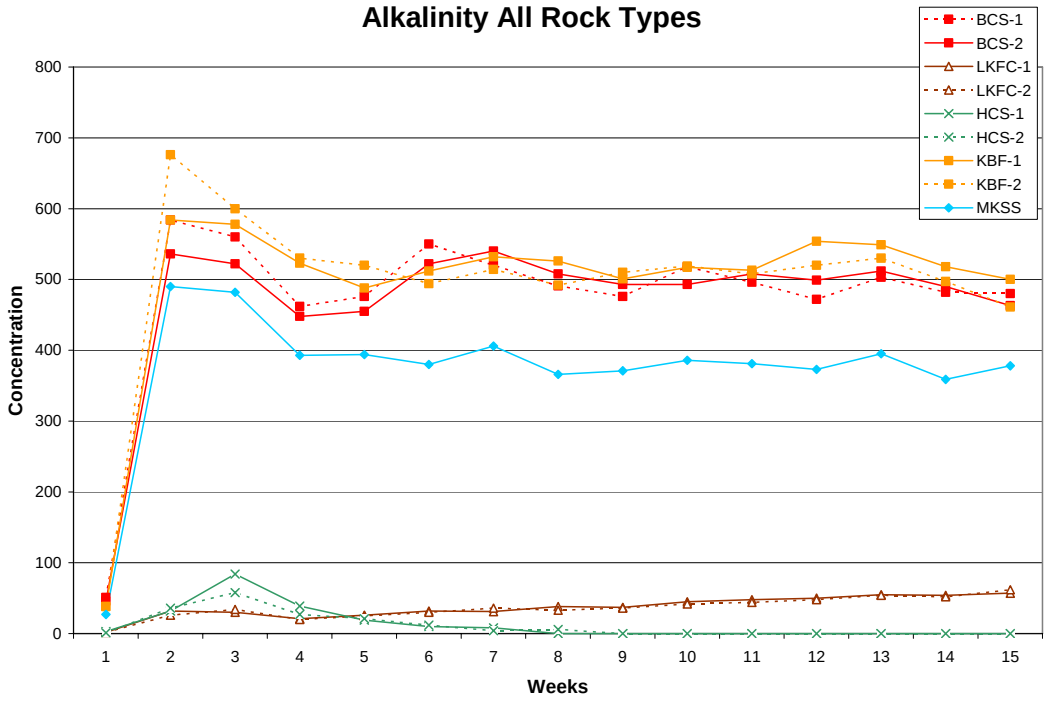


Figure 7.21. Differences in alkalinity concentrations (mg/L) of leachate from the five rock types.

Sulfur Leaching from Shales

Data Processing

Sulfur is the primary element responsible for the generation of acidity so accordingly, sulfur extraction in the leaching columns was examined in somewhat more detail. Data for four of the laboratories, numbers 1, 3, 4, and 5 were used for the analysis. The data processing was as follows:

Sulfate concentrations, as given by the analytical laboratories were multiplied by the "water-out" (mL) to give sulfate concentration as the mass released each week.

The above number was divided by 3 to convert the sulfate mass to sulfur mass (the molecular weight ratio is 96/32) and the resultant masses converted to grams.

The rock weight in each column was multiplied by the percent sulfur as determined by chemical analysis of the rock.

The grams of sulfur in the leachate for each week was divided by the total grams of sulfur in the column to give a "weekly percent of total sulfur leached".

These weekly sulfur releases were summed to give a cumulative release of sulfur. These numbers are plotted in figures 7.22 to 7.25. These plots then formed the basin for further discussion and regression analysis.

Results and Interpretation

Plots of cumulative sulfur leaching from the four shale samples show that the data are best described by a power function of the form

$$C = A t^n \qquad (7.2)$$

In equation 7.2, C = cumulative concentration of leached sulfur expressed as a percentage of the sulfur loading in the original rock, A = coefficient determined by curve fitting, t = time in units of weeks, and n = the exponent of the power function to be determined by curve fitting.

The fitting parameters for the four shale samples are listed in Table 7.4. The regression coefficient, r^2, is a measure of the goodness of fit and is generally excellent for the four laboratories and four samples. The leaching curves for the four laboratories for any given sample have similar shapes but do not completely overlap. The fit with the calculated regression curves, as shown on the figures, is also very good.

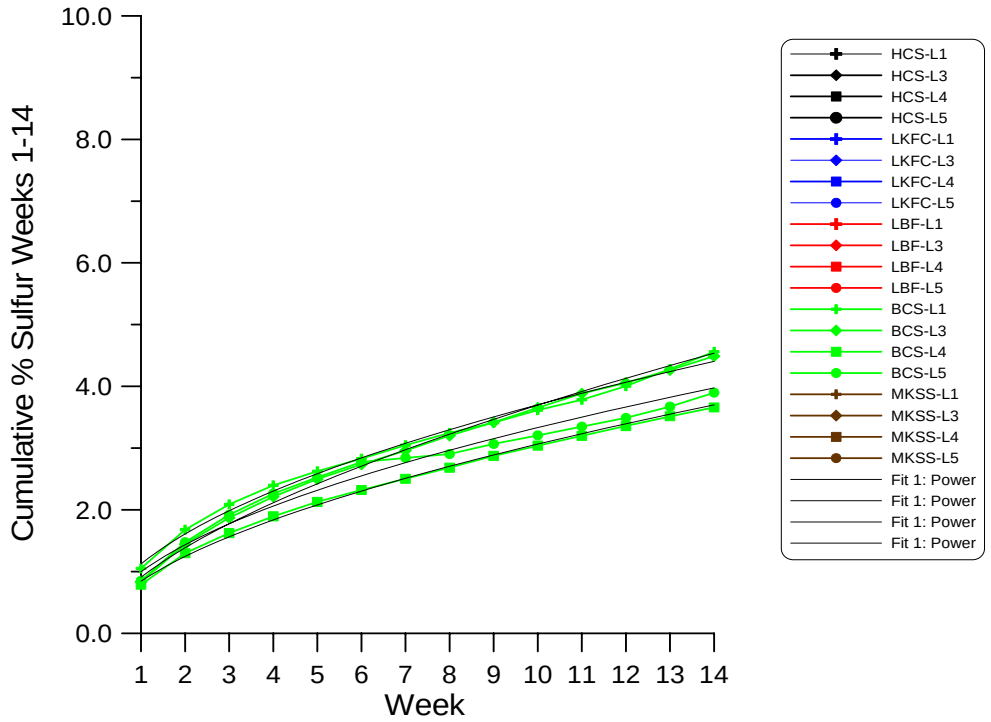


Figure 7.22. Sulfur leaching from BCS3-PA, the Brush Creek Shale.

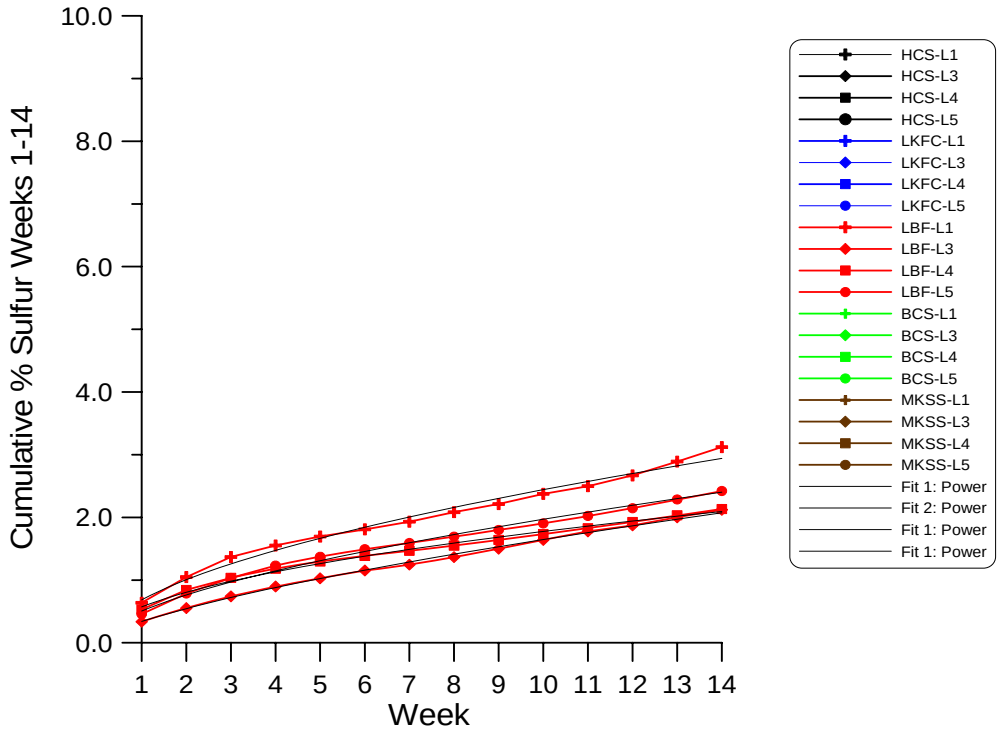


Figure 7.23 Sulfur leaching from KBF-WV, the Kanawha black flint shale.

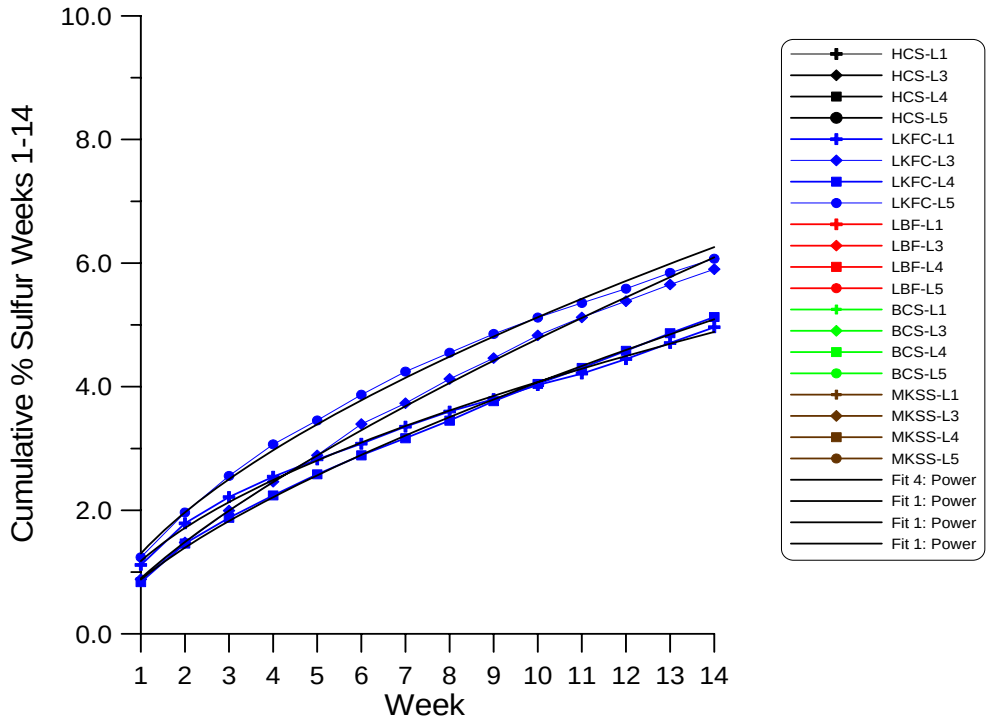


Figure 7.24. Sulfur leaching from LKFC-PA, the Lower Kittanning Shale.

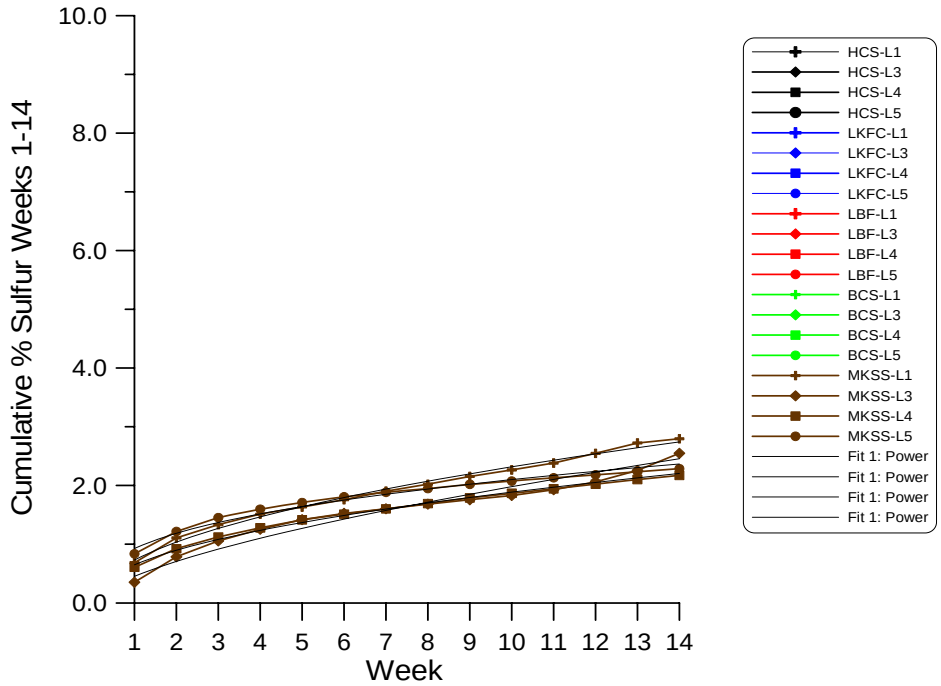


Figure 7.25. Sulfur leaching from MKSS-PA, the Middle Kittanning Sandstone.

Table 7.4 Fitting parameters for sulfur release shown in Figures 7.22 – 7.25.

Sample	A	n	R^2
BCS3-PA			
L1	1.124	0.517	0.993
L3	0.908	0.609	0.994
L4	0.845	0.559	0.995
L5	0.998	0.524	0.970
KBF-WV			
L1	0.686	0.551	0.988
L3	0.340	0.685	0.998
L4	0.573	0.491	0.991
L5	0.506	0.590	0.990
LKFC-PA			
L1	1.180	0.536	0.966
L3	0.899	0.725	0.999
L4	0.879	0.666	0.998
L5	1.301	0.595	0.997
MKSS-PA			
L1	0.732	0.500	0.992
L3	0.454	0.640	0.953
L4	0.651	0.462	0.994
L5	0.927	0.355	0.976

The exception to expected leaching pattern was HCS-IN, the Houchins Creek Shale (Fig. 7.26). Instead of leaching rates decreasing with increasing time, in this specimen, the leaching rates increased through the end of the 14-week experimental period. The HCS-IN leaching can be approximated with an exponential function with a positive coefficient.

The rapid increase in rate at the end of the experimental sequence was observed in the leaching of some other elements from the Houchins Creek Shale. The exponential form does not make theoretical sense, because it would imply a runaway process that turns on late in the experimental sequence. Clearly, these curves cannot be sustained and must eventually bend over as the sulfur in the shale is completely extracted.

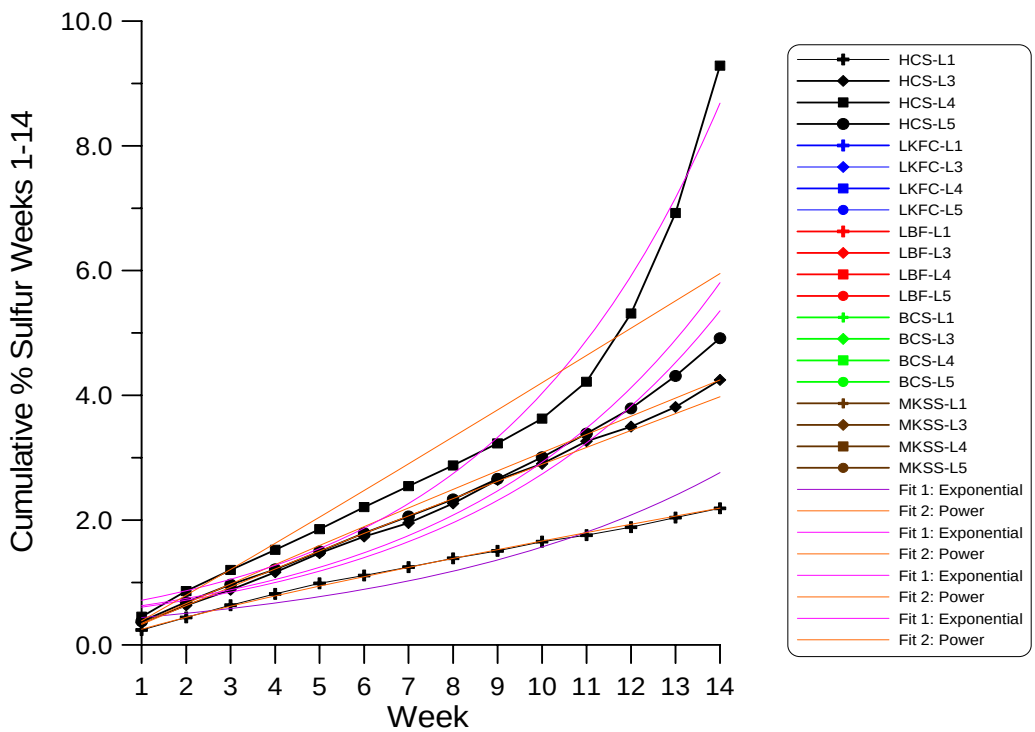


Figure 7.26. Sulfur leaching from HCS-IN, the Houchins Creek Shale. Both power law and exponential fitting curves are shown.

Carbonate Leaching

Determining Carbonate Dissolution Rates

There are two ways to calculate carbonate dissolution rates, the "cation" approach and the "anion" approach. The rate of reaction can be determined from the amount of material that is weathered each week as a portion (or percentage) of the total of that material that is in the rock. Neutralization potential was determined two ways, the traditional Sobek et al,. (1978) method and the modified Skousen et al., (1997) method that takes steps to reduce the effects of siderite interference. Hydrogen peroxide is added in order to oxidize and precipitate iron. Siderite ($FeCO_3$), a non-alkalinity generating carbonate can give falsely high NP readings if the water is not oxidized (Skousen et al., 1997; Rose and Cravotta, 1998). The Skousen method NP results are about half the Sobek method results (Table 7.5). This is consistent with the mineralogic analyses performed by Hammarstrom et al., (this volume, Table 5.4), where about half the carbonates in the Brush Creek shale are siderite. The Skousen method NP numbers were used to determine the average NP, and the calcium carbonate content, for the all rocks in this study.

Although NP does not in and of itself specify the forms of carbonate, with the improved NP method of Skousen et al., it is reasonable to assume that most of the NP is from alkaline earth carbonates. For simplicity and accuracy, results are expressed as calcium carbonate equivalent.

Table 7.5. Acid-Base Accounting data for the Brush Creek Shale.

NP Sobek	NP Skousen	%S
96.97	49.68	0.59
96.96	49.31	0.59
96.98	47.61	0.56
96.97	47.07	0.59
Ave 96.97	**Ave 48.42**	**Ave. 0.58**

The following steps illustrate how carbonate dissolution rates were determined.

Step 1. Determine the amount of calcium carbonate (equivalent) in the column.

Using the Average NP number (Table 7.5) and the known mass of sample in a column, the amount of calcium carbonate equivalent can be computed for the material in that column. For example, Lab 5's Brush Creek Shale, Column 1 contained 1879.2 grams of material. The units for NP are tons/1000 tons $CaCO_3$ equivalent. The amount of calcium carbonate equivalent contained in the column can be computed as follows:

$$1879.2 \text{ grams} \times (48.42/1000) = 91.0 \text{ grams } CaCO_3 \text{ equivalent.}$$

Thus, this column contains the carbonate equivalent of 91 grams $CaCO_3$. This number will be used later to determine weathering rate.

Step 2. Determine the amount of calcium carbonate weathered each week. This is done by determining the mass of the weathering products produced each week in the leachate. There are two ways this can be done, the "cation approach" and the "anion approach" discussed below.

Step 2a. *The "Cation" Approach*

The Cation Approach involves computations using the two cations that are commonly associated with acid-neutralizing carbonates, namely calcium and magnesium. These are evaluated in terms of calcium carbonate equivalent by summing Ca as $CaCO_3$ and Mg as $CaCO_3$. Three assumptions are made:

(1) all Ca and Mg in solution are derived from carbonate dissolution,
(2) Ca and Mg have not been lost from the solution and retained in the column, and
(3) gypsum is not present in the material being leached.

If gypsum is present, then there is calcite from a source that is not directly related to carbonate dissolution. Thus, the calcium carbonate dissolution rate can not be accurately determined, unless one determines the amount calcium from gypsum dissolving per week and subtracts this portion.

Assumption 1. By far the most common and most soluble minerals containing calcium and magnesium on mine sites are calcite, dolomite and ankerite. Calcium is almost exclusively present in carbonate minerals. Although there are other sources of magnesium, the carbonates are by far the most soluble sources of magnesium found in overburden rocks. There is more discussion on this topic below.

Assumption 2. Gypsum and calcite are the most common calcium-bearing minerals that are likely to precipitate from solution. It is recommended that gysum and calcite solubility be calculated to determine whether the solutions are saturated or under- or over-saturated with these minerals. If gypsum or calcite are precipitating then some of the calcium that has dissolved will not be measured in the leachate, but in fact is being retained in the column.

Assumption 3. The presence of gypsum in a sample can be determined through hand sample observation, X-ray diffraction or other mineral determining techniques.

The mass of Ca and Mg leached each week is determined from the mg/L of Ca and Mg leach multiplied by the volume of leachate.

$$Analyte,\ mg = \left(\frac{mg}{L}\right) \times \left(Leachate\ Volume\ Out,\ L\right)$$

The examples used below are of actual leachate obtained from the same column during the same week. That is, all data are all from the same sample event.

Calculating $CaCO_3$ from Ca The mass of calcium carbonate (equivalent) can easily be determined from the mass of calcium. The atomic weight of Ca is 40, and the molecular weight of $CaCO_3$ is 100. Thus, $CaCO_3$ is 2.5 times the weight of Ca alone, and 40 grams of Ca converted to calcium carbonate equivalent is 100 grams of $CaCO_3$. For example, a sample leaches 176 mg/L Ca and the volume drained from the column is 279 mL.

$$\left(176.0\frac{mg}{L}\right) \times \left(0.279\ L\right) = 49.1\ mg\ Ca$$

and

$$49.1\ mg\ Ca \times 2.5 = 122.8\ mg\ as\ CaCO_3$$

Therefore, during this sample event 122.8 mg of $CaCO_3$ equivalent weathered from the rock.

Calculating $CaCO_3$ from Mg The conversion of Mg to $CaCO_3$ is the same process as that for calcium. The atomic weight of Mg is 24.3. Dividing the molecular weight of $CaCO_3$ of 100 by 24.3 gives a conversion factor of 4.1.

$$\left(83.1\,\frac{mg}{L}\right)\times\left(0.279\ L\right)=23.2\ mg\ Mg$$

and

$$23.2\ mg\ Mg\times 4.1=95.0\ mg\ as\ CaCO_3$$

<u>*Calculating $CaCO_3$ equivalent from Ca + Mg*</u> The next step is to simply sum the calcium carbonate equivalents calculated above:

$$122.8\ mg\ Ca+95.0\ mg\ Mg=217.8\ mg\ as\ CaCO_3$$

Therefore, during the course of the previous week, 217.8 mg of carbonates, measured as $CaCO_3$ equivalent, were dissolved.

Step 2b. *The "Anion" Approach*

The Anion Approach involves determining excess alkalinity and neutralized alkalinity produced by evaluating two anions that are commonly associated with neutralized mine drainage, bicarbonate and sulfate. The sulfate part of the equation is not necessarily intuitive and requires some explanation. This approach only works where the water is alkaline. It will not work for acidic samples. Again, assumptions are made: (1) sulfate has not been lost from the solution and retained in the column, and (2) gypsum is not contributing to the sulfate load.

Assumption 1. The most common sulfate-bearing mineral that is likely to precipitate from solution is gypsum. If gypsum is precipitating then some of the sulfate that has dissolved will not be measured in the leachate, but in fact is being retained in the column.

Assumption 2. The presence of gypsum can be determined through hand sample observation or X-ray diffraction or other mineral determining techniques.

Bicarbonate alkalinity. Bicarbonate alkalinity is generally reported as $CaCO_3$ equivalent, so no conversion is necessary. If it is not reported as $CaCO_3$ equivalent, HCO_3 can be converted to $CaCO_3$ using the following equation:

$$\text{mg/L } HCO_3 \times 0.8202 = \text{mg/L } CaCO_3$$

Determining milligrams of $CaCO_3$ is performed using the same process as that for calcium and magnesium discussed above, except no conversion is typically necessary to obtain calcium carbonate equivalent. Using the same sample event as the examples above, the concentration of alkalinity as $CaCO_3$ was 520 mg/L.

$$\left(520\,\frac{mg}{L}\right)\times\left(0.279\ L\right)=145.1\ mg\ CaCO_3$$

Thus, the alkalinity times the volume of leachate represents 145.1 mg of dissolved $CaCO_3$.

Alkalinity Neutralized The alkalinity measured in a mine water is the "excess" alkalinity that has been produced. For samples with pyrite oxidation occurring (indicated by elevated sulfate), some alkalinity has been neutralized by the acid. The amount of acidity that has been produced can be calculated based on the following stoichiometry:

$$FeS_2 + 3.25\ O_2 + 3.5\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+$$

For every mole of pyrite oxidized there are 2 moles of sulfate produced and 4 moles of H^+. It takes 2 moles of $CaCO_3$ to neutralize 4 H^+. This relationship can be written as:

$$\frac{4 \text{ mol } H^+}{2 \text{ mol } SO_4^{2-}} = \frac{2 \text{ mol } CaCO_3}{2 \text{ mol } SO_4^{2-}} = \frac{200 \text{ g } CaCO_3}{192 \text{ g } SO_4^{2-}}$$

Therefore, for every 1 mg/L (or gram) of sulfate, 1.04 mg/L (or gram) of acidity, as $CaCO_3$, are produced.

Therefore, if a sample is net alkaline, the neutralized alkalinity can be calculated from sulfate, by using the following equation:

$$\text{mg/L } SO_4 \times 1.04 = \text{mg/L } CaCO_3$$

Using a sulfate value of 298 mg/L, we get:

$$\left(298\ \frac{mg}{L} \times 1.04\right) \times (0.279\ L) = 86.5\ mg\ neutralized\ alkalinity\ as\ CaCO_3$$

<u>*Calculating $CaCO_3$ from Alkalinity + Sulfate*</u> The next step is to simply sum the calcium carbonate equivalents calculated above:

$$141.1\ mg\ Alkalinity\ CaCO_3 + 86.5\ mg\ neutralized\ alkalinity = 227.6\ mg\ as\ CaCO_3$$

Therefore, during the course of the previous week, 227.6 mg of carbonates, measured as $CaCO_3$ equivalent, were dissolved. We had calculated earlier that there is a total of 91.0 grams of $CaCO_3$ equivalent in the column. Thus, during this one week

$$\left(\frac{0.2276\ g}{91.0\ g}\right) \times 100 = 0.25\%\ CaCO_3\ weathered$$

That is, one-quarter of one percent of the total $CaCO_3$ dissolved during that week.

Step 2 c. Compare the anion derived numbers to the cation derived numbers.

Cumulative Weathering Rates

The above calculations were performed for each week, for each column and for each laboratory. The only reasonable way to do the multiple calculations was to use a spreadsheet. The types of calculations presented in spreadsheet format are displayed in Table 7.6. The percentage weathered each week can be added cumulatively to determine the amount of carbonate (or sulfur) weathered through the duration of the test. This also allows for the evaluation of whether or not the rate of weathering changes throughout the course of the test. Figures 7.27 through 7.32 show cumulative weathering plots for calcium carbonate weathering rates calculated using the cation and anion approaches. The carbonate weathering results for the Brush Creek Shale and the Lower Kittanning FC shale are illustrated below.

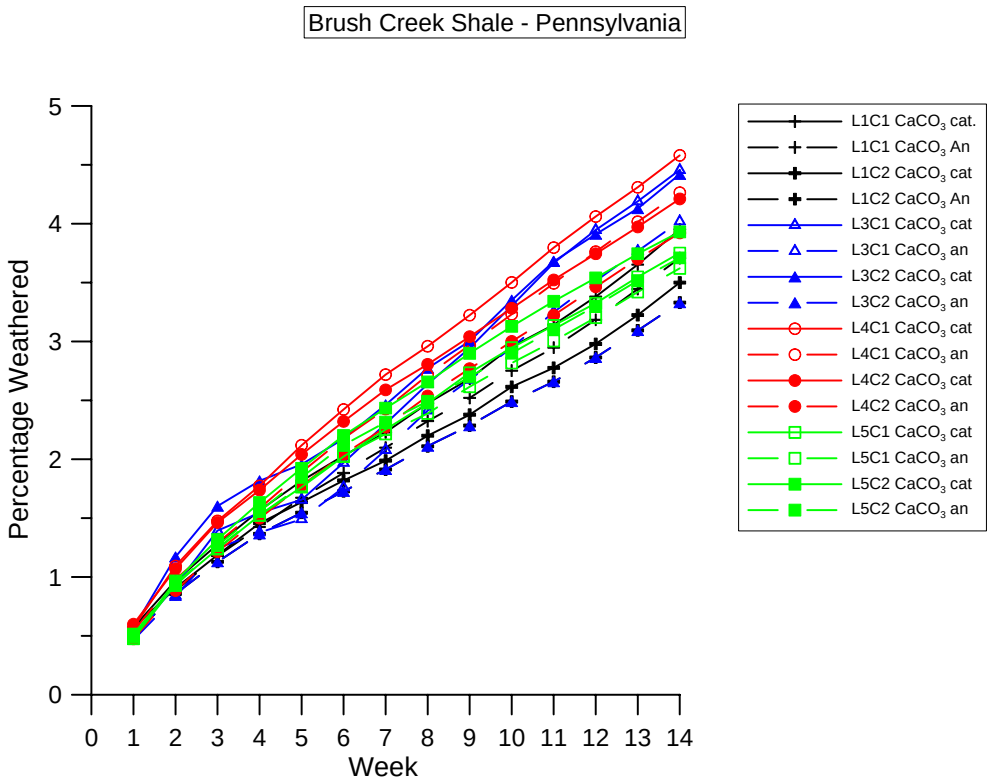


Figure 7.27. Cumulative carbonate dissolution rate determined using cations and anions for the Brush Creek Shale. Data are for laboratories 1, 3, 4 and 5.

Table 7.6. Example table of the computational steps to determine CaCO3 weathering rate. Column 1 identifies the week that was leached. Week "0" is the initial flush. Weeks 1 through 14 are the actual weeks that the sample is weathered. Column 2 is the leachate volume collected. Column 3 is mg/L calcium. Column 4 is the mg calcium computed from columns 2 and 3. Column 5 is the mg calcium displayed cumulatively. Column 6 is calcium displayed as calcium carbonate. Columns 7 through 10 are the same as those described above, but for manganese. Column 11 is the sum of columns 6 and 10. Column 12 is column 11 divided by the total mass of calcium carbonate equivalent in the column, expressed in percent.

1	2	3	4	5	6	7	8	9	10	11	12
Week	VolOut mL	mg/L Ca	mg Ca	cumulative mg Ca	cumulative mg Ca as CaCO3	mg/L Mg	mg Mg	cumulative mg Mg	Cumulative mg Mg as CaCO3	Cumulative Ca + Mg as CaCO3	% CaCO3 weathered each week from 91.0 g
0	1356	99.8	135.33	135.33	338.32	57.1	91.83	91.8	377.90	716.22	0.79
1	310	270.0	83.70	219.03	547.57	148.0	54.41	146.24	601.82	1149.39	1.26
2	340	240.0	81.60	300.63	751.57	131.0	52.82	199.07	819.20	1570.77	1.73
3	295	186.0	54.87	355.50	888.75	93.3	32.64	231.71	953.53	1842.28	2.02
4	309	175.0	54.08	409.57	1023.93	82.7	30.31	262.02	1078.25	2102.19	2.31
5	270	170.0	45.90	455.47	1138.68	78.8	25.23	287.25	1182.09	2320.78	2.55
6	279	176.0	49.10	504.58	1261.44	83.7	27.70	314.95	1296.07	2557.51	2.81
7	296	147.0	43.51	548.09	1370.22	68.7	24.12	339.06	1395.32	2765.54	3.04
8	285	153.0	43.61	591.69	1479.24	68.4	23.12	362.18	1490.46	2969.70	3.26
9	285	163.0	46.46	638.15	1595.37	84.3	28.49	390.68	1607.72	3203.09	3.52
10	268	156.0	41.81	679.96	1699.89	68.6	21.80	412.48	1697.45	3397.34	3.73
11	260	142.0	36.92	716.88	1792.19	62.7	19.33	431.82	1777.01	3569.21	3.92
12	260	148.0	38.48	755.36	1888.39	59.8	18.44	450.26	1852.90	3741.29	4.11
13	274	162.0	44.39	799.75	1999.36	68.7	22.33	472.58	1944.77	3944.13	4.33
14	264	151.0	39.86	839.61	2099.02	66.4	20.79	493.37	2030.32	4129.35	4.54

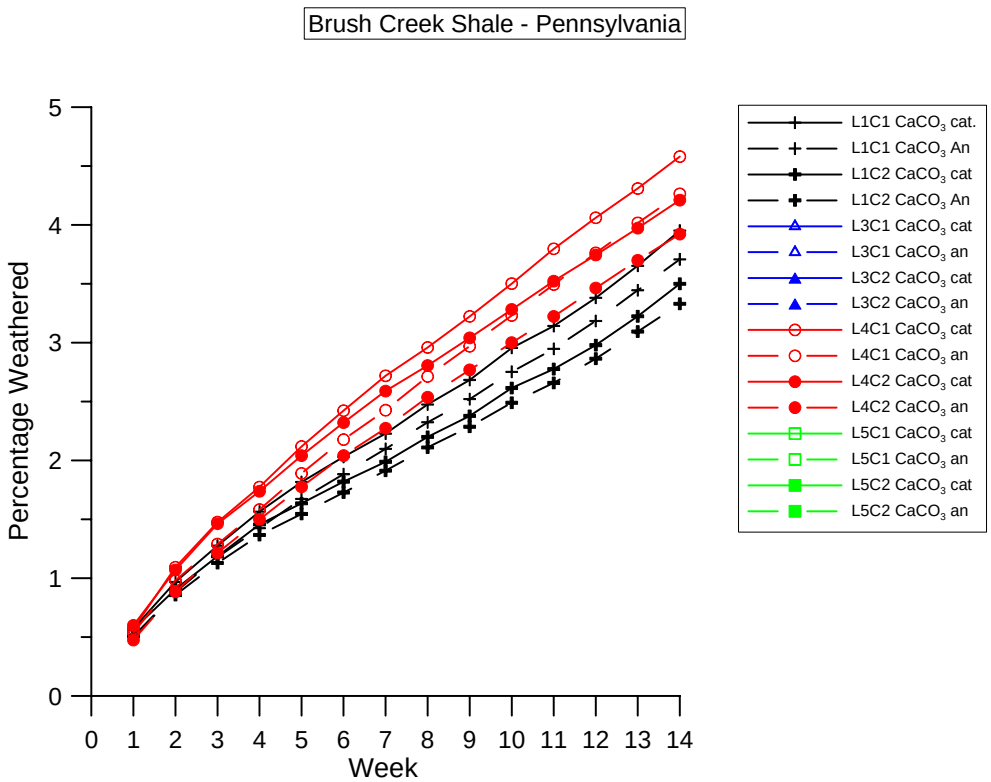


Figure 7.28. Same data as in Figure 7.27, but showing only Labs 1 and 4.

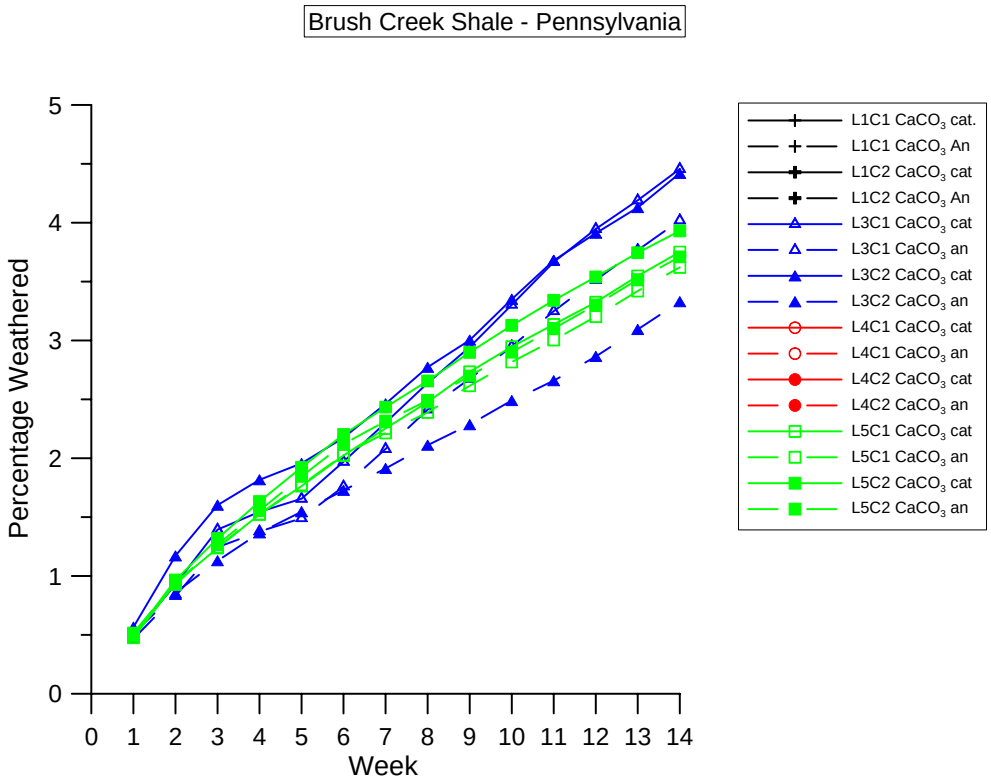


Figure 7.29. Same data as in Figure 7.27, but showing only Labs 3 and 5.

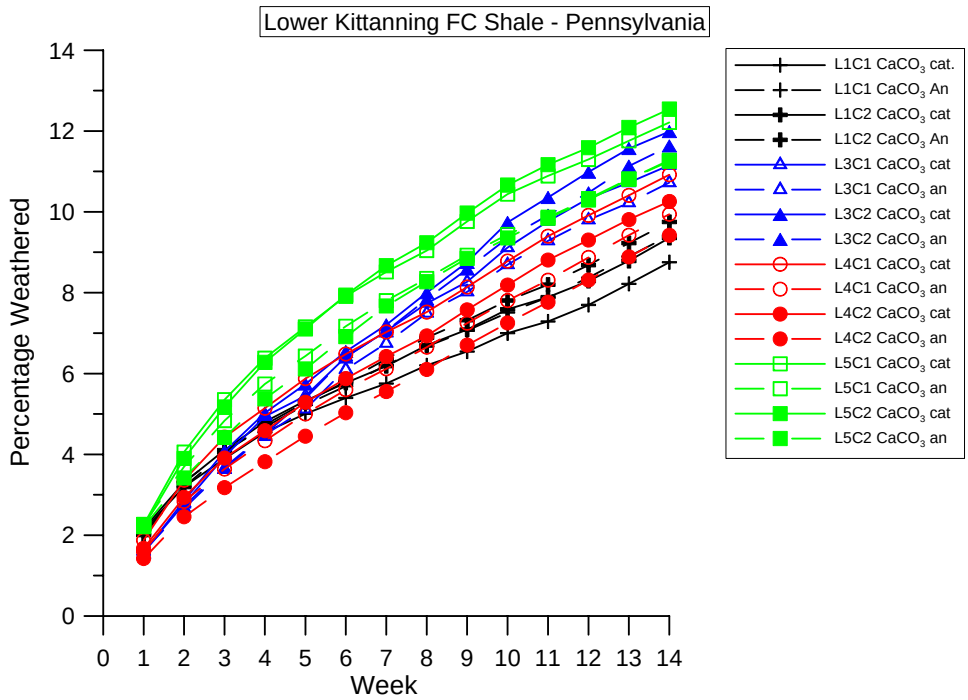


Figure 7.30. Cumulative carbonate dissolution rate determined using cations and anions for the Lower Kittanning FC Shale. Data are for laboratories 1, 3, 4 and 5.

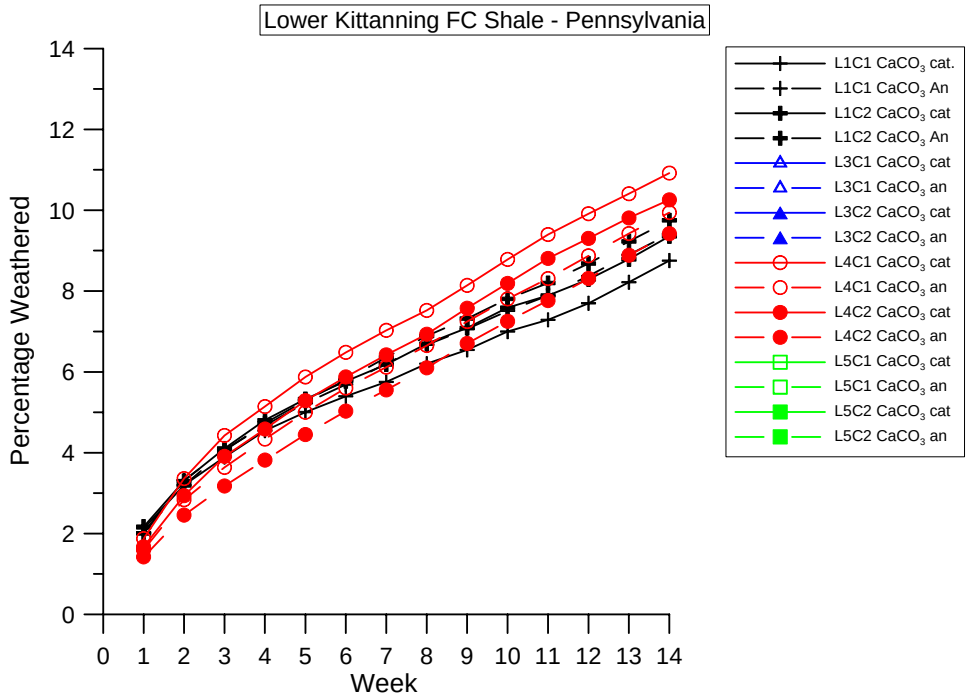


Figure 7.31. Same data as in Figure 7.30, but showing only Labs 1 and 4.

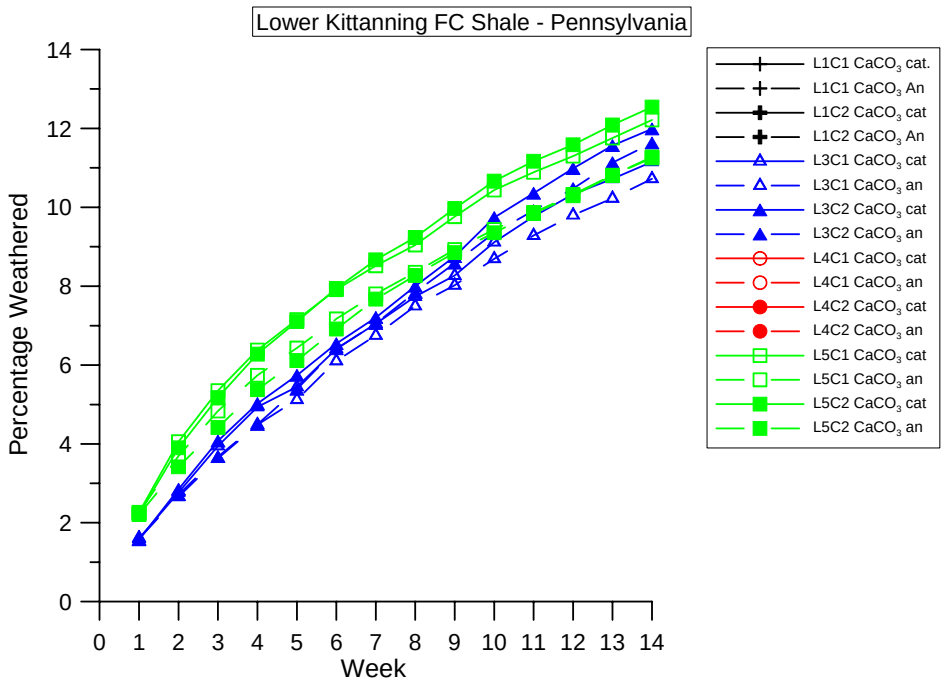


Figure 7.32. Same data as in Figure 7.30, but showing only Labs 3 and 5.

Figures 7.27 through 7.32 show that the weathering rates determined by the cation and anion approaches result in very similar values. This close relationship is also evident in Figure 7.34. The similar results of the cation and anion approaches instill confidence that the numbers from both approaches are accurate. There is generally a slightly larger percentage weathered for the cation computation. This may be due to Mg (in particular) being present in rocks other than carbonates.

Hammarstrom (Chapter 5) identified the mineralogy of the rocks used in the leaching study. Table 7.7 identifies calcium and magnesium minerals that can contribute these cations to solution. Quite a number of Mg-bearing minerals are present in these rocks. Although present, their contribution, compared to carbonate minerals, is likely minor. Figure 7.33 shows relative dissolution rates for a variety of minerals. As can be seen, most minerals are orders of magnitude less reactive than carbonates, especially under neutral pH conditions. Although chlorite is not shown on the graph, its dissolution rate is also orders of magnitude less than calcite, and in fact less than that of biotite (Freyssinet and Farah, 2000).

Table 7.8 shows the percentages of calcium, magnesium, CO_2, calcite, ankerite and chlorite. Chlorite is included because it was fairly abundant in all rock types studied and could contribute magnesium to the solutions. (Data from Hammarstrom, Chapter 5)

Table 7.7. Calcium- and magnesium-bearing minerals in rocks used for the leaching study. Formulas are simple basic formulas. Minerals are those identified by Hammarstom (Chapter 5).

Mineral	Composition	Comments
Ankerite	$Ca(Mg,Fe)(CO3)_2$	Present in all samples
Anorthite	$CaAl_2Si_2O_8$	<1% in all samples except MKSS
Apatite	$Ca_5(F,Cl,OH)(PO_4)_3$	Less than 2% except in HCS-IN (>3%)
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Only identified in KBF-WV & <1%
Calcite	$CaCO_3$	Present in all samples
Chlorite	$Mg_3(Si_4O_{10})(OH)_2$-$Mg_3(OH)_6$	Present in all samples (see Table 7.6)
Phengite	$K(AlMg)_2(OH)_2(SiAl)_4O_{10}$	Present in all samples

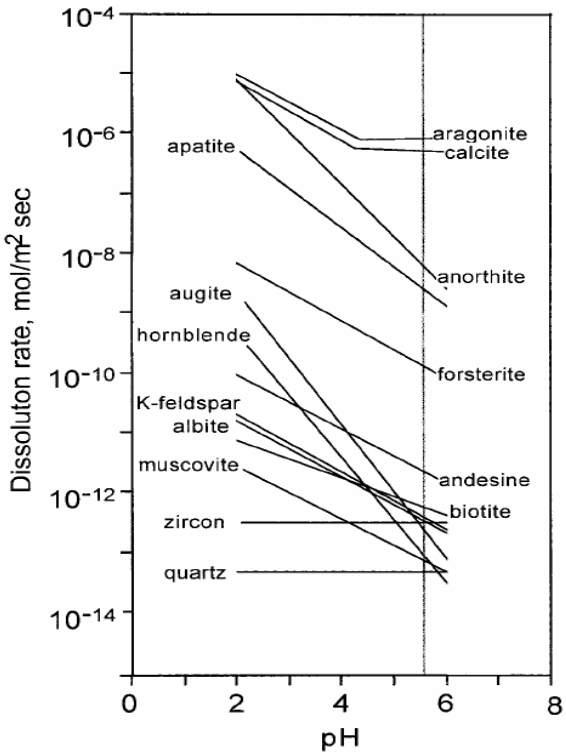


Figure 7.33. Relative dissolution rates of minerals. From Kowalewski & Rimstidt (2003).

Table 7.8. Elements and minerals relevant to Ca and Mg concentrations.

Rock Type	%Ca	%Mg	%CO2	%Calcite	%Ankerite	%Chlorite
HCS-IN	2.25	1.61	1.06	0.60	2.40	4.60
LKFC-PA	0.87	1.88	3.13	0.35	0.70	9.45
KBF-WV	1.03	1.81	1.94	0.65	1.15	7.55
MKSS-PA	1.81	0.89	1.93	3.45	1.55	5.15
BCS-PA	2.25	2.41	2.03	2.45	1.20	11.15
BCS-PA2				2.13	1.10	10.10
BCS Weighted Ave.				2.26	1.14	10.52

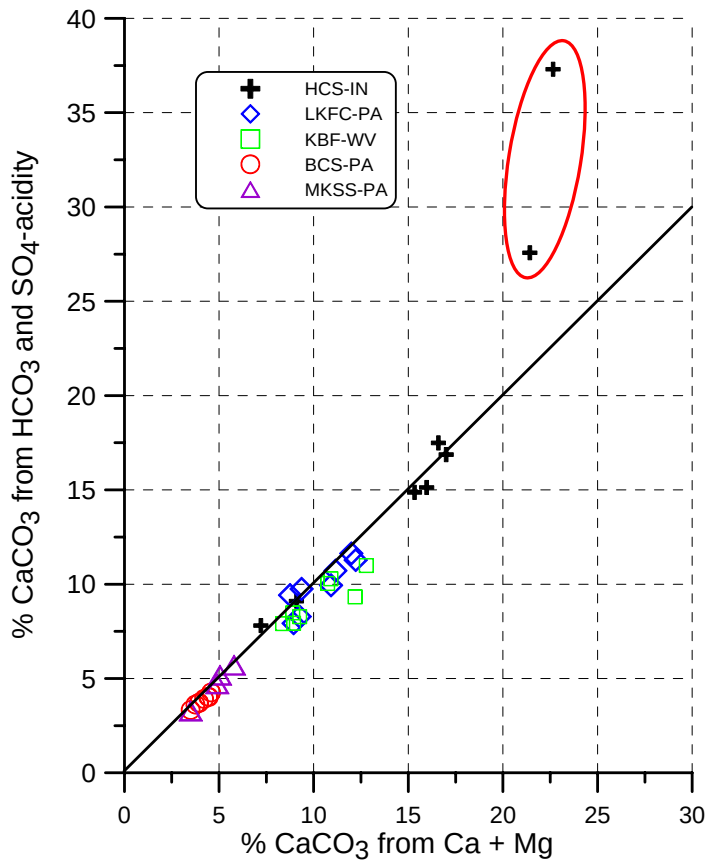


Figure 7.34. Comparison of the "anion" and "cation" methods of determining carbonate dissolution. The cumulative value at the end of 14 weeks leaching was used to construct this plot. As can be seen, most data fall on or near the diagonal line, which represents where data would fall if both methods produce the same answer. The circled values indicate columns that became acidic.

The Race to the Finish

Whether a sample through time will produce acidic or alkaline water is a function of the relative weathering rates of the carbonates and pyrite. If the carbonates exhaust first, the sample will probably become acidic. If the pyrite is exhausted first, the sample will remain alkaline. In order to determine which will win the race (remain the longest) the pyrite oxidation rate will also need to be determined. The same approach that was used for determining carbonate dissolution rates is used to determine pyrite oxidation rates and the amount of sulfur weathered each week. This is then compared to the mass of sulfur in the rock. The sulfur in the rock is determined during acid-base accounting. The examples below are analyses of the Brush Creek Shale and are for the same leaching event used above for the carbonates. The average sulfur shown in Table 7.5 was used for these calculations.

Step 1. Determine the amount of sulfur in the column from the average of the samples analyzed.

Using the average percent sulfur value (Table 7.5) and the known mass of sample in a column, the amount of calcium carbonate equivalent can be computed for the material in that column. That is, what is being computed is the amount of calcium carbonate that would be needed to neutralize the acid generated from the oxidation of the pyrite in this rock. For example, Lab 5's Column 1 contained 1879.2 grams of material. The amount of sulfur contained in the column can be computed as follows:

1879.2 grams x (.0058) = 10.9 grams Sulfur.

For the purposes of this study we used total sulfur values. This approach probably slightly overestimates the amount of pyrite present, but likely less than 10% (Brady and Smith, 1988). Forms of sulfur determinations are not used because of the plethora of analytical and other problems associated with determinations of forms of sulfur in coal overburden samples (Brady and Smith, 1988). Pyrite is 53.45% sulfur, so if one wanted to determine the amount of pyrite in a rock the percent sulfur can be multiplied by 1.873:

0.58% S x 1.873 = 1.09% pyrite

Step 2. Determine the sulfur oxidation rate.

Sulfur has an atomic weight of 32. Sulfate (SO_4) has an ionic weight of 96 (32 + (16 x 4) = 96). Thus, sulfur comprises one-third the weight of sulfate. To calculate the amount of sulfur leached each week use the following equation:

$$\frac{298\ mg/L\ SO_4}{3} \times 0.279\ L = 27.7\ mg\ S\ weathered$$

The percentage of the available sulfur that was weathered during this time period can be determined using the following equation:

$$\left(\frac{0.0277\ g}{10.9\ g}\right) \times 100 = .25\%\ S\ weathered$$

The percent sulfur that has weathered can be compared to the percent carbonate that has weathered. Figures 7.35 and 7.36 show comparisons of these two types of data for the LKFC-PA and the BCS-PA shales. The LKFC-PA (Figure 7.35) has distinctly different rates of weathering for carbonates compared to sulfides, with the carbonates weathering faster than the sulfides. The weathering rates of the two mineral groups are similar for the BCS-PA (Figure 7.36).

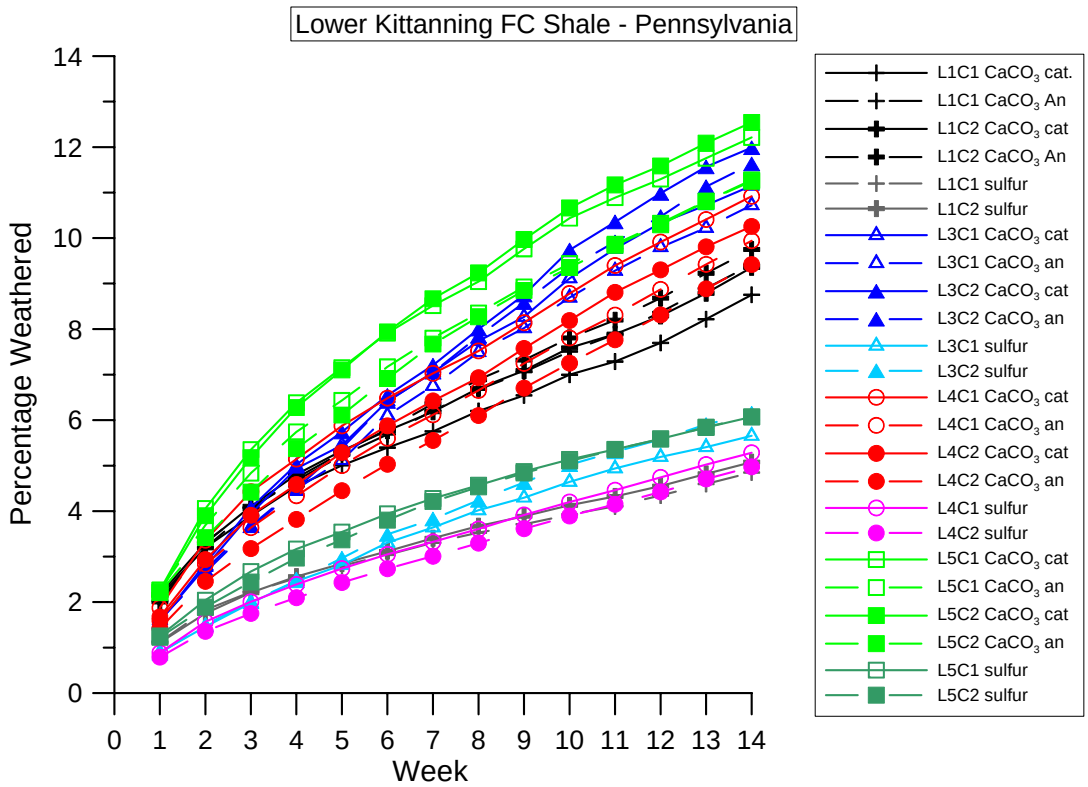


Figure 7.35. Weathering rates through time for carbonates and sulfur for the LKFC shale. The weathering rates for the two mineral groups form two distinct groups, with the sulfur weathering at a slower rate than the carbonate minerals.

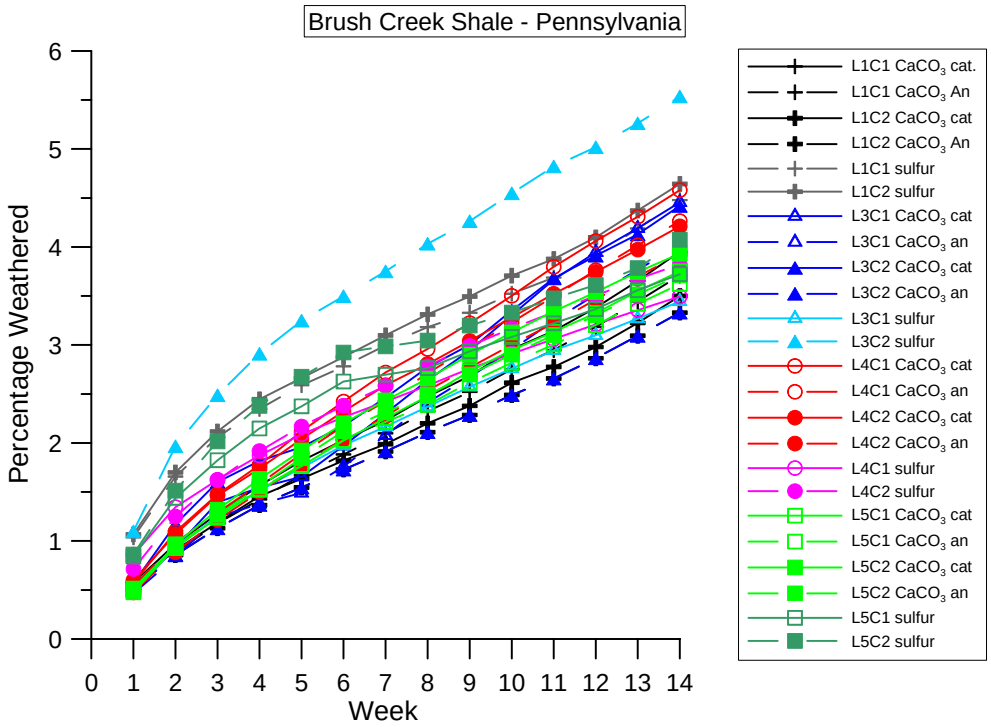


Figure 7.36. Weathering rates through time for carbonates and sulfur for theBCS shale. The weathering rates for the two mineral groups overlap, with the sulfur weathering at more or less the same rate as the carbonate minerals.

Figure 7.37 shows the cumulative percent sulfur and carbonates weathered at the end of 14 weeks of leaching for the five rocks examined in this study. The plot represents data from four labs, and the duplicate columns. Other than the Brush Creek Shale all the samples at the end of 14 weeks had weathered more calcite than pyrite. The Brush Creek seems to have carbonate and pyrite weathering at about the same rate.

The diagonal black line on Figure 7.37 is drawn where carbonate weathering equals pyrite weathering. Even though there were weathering rate differences among the labs, the sample results for a given rock type cluster together. That is, the differences among labs are less than the differences between rock types. The one sample that displays extreme scatter is the LKFC-PA shale, which in some labs remained alkaline, while in others, by the end of the test, the water was acidic. Thus there were big differences in the rate of weathering among the labs for this sample. Figure 7.37 illustrates that the laboratories produced very similar results with similar predictions for a given rock type.

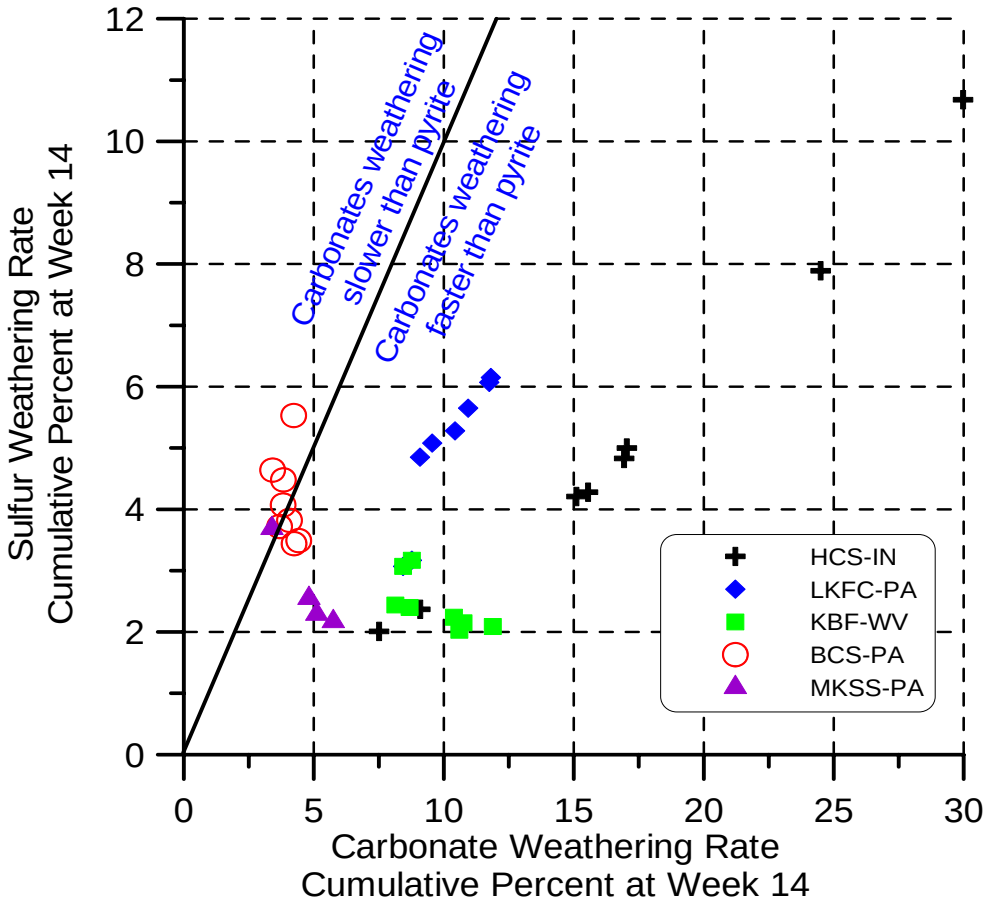


Figure 7.37. Comparison of weathering rates for pyrite and carbonates for five rock types by four laboratories. Most rock types are represented by eight points (two columns each lab), the exception being the MKSS-PA, where there was a single column in each lab.

Leaching of Minor Elements

Data Analysis

The overall objective of this study was to determine inter-laboratory reproducibility of the leach data. As indicated earlier in this report, the inter-laboratory variability was considerable. Rather than attempt to interpret the laboratory results individually or weight one laboratory against another, the seven laboratories' results were averaged over the seven data sets for each species of interest and each rock type. Tables of means were constructed for each species and each sample. A second set of tables was then constructed for the accumulated extraction of the given species from the given sample. Both tables were then plotted against time. The plots of accumulated release give the best indication of the overall kinetics of the column leaching experiments. The tables of accumulated release were than fitted to a power function by regression analysis and the fitting parameters of equation 7.2 were extracted. The first flush is included at time = zero in the data plots. For this reason, most of the plots do not go through zero at time = zero. The time = zero point was excluded from the regressions but the accumulative concentrations include material released on the first flush.

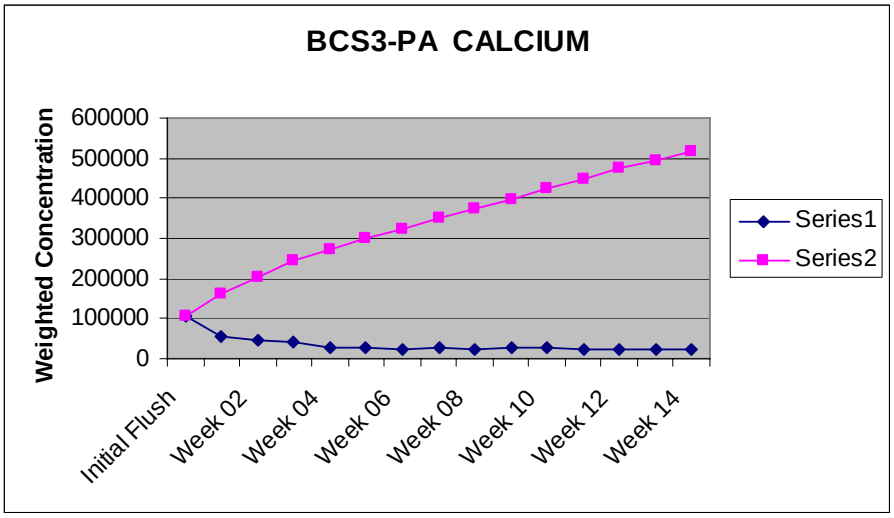
The experimental columns were loaded with a known mass of rock sample and filled with a known volume of water. These numbers varied somewhat from experiment to experiment and were determined by direct measurement for each experiment. Two data sets were then available – the raw concentrations as reported by the analytical laboratory and a weighted concentration that takes account of the specific weight of sample and volume of solution for each experiment. Numerically, the weighted concentrations would be

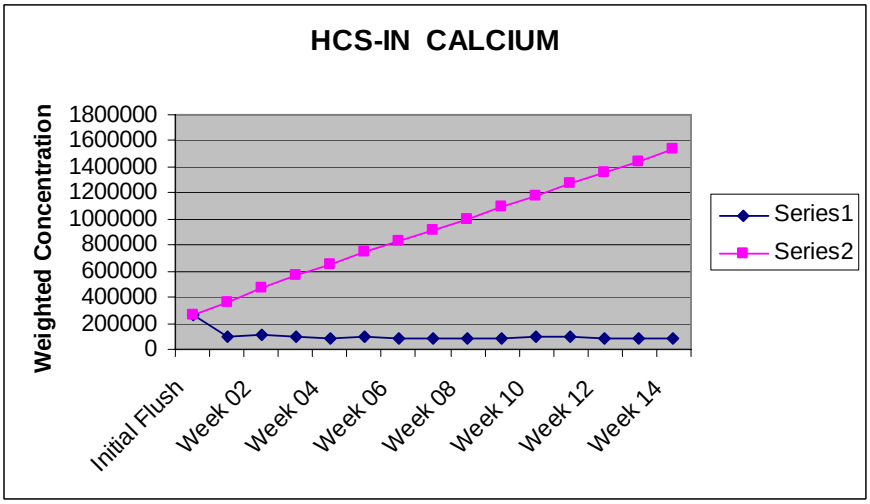
$$Weighted\ Concentration \quad = \quad \frac{Concentration\ (\mu g\ /\ L)\ x\ Volume\ (mL)}{Sample\ Mass\ (g)}$$

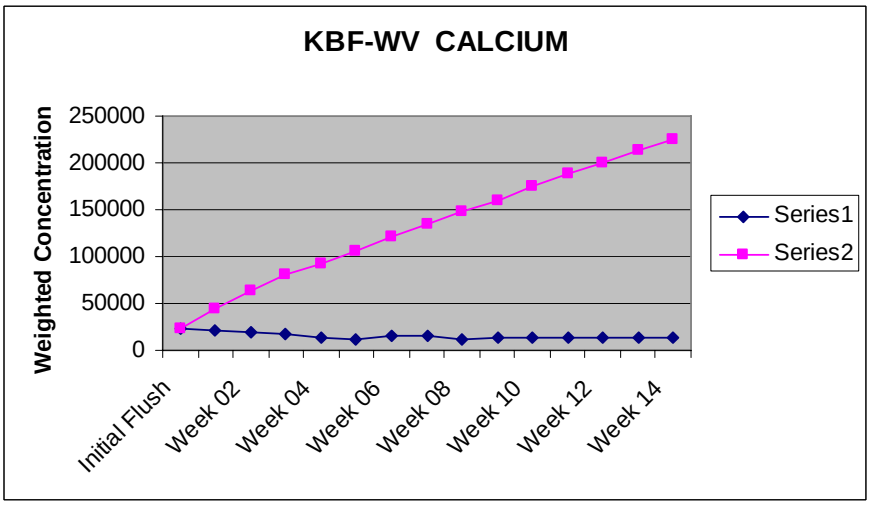
Combining units, the weighted concentration has units of μg/kg of solid.

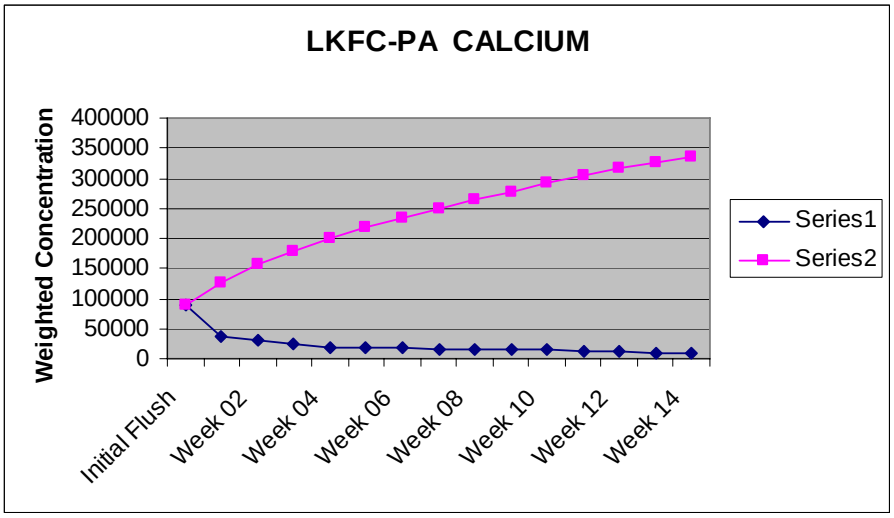
Major Cations: Calcium, Magnesium, and Potassium

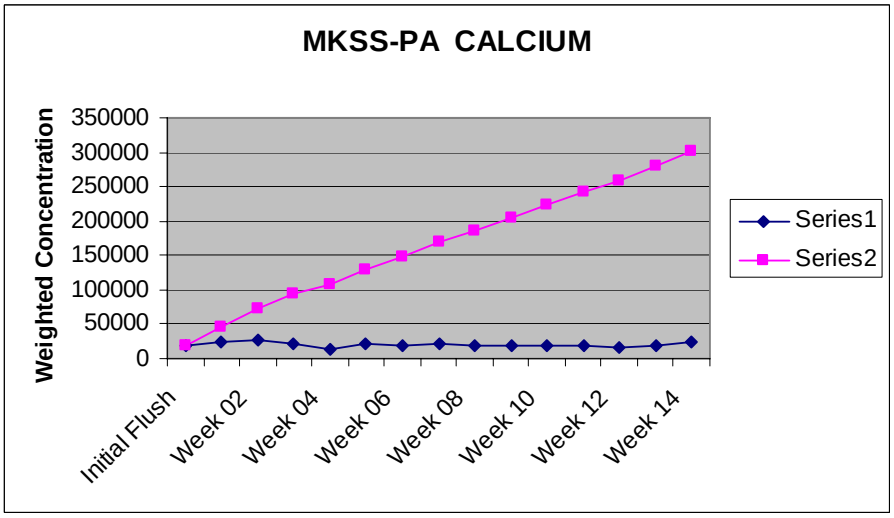
Individual plots showing the cumulative leaching of the three major cations from each rock type are given in Figure 7.38. Averaging the results from all of the laboratories has the effect of smoothing the data. The cumulative leaching curves are all rather similar. There is a slight flattening with increasing time but no indication that the sources of these elements are reaching depletion at the end of the 14-week experiment.

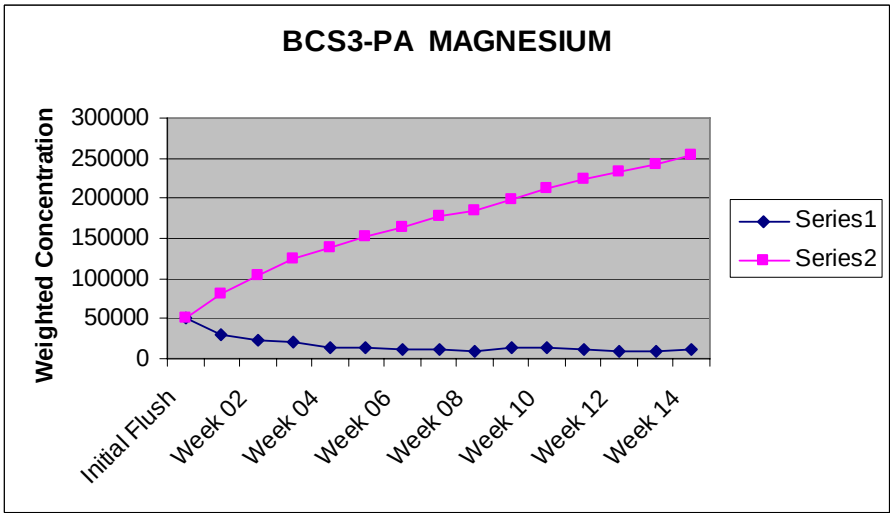

BCS3-PA CALCIUM
Weighted Concentration
600000
500000
400000
300000
200000
100000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2

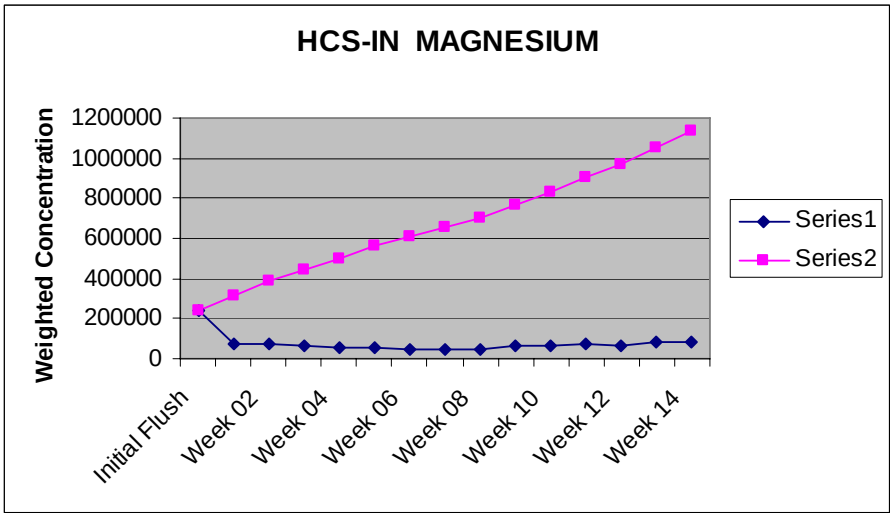

HCS-IN CALCIUM
Weighted Concentration
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


KBF-WV CALCIUM
Weighted Concentration
250000
200000
150000
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


LKFC-PA CALCIUM
Weighted Concentration
400000
350000
300000
250000
200000
150000
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


MKSS-PA CALCIUM
Weighted Concentration
350000
300000
250000
200000
150000
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


BCS3-PA MAGNESIUM
Weighted Concentration
300000
250000
200000
150000
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


HCS-IN MAGNESIUM
Weighted Concentration
1200000
1000000
800000
600000
400000
200000
0
Initial Flush
Week 02
Week 04
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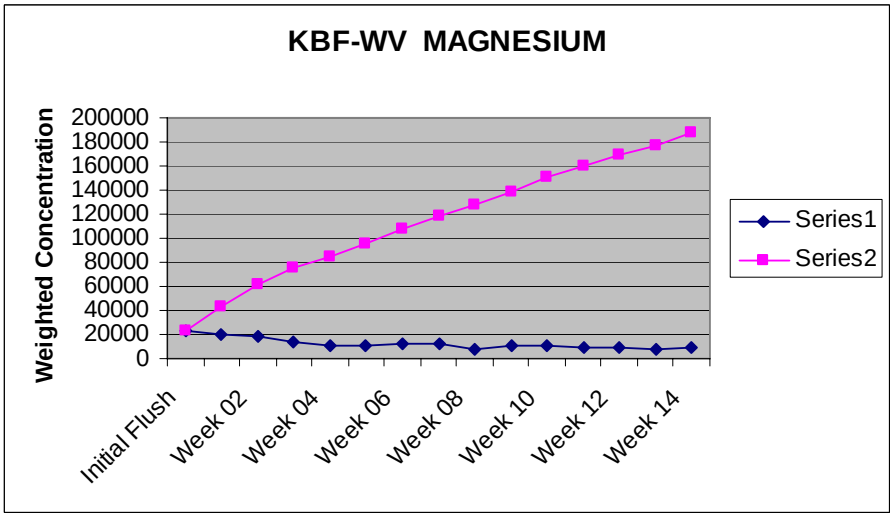
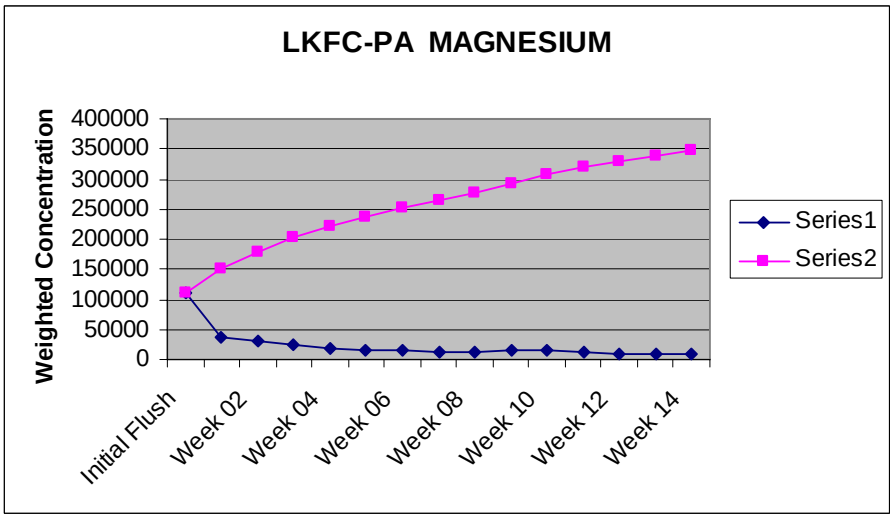
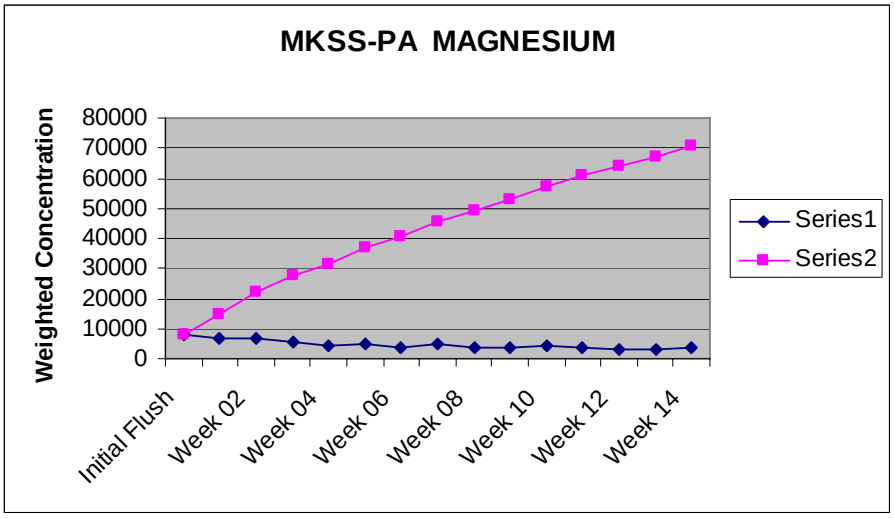
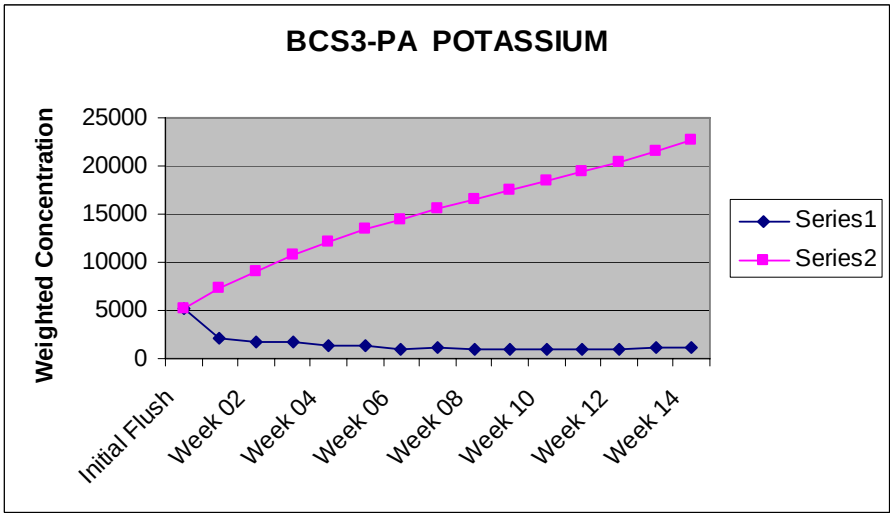
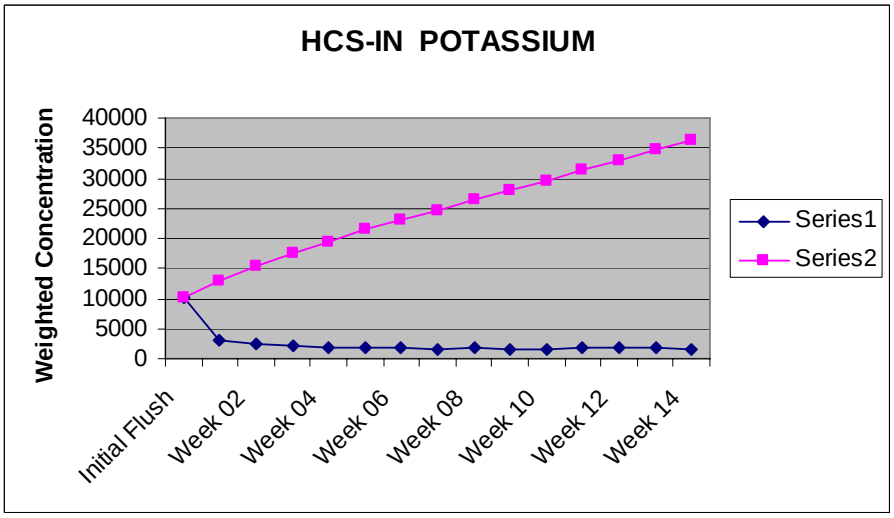
Week 08
Week 10
Week 12
Week 14
Series1
Series2

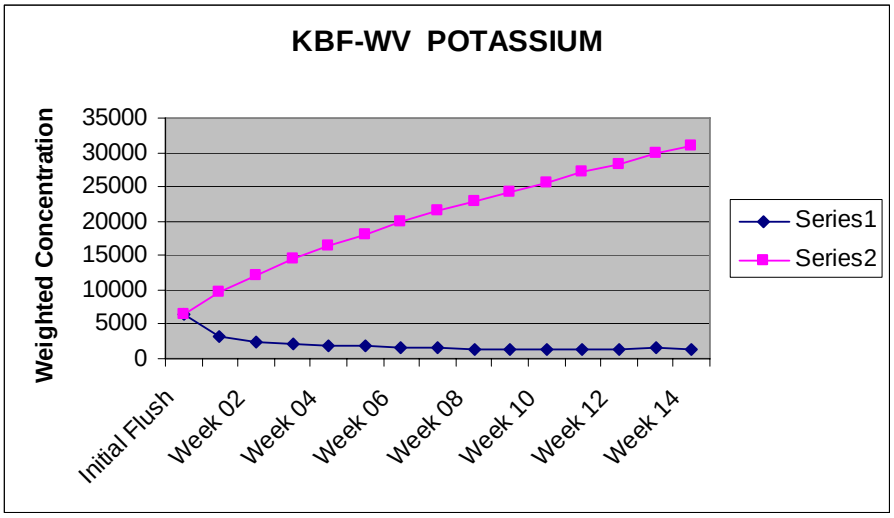

KBF-WV MAGNESIUM
Weighted Concentration
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2

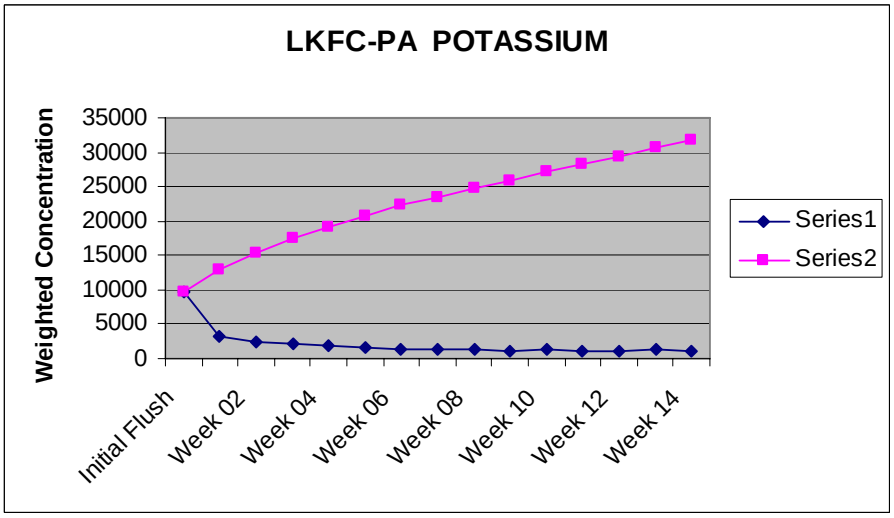

LKFC-PA MAGNESIUM
Weighted Concentration
400000
350000
300000
250000
200000
150000
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


MKSS-PA MAGNESIUM
Weighted Concentration
80000
70000
60000
50000
40000
30000
20000
10000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


BCS3-PA POTASSIUM
Weighted Concentration
25000
20000
15000
10000
5000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


HCS-IN POTASSIUM
Weighted Concentration
40000
35000
30000
25000
20000
15000
10000
5000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2





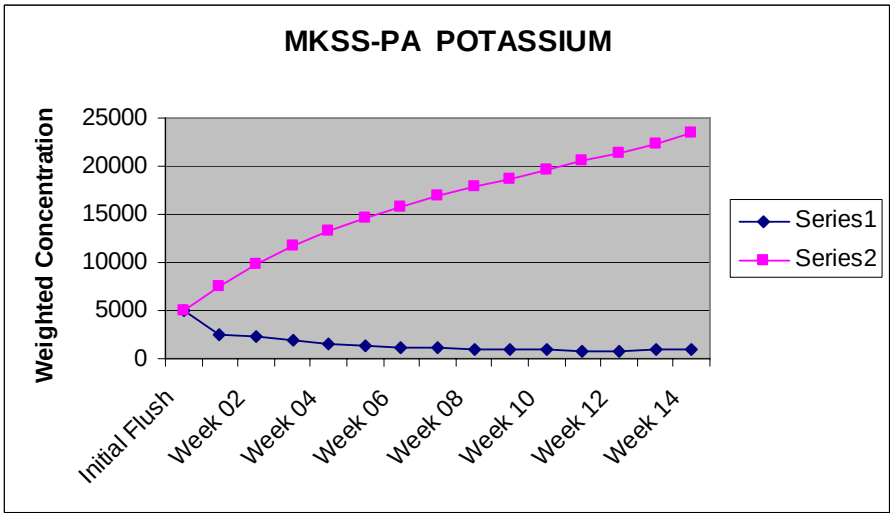
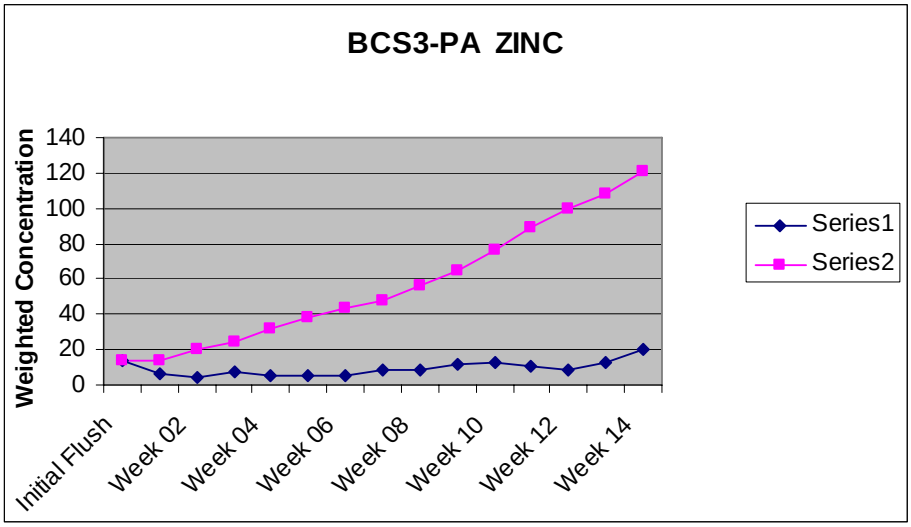
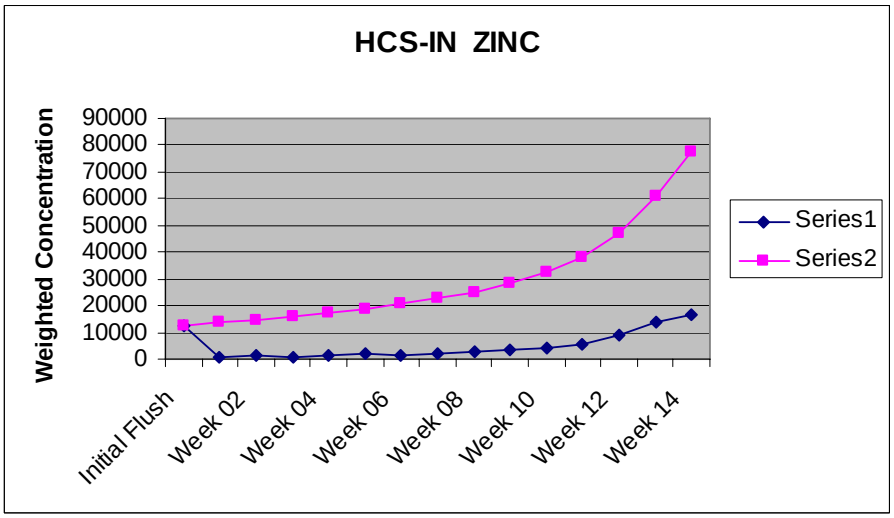


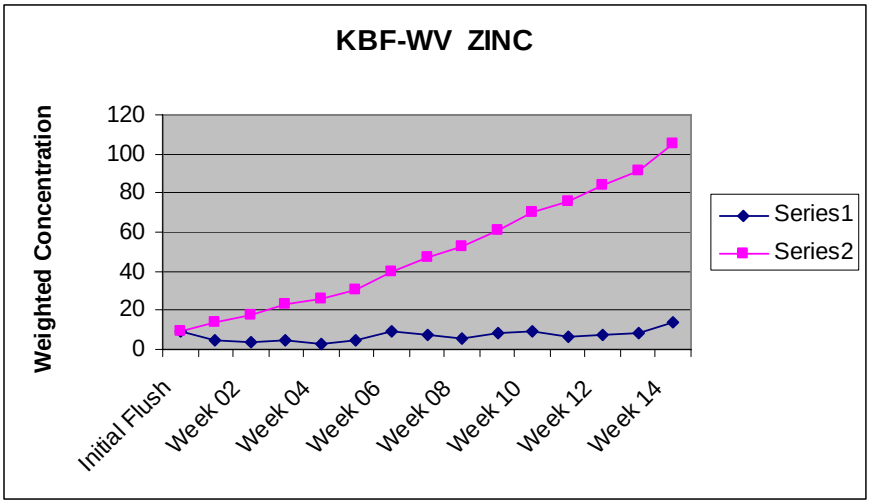
Figure 7.38. Plots of week-by-week release (series 1) and cumulative release including the first flush (series 2) of calcium, magnesium, and potassium.

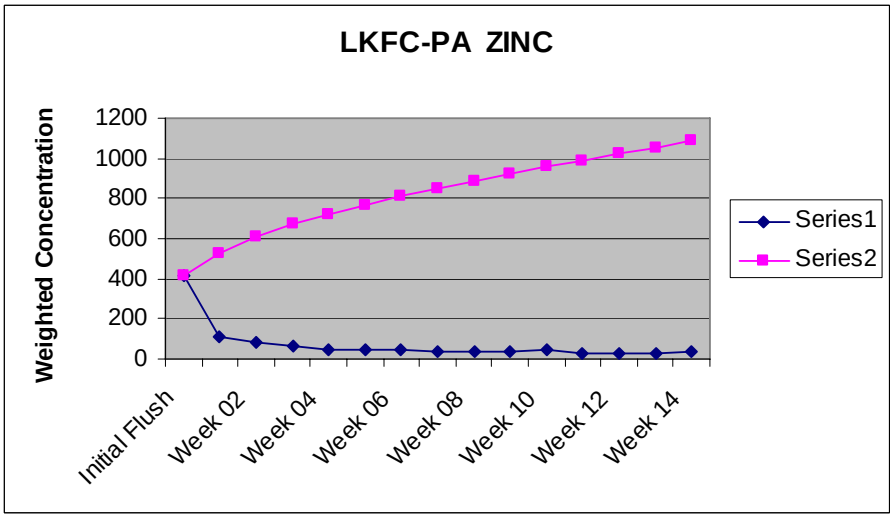
Zinc

Of the various transition metals that occur in minor amounts in the reference rock samples, zinc is leached in sufficient quantities to justify examining the rate of release. Even so, the concentrations are low and some scatter in the data is to be expected. The zinc release data are shown in Figure 7.39. The shapes of the cumulative zinc release curves vary considerably from one rock sample to another. In particular, the zinc release from the Houchins Creek Shale increases rapidly during the last several weeks of the experiment.









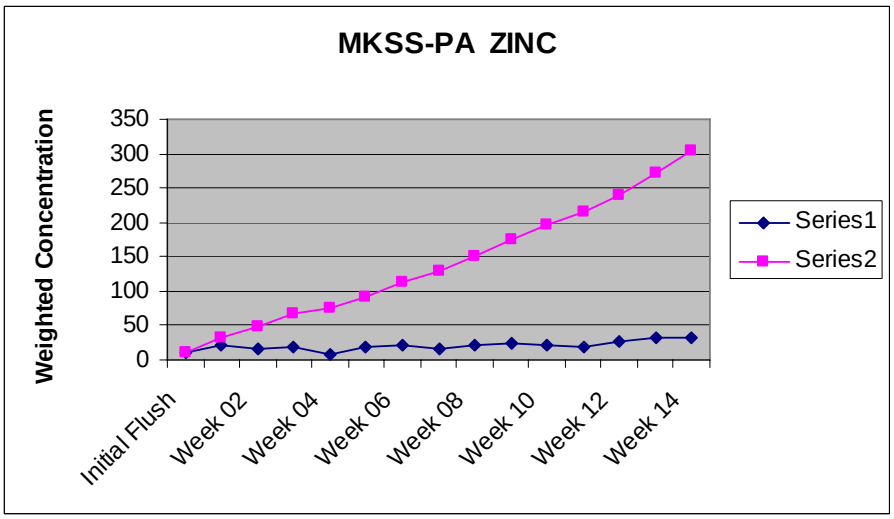
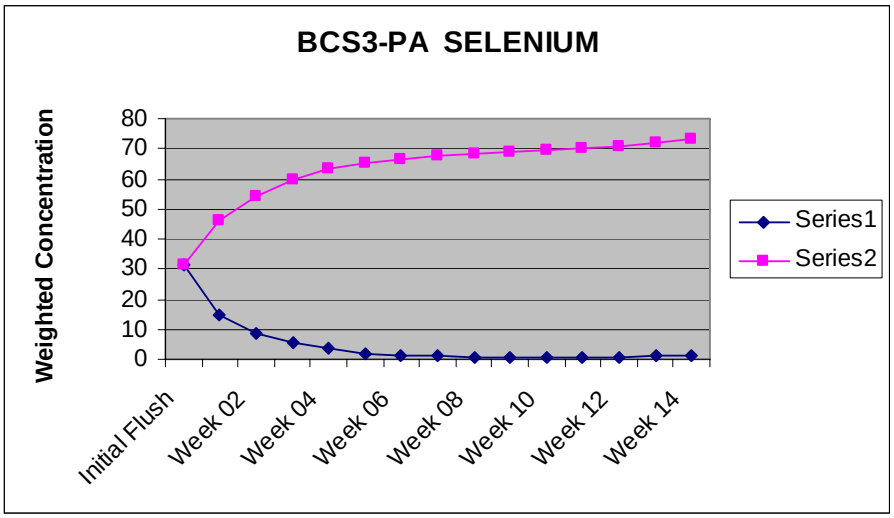
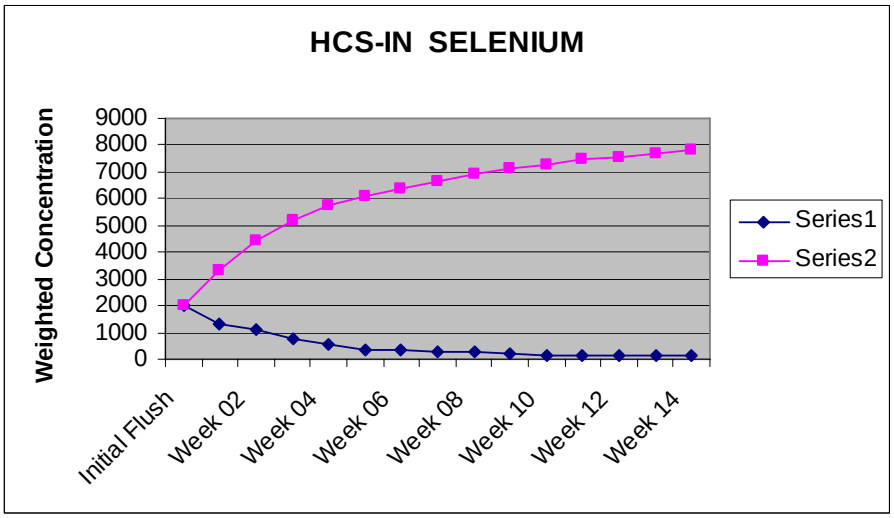


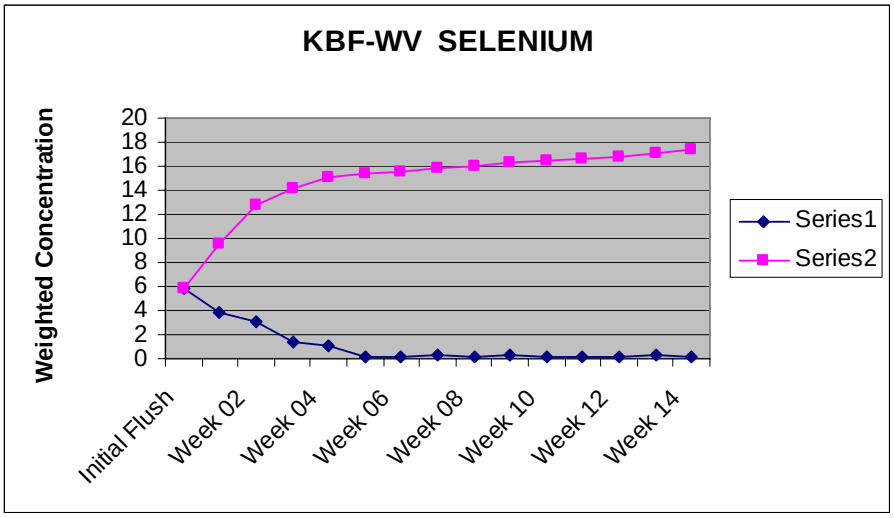
Figure 7.39. Plots of week-by-week (Series 1) and cumulative (Series 2) release of zinc.

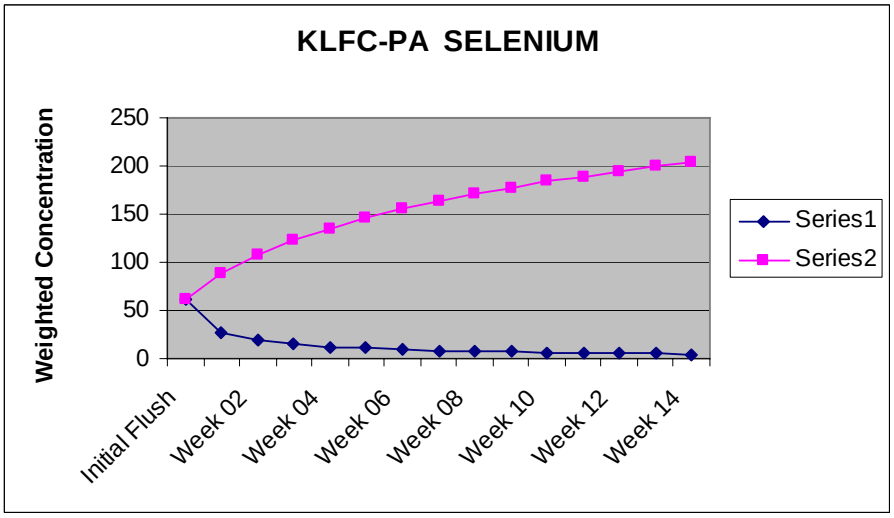
Selenium

Selenium is an element of concern. Release of selenium is described in Figure 7.40. Many of the samples show rapid initial release of selenium followed by a flattening of the rate curves although the curves never become completely horizontal.









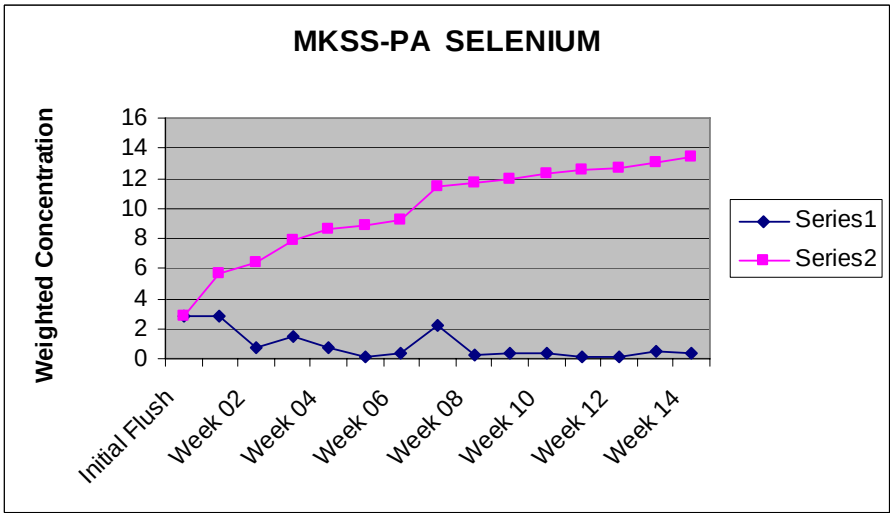
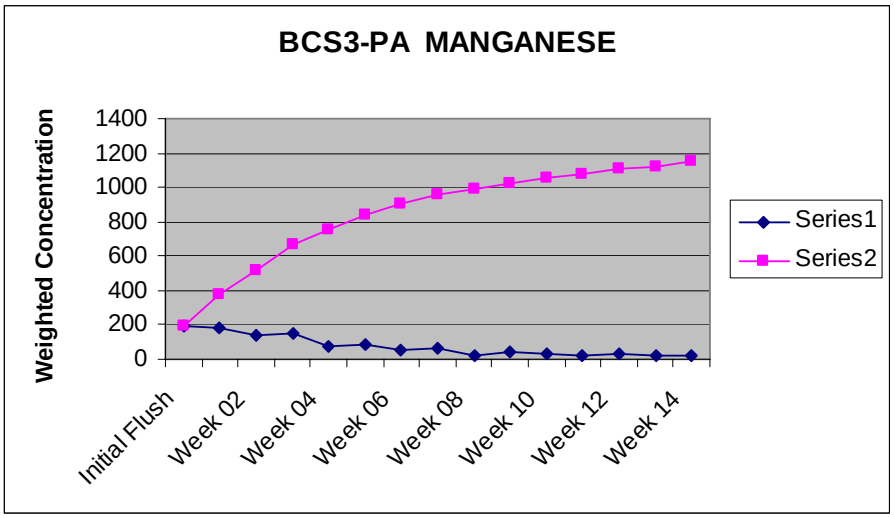
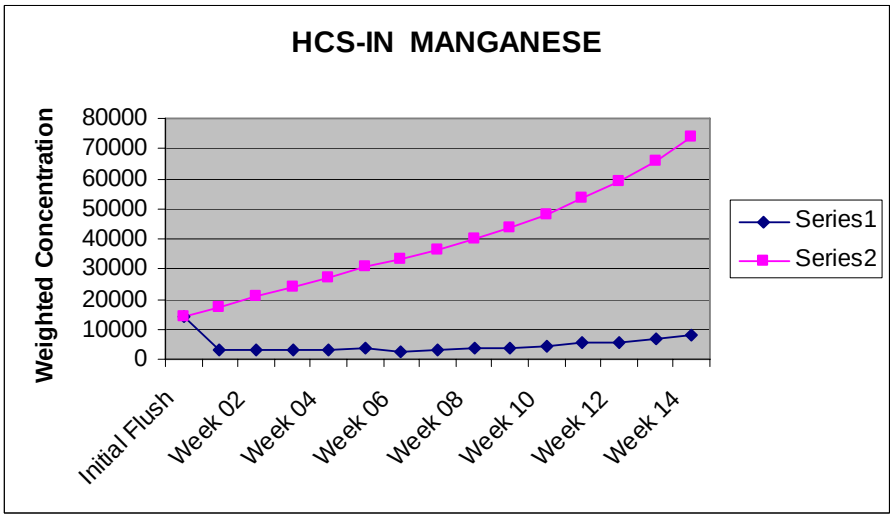


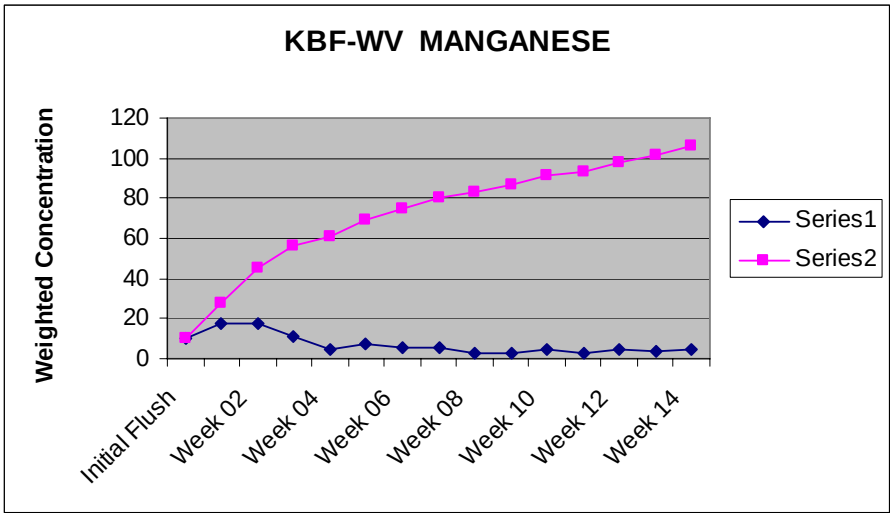
Figure 7.40. Plots of week-by-week release (Series 1) and cumulative release (Series 2) of selenium.

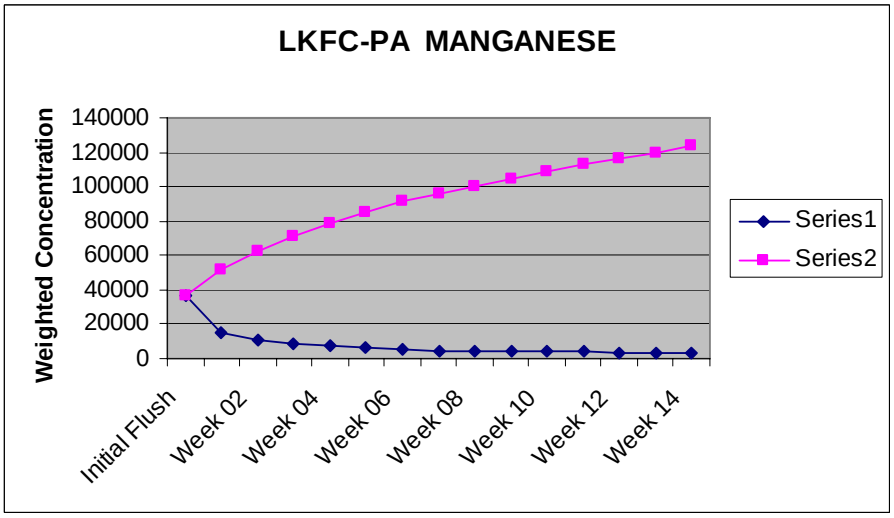
Manganese, Iron and Aluminum

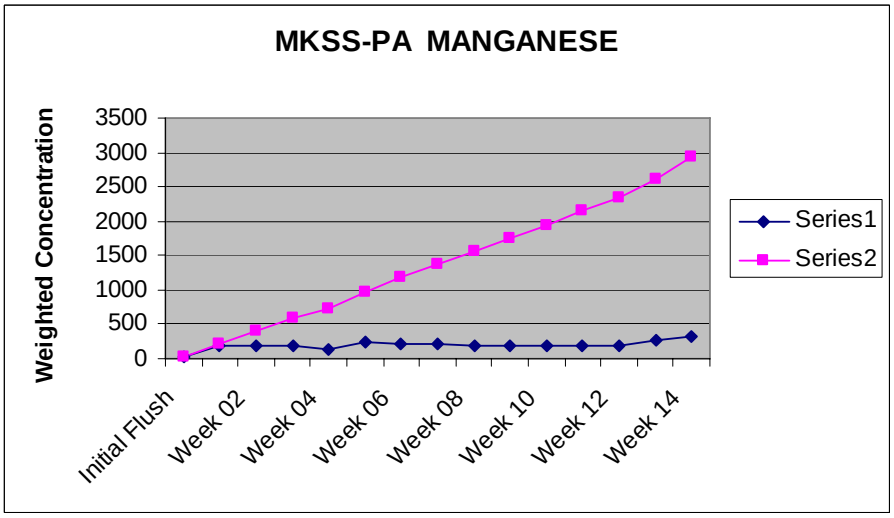
Manganese, iron, and aluminum are common constituents of most rocks. Manganese and iron are highly insoluble in neutral to alkaline environments but can be leached by low pH waters and, as such, are of concern when there is production of acid. Manganese was extracted from the columns in sufficient quantity to produce smooth leach curves. Iron concentrations were lower and so the plots are more erratic. Aluminum was mostly below the detection limit in the analyses, and is not further discussed in this section. The leach curves for manganese and iron are shown in Figure 7.41.

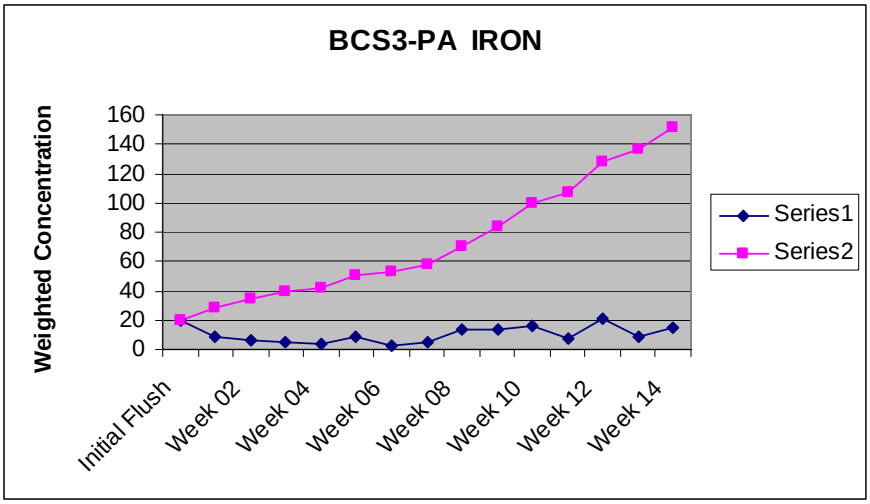


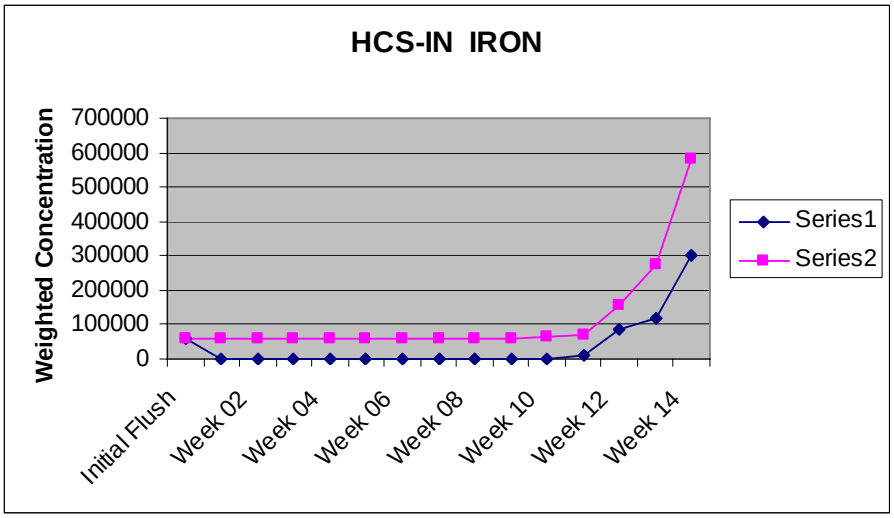


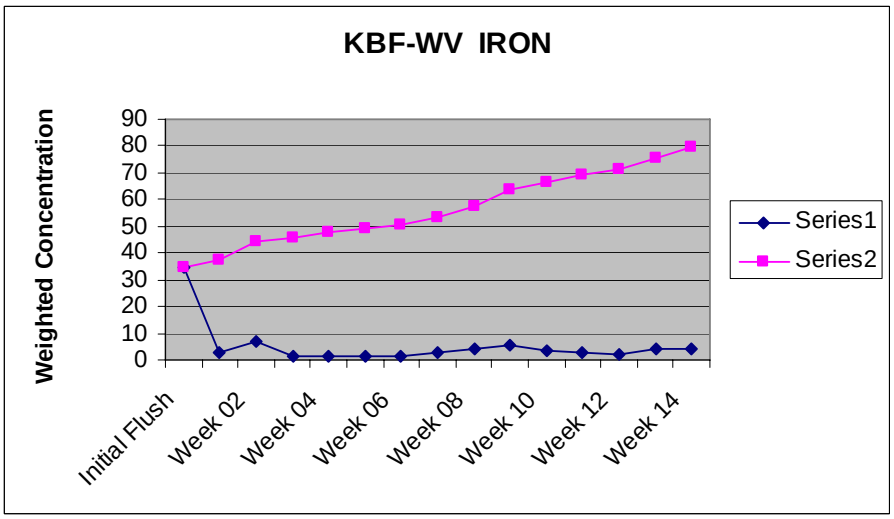

KBF-WV MANGANESE
Weighted Concentration
120
100
80
60
40
20
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2

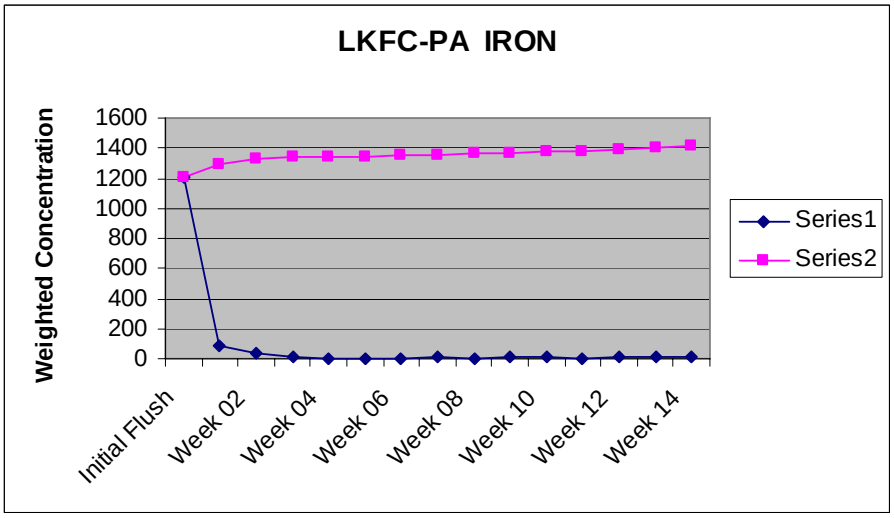

LKFC-PA MANGANESE
Weighted Concentration
140000
120000
100000
80000
60000
40000
20000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


MKSS-PA MANGANESE
Weighted Concentration
3500
3000
2500
2000
1500
1000
500
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


BCS3-PA IRON
Weighted Concentration
160
140
120
100
80
60
40
20
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


HCS-IN IRON
Weighted Concentration
700000
600000
500000
400000
300000
200000
100000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


KBF-WV IRON
Weighted Concentration
90
80
70
60
50
40
30
20
10
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2



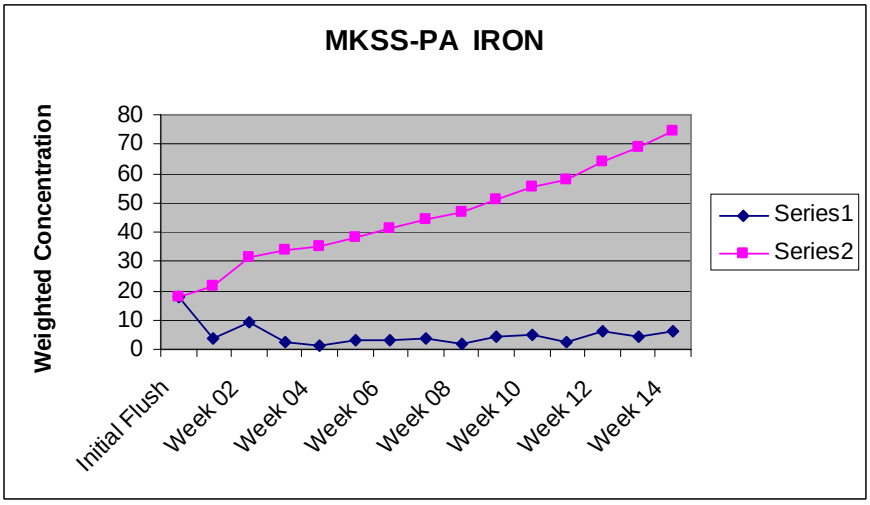


Figure 7.41. Leach curves for manganese and iron.

Discussion and Conclusions Concerning Minor Elements

Considering the inter-laboratory variations, the averaged data give remarkably smooth rate curves for the cumulative release of various minor elements. Regressions based on a power law fit (equation 7.2) were calculated for each of the cumulative release curves (Table 9).

The data for the major cations, calcium, magnesium and potassium plot on very smooth curves that give excellent power function fits with values of the statistical goodness of fit parameter, R^2, in the range of 0.94 to 0.99. If the leaching process were purely diffusion controlled, the exponent, n, should be 0.500. The fitted values scatter around the ideal value with the rather wide range of 0.3 to 0.7. It is probably reasonable to conclude that the release of these elements from the columns is a diffusion-controlled process.

Because of dissolution kinetics of calcite, dolomite, and gypsum – a main calcium and magnesium-bearing minerals, are not diffusion controlled when measured on single phases, it can be further concluded that the movement of these ions through the mass of generally inert material in the columns is the source of the diffusion barrier.

Table 7.9 Fitting parameters for power law regression of minor element data.

	BCS3-PA	HCS-IN	KBF-WV	LKFC-PA	MKSS-PA
CALCIUM					
A	150276	320331	40638	120685	42966
n	0.451	0.564	0.630	0.381	0.715
R^2	0.988	0.978	0.991	0.995	0.992
MAGNESIUM					
A	78068	272488	40836	143448	14330
n	0.432	0.490	0.561	0.326	0.597
R^2	0.993	0.944	0.992	0.993	0.998
POTASSIUM					
A	6879	11790	9030	12212	7391
n	0.431	0.400	0.453	0.346	0.427
R^2	0.989	0.974	0.993	0.988	0.998
ZINC					
A	10.7	8988	10.3	504	26.0
n	0.849	0.604	0.812	0.279	0.872
R^2	0.937	0.634	0.943	0.988	0.962
SELENIUM					
A	48.7	3556	10.8	86.9	5.3
n	0.160	0.313	0.192	0.324	0.354
R^2	0.956	0.982	0.907	0.999	0.970
IRON					
A	20.4	32987	34.2	1288	20.7
n	0.663	0.518	0.279	0.031	0.432
R^2	0.854	0.144	0.893	0.920	0.923
MANGANESE					
A	406	13979	31.4	50388	209
n	0.413	0.548	0.468	0.334	0.973
R^2	0.971	0.897	0.989	0.998	0.994

The cumulative rate data for zinc give relative good fits for all samples except the Houchins Creek Shale. Because of the low concentration of zinc in the leachate, the data points have somewhat larger scatter then do the points for calcium, magnesium, and potassium but the R^2 values remain in the range of 0.94 to 0.98. The fit for the Houchins Creek Shale is 0.634 in spite of the data fitting a very smooth curve. Normally, an R^2 this low would imply a tremendous scatter in the data. The explanation is that the plot curves upward at long times, a shape that is not compatible with the power function rate equation. It shows that the release of zinc from the Houchins Creek Shale involves a more rapid rate process that is activated after the experiments are well underway.

The behavior of selenium is unique among the elements examined. The initial release is very rapid, followed by a flattening of the rate curves are long times. The fits are reasonably good – R^2 = 0.90 to 0.999 – but the exponents are in the range of 0.16 to 0.35, well outside of expected values for a diffusion controlled process. Again, the hypothesis is that there is more than one process involved. It appears possible that selenium occurs in several of the phases in the spoil sample. One dissolves rapidly giving the initial burst o selenium. The later release of selenium is due to a second phase that dissolves for slowly after the first phase is completely dissolved.

Manganese produces smooth rate curves with good fitting values. The only value of R^2 below 0.97 is the Houchins Creek Shale and the value there is 0.897. Three of the exponents are in the range expected for diffusion-controlled processes. However, the Lower Kittanning Shale has n = 0.334 which is somewhat outside the expected range. In contrast, the Middle Kittanning Sandstone has n = 0.973, almost linear behavior.

Iron is present in the leachates only a low concentration. The fitting parameters for the average cumulative release curves are highly erratic. It does not seem useful to attempt any interpretation.