Chapter 8: Leaching Behavior of Elements

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Nine elements and four general chemistry parameters exhibited distinctive behavior during the 14 week test among the five rocks and seven laboratories. The test successfully distinguished weathering characteristics of the five rocks on concentration, flux and leachate composition bases. Solid rock chemistry and mineralogy, mineral solubility, gas pressure, pyrite and carbonate content all combined to influence the rate and intensity of chemical weathering and leachate chemistry. Pyrite content, as represented by sulfur measurements and mineralogical studies described in chapter 5, was one of the most important influences on leachate chemistry. Pore gas composition, including the partial pressure of carbon dioxide (CO_2), strongly influenced the observed solution alkalinity concentrations and carbonate mineral dissolution.

Chemical Concentration

Calcium, magnesium, sodium, potassium, sulfate and alkalinity were typically present as macro constituents (mg/L range) in all samples. Selenium and zinc are present in trace amounts in the rocks, and were usually as micro constituents (ug/L to a few mg/L) in leachates. Iron and aluminum, although major components in the rocks, were present at detections levels or ug/L, for most of the leaching cycle in four rocks. The low concentrations reflect pH and redox solubility controls on these metals. Sample HCS-IN, which produced acidic leachate during the test, leached significant quantities of iron and aluminum.

The rocks leached varying concentrations of the major constituents, and were generally consistent with minerlogical compostion. Figure 8-1 shows the concentration distribution at weeks 1 and 14 for calcium, magnesium, sodium, potassium, and alkalinity in the five rocks. Other data for weeks 1 and 14 include sulfate concentration and specific conductance (Figure 8-2), selenium and zinc (figure 8-3), and iron, aluminum and manganese (Figure 8-4).

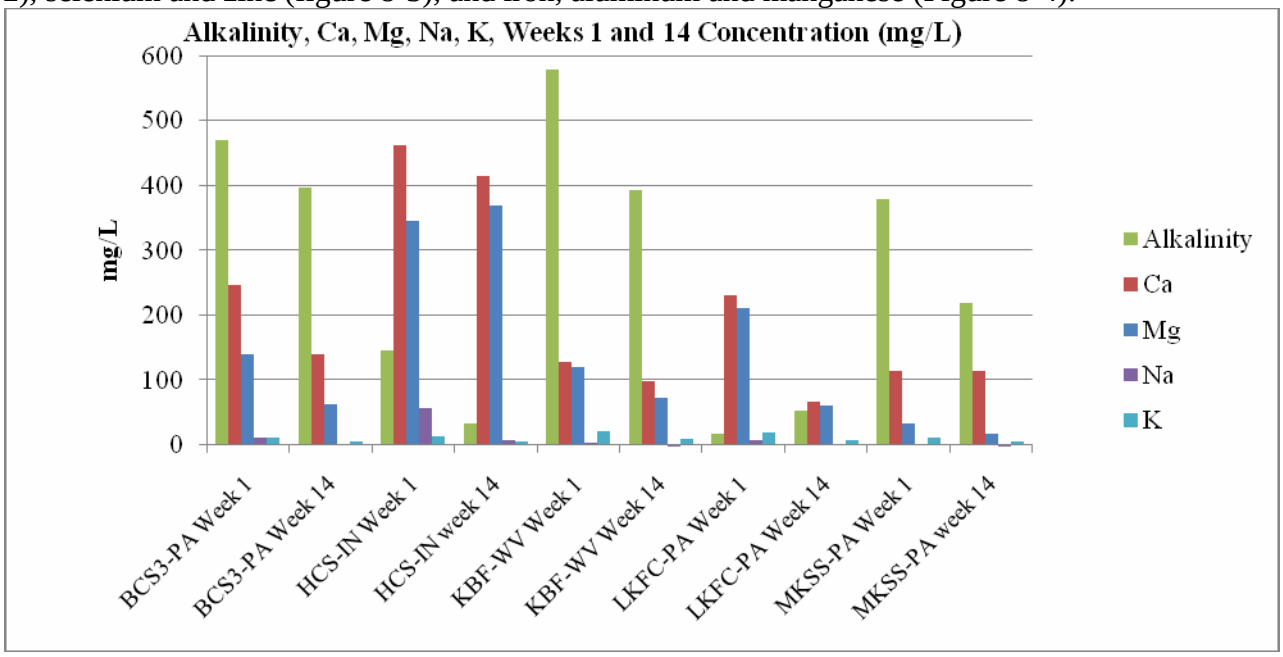

Figure 8-1. Alkalinity, Calcium, Magnesium, Sodium and Potassium Concentrations at Weeks 1 and 14 for 5 Rocks. Values are medians of all labs in mg/L.

Samples BCS3-PA and HCS-IN, which contain the most carbonate, also produced the highest calcium and magnesium leachate concentrations. HCS-IN which generated acidic leachate consumed carbonate and/or other minerals most aggressively. It produced the highest concentration data for most chemical parameters. The "blank" sample MKSS-PA generallly produced low concentrations of major and minor constituents, and KBF-WV and LKFC-PA leachate concentrations were intermediate between the end members.

Elemental concentrations declined substantially from week 1 to week 14. Calcium and magnesium concentrations at week 14 were 22 to 71% lower than initial values for 4 rock types and sulfate values were 60 to 88% lower (Figure 8-1 and 8-2). The single exception was sample HCS-IN where magnesium and sulfate concentrations actually increased through the test, indicating that mineral weathering and leaching intensified as conditions became acidic. Alkalinity concentration declined the least (about 16%) in sample BCS3-PA and the most in HCS-IN as that sample consumed its' neutralizers. One sample, LKFC-PA, had higher alkalinity at the week 14 than at week 1. The reason for this increase or slower release of alkalinity during the test is not clear. The trace element selenium declined in concentration about 90 to 95% from week 1 to week 14 in all 5 rocks (Figure 8-3). The rapid decrease suggests that selenium leaching might be a short term event.

Alkalinity data in Figure 8-1 reflect both carbonate content and mineralogy, and the high partial pressure of CO_2 used in the columns. Each rock produced significant alkalinity, and two rocks generated water with more than 400 mg/L. These data show that the test produced a weathering environment similar to that found in a spoil pile or underground mine. Under atmospheric conditions, calcium carbonate dissolution can only produce about 60 mg/L alkalinity, yet mine waters frequently contain carbonate alkalinity well in excess of that, and measured or calculated pCO_2 is above atmospheric conditions. Cravotta (2008b) in a detailed study of 140 mine discharges in Appalachia, USA, reported a mean pCO_2 of about 0.1 atmospheres; the same condition specified for the test columns. Alkalinity, carbonate solubility and pCO_2 relationships are discussed under "Solubility Controls" later in this chapter.

Specific conductance data in figure 8-2 are a surrogate measure of the dissolved solids content. They are consistent with the elemental analyses, and show a decline in dissolved solids content for 4 samples through the test period, and an increase in the acid weathering HCS-IN sample. The "blank" sample MKSS-PA had the lowest dissolved solids content as would be expected based on its' mineral composition, which includes a high percentage of quartz. The highest chemical concentrations are typically observed during initial weathering and leaching, followed by gradual declines through time. Younger (1997) describes an early flush of weathering products from flooded underground mines in Britain, followed by a decline in pollutant concentrations. After 10 to 20 years, the curves become asymptotic or nearly so. Similar behavior has been described for coal mines in Appalachia (Perry and Rauch, 2006). The increasing specific conductance in HCS-IN from week 1 to 14 reflects two phases of weathering; the first with circumneutral leachate as alkalinity is generated; and the second, an acidification phase as pyrite oxidation dominates. The solubility of many minerals and elements increases at low pH, and this is reflected by the higher conductance readings at week 14.

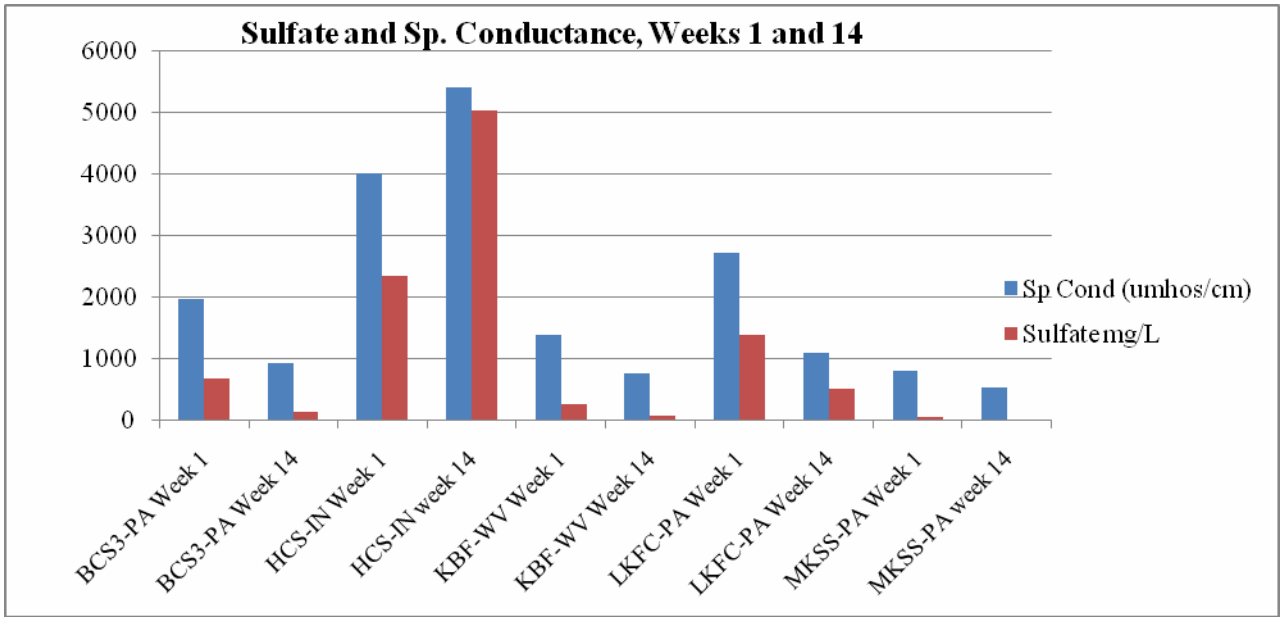

Figure 8-2. Sulfate and Specific Conductance, Weeks 1 and 14 For 5 Rocks. Sulfate in mg/L, Specific Conductance in umhos/cm. Values are medians of all labs.

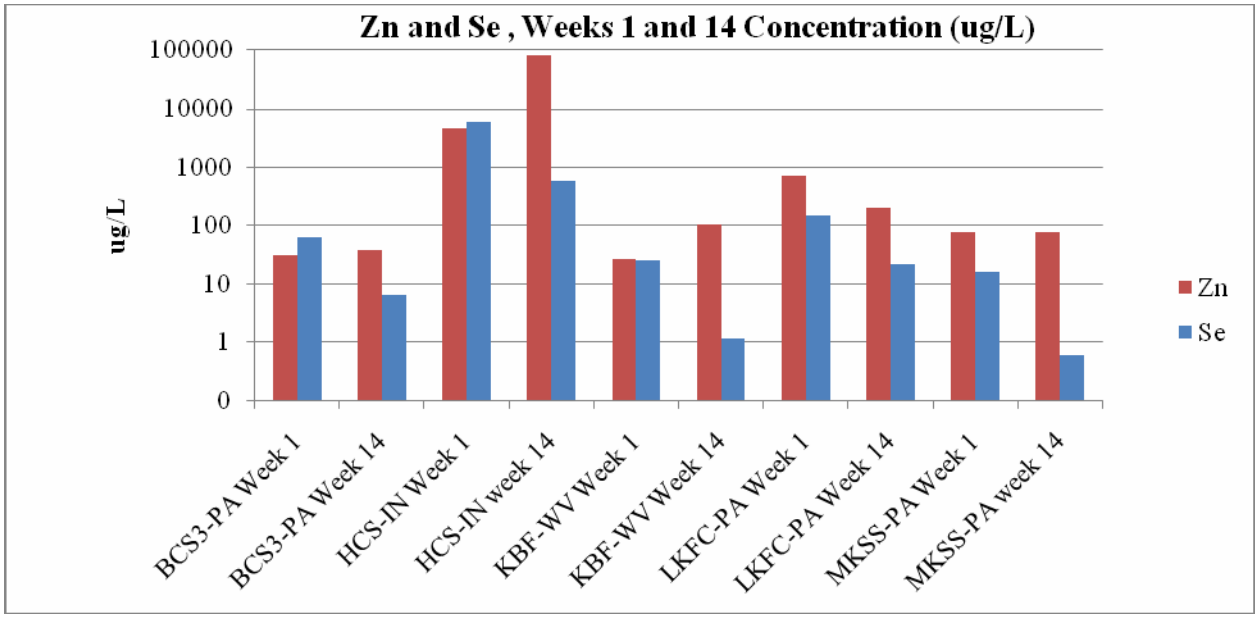

Figure 8-3. Selenium and Zinc Concentration, Weeks 1 and 14 for 5 Rocks. Data are median values of all labs. Concentration is ug/L, log scale. Values are medians of all labs.

Figure 8-3 shows weeks 1 and 14 zinc and selenium concentration data. Four rocks leached these elements at concentrations of a few ug/L, and concentrations declined during the test. Sample HCS-IN produced the highest leachate concentrations and zinc actually increased from week 1 to 14 as the sample acidified. Selenium concentration declined about 90 to 95% for all five rocks from week 1 to week 14. Sample KBF-WV was collected from a mining area in

West Virginia where selenium has been identified as mostly closely associated with coal and carbon rich shales in parts of the Kanawha formation in West Virginia (Vesper et al, 2008). This sample leached negligible quantities of selenium.

Figure 8-4 shows weeks 1 and 14 concentration data for the mine water metals iron, aluminum and manganese. Most leachate analyses were at or near detection levels for iron and aluminum, so few trends are evident. The low concentrations are consistent with the test protocol, and geochemical behavior of these elements. The column is a strongly oxidizing environment, with oxygenated air continually passing through the apparatus. Under strongly oxidizing conditions, conversion of Fe(II) to Fe(III) is favored, and occurs as:

$$Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{+3} + 0.5\ H_2O$$

At circumneutral pH, the conversion can progress rapidly, followed by formation of solid phase Fe(III) oxyhydroxide minerals (Langmuir, 1997). Aluminum solubility is strongly pH dependent, with a minimum concentration at circumneutral pH leachates such as those produced in four of the rocks. Only the acidic HCS-IN leachates contained appreciable soluble aluminum and iron. Manganese, which is soluble over a wide range of pH and redox conditions, is present in small to moderate amounts in all samples.

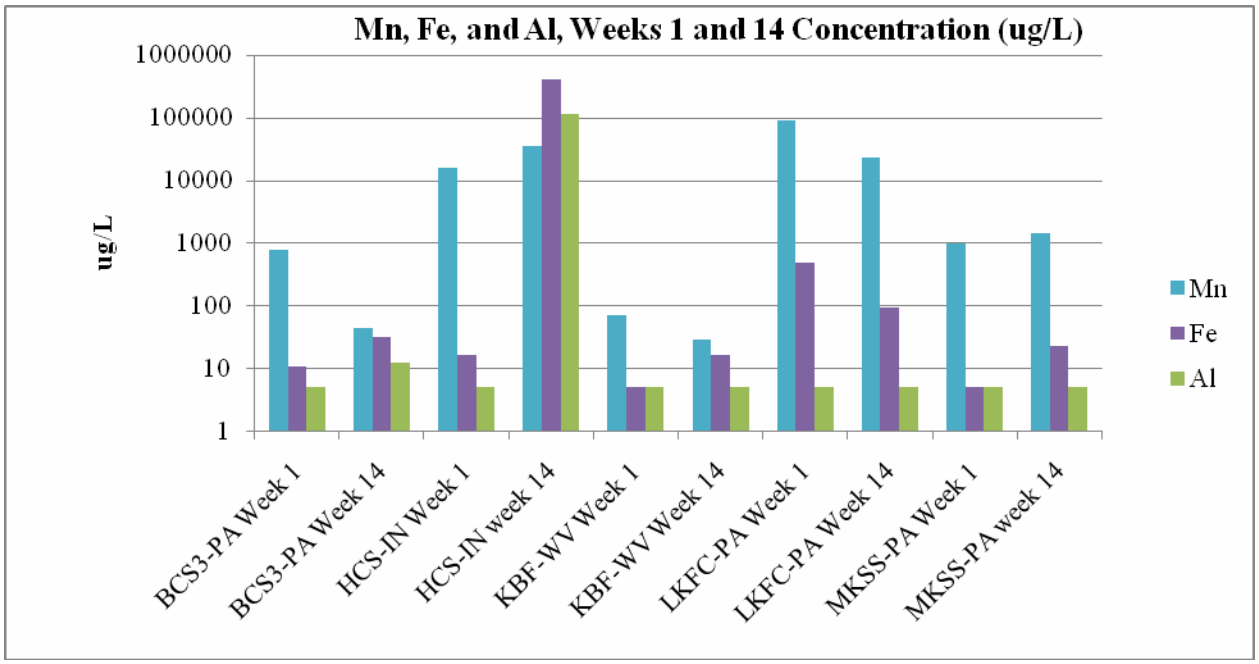

Figure 8-4. Iron, Manganese and Aluminum Concentration, Weeks 1 and 14 For 5 Rocks. Values are medians of all labs. Concentration is ug/L, log scale.

The lack of significant concentrations of iron and aluminum in most leachates should not be interpreted as lack of weathering of iron and aluminum bearing minerals. Significant weathering did take place within the columns, as described in the Chapter 5 comparisons of pre and post leaching mineralogical observations and as shown in the cumulative weathering graphs in Chapter 7. Iron and aluminum were largely removed from solution by the formation of new minerals in four samples, rather than being leached from the columns.

Mineral solubility, pH and redox controls on elements leaching are discussed in the section "Solubility Controls" later in this chapter.

Leachate Composition

The five rocks produced water of various compositions. Figure 8-5 is a Durov plot, a graphical display of week 1 and week 14 leachates, based on dominant cations and anions expressed in percentage milliequivalents. The plot also displays pH and dissolved solids content (estimated

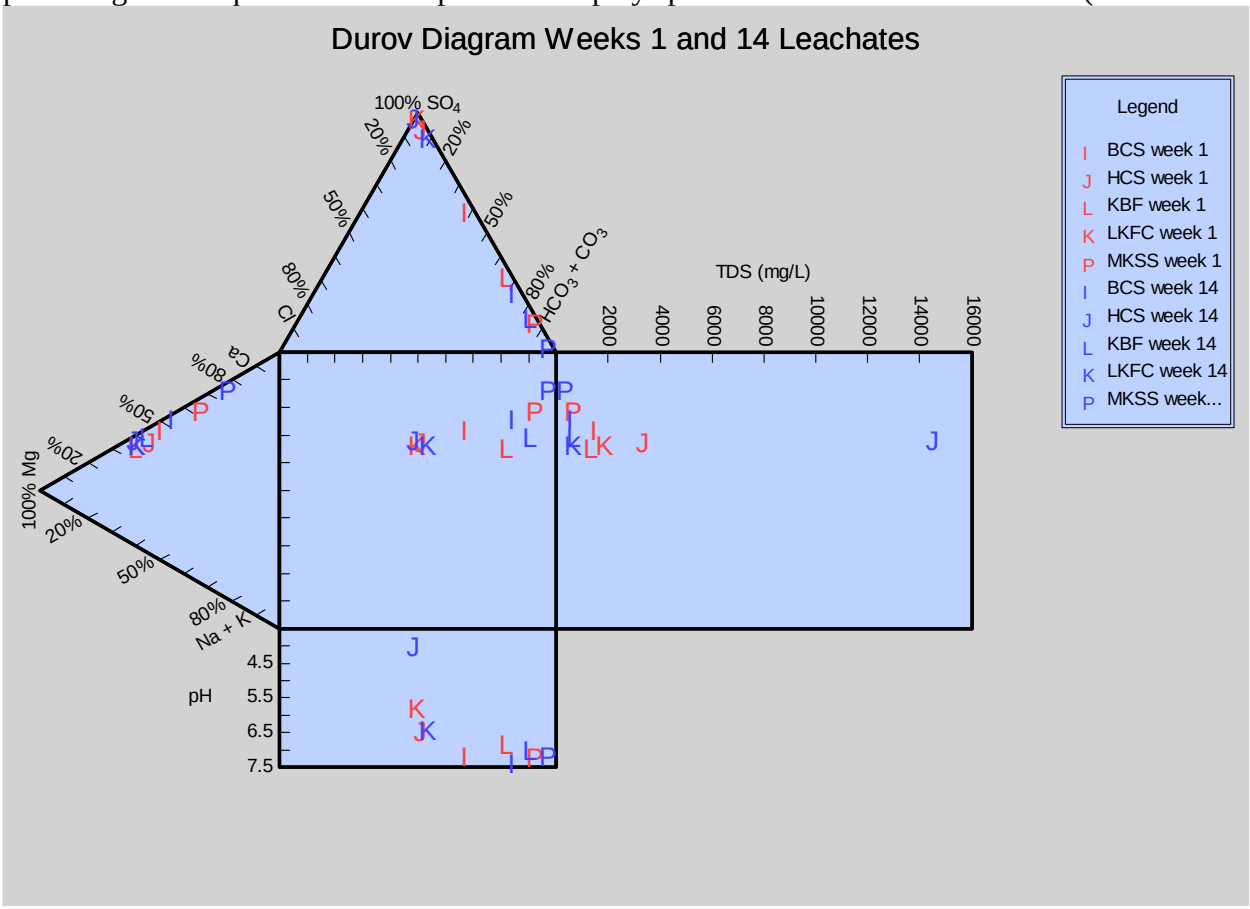

Figure 8-5. Durov (Composition) Plot of Weeks 1 and 14 Leachates. Values are medians of all labs.

from specific conductance). The cation fraction is dominated by calcium and magnesium, while sulfate and bicarbonate are the principal anions. These findings are summarized in table 8-1. The chemical signature for four of the five rocks did not change overall from week 1 to week 14; indicating weathering reactions were consistent throughout the test. Sample BCS3-PA shifted from a sulfate-bicarbonate water at week 1, to a bicarbonate-sulfate type water at week 14. This suggests a gradual depletion of pyrite weathering products, and continued alkalinity production from carbonates. Two samples, HCS-IN, and LKFC-PA produce sulfate dominated water. These two rocks have the highest sulfur contents. The other three rocks produce bicarbonate dominated leachate and have low sulfur contents. Three samples are approximately saturated for the mineral calcite. These waters have dissolved all of the calcium carbonate they can hold, and calcium and bicarbonate concentrations are at a maximum for the conditions in the column.

Table 8-1
Leachate Water Type at Weeks 1 and 14

Sample	BCS3-PA	HCS-IN	KBF-WV	LKFC-PA	MKSS-PA
Week 1 Water Type	Ca-Mg- SO_4 - HCO_3	Mg-Ca - SO_4	Mg-Ca - HCO_3	Mg-Ca - SO_4	Ca -Mg- HCO_3
Week 14 Water Type	Ca-Mg- HCO_3- SO_4	Mg-Ca - SO_4	Mg-Ca - HCO_3	Mg-Ca - SO_4	Ca -Mg- HCO_3
Calcite Saturated	Yes	No	Yes	No	Yes

The column leaching waters have compositions characteristic of mine waters. Cravotta (2008a, 2008b) sampled about 140 surface and underground mine discharges in Appalachia, including strata that is similar to some of the study samples. Cravotta's data when replotted to show cation/anion composition, shows water much like those in Figure 8-5.

The test produced leachates of different chemical composition as shown by comparing mean (average) leachate composition for the five rocks over the 14 week test. These data are summarized in Table 8-2 for the major elements, pH and specific conductance. Chemical concentrations were compared using analysis of variance techniques (ANOVA). The test compares the mean values of 14 weeks of data among the different rocks. Statistically significant differences occur for each chemical parameter. The ANOVA F-test showed that that the differences are not likely due to chance. Alkalinity concentrations were distinct for each rock, and specific conductance values were divided among four categories. Calcium and magnesium concentration also shows distinct difference, with the BCS3-PA and HCS-IN leaching the highest concentrations of these two elements. These rocks contained the most carbonates. Sulfate concentrations were also divided among several categories and generally follow the total sulfur content of the rocks. Table 8-2 shows that the test produces waters of different composition from both geochemical and statistical bases, and has value for discriminating among the weathering behavior of rocks. Leaching of the trace element zinc was distinct only for the HCS-IN.

Table 8-2
Mean Leachate Composition for Five Rocks(1)

Sample	**pH**	**Alkalinity (mg/L)**	**Specific Conductance**	**Calcium (mg/L)**	**Magnesium (mg/L)**	**Sulfate (mg/L)**	**Zinc (ug/L)**
BCS3-PA	7.23*	368****	1131**	157**	75**	220*	35.2*
HCS-IN	5.12***	76**	3851****	458***	337***	2609***	19862**
KBF-WV	6.99*	427*****	958**	99*	83**	592**	44*
LKFC-PA	6.10**	38*	1464***	109*	100**	95*	283*
MKSS-PA	7.14*	250***	604*	102*	22*	17*	74*

(1) Values followed by the same number of asterisks (*) are **not** statistically significantly different at a probability level of p=0.05. Values with differing number of asterisks **are** statistically significantly different. Means computed from week 1 to week 14 data inclusive. F-test indicates ANOVA model is statistically significant.

Chemical Flux (Load)

Chemical flux or load varied among the rocks, both on an absolute basis, and as relative fraction of the total elemental content. HCS-IN leached chemicals most aggressively, while the blank MKSS-PA and KBF-WV were the least reactive rocks.

Fraction Leached

Table 8-3 shows the total elemental content and fraction leached for the five rocks. These data represent only the elemental fraction removed completely from the column. It does not account for materials that weathered and were retained in the column by the formation of other minerals, adsorption or exchange reactions. Four of five rocks leached about 0.001% or less of the Fe and Al present. Only the acidic leachate from sample HCS-IN contained appreciable quantities of Fe and Al. Less than 1% of total Mn was leached, except in sample HCS-IN where nearly 18% of Mn was removed. Between about 3 to almost 9% of total Ca was removed during the test and about 1 to 2 % of Mg was leached. For sulfur, initially present mostly as sulfides, about 2 to 4.5 % of total sulfur was removed during leaching. The trace element Se is in low concentrations (<3 ppm) in four of the five rocks, and less than one to about 7% of the total was removed during the test.

The rocks were ranked from most (1), to least (5) based on the fraction leached from the original content for each element. An overall average rank was computed from all parameters, and is shown in table 8-3. HCS-IN leached the most element fractions overall, while KBF-WV and MKSS-PA leached the least. As described in chapter 5, these rocks both contain more quartz and other less reactive minerals than the other three samples.

Table 8-3Total Elemental Content and Relative Fraction Leached(1)

Sample	BCS3-PA		HCS-IN		KBF-WV		LKFC-PA		MKSS-PA	
Element	Total(2) (%)	Leached Fraction	Total (%)	Leached Fraction	Total (%)	Leached Fraction	Total (%)	Leached Fraction	Total (%)	Leached Fraction
Fe	6.66	$< 10^{-5}$	6.36	0.0015	6.14	$< 10^{-5}$	7.74	10^{-5}	2.25	$<10^{-5}$
Mn	0.10	0.0009	0.04	0.18	0.10	0.0001	0.18	0.07	0.05	0.006
Al	10.83	$< 10^{-5}$	6.66	3×10^{-4}	8.49	$<10^{-5}$	9.41	9×10^{-5}	5.89	3×10^{-5}
Ca	1.61	0.033	1.61	0.089	0.74	0.027	0.62	0.052	1.29	0.023
Mg	1.45	0.018	0.97	0.11	1.09	0.015	1.13	0.018	0.54	0.008
Na	0.18	0.012	0.37	0.032	0.55	0.0009	0.16	0.008	0.10	0.003
K	2.91	0.0007	2.28	0.0012	2.85	0.001	3.05	0.0009	1.99	0.001
S	0.53	0.035	5.54	0.045	0.20	0.024	0.81	0.043	0.09	0.021
Se	<3	0.021	81	0.11	<3	0.004	<3	0.068	<3	0.002
Zn	171	0.0055	456	0.088	126	0.0006	151	0.007	86	0.002
pH Week 1	7.12		6.61		7.19		5.45		7.20	
pH Week 14	7.14		3.24		7.18		6.27		7.16	
Average Rank	3.4		1		4.2		2.3		4.0	

(1) Median values of all columns, all labs.
(2) Se and Zn total concentrations are in ppm.

Table 8-4 summarizes elemental leaching on an absolute basis, in cumulative mg of element leached per Kg of sample during the 14 week test. The trends are similar to the relative fraction data in table 8-3. Sample HCS-IN leached about 4 times as much sulfur as the next most active sample, LKFC-PA. The blank sample MKSS-PA leached the least. BCS3-PA leached more calcium than four other rocks and has the largest neutralization potential values. The rocks were also ranked from most (1), to least (5) based on the total leached for each element, and an overall average rank computed.

Table 8-4
Total Element Content and Absolute Amount Leached

Sample	BCS3-PA		HCS-IN		KBF-WV		LKFC-PA		MKSS-PA	
Element	Total(2) (%)	Leached(3) (mg/Kg)	Total (%)	Leached (mg/Kg)	Total (%)	Leached (mg/Kg)	Total (%)	Leached (mg/Kg)	Total (%)	Leached (mg/Kg)
Fe	6.66	0.73	6.36	96.1	6.14	0.32	7.74	0.946	2.25	0.069
Mn	0.10	0.996	0.04	68.5	0.10	0.102	0.18	127	0.05	3.12
Al	10.83	0.032	6.66	20.8	8.49	0.015	9.41	0.086	5.89	0.018
Ca	1.61	543	1.61	1443	0.74	205	0.62	323	1.29	300
Mg	1.45	268	0.97	1123	1.09	191	1.13	371	0.54	70.9
Na	0.18	22.9	0.37	119	0.55	5.4	0.16	12.7	0.10	3.33
K	2.91	1.07	2.28	1.24	2.85	1.25	3.05	1.07	1.99	0.093
S	0.53	1066	5.54	8576	0.20	299	0.81	2187	0.09	111
Se	<3	0.065	81	8.97	<3	0.013	<3	0.204	<3	0.014
Zn	171	0.095	456	.043	126	0.084	151	1.13	86	0.188
pH Week 1	7.12		6.61		7.19		5.45		7.20	
pH Week 14	7.14		3.24		7.18		6.27		7.16	
Average Rank	2.7		1.5		3.7		1.8		3.7	

(1) Median values of all columns, all labs.
(2) Se and Zn total concentrations are in ppm.
(3) Leached fraction calculated as cumulative total mass of element in leachate / Kg of sample.

The acid forming shale HCS-IN leached the greatest elemental fraction and absolute amounts for most parameters in tables 8-3 and 8-4. The samples rank for overall weathering intensity and element leaching as follows, using either relative or absolute amount leached:

HCS-IN(%S=5.15) > LKFC-PA(%S=0.91) > BCS3-PA(%S=0.59) > KBF-WV(%S=0.31) ≈ MKSS-PA(%S=0.04)

Weathering intensity follows the same ranking order as the original sulfur content of the rocks. Pyrite content indicates in general terms, how intensely the rock will weather.

Solubility Controls

The leaching behavior of elements, and interpretation of leaching test results, is influenced by mineral solubility, oxidation-reduction state, and for carbonate minerals, the partial pressure of carbon dioxide. A proper interpretation of column leaching results and estimation of field performance requires consideration of solubility controls imposed on elements.

Carbonates, Alkalinity and Carbon Dioxide Partial Pressure

The aqueous carbonate system is described by a series of equilibrium equations including carbon dioxide gas as follows:

$$CO_{2\,(g)} + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

and the dissolution of carbonate minerals, such as calcite as:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

These reactions collectively determine the amount of carbonate that dissolves and the subsequent alkalinity concentrations. Figure 8-6 illustrates the effects of carbon dioxide pressure on pH and alkalinity when dissolving calcium carbonate in pure water. At normal atmospheric conditions, solution pH is about 8.3 and calcite solubility produces around 60 mg/L alkalinity. At the column test condition of 10% CO_2, or pCO_2 of 0.1, calcite solubility is increased to produce alkalinity approaching 350 mg/L. The use of 10% CO_2 for the test protocol had a significant effect on carbonate weathering and alkalinity concentrations.

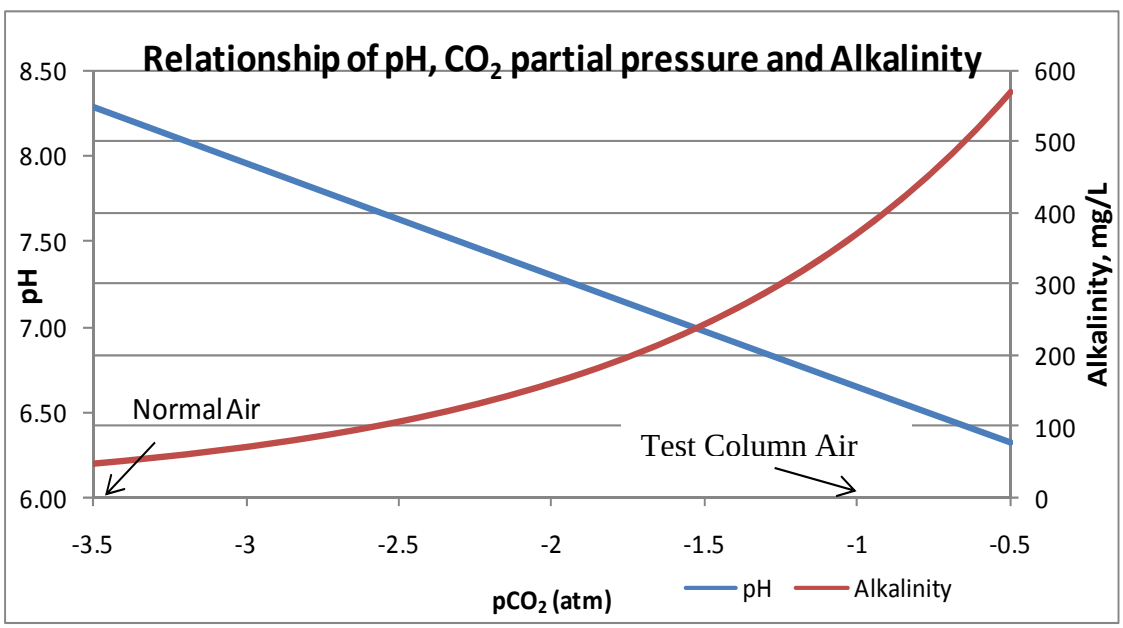

Figure 8-6. Effect of pCO2 on Alkalinity, pH and Calcium Carbonate Dissolution.

Figure 8-7 shows median alkalinity concentrations for the five samples over the 14 week test period. Three rocks BCS3-PA, KBF-WV and MKSS-PA produced significant alkalinity, with concentrations ranging from about 200 to 400 mg/L from weeks 4 to 14. These three rocks also produced leachates that were at saturation for the mineral calcite throughout the 14 week test (Figure 8-6). These samples were able to continuously dissolve the maximum amount of calcite

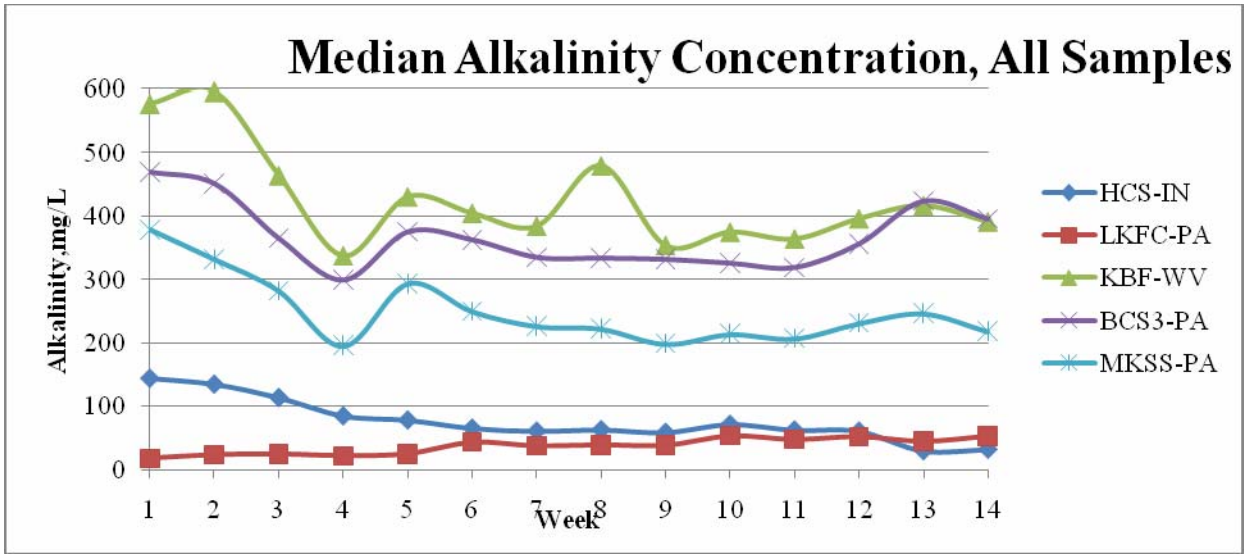

Figure 8-7. Alkalinity Concentration Weeks 1 to 14 for Five Rocks. Values are medians of all labs.

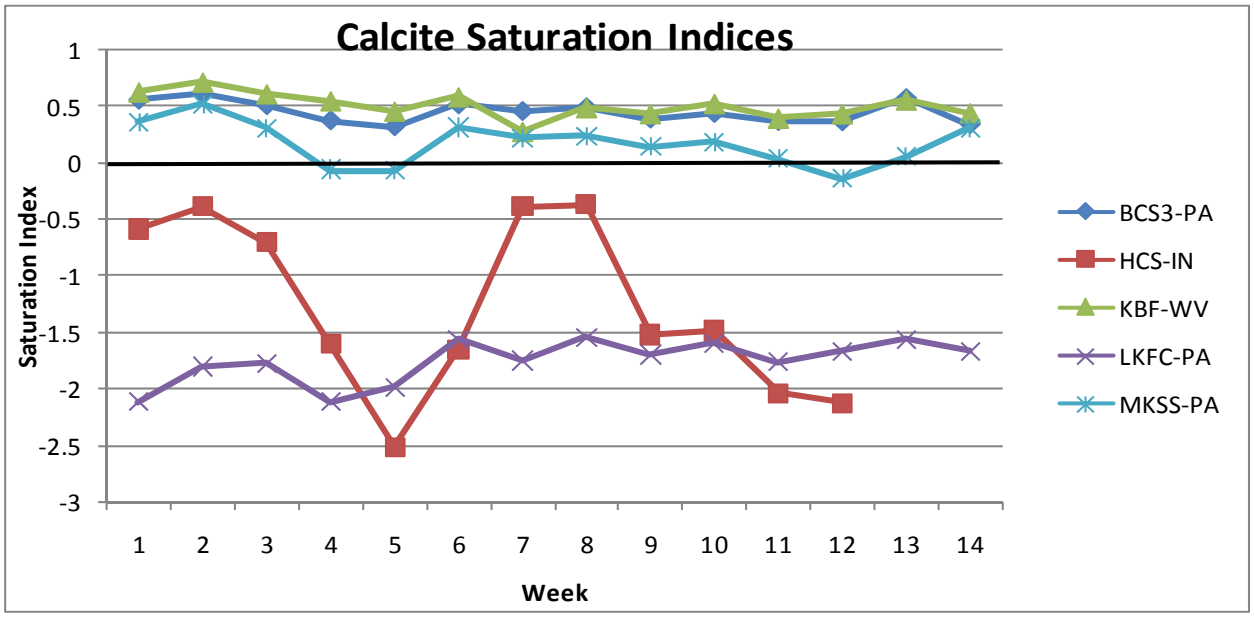

Figure 8-8. Calcite Saturation Indices Weeks 1 to 14 for Five Rocks. Values are medians of four labs.

that the water could hold during the test and are significant sources of acid neutralization in the test. The saturation index calculations are based on chemical equilibrium concepts, and are described in Appendix B of Draft Method 1627 document (2008). The computer code PHREEQCI (Parkhurst and Appelo, 1999) was used to calculate calcite and other mineral

saturation indices. Leachates with a saturation index value greater than zero are over-saturated and cannot dissolve more of that mineral. Leachates with saturation index less than zero are under-saturated and the mineral, if present, can dissolve, because the solution is holding less than the maximum. HCS-IN and LKFC-PA produced leachates that were under-saturated for calcite. These rocks have less significant sources of neutralization.

Sulfate Minerals

Gypsum ($CaSO_4$*2 H_2O) and other sulfate bearing minerals could influence the amount of sulfate in leachates. Gypsum was identified in sample HCS-IN (chapter 5). Gypsum saturation indices, calculated using PHREEQCI, are shown in figure 8-9. Sample HCS-IN is at approximate equilibrium for gypsum, indicating solubility of that mineral is likely controlling the amount of sulfate in solution. The other four rocks are under-saturated for gypsum, and have no gypsum solubility limitations on their leachate composition.

Sulfate concentration is often used as a surrogate estimate of acid production from pyrite. For samples like HCS-IN, where sulfate concentration may be limited by solubility controls, actual acid production may be greater than estimated. Other metal-sulfate minerals such as schwertmannite, the jarosite series, and jurbanite could also control the solution concentrations of sulfate and various metals. Mineral solubility constraints should be part of the evaluation scheme for leachate interpretation.

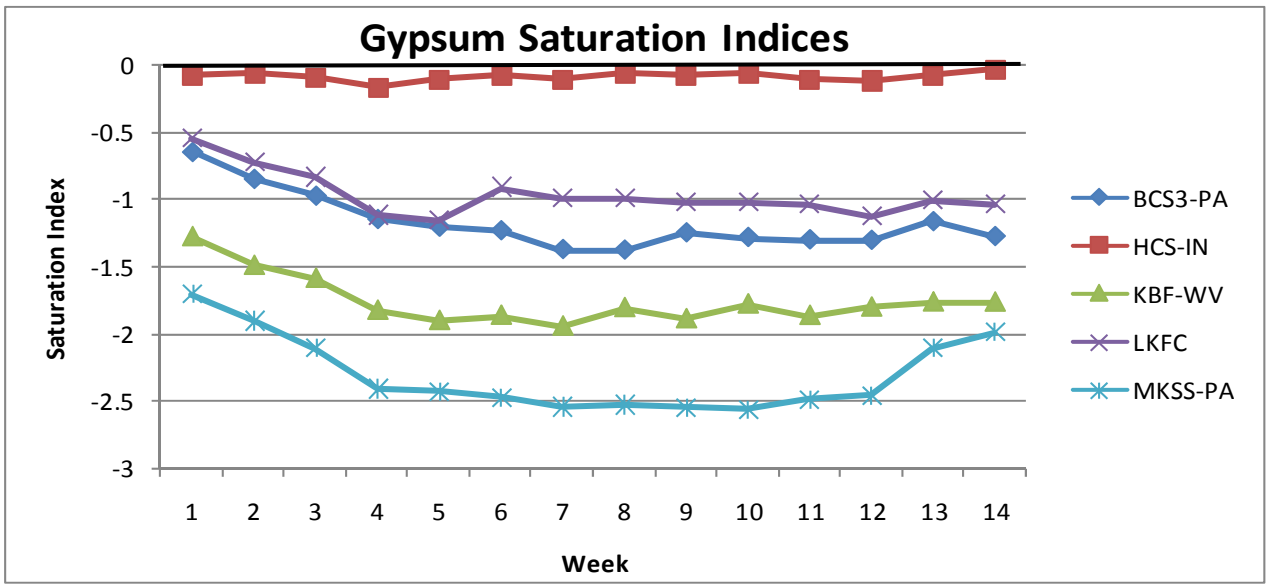

Figure 8-9. Gypsum Saturation Indices for Five Rocks. Values are medians of four labs.

Oxidation-Reduction

Oxidation reduction reactions can exert a strong influence on elements with more than one possible valence state. More than one potential valence state is possible for the elements iron(+2,+3), manganese(+2,+3,+6,-7) and selenium(-2,+4,+6). Their behavior can be estimated from the use of equilibrium calculations and graphically illustrated in Eh/pH diagrams. One laboratory measured the Eh, or oxidation reduction status of the weekly leachate samples, even though this was not a requirement of the test protocol. These data confirmed that oxidizing conditions existed, and allow equilibrium calculation of leachate speciation.

Figure 8-10 shows the distribution of iron species of week 14 leachates for the 5 rocks. Four of the five samples are in the stability field for the solid, poorly crystalline Iron Hydroxide, $FeOH)_3$(ppd). This is consistent with very low leachate iron concentrations, oxidizing conditions, generally low solubility of Fe (III) at circumneutral pH, and post leaching observations discussed in chapter 5. Soluble forms of iron are the preferred state for the acidic HCS-IN leachate. Cravotta (2008b) found that iron concentration in many mine waters is controlled by iron oxyhydroxides or hydroxysulfate minerals.

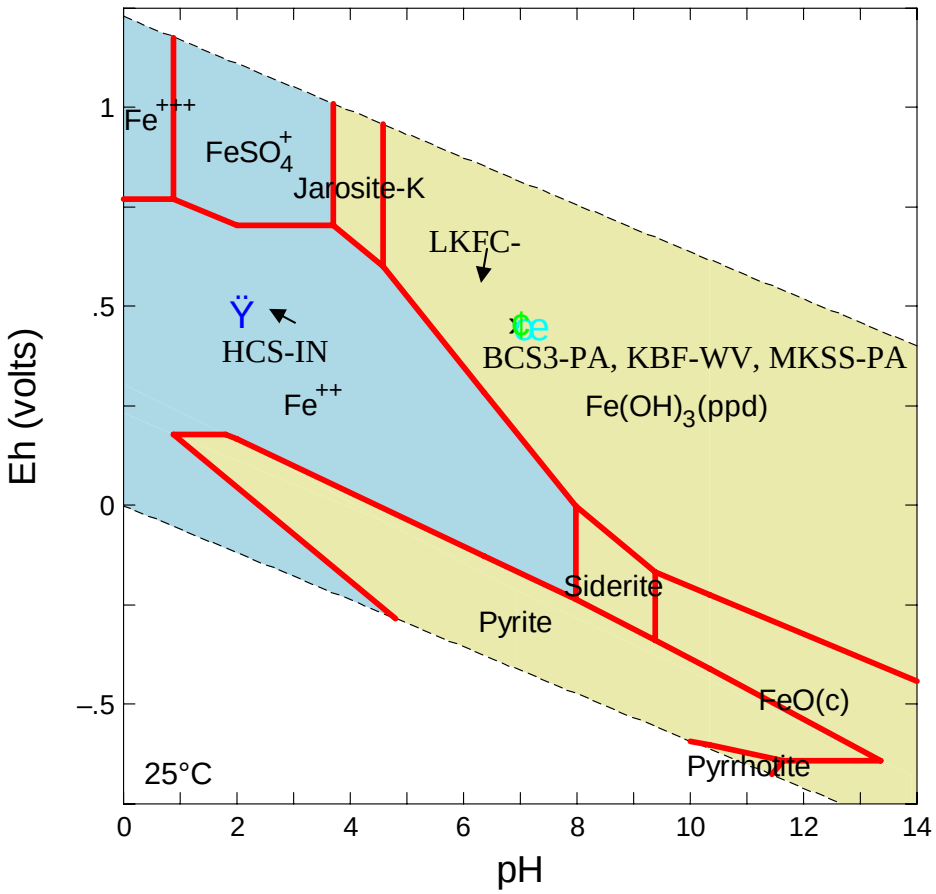

Figure 8-10. Eh/pH Plot of Selected Iron Minerals and Week 14 Leachates.

<u>pH</u>

pH is the principal solubility control for aluminum, and strongly influences the behavior of iron and other elements. Figure 8-11 shows aluminum solubility for leachates containing sulfate, potassium and silica at chemical activities representative of week 14 conditions. Aluminum solubility is at a minimum at about pH 6, and increases rapidly at pH conditions less than about 5. Aluminum solubility is controlled by alumino-silicates such as the clay mineral kaolinite, sulfate minerals such as alunite or others at low pH, and oxyhydroxides such as $Al(OH)_3$. Four of the five rocks produced leachates with pH between 6.1 and 7.2 and all contain kaolinite in the clay fraction. Aluminum concentrations were at or near detection for these rocks. The acidic conditions in HCS-IN leachate allow much higher concentration of soluble aluminum.

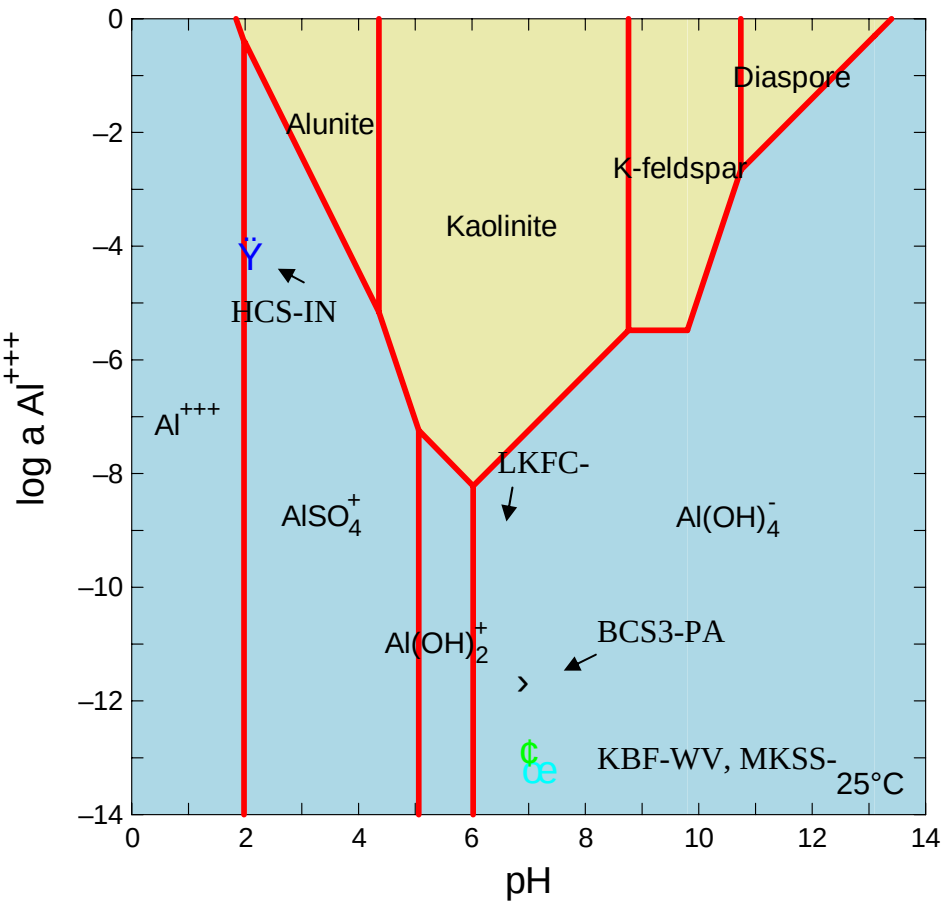

Figure 8-11. Aluminum Solubility as a Function of pH for selected Sulfate and Clay Minerals. Aluminum activity (y-axis) on log scale.

Weathering Rates

Chemical Concentration

Time series plots of chemical concentrations in the columns often exhibited curvilinear behavior. This behavior, which is observed in many chemical and biological systems, has been described using an exponential decay function of the general form:

$$C_t = C_o \times e^{-kt}$$

where: C_t = concentration at time t
C_o = concentration at time zero
e = base e, approximate value of 2.718
k = decay constant, rate of concentration change per unit time
t = time

The exponential changes with time in mine water chemistry are not, strictly speaking, decay processes, but are a rate of change with a mathematical description. The term decay is used for convenience in this chapter in the context of describing rate of change in column leachate chemical concentration. For chemical processes that follow a decay function, it is possible to estimate concentration values at different times, and provide some insight into longer term leachate composition. The decay function implicitly assumes constant conditions, and does not account for variations such as change in pCO_2 or other test variables.

Decay constants were calculated by plotting the ratio $\ln(C_t/ C_o)$ versus time. The slope of that plot, determined by linear regression, gives an estimate of k, the decay constant. Estimated k values for concentration change are shown in table 8-5, for calcium, sulfate, alkalinity, specific conductance as a surrogate for dissolved solids, and selenium, along with their R^2 values. The R^2 indicates the percentage of variation explained by the regression, and is shown in parentheses in Table 8-5. R^2 values approaching 100% show a strong relationship for estimating decay constants, while lesser values indicate a weaker association.

Calcium concentration decay was statistically insignificant for two rocks; HCS-IN and MKSS-PA. Both rocks have calcium solubility constraints; gypsum for HCS-IN, and calcite for MKSS-PA. For these two rocks, mineral dissolution was rapid enough to prevent significant change in calcium concentration during the 14 weeks of leaching. The remaining 3 rocks differ by about a factor of 4, with the slowest rate of calcium change in BCS3-PA. This rock had the largest carbonate content.

Table 8-5
Estimated Decay Constants for Calcium, Sulfate,
Alkalinity and Selenium Concentration, and Specific Conductance

Sample	Calcium(1)	Sulfate(1)	Alkalinity(1)	Specific Conductance(1)	Selenium(1)
BCS3-PA	-4.2×10^{-3} (48.3%)(2)	-1.5×10^{-2} (73 %)	-3.4×10^{-3} (41.4%)	-6.2×10^{-3} (57%)	-4.1×10^{-2} (89.6%)
HCS-IN	N.S. (3)	$+6.4 \times 10^{-3}$ (52.4%)	-1.3×10^{-2} (82%)	$+ 1.0 \times 10^{-2}$ (91%)	-2.4×10^{-2} (94.5%)
KBF-WV	-1.7×10^{-2} (39%)	-3.7×10^{-2} (89.4%)	-4.8×10^{-3} (42.7%)	-5.5×10^{-3} (66.6%)	-5.0×10^{-2} (77.1%)
LKFC-PA	-1.0×10^{-2} (75%)	-1.2×10^{-2} (71.6%)	$+1.1 \times 10^{-2}$ (83%)	-9.7×10^{-3} (83.9%)	-1.6×10^{-2} (91.6%)
MKSS-PA	N.S.	-2.0×10^{-2} (78%)	-6.2×10^{-3} (55%)	N.S.	-

(1) Constant in $^{-day}$. Calcium, Sulfate in mg/L. Alkalinity as $CaCO_3$Eq. Specific Conductance data in µmhos/cm. Selenium in µg/L.
(2) Values in parentheses are R^2 values, or percentage of variation explained by the regression
(3) N.S. = not significant.

Sulfate decay, like calcium, is on the order of 10^{-2}/day for 4 rocks. The larger R^2 values indicate a stronger relationship to the decay function for sulfate than calcium. The sulfate values are closely spaced within a factor of about 2.5, indicating very similar sulfate leaching behavior.

The + value for HCS-IN shows that sulfate concentration increased in this leachate, rather than decreased.

Alkalinity concentration decay is about 4 to 5 times less than for sulfate for 3 rocks (BCS3-PA, KBF-WV and MKSS-PA), suggesting that carbonate neutralization may persist longer than acid generation for these samples. Alkalinity decayed most rapidly in HCS-IN, as that sample ultimately produced acidic leachate. The + value for LKFC-PA reflects the increase in alkalinity in this leachate through time. The lowest R^2 values are associated with rocks whose leachates are at saturation for calcite, and may therefore not completely follow a simple time-concentration decay function.

Specific conductance values, representing dissolved solids concentration, are grouped within a factor of about 1.5 for three rocks. This suggests consistent leaching behavior, and the potential to estimate dissolved solids behavior for rocks with similar mineralogical composition. The "blank" sample, MKSS-PA, showed no significant decay in dissolved solids. This rock has the lowest specific conductance, and the highest content of quartz and other weathering resistant minerals. The + value for HCS-IN shows that dissolved solids concentration increased in this leachate through time.

Selenium decay values are within a factor of about 3, and had the highest R^2 values of any parameter in table 8-5. Like the conductance data, selenium decay suggests consistent and predictable behavior for this parameter. Decay was not estimated for MKSS-PA because of the number of non-detect readings.

Gzyl and Banks (2007) estimated decay constants to describe the rate of change in pH and sulfate concentration in flooding underground coal mines in Poland. They reported decay constants on the order of 3 to 5 x 10^{-3} per day, or about an order of magnitude slower than the column tests. Underground mine flooding is a different hydrologic regimen than the weekly flushing cycle of the column test protocol. However, the two data sets suggest that the column test does provide an accelerated chemical weathering cycle that represents field behavior on the order of at least a few years. The leaching column is intended to simulate surface mine conditions, however no comparable published decay constant values were found for surface mine-spoil.

Chemical Flux

Chemical flux or load leached each week was greatest during the first five weeks of weathering for most parameters. Thereafter, weekly flux declined slowly or remained near constant. Figure 8-12, weekly sulfate flux for sample BCS3-PA is typical of the observed leaching behavior. Week 1 flux exceeds 140 mg/Kg, but rapidly declined to about 40 mg/Kg by week 5, and to about 25 mg/Kg by the last week. The first five weeks may represent a rapid initial weathering and flush, followed by slower leaching, more representative of long term chemical weathering. Other major and trace elements generally displayed similar behavior. The rapid initial flux, followed by a slow decline is consistent with the authors' unpublished data and collective experience with mine discharge behavior in the Appalachian region. The column leaching mimics field behavior.

The data plotted in Figure 8-12 exhibit a curvilinear behavior, suggesting that some type of log or exponential function can be fitted. Cumulative flux data were plotted and found to fit

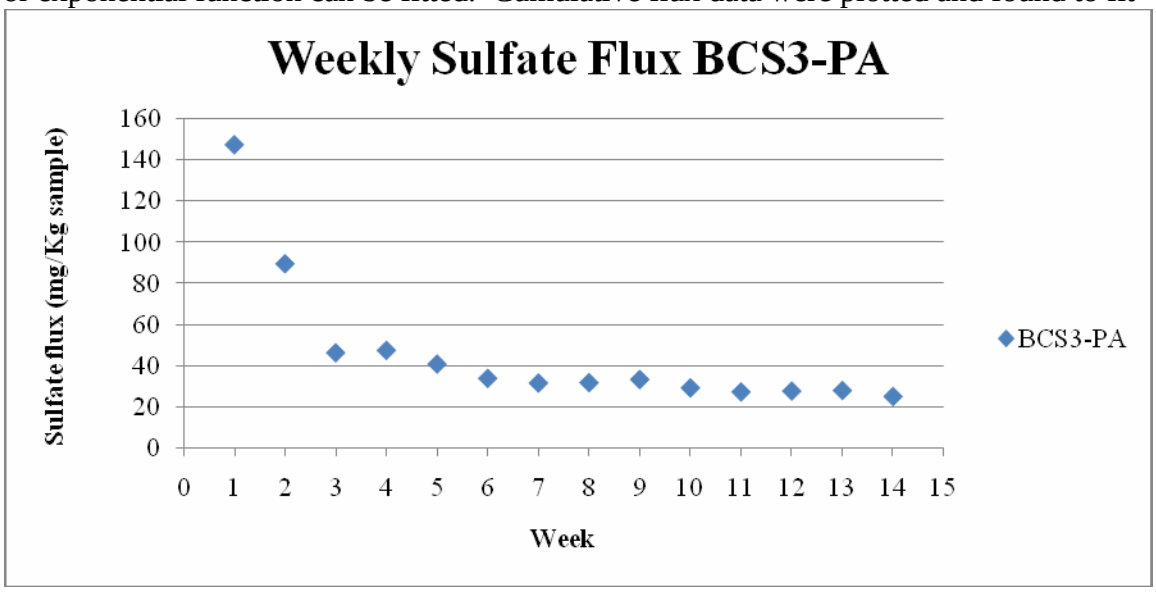

Figure 8-12. Weekly Sulfate Flux (mg/Kg sample) for BCS3-PA. Values are medians of all labs.

either a power or natural log functions of the general forms:

$$y = bx^m \qquad \text{(power)}$$
$$y = m*\ln(x) + b \qquad \text{(natural log)}$$

Figure 8-13 shows sulfate flux data for BCS-PA (same as figure 8-12) plotted on a cumulative

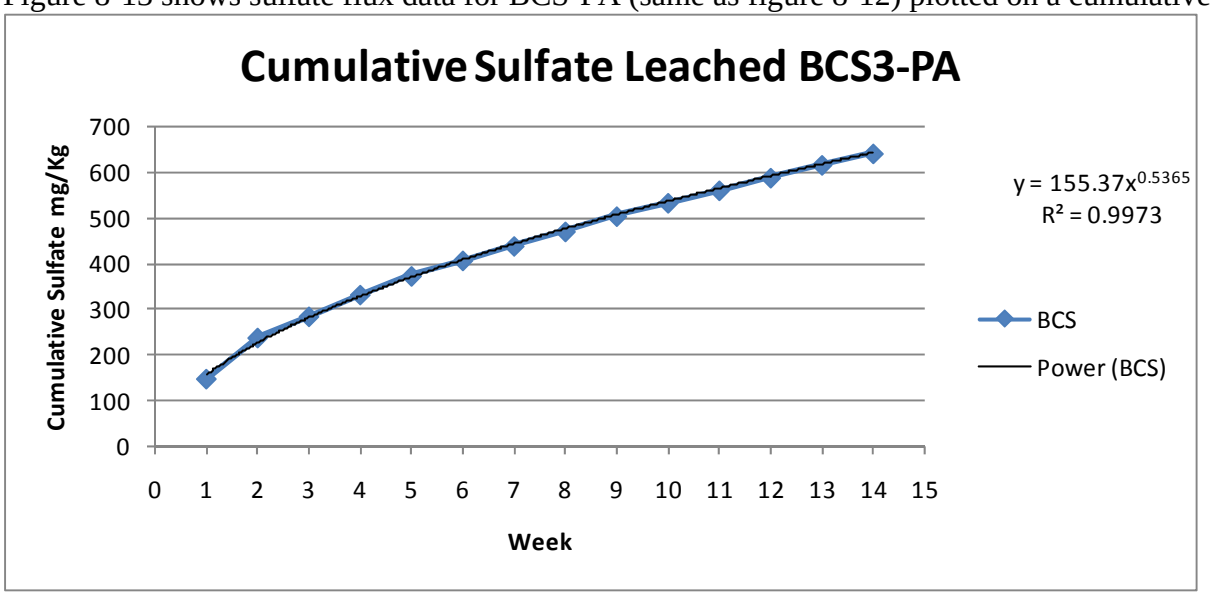

Figure 8-13. Cumulative Sulfate Leaching (mg/Kg sample), BCS3-PA. Values are medians of all labs.

basis with a fitted power function. Other samples and element flux data showed behavior similar to figures 8-12 and 8-13, and generally fit either a power or natural log function. The fit of these functions shows that element flux can be estimated; if leaching conditions are constant and mineral solubility influences are absent.

Calcium flux data displayed a linear trend for four rocks (BCS3-PA, HCS-IN, KBF-WV, and MKSS-PA) that produced leachates saturated for calcite or gypsum. Only LKFC-PA, which was under-saturated for both calcite and gypsum, produced a log fit plot. Figure 8-14a and b shows the two types of cumulative plots. The linear plots exemplified by Figure 8-14a show that these rocks dissolve minerals containing the constituent element and leach at a constant rate. Elemental flux is constrained by mineral solubility. The curvilinear log or power function plots are typical of "shrinking core" models of rock weathering, where diffusion is an important leaching control. Plots of cumulative flux can provide insight into leaching mechanisms and constraints.

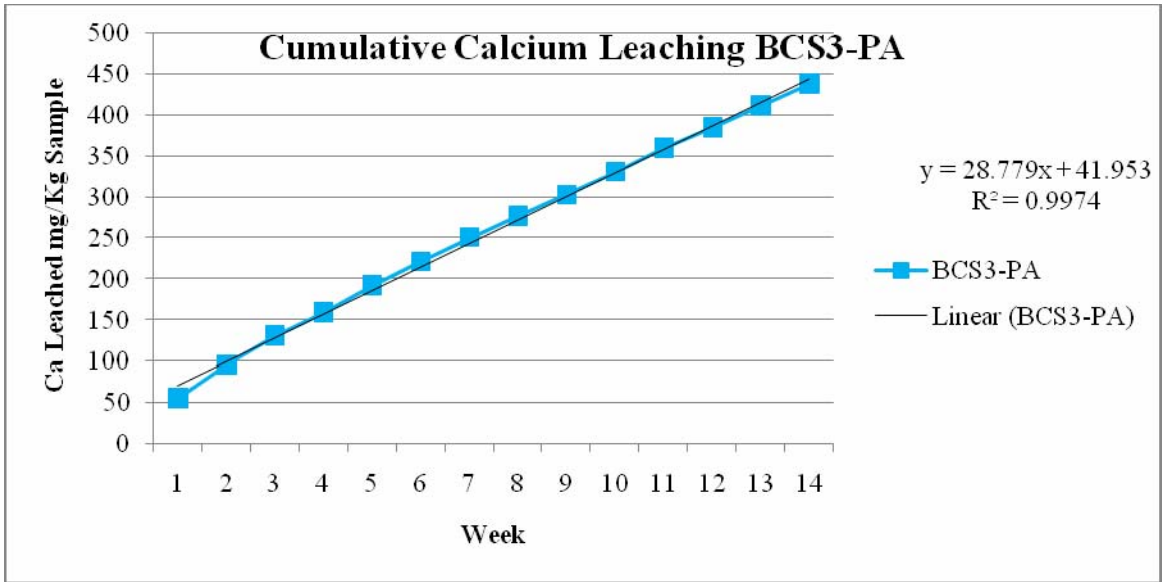

Figure 8-14a. Calcium Flux(mg/Kg sample), BCS3-PA with linear trend. Leachate is Calcite Saturated.

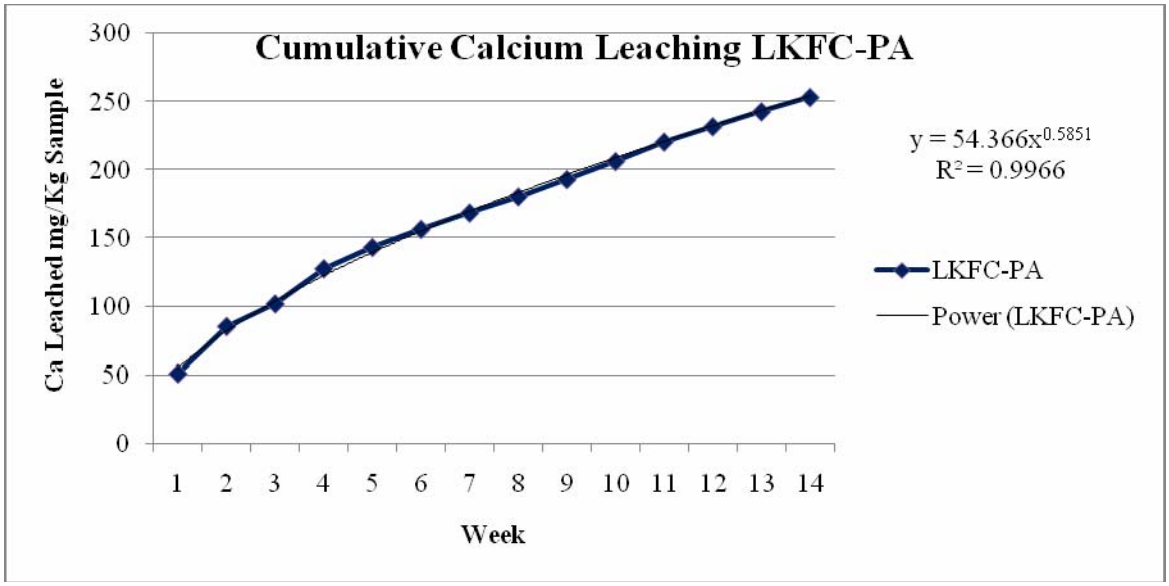

Figure 8-14b. Calcium Flux(mg/Kg sample), LKFC-PA. Leachate is Under-Saturated for Calcite.

Chapter Summary

The inter-laboratory study produced a large body of elemental leaching data that demonstrated the utility of the column leaching test. The five rocks produced leachates that:

- Had distinct chemical composition. The test discriminates among rocks of differing mineralogical make-up. Calcium and magnesium were the dominant cations, while sulfate and bicarbonate were the principal anions. The different leachate chemistries can be distinguished by graphical techniques like Durov, Stiff or trilinear (Piper) plots, or statistical methods.
- Weathered at different intensities on both a relative and absolute basis. Weathering intensity paralleled sulfur content. High sulfur rocks weathered most aggressively, while low sulfur rocks leached the least.
- Had significant alkalinity concentrations. The inclusion of pCO_2 of 0.1 atmospheres produced leachates more like that observed in field collected samples. One rock consumed all its alkalinity during the test and produced acidic leachate by week 14. Rocks with limited self neutralization capacity may be identified with the test. pCO_2 is a critical variable for simulating field conditions for alkalinity concentration.
- Had declining concentrations through time. Only HCS-IN concentrations increased during the test, after the sample began producing acidic leachate. Time dependent concentration trends were approximated by a natural log decay function for most elements. The decay equation, or other appropriate models, can be useful for estimating leachate chemical concentration chemistry through time. Alkalinity decay was slower than sulfate for most rocks, suggesting it will persist over acid generation in those samples. Laboratory decay values were about an order of magnitude greater than reported for flooding underground mines, suggesting that the column test does accelerate weathering over field conditions. No comparable decay data for surface mines was found.
- Leaching of minor and trace elements like zinc and selenium was similar to the major elements. Selenium behavior closely followed the natural log decay function, and concentrations declined significantly during the 14 week test.
- Produced the largest chemical fluxes in the first few weeks of the test. Thereafter, fluxes decreased slowly. Time dependent fluxes were well described by power function or natural log regression models. Chemical flux behavior can be estimated through time. The curvilinear models are similar to the behavior expected from “shrinking core” weathering models where diffusion controls leaching.

Cumulative calcium chemical fluxes, unlike most other parameters, produced linear time dependent plots. This behavior is attributable to soluble calcite and gypsum maintaining solution concentrations of calcium. The shape of the plot can give insight into the mechanisms influencing leachate chemistry.

Four of five rocks produced circumnutral pH leachates with very low concentrations of soluble aluminum and iron. The results are consistent with pH and redox behavior of the elements. Only the acidic HCS-IN leachate contained appreciable iron and aluminum. The lack of soluble metals does not necessarily indicate non-weathering of iron and aluminum bearing minerals. Information in Chapter 5 showed the formation of secondary minerals within the columns. Calcite, gypsum, other metal sulfates and metal oxyhydroxides may influence the leachate behavior of various elements. Mineral and element solubility properties should be part of any interpretive scheme for leaching test data.

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