

**Observations on the Mine Water Leaching Procedure and the  
Effects of Placing CCBs in Contact with Mine Spoil**

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## **Abstract**

Studies of the Mine Water Leaching Procedure (MWLP) using acidic mine water and a coal combustion by-product determined that many metals are controlled in solution by solubility, or solubility-like processes. Gypsum and barite were found to be supersaturated in the extracting solutions. The results of an extraction do not depend, within limits, on the volume of extractant, although the total mass extracted is a function of the volume.

Addition of mine spoil, as exemplified by sandstone or shale, did not substantially change the extraction behavior of the constituents. The solution pH of the first extraction was lower in the presence of mine spoil. Certain constituents were leached to a greater degree in the first cycle in the presence of spoil, but the total amount extracted (mass) over multiple cycles were usually the same.

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## Introduction

The Mine Water Leaching Procedure (MWLP) is a recently developed method (1,2,3) to assess the interaction of specific mine waters with coal combustion byproducts (CCBs) that may be deposited at the mines during reclamation. The method is styled after the Toxic Component Leaching Procedure (TCLP) which the United States Environmental Protection Agency uses to evaluate the leaching potential of material to be deposited in landfills and the Synthetic Precipitation Leaching Procedure (SPLP) (EPA Method 1312) which evaluates the interaction of precipitation with waste materials.

The TCLP method leaches a suspect solid material with a solution meant to simulate the organic acids found in landfills. The SPLP method (4) leaches with a synthetic precipitation composed of sulfuric and nitric acid at pH 4.2 or 5. The method is used to evaluate leaching due to contact of solid materials (often contaminated soils) with rain. The MWLP method leaches with drainage collected from the target mine rather than a standardized solution and is thus site specific. Good reasons can be advanced to restrict the TCLP and SPLP to standardized solutions; landfills are difficult to sample and have gross similarities among them and rainwater is fairly chemically consistent, if not pH consistent. Mine water has, on the other hand, chemical consistency at any one site and gross differences from site to site. Any attempt to construct a synthetic mine water to interact with a CCB would grossly misrepresent conditions at actual mines.

A National Research Council study (5) concluded that “putting CCRs [CCBs] in coal mines as part of the reclamation process is a viable management option as long as ...CCR placement is properly planned and is carried out in a manner that avoids significant adverse environmental and health impacts..”. The rather benign statement above is somewhat clarified by subsequent language. The committee worries that “..little is known about the potential for minefilling to degrade the quality of groundwater and/or surface waters over longer time periods. Additionally, there are insufficient data on the contamination of water supplies by placement of CCRs in coal mines, making human risk assessments difficult.” The committee thus concludes that “the presence of high contaminant levels in many CCR leachates [presumably TCLP leachates] may create human health and ecological concerns at or near some mine sites over the long term.”

Despite their dire predictions, the Committee also notes that “The EPA has not identified any cases in which exceedances of water quality standards could be attributed directly to CCR mine placement.” Apparently, although there is no evidence of any effects, the Committee worries about long term effects.

The Mine Water Leaching Procedure was designed to provide laboratory data that can be used to determine “the potential for minefilling to degrade the quality



of groundwater and/or surface waters over longer time periods”, to use the NRC Committee’s wording once again. The method, once fully developed and characterized, seeks to provide meaningful information regarding long term water quality at target mines that beneficially use CBCs.

Previous use of the MWLP (1-3) has focused on refinement of the method and the first generation observation of its behavior. Although the MWLP is structurally similar to the TCLP and SPLP, it has substantial differences. TCLP is a regulatory defined method that attempts to determine what is leached from waste by a specifically prepared acetic acid solution. The amount of solid used, the amount of acetic acid used, the reaction (shaking) time and the number of extractions (one) are specified in order to provide comparable results from waste to waste. The outcome (the chemical composition of the leachate) is used by regulatory agencies to determine the suitability for disposal of the waste in a landfill.

The SPLP seeks to evaluate the degree to which contaminated soils, and other materials left in place, release contaminants that may detrimentally affect surface and ground water quality. The method is used to evaluate in natural settings, where transport of contaminant is due to rainwater. A positive determination could lead to the requirement that soil be removed and treated or placed in a landfill.

The MWLP proposes to derive the leaching (or more properly reaction) behavior of a CCB that is to be used in mine reclamation when it is exposed to successive aliquots of drainage from the target mine. The mass of CCB solid to volume of leaching solution ratio is not fixed. The influence of shaking time is yet to be derived. The eventual output of an MWLP will be a cogent analysis of the long term chemical reactivity of CCBs when exposed to mine water, not a simple list of chemical concentrations as in the TCLP or SPLP. Part of the gradual development of the method and its data treatment methods is undertaken here. Specifically, certain observables from the method are expanded and compared to earlier work and the influence of the addition of relatively inert mine spoil is investigated.

Mine spoil is any material excavated by a coal mine that is not coal. The spoil is some sort of rock, often overwhelmingly shale or sandstone with inclusions of other minerals. In many cases, the geologic layer above the coal seam is isolated and handled separately. This seam tends to have the potential for pyrite oxidation and is not purposefully reinserted into the reclaimed mine. The mine excavated spoil, most commonly from a surface coal mine, is used as the backfill material during reclamation.

Reclamation of a coal mine using CCBs can be accomplished in many ways; the general objective is to place the alkaline CCBs to allow contact with acidic mine water to provide neutralization. Coincident mine spoil will tend to be in edge

contact with the CCB and also be exposed to the mine water that is neutralized by the CCB. An objective of this project was to determine possible influences of mine spoil material on the reaction of the CCB with the mine water.

The spoil is mixed with the CCB in this study, which is a situation that normally is not found in reclaimed mines (although the mixing could be affected before placement if advantageous). Normally, CCB and spoil are placed separately in truck loads. Any mixing that occurs is due to disturbances during bulldozing for final placement and contouring. Normally the water that has reacted with the CCB subsequently passes through the spoil; spoil and ash are seldom intimately mixed. Whether the spoil retards materials that are released from the CCB will be investigated. Any subtleties to be found in the reaction of coincident spoil and ash, versus ash reaction with subsequent mine spoil contact are deferred.

The objectives of this study involve fairly gross trends; no extensive statistical evaluation is conducted. In certain of the cases, conclusions will be uncertain because propagation of error overwhelms the final result. Such situations will be noted.

## Executive Summary

The Mine Water Leaching Procedure was evaluated with respect to reproducibility, extraction volume, constituent release and interaction with mine spoil, in this case sandstone and shale. The method involves interacting acidic mine water from a target mine with a coal combustion by-product (CCB) that would be used to help remediate the mine. In the course of the trial, alkalinity from the CCB neutralizes the acidity of the mine water, initiating chemical reactions, generally precipitation. After reaction (18 hours), the solid is separated from the liquid, and then used in the next cycle.

These studies used two CCBs, a fluidized bed combustor ash (FBC) and a class F fly ash (PCF). In addition to leaching the pure CCBs, trials were conducted using a CCB plus either sandstone or shale, common mine spoil materials.

Two separate series of leachings were conducted at widely separated times. Different technicians used the same mine water and CCB. Inter-series reproducibility was evaluated using pure CCB extractions. The standard deviations of supposedly identical trials in the two different series reveal disparate analytical results. Relative standard deviations ranged from 0% (Fe, which was completely precipitated) to 277% for thallium. Intra-series results were improved. Series A had relative average deviations (only duplicates were run) from 0.16% (boron) to 12% (manganese). Series B ranged from 1.2% (sulfate) to 37% (calcium). The reproducibility must improve if subtle chemical behavior is to be studied. Inhomogeneous CCB material and poor mine drainage stability may contribute to irreproducibility.

One series specifically investigated the relationship between outcome and extraction volume. Two volumes were used (1L and 1.5L) with 100g of CCB. In all cases except when a substance was exhausted or nearly so from the CCB, the concentrations of constituents were constant regardless of volume used. Boron, thallium and beryllium approached total leaching and disobeyed the generality. These elements more closely released equal masses from the CCB.

Larger volumes with the same concentrations of a substance contain a larger mass of that substance, thus 1.5L leaches a CCB faster (fewer leach cycles). In general, aside from substances that undergo depletion, 1.5 times as much substance is removed.

Some constituents of the CCBs leach into solution (Ca, Mg, Al, As, B, Ba, Be, Cr, Hg, Ni, Tl and V. Other substances precipitate from the solution, iron as notably ferrihydrite and sulfate as gypsum. Ferrihydrite co-precipitates metals as well, notably copper. Other metals that drop out of solution are manganese, antimony, cadmium, lead, silver and zinc. Gypsum (calcium sulfate) is supersaturated in almost every solution, to the greatest degree in the high pH solutions.

Sandstone and shale leach similar arrays of substances when subjected to the MWLP and, with a few exceptions, similar concentrations. When a mass of either additive was included with a CCB, the pH of the first cycle invariably was lower than for pure CCB. The total (cumulative) mass release over all cycles was the same regardless of the amount of added sandstone or shale.

## **Experimental**

The Mine Water Leaching Procedure as developed by Ziemkiewicz (1) and subsequently modified (3) was used.

### **Equipment and Supplies**

Extractions were performed using a TCLP rotating mixer using 2L plastic TCLP containers. All solid samples were weighed on an electronic balance. All samples were filtered using a TCLP vacuum filter unit.

### **Materials and Chemicals**

Fluidized bed combustor ash (denoted FBC) was obtained from a local fluidized bed electric generating plant. Class F fly ash (denoted PCF) was acquired from a conventional coal power plant. PCF ash was analyzed for Ca, Fe, Al, Mn, Sb, As, B, Ba, Be, Cd, Cr, Pb, Se, Ag, Cu, Ni, Tl, V, and Zn. The FBC ash was analyzed for the same elements as the PFC ash with the addition of Mg. The neutralization potential of the FBC was also determined.

Sandstone was collected from a road cut near Morgantown, WV. Shale was collect from a different road cut near Morgantown, WV.

Mine drainage was acquired from an abandoned surface mine in Preston County, WV. The water is mine water P as found in (3). The drainage was analyzed for pH, acidity, alkalinity, Mg, Ca, Fe, Al,  $\text{SO}_4^-$ , Mn, Sb, As, B, Ba, Be, Cd, Cr, Pb, Se, Ag, Cu, Ni, Tl, Hg, V, and Zn.

### **Extraction**

One hundred grams of CCB was added to a 2L TCLP container, followed by from 0 to 75g of sandstone or shale. Certain trials contained only 100g of sandstone or shale. All extractions used the acidic mine drainage collected from Preston County, WV.

The newest MWLP protocol requires a leaching volume ten times the mass of extracted solid, thus 1000 mL (roughly 1000g) of mine water is used for a 100g sample. Trials were conducted to evaluate the influence of extraction volume on the process. In these trials, 1000 mL or 1500 mL of extracting liquid were used for 100 or 150g samples of PCF and PCF with added sandstone or shale. Extracting liquid to sample ratios of 6.7 (1000mL:150g), 10 (1500mL:150g or 1000mL:100g) and 15 (1500mL:100g) were thus evaluated. All of the varied extracting solution experiments were conducted in duplicate. This set of trials was denoted Series A (Table 1).

Another series of trials consistently used an extracting liquid volume to sample

**Table 1. List of Series A Experiments.**

Run	PCF, g	Sandstone, g	Shale, g	Mine Water, mL	Reps
1	100	0	0	1000	2
2	100	0	0	1500	2
3	100	50	0	1000	2
4	100	50	0	1500	2
5	100	0	50	1000	2
6	100	0	50	1500	2
7	0	100	0	1000	2
8	0	100	0	1500	2
9	0	0	100	1000	2
10	0	0	100	1500	2

mass ratio of 10. These trials used both PCF and FBC ash with either 0, 25, 50, or 75g of added sandstone or shale. Extracting liquid volumes were, respectively, 1000mL, 1250mL, 1500mL and 1750mL. Additional trials using 100g of sandstone or shale with 1000mL of extracting liquid were conducted. No replicates were run for these trials. This set of trials was denoted Series B (Table 2).

**Table 2. List of Series B Experiments.**

Run	FBC, g	PCF, g	Sandstone, g	Shale, g	Mine Water, mL	Reps
1	100	0	0	0	1000	2
2	100	0	25	0	1250	1
3	100	0	50	0	1500	1
4	100	0	75	0	1750	1
5	100	0	0	25	1250	1
6	100	0	0	50	1500	1
7	100	0	0	75	1750	1
8	0	100	0	0	1000	2
9	0	100	25	0	1250	1
10	0	100	50	0	1500	1
11	0	100	75	0	1750	1
12	0	100	0	25	1250	1
13	0	100	0	50	1500	1
14	0	100	0	75	1750	1

All samples were reacted/extracted on the rotating mixer for 18 hours and then filtered. The recovered solid was saved for subsequent use (further extraction)

and a portion of the solution was sent for chemical analysis. Each extraction is called a cycle. The laboratory analyzed each solution for the analytes noted above for the original mine water.

All samples were extracted for multiple cycles. The protocol requires extraction until the pH of the extracting solution equals the pH of the original solution. Series A samples were extracted up to 8 times to achieve this objective. Series B samples were extracted three times each. Series B was actually conducted before Series A.

## Results and Discussion

### The MWLP Method

#### System Behavior and Data Handling.

The operational model for the MWLP is the TCLP, the Toxic Characteristics Leach Procedure. Whereas TCLP is functionally a leaching procedure using acetic acid, the MWLP is more fairly an interaction or reaction procedure. The contact solution in MWLP not only dissolves and desorbs components from the solid sample, but components dissolved from the solid sample (alkaline materials) change the chemistry of the contact solution, leading to the precipitation of components. The MWLP method is explicitly designed (1) to evaluate the specific nature of the beneficial use of the ash material.

One unique outcome of the new procedure versus TCLP or SPLP is the loss of material from the contact solution, in this case the acidic mine drainage water. In the TCLP, the only observable is an increase of some substance after administering the TCLP procedure from the zero baseline of the acetic acid solution. Similar results are found with the Synthetic Precipitation Leach Procedure (SPLP), which is a solution with a higher pH.

Material loss from the contact solution leads to a new data type, negative concentrations, not found in TCLP or SPLP. Negative concentration is a measure of constituent removal from solution. A reaction experiment, the 18 hour rotating solution contact procedure, can lead to less of a species in the resulting solution than was initially present. Precipitation of iron due to the increase in pH provided by the dissolution of alkaline ash is an example. In data analysis, the original concentration of the species in the mine water is often subtracted from the resultant concentration after the extraction/reaction. This process results in what will be termed **normalized** concentrations. If less material is present after extraction/reaction, the species has been removed to some degree from the contact solution. All reported concentrations will be actual solution concentrations, not normalized concentrations. Normalized concentrations will be used in the determination of the total mass of a constituent that is added or removed over the cycles in a leaching trial. The **limit of removal**

is defined as the negative value that corresponds to the loss of all of a species from the contact solution.

Certain constituents increase in the contact solution after a cycle. For multiple cycles, a mass of removed material can be determined by multiplying the normalized concentration and the volume. The cumulative total should allow a mass balance as it approaches the total mass of the constituent found in the original ash sample. Aluminum, for example, tends to be dissolved from the ash into solution. The total mass of dissolved Al from all cycles should approach the amount in the original ash (2 g for the 100g PCF sample, Table 3).

Material precipitation or adsorption leads to two results that are not found in TCLP or SPLP. As noted, the contact solution can lose amounts of certain species up to the limit of removal. In addition, the amount lost from solution changes the nature of the recovered solid material, which now contains additional solid material. The implications of this added solid are important, but were not addressed in this study. Extraction cycles continued beyond the end point where the final pH equals the initial pH (the definition of the stop point for MWLP), may begin to dissolve the accumulated material deposited from the contact solution.

Ash and Mine Water Analyses, Acidity and Alkalinity

The fluidized bed combustor ash (FBC) is decidedly more alkaline than the fly ash (PCF) (Table 3; the Ca value roughly represents the CaCO<sub>3</sub> content). In a

	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>Sb</b>	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Cd</b>
<b>PCF</b>		943	4603	2062	6.4	0.6	6.4	14	15	0.15	0.5
<b>FBC</b>	531	15860	2777	3833	15	BDL	1.4	7.6	29	1.0	0.08
	<b>Cr</b>	<b>Pb</b>	<b>Hg</b>	<b>Se</b>	<b>Ag</b>	<b>Cu</b>	<b>Ni</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>	
<b>PCF</b>	4.8	1.3		1.2	1.5	2.5	3.6	1.2	7.6	3.3	
<b>FBC</b>	2.2	0.9	BDL	0.3	BDL	1.2	1.7	BDL	4.7	1.6	

previous study (3) the FBC ash was exposed to two mine drainages (using an elevated volume to mass ratio of 200) and still had not been exhausted in one case (Water M) after 15 cycles. A second case (Water P) required 5 cycles. The neutralization potential (NP) of the FBC was reported as 300 tons of CaCO<sub>3</sub> per 1000 tons of ash or 3g (0.03 mole) per 10g of ash sample in their experiments. Their experiments used 10g of FBC ash with 2L of mine drainage (v/m of 200).



The calculated acidity (766 mg CaCO<sub>3</sub> /L) of water P can be determined by Equation 1,

$$\text{Calculated Acidity} = 50[(1000)(10^{-\text{pH}}) + \sum Z_i C_i] \quad (1)$$

where  $Z_i$  and  $C_i$  are the charge and concentration (in mmoles/L) of the  $i$ th ion that reacts with base, summed over all such ions. The units of calculated acidity are as mg CaCO<sub>3</sub> /L. These base reacting ions are most commonly Fe<sup>+3</sup>, Al<sup>+3</sup>, and Mn<sup>+2</sup> in coal mining applications. Obviously other metals need to be considered in metal mining drainages. The acidity calculated by Ziemkiewicz and Knox (3), 766 mg/L as CaCO<sub>3</sub>, differed from the measured acidity of 643 mg/L as CaCO<sub>3</sub> (Table 4). Ziemkiewicz and Knox (3) used the calculated value of acidity in their discussion.

Using Eq. 2,

$$\text{Number of cycles} = \text{NP} / (A_c V) \quad (2)$$

where NP is the neutralizing potential of the ash for the mass used (in mg/L as CaCO<sub>3</sub>),  $A_c$  is the acidity of the water in mg/L as CaCO<sub>3</sub> and V is the volume of contact water in L, roughly two cycles of water P should be required to exhaust the neutralizing capability of the ash.

Water M had an acidity of 144 mg/L as CaCO<sub>3</sub>, which, using Eq.2, should have required 10 cycles, fewer than the more than the 15 cycles actually needed. Use of the neutralization potential of the ash and the measured mine water acidity does, however, provide a reasonable initial estimate of the required number of cycles. The amount of ash used, and the v/m ratio, can be adjusted to provide completion in roughly 5 cycles.

The same FBC ash and mine water P (Table 4) were used in our experiments. both the ash and mine water were analyzed a single time.

Both the ash and mine water were analyzed a single time. With a volume to mass (v/m) ratio of 10 to 17.5, rather than 200, the expected number of extractions to exhaust the reactivity of the FBC ash was nearly 50, which was experimentally impractical.

The NP of the PCF was not measured, but its functional exhaustion after only a few cycles, even at a 10 to 17.5 v/m ratio, indicated a weakly alkaline material. The results for pure PCF were unfortunately contradictory for the Series A and Series B experiments.

Series B was run using single samples, but the pure PCF sample was fortuitously run twice, once each for the sandstone and shale addition experiments. Table 5 lists the average values found for those two trials. The calculated acidity, which

<b>Field pH*</b>	<b>pH*</b>	<b>acidity<sup>#</sup></b>	<b>alkalinity<sup>#</sup></b>	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>
2.88	2.73	643	0	37	49	169	39	2.0
<b>SO<sub>4</sub><sup>=</sup></b>	<b>Sb</b>	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Cd</b>	<b>Cr</b>	<b>Pb</b>
1529	0.05	0.03	0.25	0.01	0.009	0.004	0.006	0.004
<b>Hg</b>	<b>Se</b>	<b>Ag</b>	<b>Cu</b>	<b>Ni</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>	<b>Cond.<sup>^</sup></b>
0.001	0.016	0.002	0.18	0.19	0.021	0.003	1.24	2910
* Standard pH units								
# as mg/L CaCO <sub>3</sub>								
^ uS/cm								

<b>Cycle</b>	<b>pH</b>	<b>acidity*</b>	<b>Calc. acidity*</b>	<b>alkalinity*</b>
0	2.73	643	766	0
1	6.45	1	2	19
2	4.95	33	19	2
3	4.30	190	197	1
* mg/L as CaCO <sub>3</sub>				

is found by Eq. 1, tracks well with the measured acidity. The parameters of the initial water are listed as Cycle 0. The pH of the recovered solution has not decreased to the original value of 2.73, further extraction cycles would normally be indicated.

Series A (Table 6) does not have good correspondence between the measured and calculated acidity. All of the trials showed the same lack of agreement. Since the same ash and water were used for both experiments, the discrepancy could be due to analytical error (of a very systematic sort), because the reproducibility of the duplicates was good. As an example, for cycle 3 in Table 6, the measured average acidity of 624 mg/L as CaCO<sub>3</sub> is double the calculated value of 314 mg/L as CaCO<sub>3</sub>. The 624 mg/L as CaCO<sub>3</sub> value is the average of the duplicate values 618 mg/L as CaCO<sub>3</sub> and 631 mg/L as CaCO<sub>3</sub>. The acidity titration is highly reproducible between samples, but unnaturally high. Consider

**Table 6. Series A pH and Acidity MWLP Results for PCF Ash**

Cycle	pH	Acidity*	Calc. Acidity*	Alk.*
0	2.73	643	766	0
1	6.58	106	56	12
2	4.15	470	237	0
3	3.72	624	314	0
4	3.63	934	469	0
5	3.48	769	386	0
6	3.39	595	299	0
7	2.86	597	300	0
8	2.66	622	312	0

\* mg/L as CaCO<sub>3</sub>

that the original water had a pH of 2.54 and an iron concentration of 169 mg/L and cycle 3 has an average pH of 3.72 and a mean iron concentration of 0.2 mg/L, yet the measured acidities are 643 and 624 mg/L as CaCO<sub>3</sub> respectively. The respective calculated acidities are 766 and 314 mg/L as CaCO<sub>3</sub>, which are more sensibly related. In addition, certain of the measured acidities in Table 6 (cycles 4 and 5) exceed the acidity of the original water. The PCF is not acidic, so it cannot be the cause extra acidity. Iron is lowered in all of the treated samples (and Al and Mn are close to the values of the original water), so the increased acidity values are logically artifacts. A thorough investigation of this issue seems warranted. The calculated acidities in Series A are all lower than the questionable measured acidities, while in Series B the values are reasonable close (which Tables 5 and 6 illustrate). Any further use of acidity will use the calculated values.

### Reproducibility

The largest number of replicates, the case of 100g of PCF at a v/m of 10, was four, two for each series. The two series were conducted by different technicians at different times using the same ash and mine water. The results of evaluation of the first cycle of all four trials (Table 7) demonstrate a high level of scatter in all but pH and vanadium (RSD<10%). Moderate reproducibility (10-20%) is found for Mn, Mg, SO<sub>4</sub><sup>-</sup>, Cr, Ni and Zn. Others have relative standard deviations over 20%, although large RSD values for components at very low concentration (near the limit of detection) are expected. Many of the components were undetectable and certain data are noted to be not determinable. The averages for certain components are given a zero value here, rather than being denoted as being below the limit of detection.

**Table 7. Reproducibility of 100g PCF Sample (mg/L), 1<sup>st</sup> Cycle, All Samples.**

	<b>pH*</b>	<b>Alk.#</b>	<b>Acidity#</b>	<b>Calc. Acid#</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>
Mean	6.52	15.5	53	2.2	0.03	0.16	0.65
S.D.	0.22	4.88	60.54	0.47	0.00	0.12	0.09
RSD	3.3%	31.4%	113.6%	21.8%	0.0%	72.9%	14.2%
	<b>Mg</b>	<b>Ca</b>	<b>SO<sub>4</sub><sup>-</sup></b>	<b>Sb</b>	<b>As</b>	<b>Ba</b>	<b>Be</b>
Mean	70	548	1778	0.01	0.01	0.01	0.00
S.D.	9.1	214	160	0.00	0.00	0.00	ND
RSD	13.0%	39.1%	9.0%	35.4%	28.3%	32.9%	ND
	<b>B</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Hg</b>	<b>Ni</b>
Mean	5.8	0.00	0.08	0.01	0.00	0.00	0.08
S.D.	2.3	ND	0.01	ND	ND	ND	0.01
RSD	39.8%	ND	15.8%	ND	ND	ND	12.1%
	<b>Se</b>	<b>Ag</b>	<b>V</b>	<b>Tl</b>	<b>Zn</b>		
Mean	0.00	0.00	0.11	0.02	0.03		
S.D.	0.00	ND	0.00	0.06	0.00		
RSD	0.0%	ND	2.6%	276.7%	16.6%		
ND = Not Determinable * pH Units # mg/L as CaCO <sub>3</sub>							

Isolation of the two series reveals much better reproducibility within series than between the series (Tables 8, 9). These data use the average deviation rather than the standard deviation due to the small (duplicate) sample size. In every case, the deviation is lower within a series. Solids are notoriously heterogeneous, and the ashes used here were not rigorously characterized for homogeneity, but certainly with respect to within the series, no obvious questions about homogeneity or procedure reproducibility are evident. The reproducibility within a series is adequate to discuss the significance of departures from the averages for experiments that seek information on extraction volume (v/m) or the effect of spoil.

The poor between series reproducibility may be attributable to unknown, but critical, procedural differences between technicians, but most likely, when all factors are considered, the variability is due to ash inhomogeneity. The possible lack of homogeneity will also be seen when the mass balances are discussed below.

Deviations for various cycles within a series can only be determined for Series A, which was run in duplicate. Cd, V, Pb, Se, Ag, Hg and Sb had values that generally fell below the limit of detection. No information was available for them other than the observation that the values were reproducibly undeterminable. The other constituents show scattered relative average deviation throughout the

<b>Table 8. Reproducibility of 100g PCF Sample (mg/L), 1st Cycle, Series B.</b>							
	<b>pH*</b>	<b>Alk.#</b>	<b>Acidity#</b>	<b>Calc. Acid#</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>
Mean	6.45	19	1	1.8	0.05	0.06	0.7
Avg. Dev.	0.25	3	0	0.1	0	0	0.04
RAD	3.9%	15.8%	0.0%	3.5%	0.0%	0.0%	5.7%
	<b>Mg</b>	<b>Ca</b>	<b>SO<sub>4</sub><sup>=</sup></b>	<b>Sb</b>	<b>As</b>	<b>Ba</b>	<b>Be</b>
Mean	62.05	393	1640	0.016	0.01	0	0
Avg. Dev.	2.65	144	20	0.002	0.001	ND	ND
RAD	4.3%	36.6%	1.2%	12.5%	10.0%	ND	ND
	<b>B</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Hg</b>	<b>Ni</b>
Mean	3.78	0	0.07	0.01	0	0	0.075
Avg. Dev.	0.12	ND	0	0	ND	ND	0.005
RAD	3.2%	ND	0.0%	0.0%	ND	ND	6.7%
	<b>Se</b>	<b>Ag</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>		
Mean	0.004	0	0.0005	0	0.051		
Avg. Dev.	0	ND	0	ND	0.003		
RAD	0.0%	ND	0.0%	ND	5.9%		
ND = Not Determinable * pH Units # mg/L as CaCO <sub>3</sub>							

cycles (Figures 1a through e). In many cases, the percent deviation is largest for the eighth cycle, where the release of constituents becomes somewhat smaller. Some of the cycles (e.g. cycle 4) exhibit higher deviations that appear to be occasional outliers, either through procedural or analytical imprecision, but in all cases the reproducibility is better in cycle 5. Not enough replicates were run to determine if the variations are random or systematic.

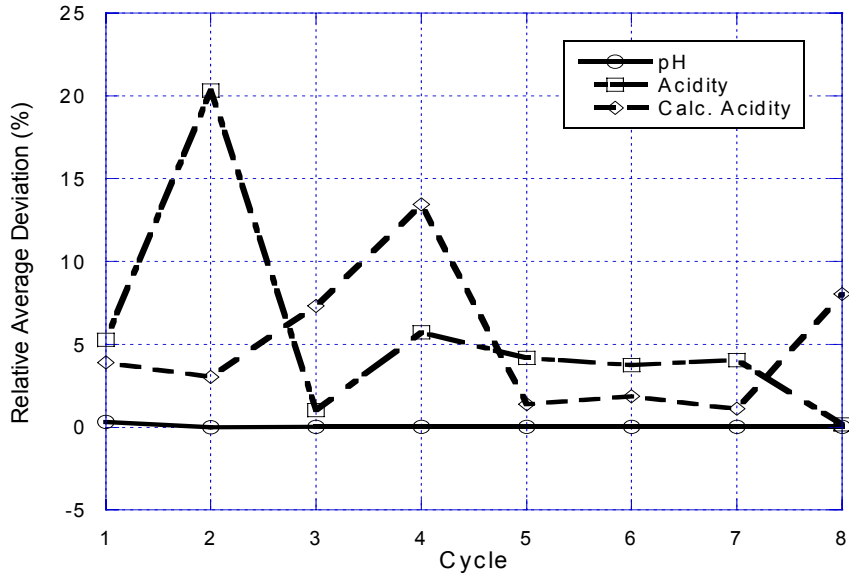


Figure 1a. Percent relative average deviation for pH, measured acidity and calculated acidity. Series A, 100g PCF, 1000mL mine water.

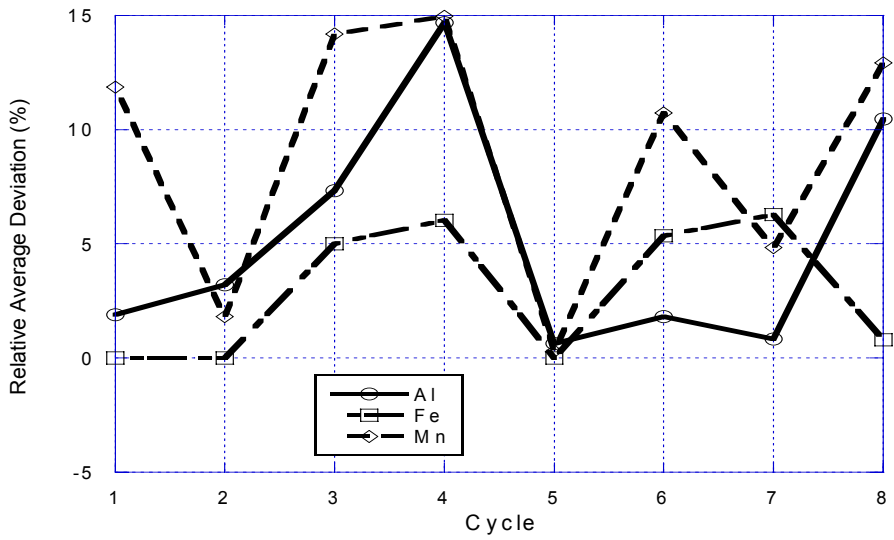


Figure 1b. Percent relative average deviation for Fe, Al and Mn. Series A, 100g PCF, 1000mL mine water.

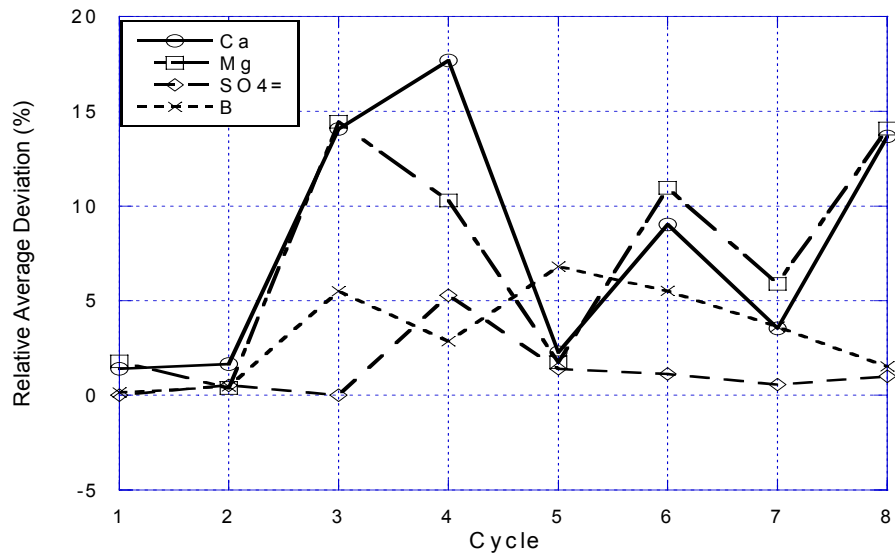


Figure 1c. Percent relative average deviation for Ca, Mg, SO<sub>4</sub><sup>=</sup> and B. Series A, 100g PCF, 1000mL mine water.

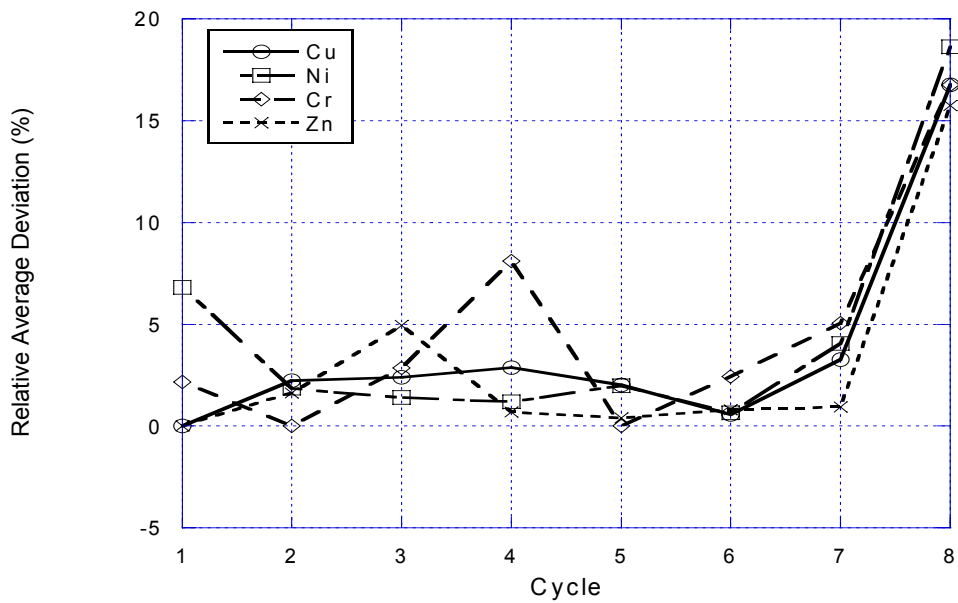


Figure 1d. Percent relative average deviation for Cu, Cr, Ni and Zn. Series A, 100g PCF, 1000mL mine water.

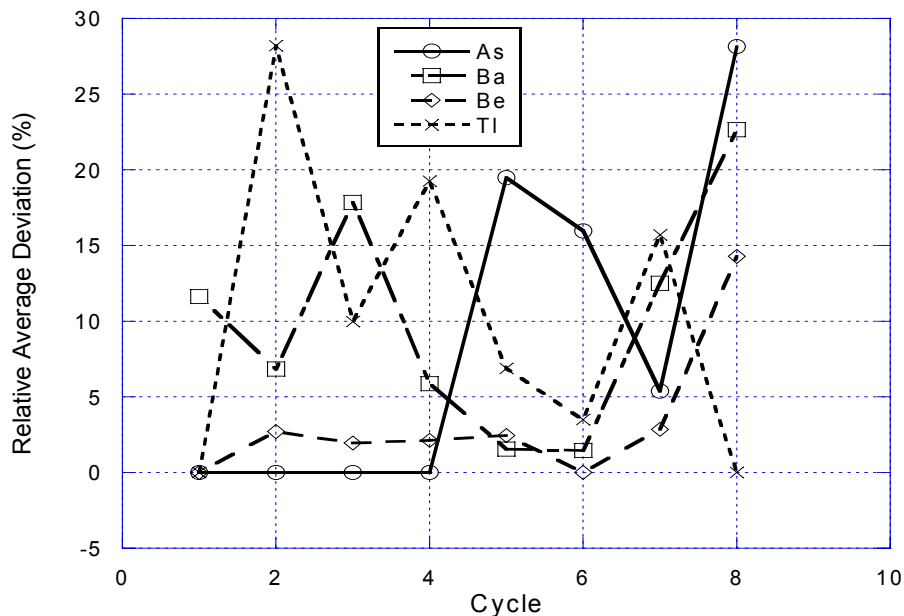


Figure 1e. Percent relative average deviation for As, Ba, Be and Tl. Series A, 100g PCF, 1000mL mine water.

### Behavior of Constituents

Twenty five constituents, or properties such as pH, alkalinity and acidity, were tracked through the cycles in the two series. In every case, pH and alkalinity decreased with increasing number of cycles and acidity increased (to a plateau roughly equal to the acidity of the original mine water). These are expected results whenever a basic material is mixed with an acid solution.

The contact of the acidic (pH 2.54) mine drainage with the alkaline CBC will initially neutralize free acid, then precipitate susceptible metals, and finally provide dissolved base. In the case of metal precipitation (usually as some hydroxide form) the process can be visualized as a reaction with water, with the metal extracting a hydroxide. The resultant proton is neutralized by the alkaline species from the CBC. When no further protons are available, alkaline material dissolves. No alkaline anion analyses were performed on the CBC ashes, but certainly, considering its genesis, the majority of alkaline material in FBC ash is as CaO. PCF ash is more likely composed of metal oxides. Oxides hydrolyze, release base and consume acid.

Constituent behavior is consistent for all trials. Magnitudes and cycle to cycle behavior varies, but in general, the following occurs;



**Table 9. Reproducibility of 100g PCF Sample (mg/L), First Cycle, Series A.**

	<b>pH*</b>	<b>Alk.#</b>	<b>Acidity#</b>	<b>Calc. Acid#</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>
Mean	6.58	12	106	2.6	0	0.27	0.59
Avg. Dev.	0.02	1.61	5.6	0.1	ND	0.005	0.07
RAD	0.30%	13.36%	5.28%	3.91%	ND	1.89%	11.86%
	<b>Mg</b>	<b>Ca</b>	<b>SO<sub>4</sub><sup>=</sup></b>	<b>Sb</b>	<b>As</b>	<b>Ba</b>	<b>Be</b>
Mean	77	702	1915	0	0	0.022	0
Avg. Dev.	1.375	9.87	0	ND	ND	0.0025	ND
RAD	1.78%	1.41%	0.00%	ND	ND	11.63%	ND
	<b>B</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Hg</b>	<b>Ni</b>
Mean	7.8	0	0.092	0	0	0	0.088
Avg. Dev.	0.012	ND	0.002	ND	ND	ND	0.006
RAD	0.16%	ND	2.17%	ND	ND	ND	6.82%
	<b>Se</b>	<b>Ag</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>		
Mean	0	0	0.046	0.22	0		
Avg. Dev.	ND	ND	0	0.002	ND		
RAD	ND	ND	0.00%	0.91%	ND		

ND = Not Determinable  
 \* pH Units  
 # mg/L as CaCO<sub>3</sub>

**pH:** The pH rises in the first cycle, to nearly neutral for PCF and to nearly 10 for FBC, then falls fairly slowly through additional cycles until a value roughly equal to the original mine drainage pH is achieved. The trend is illustrated in Table 6 for PCF.

**Alkalinity:** Alkalinity, if measurable at all, is seen in early cycles and becomes zero as the alkaline material is exhausted in later cycles. This is also seen in Table 6 for PCF. The FBC trials in Series B had measurable, but decreasing, alkalinity through the three cycles.

**Acidity:** Acidity is discussed in some detail above. It increases with cycle number and plateaus towards later cycles.

**Iron:** The mine drainage (Table 4) initially contains 168 mg/L Fe. The cycles tend to remove all iron from solution (as precipitated hydroxide species) and none is, obviously, contributed from the ash, although both ashes contain substantial iron (Table 3). In later cycles, as pH drops, more iron stays solubilized, however, even at low pH, much is still removed from solution. Cycle 8 of the 100g PCF run using 1500 mL of mine water for Series A (run 2 in Table 1) has a pH of 2.55 versus the initial drainage pH of 2.54, yet that cycle has only 33 mg/L Fe, not 168 mg/L. Use of a  $K_{SP}$  of  $2.8 \times 10^{-39}$  for  $Fe(OH)_3$  (6) determines that the iron concentration should be about 5 mg/L at pH 2. Stumm and Morgan (6) cite  $K_{SP}$  values of  $10^{-39}$  to  $10^{-37}$  for ferrihydrite forms. Use of  $K_{SP} = 10^{-37}$  calculates an Fe concentration of 176 mg/L at pH 2.54, very near the mine drainage value of 168 mg/L. The smaller values of  $K_{SP}$  used by Stumm and Morgan represent the more amorphous forms of ferrihydrite; the larger values are used for the more crystalline forms. Mine drainage may be in equilibrium with a more aged form of ferrihydrite, leading to the higher concentration of Fe in solution. The addition of new base would precipitate the more amorphous forms and lower the concentration in the leachates. As the precipitate ages in the leachate solutions, the iron concentration may increase.

**Aluminum:** Aluminum, like iron, precipitates as a hydroxide at high pH, so it is largely absent from the solution after the first extraction cycle (Table 8). Al is more soluble than iron and is found in solution at levels close to or even above those in the original mine water at pHs below 5 (Figure 2). The mean cumulative

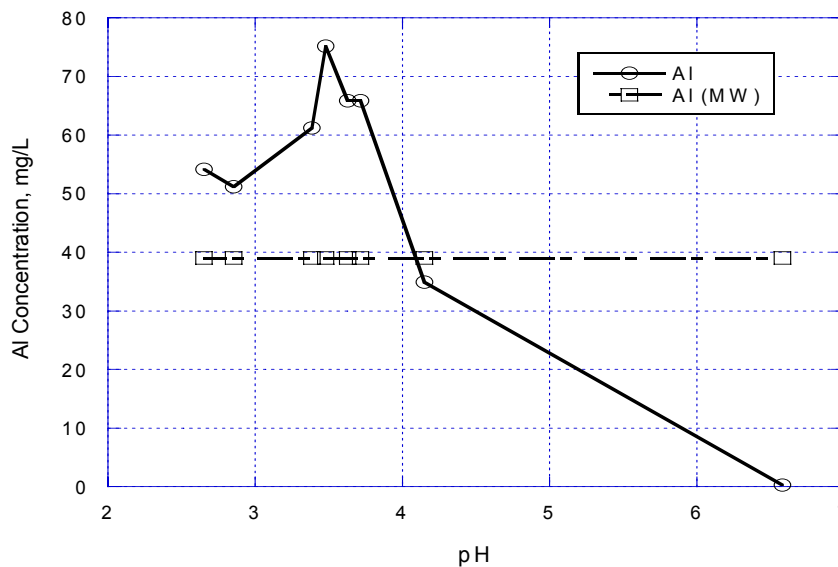


Figure 2. Aluminum concentration versus pH. Series A, 100g PCF, 1000mL

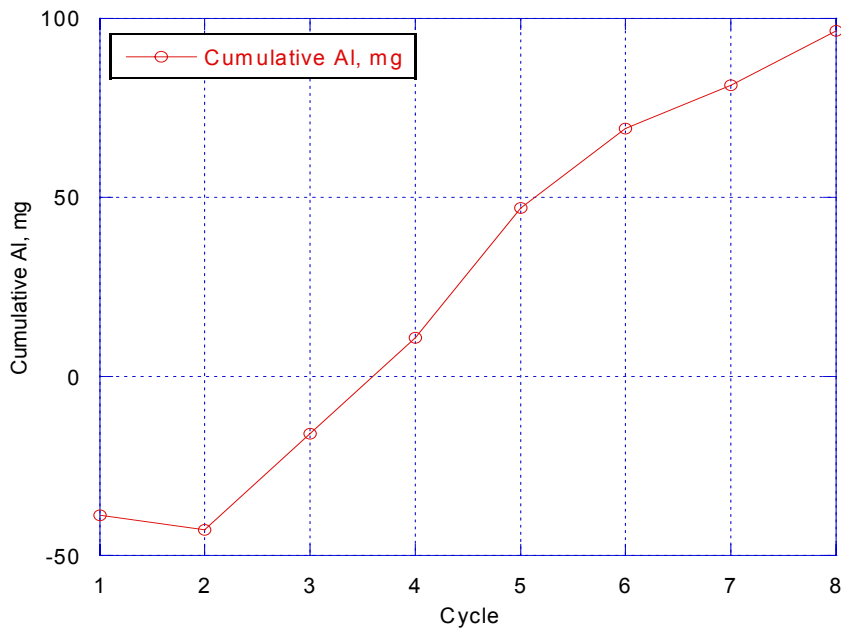


Figure 3. Cumulative aluminum release for Series A, 100g PCF, 1000mL mine water.

aluminum over the eight cycles for the duplicates in Run 1 in Table 1 is 96 mg (Figure 3) which is about 5% of the available Al in the PCF ash. The tendency is for the concentration of Al in solution to decrease in later cycles, indicating less is being dissolved from the ash. Long term studies of Al behavior have not been undertaken.

**Manganese:** The manganese content of the original ashes is small (Table 3). The Mn concentration in the solutions tends to be near the original mine water value, with less being found in the first (high pH) cycle. The only cycle that consistently has more Mn than the mine water is the second cycle, which is seen as the hump in the cumulative Mn plot (Figure 4). Overall, manganese exhibits a small removal from the system.

**Magnesium:** Magnesium exhibits a continuing release over extraction cycles for PCF. The concentration peaks in the first cycle, then falls (Figure 5). The magnesium concentration in the last cycles is indistinguishable from the mine drainage value (see Table 7). The mine drainage value is 36.6 mg/L. The

normalized value of Mg for cycle 7 of run 1 in Table is 36.7 mg/L. Certainly with

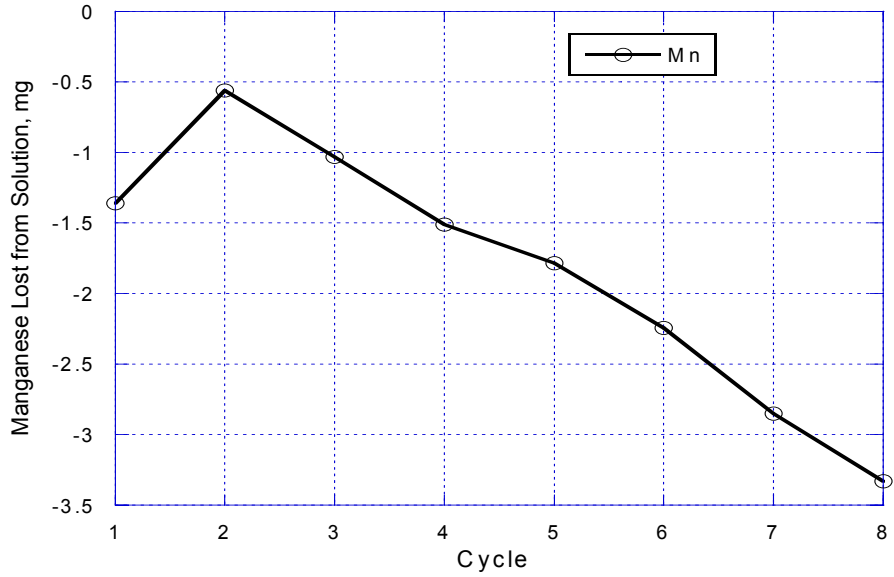


Figure 4. Cumulative manganese removal. Series A, 100g PCF, 1000mL mine water.

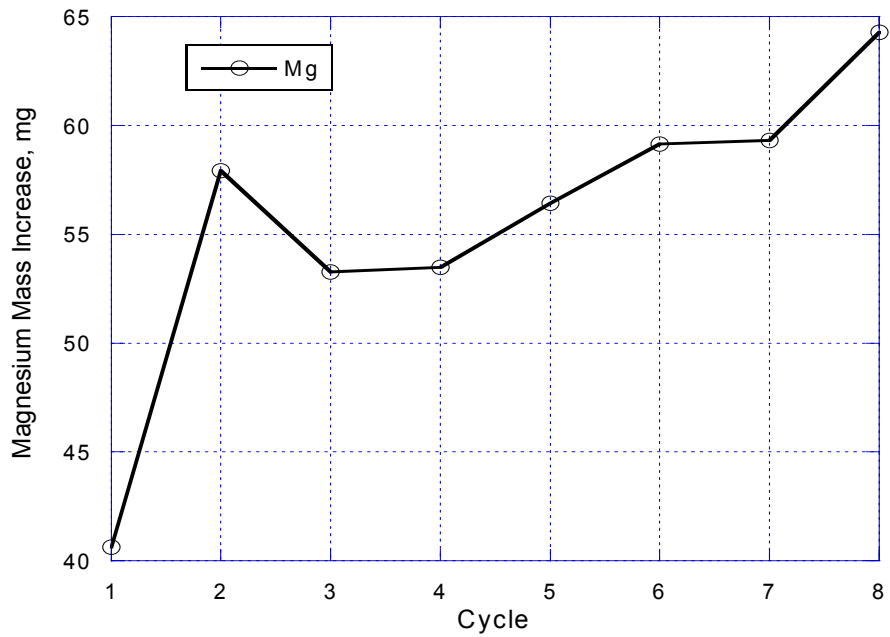


Figure 5. Cumulative magnesium removal. Series A, 100g PCF, 1000mL mine water.

a 13% RAD for Mg, the values are the same. PCF would seem to have some easily releasable Mg, then cease reacting. FBC behaves differently, although may be precipitating as carbonate or hydroxide.

**Calcium:** Calcium is released at very high levels throughout the cycles. In every trial, the cumulative Ca released exceeds the amount found to be in the PCF ash initially (Figure 6). The Ca solution analyses had a large RAD (Table 7) but the cumulative amount greatly exceeds those bounds. Either the Ca analysis of the PCF ash (Table 3) is flawed or Ca is very non-homogeneously distributed in PCF ash. Calcium is by far the most common ion released. The amount of calcium released from PCF and FBC exceeds the sum released of all other constituents.

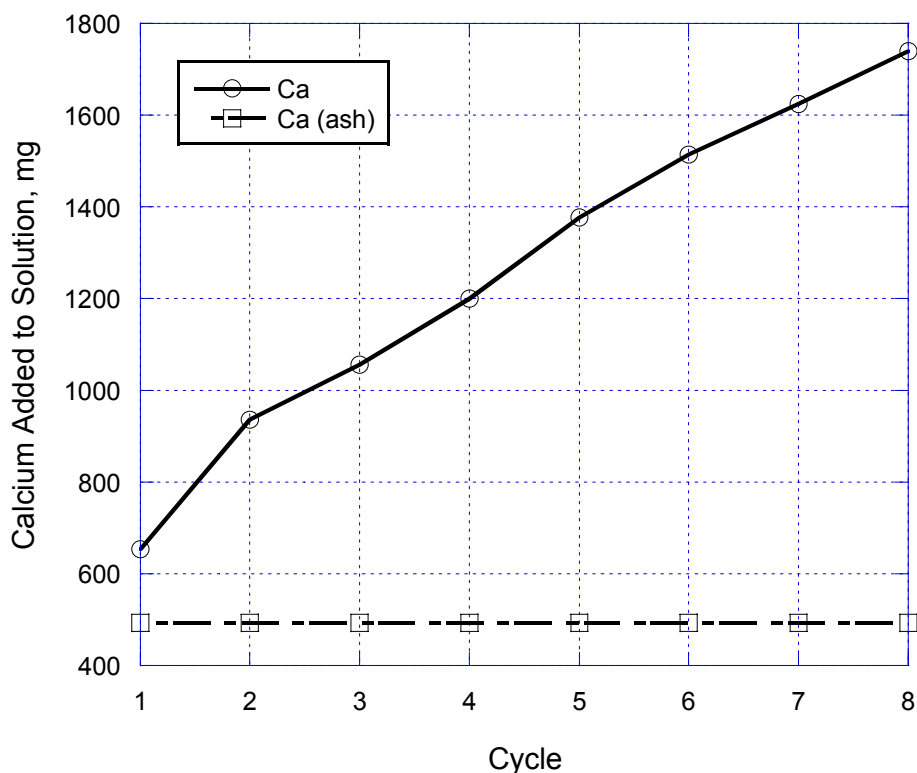


Figure 6. Cumulative calcium addition. Series A, 100g PCF, 1000mL mine water. Compared to ash content of PCF ash.

**Sulfate:** Sulfate is removed from the mine drainage solution by the added CBCs. The primary mechanism would seem to be by gypsum ( $\text{CaSO}_4$ ) precipitation due the huge Ca input. Rough calculations of gypsum solubility using a  $K_{\text{SP}}$  of  $2.5 \times 10^{-5}$  (6) indicates that for PCF, the solution is supersaturated with respect to gypsum (Table 10). The degree of supersaturation is largest

**Table 10. Supersaturation of Gypsum. 100g PCF, 1000 mL\***

Run	Ca (mg/L)	SO <sub>4</sub> <sup>=</sup> (mg/L)	Ca (M)	SO <sub>4</sub> <sup>=</sup> (M)	Product	Ratio
0	49	1529	0.00122	0.015927	1.94E-05	<b>0.78</b>
1	692	1915	0.01731	0.019948	0.000345	<b>13.81</b>
2	337	960	0.008433	0.01	8.43E-05	<b>3.37</b>
3	192	922	0.004795	0.009604	4.61E-05	<b>1.84</b>
4	227	1016	0.005667	0.010583	6E-05	<b>2.40</b>
5	231	1018	0.005778	0.010604	6.13E-05	<b>2.45</b>
6	169	1164	0.004232	0.012125	5.13E-05	<b>2.05</b>
7	153	1058	0.003831	0.011021	4.22E-05	<b>1.69</b>
8	186	1098	0.004658	0.011438	5.33E-05	<b>2.13</b>

\* Series A Run 1 in Table 1

at early cycles and decreases and stabilizes with later cycles. The mine water is undersaturated with respect to gypsum (run 0 in Table 10). FBC ash typically releases more Ca than PCF and consistently has a higher degree of supersaturation at later cycles (Table 11). Extended cycles were not run, but gypsum will re-dissolve as the calcium levels decrease if exposed to the same strength mine water. The increase in Ca and SO<sub>4</sub><sup>=</sup> in the mine drainage will not be large, however, since the system is nearly saturated. If the mine drainage stops flowing and the gypsum is exposed to water without elevated sulfate, the gypsum will dissolve.

**Table 11. Supersaturation of Gypsum. 100g FBC, 1000 mL\***

Run	Ca (mg/L)	SO <sub>4</sub> <sup>=</sup> (mg/L)	Ca (M)	SO <sub>4</sub> <sup>=</sup> (M)	Product	Ratio
1	498	1640	0.01245	0.017083	0.000213	<b>8.51</b>
2	340	1150	0.0085	0.011979	0.000102	<b>4.07</b>
3	331	1060	0.008275	0.011042	9.14E-05	<b>3.65</b>

\* Series B Run 1 in Table 2

**Antimony:** The PCF ash contains 600 mg of antimony, the FBC an undetectable amount and the original mine water has 50 ug/L. The limit of detection for Sb is 35 ug/L for the Series A runs and 5 ug/L for Series B, which makes discussion of quantitative trends difficult. In every measurable case, antimony is removed from solution. The chemistry of antimony parallels that of arsenic, the Sb(V) antimonate (or stibnate) oxyanion, SbO<sub>3</sub><sup>=</sup>, or hydrated forms, is known, like arsenate, to adsorb to iron precipitates (7). The removal of iron from the system by the alkaline ash removes the Sb. Subsequent possible re-dissolving of the

iron solids may remobilize the previously removed antimony, but no knowledge of whether the antimony in the PCF is released can be derived by the experiments as run. Antimony possibly is more strongly bound by iron than arsenic [see below].

**Arsenic:** Arsenic is added to solution from PCF over the course of ash reaction (Figure 7), although the amount added is far less than the amount found in the ash. Early cycles (which remove large amounts of iron) remove arsenic from the mine drainage, but as the pH of the cycles decreases, the iron is presumably remobilized and gains additional arsenic from the PCF. FBC contains far less arsenic than PCF and over the three cycles, demonstrates a net loss of As. The As would probably be remobilized along with iron after exhaustion of the alkaline material, but nothing can be stated about the tendency of FBC to leach As. If all of the As removed from mine drainage remobilized, the net mass change over all cycles would be zero. PCF has a substantial positive mass release. As noted, antimony, which has a similar chemistry to arsenic is not re-dissolved in late cycles. Whether this is the result of stronger binding strength or just due to the lower concentrations is unknown.

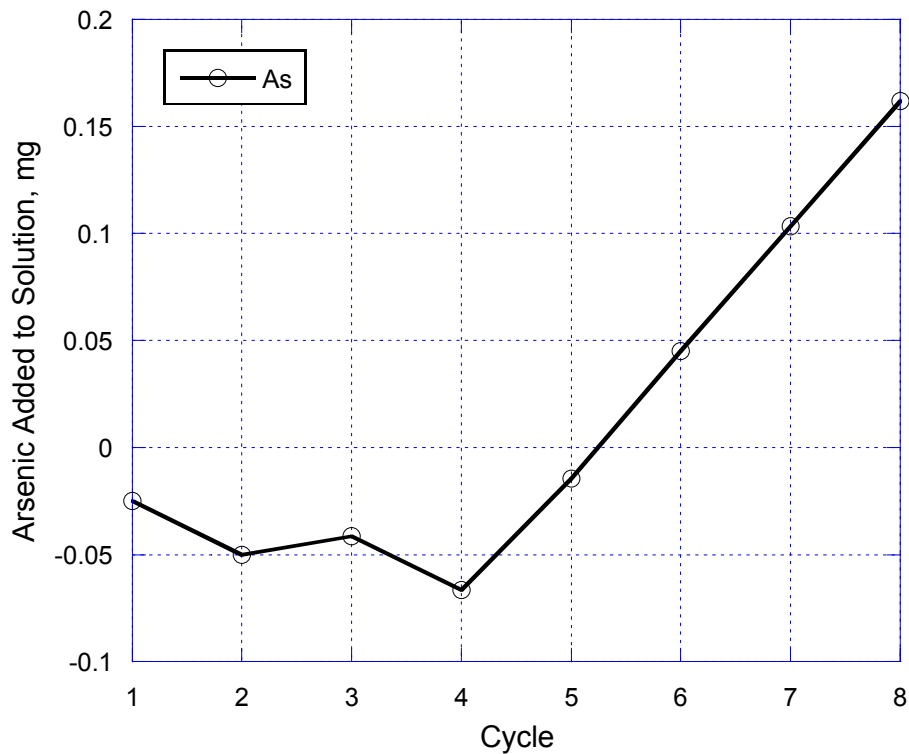


Figure 7. Cumulative arsenic addition, mg, to solution. Series A, 100g PCF, 1000mL mine water.

**Barium:** The mine water contain a low level of barium and both ashes release it over the leach cycles. A small fraction is released compared to the amount of Ba found in the ash (Table 3), 15-30 mg. All solutions are supersaturated with respect to barite (Ba SO<sub>4</sub>) for PCF (Table 12) and FBC (Table 13). All calculations used the solubility product constant of 1.0x10<sup>-10</sup> (6). The substantial precipitation of gypsum, even though the solution remains supersaturated, has no effect on barium, in fact barium is released as gypsum is lost. The supersaturation of gypsum and barite has implications for downstream

Run	SO <sub>4</sub> <sup>=</sup> (mg/L)	SO <sub>4</sub> <sup>=</sup> (M)	Ba (M)	Ba (mg/L) Calc.	Ba (mg/L Found)
0	1529	0.0159	6.7E-09	0.00092	0.01
1	1915	0.0199	5.3E-09	0.00073	0.019
2	960	0.0100	1.0E-08	0.00147	0.039
3	922	0.0096	1.1E-08	0.00153	0.023
4	1016	0.0106	1.0E-08	0.00139	0.024
5	1018	0.0106	1.0E-08	0.00138	0.032
6	1164	0.0121	8.8E-09	0.00121	0.035
7	1058	0.0110	9.7E-09	0.00133	0.035
8	1098	0.0114	9.3E-09	0.00128	0.041

\* Series A Run 1 in Table 1

Run	SO <sub>4</sub> <sup>=</sup> (mg/L)	SO <sub>4</sub> <sup>=</sup> (M)	Ba (M)	Ba (mg/L) Calc.	Ba (mg/L Found)
1	1620	0.016875	6.34974E-09	0.0009	0.19
2	1240	0.01291667	8.29563E-09	0.0011	0.13
3	1070	0.01114583	9.61363E-09	0.0013	0.12

\* Series B Run 1 in Table 2

chemistries. The long term corrective precipitation behavior of the solutions has not been investigated. A more detailed calculational evaluation of the sulfate-calcium-barium system with improved (more focused) analyses could provide additional insights.

**Beryllium:** Far less beryllium was found in PCF than FBC, yet more is released from the PCF. The FBC experiments, which all were conducted at high pH, released no Be. At high pH (pH=6) with PCF, Be shows a net removal from solution, but the Be release recovers as the pH falls in subsequent cycles. Roughly one-half of the Be found in the PCF is released in the eight cycles



(Figure 8). Beryllium solubility is controlled by the hydroxide solubility ( $K_{SP} = 6.9 \times 10^{-22}$ ). Down to pH 6, Be is soluble at levels below 1 ug/L. Solubility increases rapidly with decreasing pH; the solubility is 62 ug/L at pH 4. The lack of Be release for FBC is rationalized by the high pH of the Series B extractions (around pH 10). Whether the Be is intrinsically less labile in FBC due to structural issues cannot be determined, since low pH extractions were not performed. Ziemkiewicz and Knox (3) conducted 15 extractions with the FBC ash. Their Table 1 reports 7 ug/L Be for all extractions using water M, which appears to be a misprint of the limit of detection (0.7 ug/L). They reported the limit of detection in their table for metals that were not detected. Their last pH value (the 15<sup>th</sup> extraction) is 6.5; no Be should have been seen. They report the loss of Be in the last cycle versus the original mine drainage to be 35%, while it should be

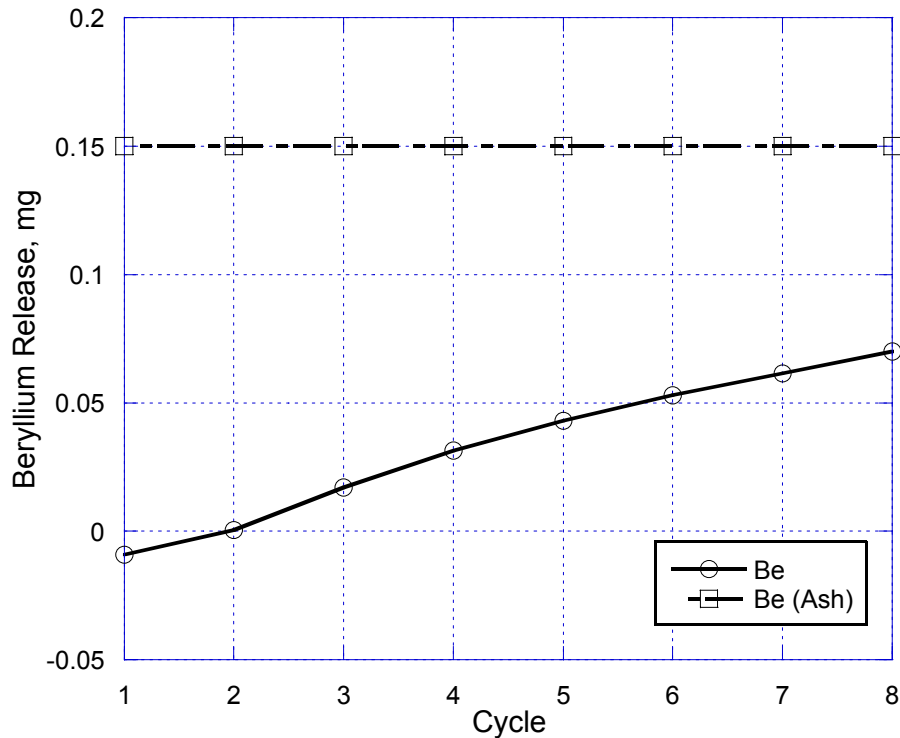


Figure 8. Cumulative beryllium addition, mg, to solution. Series A, 100g PCF, 1000mL mine water. Compared to PCF ash content, mg.

nearly 100%. Their leaching of FBC (using v/m of 200) with water P shows a weaker increase in Be with decreasing pH than is seen in our experiments. Whether this difference is an artifact of the different ashes or the different experimental conditions is unknown. The data in their Table 2, however, shows

a number of extractions in which there is a net release of Be, as seen Fig. 8 for the results of these experiments.

**Boron:** The PCF ash was found to contain 14 mg of boron per 100g (Table 3). The eight cycles for the PCF leach in Series A released a cumulative 12.6 mg, the best example in the study of a mass balance that converged (Figure 9). Boron was heavily released at the initial pH of 6.5, and then more slowly as the pH decreased. No specific conclusions can be made to explain the initial surge other than the observation that in the boric acid/borate system (the form of B expected in this study) the species is most negatively charged at pH 9.4. Boron release does not appear to be inhibited in any way; fully half of the available boron is released immediately. Series B PCF released 5.9 mg of B in the three

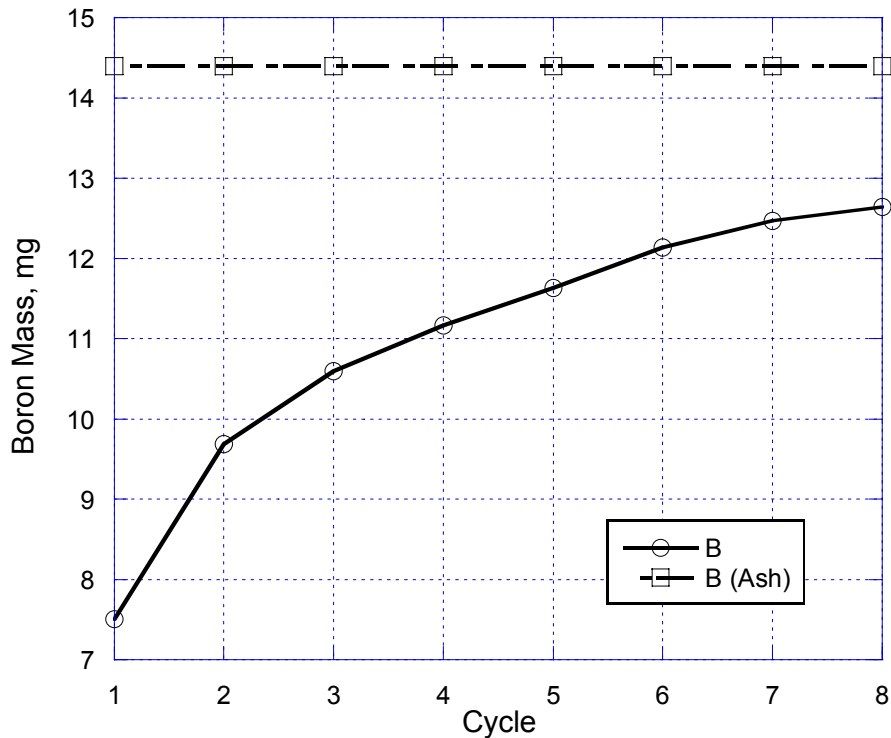


Figure 9. Cumulative boron addition, mg, to solution. Series A, 100g PCF, 1000mL mine water. Compared to PCF ash content, mg.

cycles run. The Series A leachings released 10.5 and 10.6 mg, nearly twice as much.

FBC ash released less than a mg of B over its three cycles at pH near 10. The FBC ash contained less boron initially. The lack of B release may be due to the high pH (a borate precipitation or adsorption mechanism) or to storage of boron

in an unleachable matrix in the ash. The trials of Ziemkiewicz and Knox (3) also showed little B leach for FBC ash, in fact they report a loss from solution when Water P was used. Water M, at high pH, conversely leached substantial boron, about 40% of the original content of the ash.

Boron behavior is inconsistent for the two Series here and the earlier work of Ziemkiewicz and Knox (3). Boron release is fairly reproducible within a Series (Tables 8,9), but variable across series (Table 7). Complete elucidation of its leaching behavior will require a more systematic study.

**Cadmium:** Very little cadmium is found in the two ashes (Table 3) with PCF containing the most (0.5mg). Little Cd is leached, the concentration of Cd is below the limit of detection for most samples. Although the mine water was reported to contain 4 ug/L Cd, the limit of detection reported for Cd in the cycle waters was 14 ug/L, which does not allow for any analysis of its behavior.

**Chromium:** Chromium is most likely present as chromate, although the Cr was not speciated. PCF has more Cr than FBC in a 100g sample (Table 3), 5 mg versus 2.2 mg. Chromium is released into the leachate from the PCF ash at all pHs (Figure 10), which provides indirect evidence that its form is chromate; Cr(III)

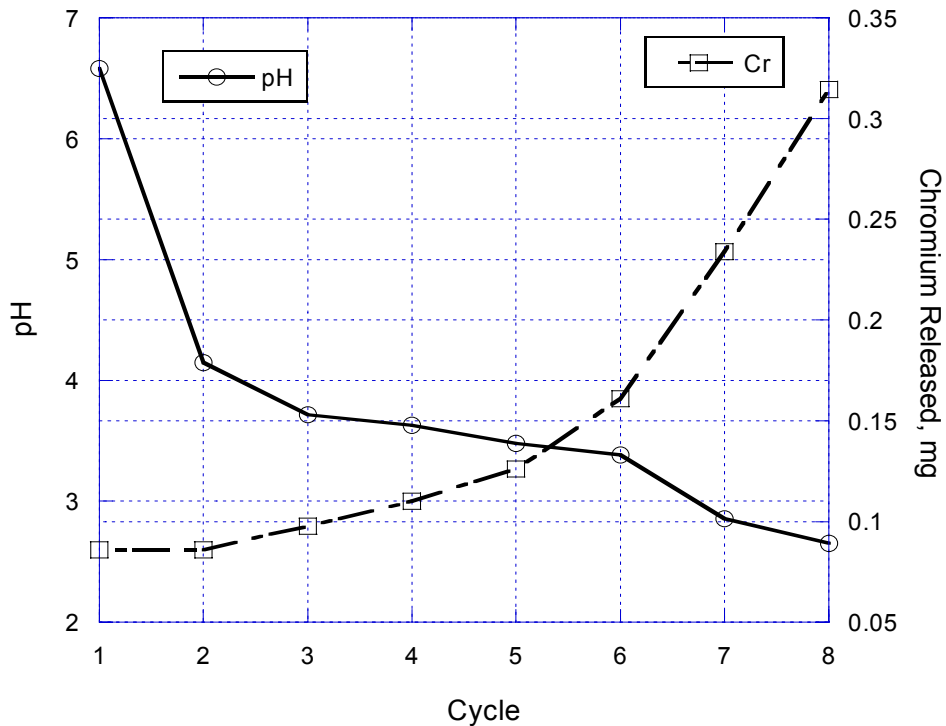


Figure 10. Cumulative chromium addition, mg, to solution. Series A, 100g PCF, 1000mL mine water. Compared to pH of cycle solution.

is insoluble as a hydroxide at moderate pH. Of course, the history of the Cr, as a component in a material resulting from an oxidation process, would favor chromate as the form. Both PCF and FBC ash release the greatest amount of Cr in the first cycle (FBC releases 0.1 mg/L from Series B (Table 2) and PCF releases 0.09 mg/L). FBC does not release measurable amounts in the other two cycles, whereas PCF has a small release (Figure 10) at intermediate pH, then an increasing release at lower pH. The first cycle may remove labile Cr regardless of pH. The increase in Cr at later cycles is more difficult to explain, since greater reaction with the ash occurs at early cycles and more entrained Cr would be expected to be released. Other processes, such as adsorption, may impeded Cr release at pHs near 4; the chromate would be in the  $\text{HCrO}_4^-$  form.

Certainly, differences in release between PCF and FBC may be related to the relative amounts in each ash. The eight cycles in Series A released less than 10 percent of the chromium from the PCF. No conclusions can be made regarding longer term leaching. The trend between cycles 7 and 8 was a constant or increasing release of Cr.

**Copper:** Copper hydroxide has a  $K_{\text{SP}}$  of  $4.8 \times 10^{-20}$  (8). The solubility of copper is normally pH controlled (using a simple argument) with solubility being negligible above pH 8. The absence of Cu in all cycles of FBC from Series B can be attributed to the insolubility of copper hydroxide. Neither ash contains much copper (2 mg or so, Table 3), but the mine drainage contains 0.18 mg/L. In all cases with measurable Cu concentrations, copper is removed from the system over the cycles (Figure 11). A particularly confusing case is copper at pH 6.5, the first cycle, for PCF in Series A and B. Although copper should be soluble to a level of around 3 mg/L, none is found, and in fact, the copper in the mine drainage is completely precipitated. Stumm and Morgan (6) note that the solubility of CuO (the stable solid phase) decreases with molar surface area, which maybe useful to explain a case where Cu is dissolved from the ash, but removal of Cu is unaffected by surface area, it is a solution phenomenon. Occlusion of copper in the precipitation of gypsum or ferrihydrite could explain the removal at pH 6, but these species also precipitate at lower pH values while copper stays in solution.

Error in the copper concentration of the mine drainage could change the system from one of net copper removal to net copper release (or stability) over the  $\text{pH} < 6$  cycles. The mean concentrations for Series A (Table 14) shows that the copper concentration in the leachate plateaus at nearly 0.180 mg/L. Given the error, it can be postulated that copper is neither removed nor added at low pH (with a small amount being removed around pH 4). Precipitation of copper is calculationaly impossible at the lower pH values, so loss would need to be through some other mechanism, such as adsorption or co-precipitation/occlusion, as mentioned above. At low pH, clearly no Cu is released from the ash. Further study of the copper behavior is warranted, particularly at longer cycles and in the precipitated material in the pH 5 to 7 range.

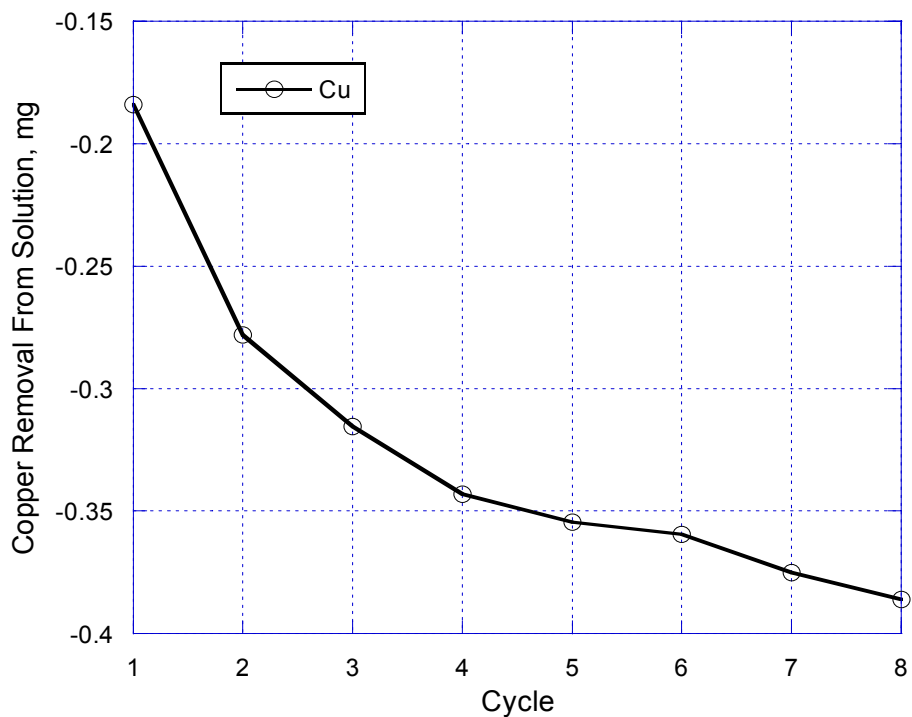


Figure 11. Cumulative copper removal, mg, from solution. Series A, 100g PCF, 1000mL mine water.

<b>Table 14. Copper Concentration, Series A,</b>			
<b>100g PCF, 1000 mL</b>			
<b>Cycle</b>	<b>Mean pH</b>	<b>Cu, mg/L</b>	<b>% Ave. Dev.</b>
0*	2.54	0.18	
1	6.58	<0.015	
2	4.15	0.090	2.2%
3	3.72	0.147	2.4%
4	3.63	0.157	2.9%
5	3.48	0.173	2.0%
6	3.39	0.179	0.6%
7	2.86	0.169	3.3%
8	2.66	0.173	16.8%

\* Mine Drainage

**Lead:** No lead was detected in any solution from any cycle. The two ash samples contained about 1 mg/100g (Table 3). The mine drainage contained 4 ug/L (Table 4), so normally a removal of lead would be indicated. Unfortunately the reported limit of detection for lead in the leachates was either 5 ug/L (Series B) or 32 ug/L (Series A). No conclusions can be drawn concerning the behavior of lead, other than it is not released to measurable levels.

**Mercury:** The Hg concentration in the original mine drainage was 1 ug/L. Neither the PCF nor FBC ash had detectable amounts and the leachate water often had undetectable amounts (two leachate waters had detectable amounts and both were below 1 ug/L). Not enough information was available about mercury to draw any conclusions.

**Nickel:** Nickel is released from the PCF ash in all cycles, but is removed from the FBC cycles. Ni hydroxide has a  $K_{SP}$  of  $5.5 \times 10^{-16}$  (8), much larger than copper for example. Calculations indicate nickel should be measurable in the ug/L range near pH 10. The behavior of Ni with FBC ash in Series B is somewhat consistent with removal of solution by hydroxide precipitation; the pH is at the limit where Ni can be dissolved. More than likely, Ni is also removed from solution as an occlusion with iron precipitation, a process more noticeable with PCF ash. PCF ash in Series A has a continuous release of nickel with cycle that eventually released (Figure 12) over one-third of the nickel originally found in the PCF (3.6g, Table 3)). Nickel release is smallest in cycle 1 (as with copper) and gradually

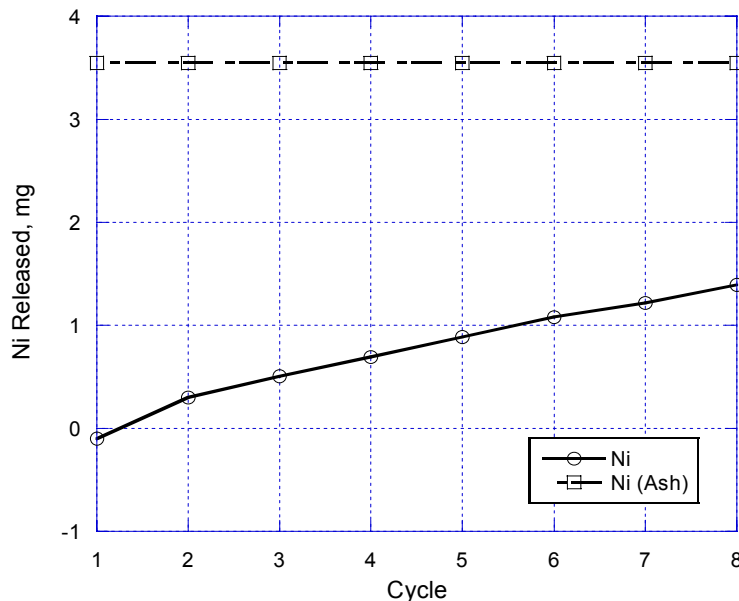


Figure 12. Cumulative nickel addition, mg, to solution. Series A, 100g PCF, 1000mL mine water. Compared to mg of Ni in the ash.

stabilizes to what could be interpreted as equilibrium values. As noted with copper, and FBC above, the nickel in the first cycle may be removed as a co-precipitant/occluded ion with iron hydroxides. The concentration of Ni released becomes almost constant at later cycles, a behavior akin to solubility control. At pH 3, no known nickel solid can be controlling; some unknown ash related property appears to control the Ni release. A series of careful extractions with mine water that used Ni exhaustion as the end point might clarify the nickel process.

**Selenium:** Selenium is removed from the drainage solution (16 ug/L, Table 4)) in all PCF cycles in Series A and B to below the detection limit. Although the PCF ash has four times the selenium content of the FBC (12 mg/100g versus 0.3 mg/100g), the FBC ash had more Se in solution in Series B. Selenium should be in the form of selenate (6), which has no useful precipitation chemistry with the major ions in solution. Selenate is known to co-precipitate with iron (9), which may explain its net removal from solution ( Figure 13). The linear removal of Se in Fig. 13 is merely the additive removal of 0.016 mg each cycle from the mine water. The precipitation of iron at higher pH (pH 9 or 10) may co-precipitate Se less efficiently than pH 6 and below. The loss of Se at pH 2.55 is an indication that the Fe in the mine drainage precipitates even at these low pH values. No other obvious mechanism for Se removal is evident.

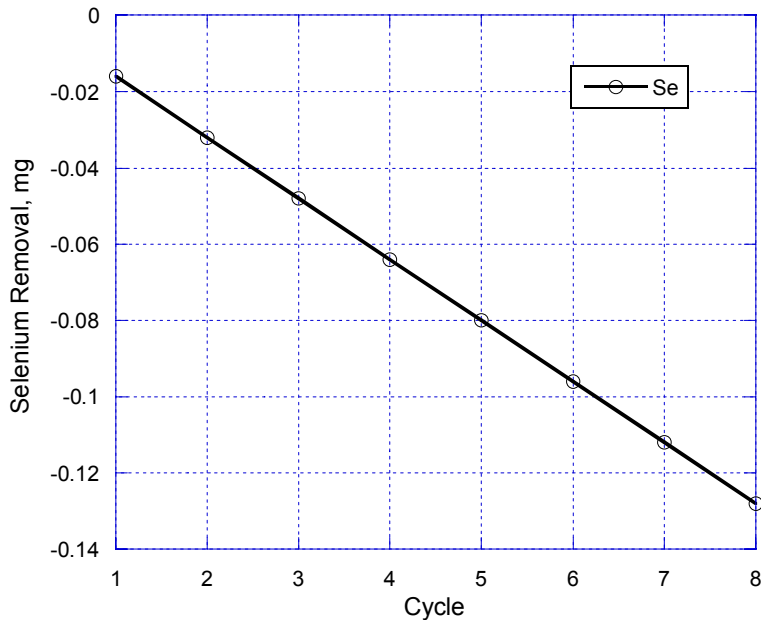


Figure 13. Cumulative selenium removal, mg, from solution. Series A, 100g PCF, 1000mL mine water.

**Silver:** In the v/m = 10 experiments, silver, which was present at 2ug/L in the mine water, was below the limit of detection, which was greater than 2 ug/L for the leachate solutions. Silver was at a low level in PCF (1.5 mg) and undetectable in FBC ash (see Table 3). No detailed information about the behavior of silver can be derived.

**Vanadium:** The mine water contained 3 ug/L vanadium, which is soluble as a variety of oxy cations and anions. Vanadium is removed from the FBC solutions in Series B, but the limit of detection is higher than the amount initially in the mine water, so no information can be derived. Vanadium in PCF behaves differently. The first cycle, in every case in Series A had a net release of V. PCF had 7.6 mg of vanadium (FBC had 4.7 mg, Table 3). The first cycle reproducibly had a large amount of vanadium released and all other cycled (pH below 5) had a net removal of vanadium (Figure 14). Unlike Se, Fig. 13, V falls off linearly, not from zero, but from the value of the initial input of vanadium in cycle 1 at pH 6.5.

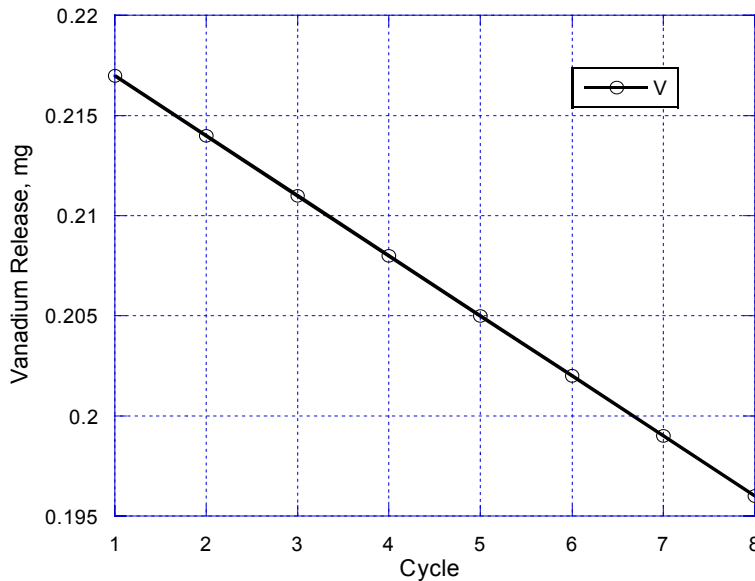


Figure 14. Cumulative vanadium addition, mg, to solution. Series A, 100g PCF, 1000mL mine water.

Vanadium is more likely to exist as an anion at pH 6 (10), which seems to be fairly soluble. Below pH 5, vanadium is more likely to be cationic. Vanadium is known to co-precipitate with Al and Fe hydroxides (11), most likely in the cationic forms. Much more needs to be known about the aqueous chemistry of vanadium at low levels to fully explain its unusual behavior.



**Thallium:** Thallium is a monovalent or trivalent cation in aqueous solution. The mine water contains 21 ug/L (Table 4), the PCF ash has 1.2 mg per 100g and the FBC has an undetectable amount. Thallium is completely removed from the mine water in the three FBC cycles in Series B. The PCF cycles in Series B have essentially no TI, indicating a net removal, but the PCF intermediate cycles in Series A all are net contributors of TI (Figure 15). The overall TI released is

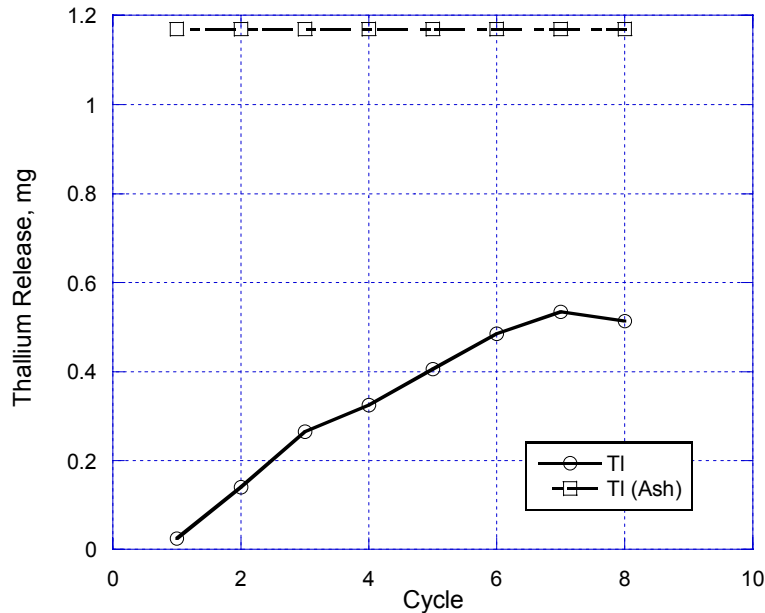


Figure 15. Cumulative thallium addition, mg, to solution. Series A, 100g PCF, 1000mL mine water. Compared to thallium content of ash.

roughly half of the amount found in the original ash. TIOH is a very soluble base, and at most pHs it is soluble. The net removal from solution of TI at pH 6 and pH 2.5 in Series B is currently unexplainable. The presence of the TI (III) oxidation state is unknown, but if present, its hydroxide is insoluble and could explain the loss of TI at high pH.

**Zinc:** Zinc hydroxide,  $K_{SP}$  of  $3 \times 10^{-17}$  (8), is soluble in all but basic solution (much like copper), yet, like copper, it undergoes net removal from the mine water solution. A mechanism of co-precipitation seems most likely, but the removal is inefficient, a significant portion of the original zinc is left in solution (Table 15). The removal is fairly consistent for cycles 3 through 7, but the zinc is totally removed at pH 6.58 and less efficiently removed in cycles 2 and 8. At pH 2.66, iron is becoming more soluble which may account for the increase, but the less efficient removal at pH 4.15 is not easily explained. One advantage of the direct study of species that are removed is the ability to spike the mine

**Table 15. Zinc Concentration, Series A, 100g PCF, 1000 mL**

Cycle	Mean pH	Zn, mg/L	% Ave. Dev.
0*	2.54	1.24	
1	6.58	<0.016	
2	4.15	1.047	1.6%
3	3.72	0.8995	4.9%
4	3.63	0.868	0.7%
5	3.48	0.8605	0.4%
6	3.39	0.8295	0.8%
7	2.86	0.843	0.9%
8	2.66	0.959	15.7%

\* Mine Drainage

drainage to aid study of the phenomena involved. Such a study with zinc (and copper) may be warranted.

Mass Removal

Over the course of eight cycles, mass is either removed or added to the overlying solution by each constituent. The mass changes are explicitly discussed in a number of cases above. An overview of all constituents (Table 16) identifies those which are removed from solution (negative, underlined ) and those which enrich the solution (italics). Additionally the limit for each constituent is given. In the case of removal, the limit is the sum of the mass of the constituent in the original mine drainage for all cycles. For cases of addition, the limit is the total mass of the constituent in the PCF ash.

Iron, manganese, sulfate, antimony, cadmium, copper, lead, selenium, silver and zinc are removed from solution. The degree of removal is determined by certain properties of the ash, notably the alkaline content, but removal is less likely a function of the composition of the solid than is addition. This will be reiterated in the section on the addition of sandstone and shale.

Calculation of Mass Loss or Gain, Propagation of Error

Using the zinc (Table 15) results, the effect of error propagation can be shown. Calculating the total mass of constituent gained or lost involves subtracting the solution concentration in the original mine water from the value found in an individual cycle. Each solution measurement has an average deviation derived

**Table 16. Mass Changes Over Eight Cycles for Series A, 100g PCF. 1000 mL**

Underlined Constituents are Removed from Solution

	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>SO<sub>4</sub><sup>=</sup></b>	<b>Sb<sup>1</sup></b>	<b>As<sup>2</sup></b>
<b>Mass Change, mg</b>	64	1739	<u>1328</u>	97	<u>3.3</u>	<u>3181</u>	<u>0.38</u>	0.16
<b>Limit, mg</b>	ND	943	<u>1349</u>	2062	<u>16</u>	<u>12232</u>	<u>0.38</u>	6.4
	<b>B</b>	<b>Ba</b>	<b>Be<sup>2</sup></b>	<b>Cd<sup>2</sup></b>	<b>Cr</b>	<b>Cu<sup>2</sup></b>	<b>Pb<sup>1</sup></b>	<b>Hg</b>
<b>Mass Change, mg</b>	12.6	0.19	0.07	<u>0.01</u>	0.31	<u>0.39</u>	<u>0.032</u>	0.0003
<b>Limit, mg</b>	14	15	0.2	<u>0.032</u>	4.8	<u>1.50</u>	<u>0.032</u>	ND
	<b>Ni</b>	<b>Se<sup>1</sup></b>	<b>Ag<sup>1</sup></b>	<b>Tl</b>	<b>V<sup>2</sup></b>	<b>Zn</b>		
<b>Mass Change, mg</b>	1.39	<u>0.13</u>	<u>0.016</u>	0.47	0.20	<u>3.6</u>		
<b>Limit, mg</b>	3.6	<u>0.13</u>	<u>0.016</u>	1.2	7.6	<u>9.9</u>		

1- Below Limit of Detection in All Cycles

2- Below Limit of Detection in Some Cycles

from the duplicate determinations in Series A. The resultant adjusted, or normalized, concentration is then added over all cycles to give the total loss or gain for the trial. The sum over all cycles carries the error for each cycle with it.

In this study, the original mine water has no known deviation, assume it is 1%. Calculation of the mass in Table 17 demonstrates the propagation of error for zinc. Each normalized zinc concentration has the summed error (second Av. Dev. Column) from the mine water (0.0124 mg/L) and the cycle analysis (the first Av. Dev. column). As each cycle is summed the average deviations are summed (last column) to give a final average deviation of 0.336, which is 9.3%. Any comparison of zinc masses between systems must consider this level of error. The error level can be problematic in situations where two large numbers are subtracted to yield a small number.

## The Influence of Extraction Volume

### pH and Acidity

During the initial trials (Z REF) the volume to mass ration was 200 (2 liters of mine water for 10g ash). The current trials, all of which added spoil to the initial 100g of ash, were initially to be run at v/m values of between 5.7 and 10, but were subsequently changed to a constant v/m = 10 after interpretation difficulties arose with the varying v/m values used. Series A (Table 1) was subsequently run to evaluate aspects of volume to mass differences.

Cycle	Zn, mg/L	Av. Dev.	Norm. mg/L	Av.Dev.	Mass, mg	Sum AvDev
0*	1.24	0.0124				0.0124
1	<0.016	0.000	-1.24	0.012	-1.24	0.012
2	1.047	0.017	-0.193	0.029	-1.433	0.042
3	0.8995	0.045	-0.3405	0.057	-1.7735	0.099
4	0.868	0.006	-0.372	0.018	-2.1455	0.117
5	0.8605	0.004	-0.3795	0.016	-2.525	0.133
6	0.8295	0.007	-0.4105	0.019	-2.9355	0.152
7	0.843	0.008	-0.397	0.020	-3.3325	0.172
8	0.959	0.151	-0.281	0.163	-3.6135	0.336

\* Mine Drainage

Two situations can be envisioned for the interaction of the ash with differing volumes that lead to increases in the constituent in the solution. For constituents that behave as if under solubility rules, as long as solid is present, the concentration of the constituent in the liquid will remain constant. In this case, use of a v/m ratio of 10 will produce the same solution concentration as v/m of 200. The total mass increase will be much larger (20 times larger) with v/m equal to 200. This is the solubility control case, which leads to constant concentrations.

Removal processes, such as for iron, should be controlled by solubility considerations. Certain minor ions may be removed by co-precipitation or adsorption. If the v/m ratio is increased, more solution is present, more iron precipitates and more of the minor substance is co-precipitated. A larger solution volume will result in more precipitated iron and more co-precipitated trace material. All of the total removal cases are trivially solubility controlled, since a large solution volume by definition has a proportionately larger total ion mass.

In certain cases the amount of constituent released is constant over a period of time. The amount of contact solution that actually surrounds the solid particles at any one time is fixed, it does not matter how many liters lie beyond that contact amount. Over time, surface reactions occur and the constituent is released, essentially with kinetic or mass transfer control. The same mass of material is released; the concentrations vary with volume. This is the case of constant mass.

The neutralization potential of the ash is a finite property, which the MWLP method is designed to exhaust. Use of larger extraction volumes provides more acid and exhausts the alkaline material earlier. The pH and acidity profiles (Figure 18) for v/m at 10 and 15 illustrate this. Only 7 of the 8 v/m cycles are

**Table 18. pH and Acidity at Different v/m Ratios for 100g PCF.**

Cycle	pH		Calc. Acidity, mg/L	
	v/m = 10	v/m = 15	v/m = 10	v/m = 15
1	6.58	5.54	3	4
2	4.15	3.85	203	370
3	3.72	3.58	379	377
4	3.63	3.22	382	434
5	3.48	2.78	439	483
6	3.39	2.66	367	492
7	2.86	2.56	374	447

used. All values are the means of duplicate trials. The seven v/m = 10 cycles correspond to 7 liters, the v/m = 15 cycles correspond to 10.5 liters. A straight proportionality would predict that v/m = 15 should lower the ash pH to about 2.86 at 5 cycles. The pH is close, but the acidity after 5 v/m cycles is much higher at a ratio of 15 than the ratio of 10 after 7 cycles. The v/m = 10 trial should take about 11 cycles to finish, but takes only 8, which indicates that release of alkaline material has a mass transfer/kinetic component. The higher ratio trial is less efficient in transferring alkalinity to the solution in the first cycle (the pH is much lower), another indication of mass transfer limitations. Using larger v/m ratios will exhaust the ash sooner, but the scaling relationships between different ratios for pH and acidity are non-intuitive and require much more study.

Major Ions

The major ions, Ca, Al, Fe, Mg, Mn and sulfate are both added and removed (Fe, Mn, SO<sub>4</sub><sup>-</sup>) from the solution. The normalized solution concentrations for the metals that increase in concentration, Table 19, shows that in almost every case the solution concentration is roughly the same regardless of extraction volume.

**Table 19. Concentrations, mg/L for Different v/m Ratios for 100g PCF**

Cycle\ v/m	Al		Ca		Mg	
	10	15	10	15	10	15
1	0.3	0.13	702	685	77	75
2	35	65	332	251	54	46
3	66	65	168	151	32	32
4	66	71	193	162	37	34
5	75	62	226	242	40	44
6	61	53	186	207	39	41
7	51	39	159	154	37	35

These four metals have RAD values (Table 9) that indicate good reproducibility, but no obvious trend other than the rough equivalence of concentration can be seen. If the release of these elements from the solid were kinetically controlled, the v/m = 15 values would be consistently 2/3 of the v/m = 10 values. The strange anomaly in manganese is unexplainable, but corrects in the third cycle.

Although the concentrations are roughly the same, the total mass released (Table 20) in the 15 column reflects the 1.5 times large volume for the v/m = 15 extractions.

Cycle/v/m	Al		Ca		Mg	
	10	15	10	15	10	15
1	-39	-58	654	954	41	58
2	-43	-20	937	1258	58	72
3	-16	19	1056	1411	53	64
4	11	67	1200	1581	54	61
5	47	101	1377	1871	56	72
6	69	122	1514	2108	59	79
7	81	122	1624	2266	59	76

The values in the table are the normalized cumulative mass released for each cycle. The mass of the constituent in the mine water has been subtracted. All of the ions are generated from the ash. Aluminum has the best adherence to pure solubility behavior, magnesium the worst. Clearly, of operational interest, v/m of 15 removes material from the ash faster than v/m of 10.

Ions removed from the mine drainage (Table 21) also show the 1.5:1 ratio. The negative value indicates that the ions are removed from the mine drainage.

Cycle/v/m	Fe		Mn		SO <sub>4</sub> <sup>=</sup>	
	10	15	10	15	10	15
1	-169	-253	-1.4	-0.1	386	223
2	-337	-505	-0.6	-0.3	-188	-616
3	-505	-758	-1.0	-1.3	-795	-1495
4	-674	-1008	-1.5	-2.3	-1359	-2329
5	-842	-1232	-1.8	-2.8	-1884	-3154
6	-1009	-1439	-2.2	-3.5	-2262	-3767
7	-1171	-1641	-2.9	-4.6	-2739	-4454

These ions in their precipitated forms add to the mass of the ash. The use of v/m = 15 removes roughly 1.5 times as much of each ion from solution.

### Trace Constituents

Many trace constituents had analytical values below the limit of detection and were unable to be evaluated. Of those with sufficient measurements (Table 22),

v/m	<b>B</b>		<b>Ba</b>		<b>Be</b>		<b>Cr</b>	
	mass, mg	RAD*	mass, mg	RAD	mass, mg	RAD	mass, mg	RAD
10	12.47	0.1%	0.15	7.7%	0.062	0.8%	0.23	0.4%
15	13.96	1.6%	0.26	15.4%	0.065	23.3%	0.41	17.7%
v/m	<b>Cu</b>		<b>Ni</b>		<b>Tl</b>		<b>Zn</b>	
	mass, mg	RAD	mass, mg	RAD	mass, mg	RAD	mass, mg	RAD
10	-0.38	2.4%	1.22	1.0%	0.53	8.3%	-3.33	1.7%
15	-0.62	24.3%	1.58	19.1%	0.50	19.6%	-5.48	13.8%

\* Relative Average Deviation of Duplicate

two were removed from solution (copper and zinc) and six were added to solution from the ash. Table 22 shows the total mass of the species either added or removed from solution for 7 cycles. The RAD values quoted are derived from the differences in total mass of the duplicates and is not a propagation of error calculation. Note that for zinc, the RAD for v/m = 10 is much lower than the propagation of error calculation in Table 16 (9.3%). Copper and zinc conform to the 1.5:1 ratio, given some large average deviations in the values. The removal of these metals is a function of the concentration in solution such that increasing the solution volume increases the mass removal by the same proportion. Copper and zinc removal cannot be strictly through precipitation (see above); some other unknown concentration dependent mechanism needs to be invoked.

Of the six constituents that are net contributors to the solution, barium and chromium clearly conform to the 1.5:1 ratio and nickel marginally conforms. These constituents appear to be released to the solution by some concentration dependent process. Beryllium, boron and thallium are more closely 1:1 ratios. Boron is almost completely released during the extractions (see Fig. 9), so equal amounts should be seen for either volume, or for that matter any larger volume. The ash releases one-third of the available Be (Fig. 8) and 40% of available thallium (Fig. 15), based on the analyses. This degree of release is large compared to Ni, Cr, or Ba and may have an enormous influence on the lower mass ratio. A closer look at the release of the three (Table 23) Shows that Be follows the 1.5:1 trend early in it cycles. Cycle 4 for v/m = 10 is 0.032 mg

**Table 23. Mass Change by Cycle for B, Be and Tl, Series A, 100g PCF**

Cycle	B		Be		Tl	
	(v/m =10) Mass, mg	(v/m =15) Mass, mg	(v/m =10) Mass, mg	(v/m =15) Mass, mg	(v/m =10) Mass, mg	(v/m =15) Mass, mg
1	7.5	8.8	-0.009	-0.014	0.02	0.08
2	9.7	10.7	0.001	0.010	0.14	0.17
3	10.6	11.6	0.017	0.031	0.26	0.27
4	11.2	12.4	0.032	0.050	0.32	0.39
5	11.6	13.0	0.043	0.049	0.41	0.43
6	12.1	13.6	0.053	0.056	0.48	0.48
7	12.5	14.0	0.062	0.065	0.53	0.50
8	12.6		0.070		0.51	

(accumulated mass) and v/m = 15 has 0.050 mg accumulated. Also cycle 4 for v/m = 15 (6L) corresponds to cycle 6 of v/m=10 (also 6L) which has a mass of 0.53 mg. Beryllium is consistent with a concentration dependent mechanism until the later cycles, which may indicate that Be has been depleted from the ash.

Boron and Tl release nearly the same mass of material regardless of volume (1:1). More than half of the boron in the ash is released in the first cycle, however, which may skew the boron results. Calculations of reaction with diminishing starting material may provide clarification, but release of both B and Tl appears superficially to be mass transfer or kinetically controlled. Usually any reaction that depends on a solid material has a steady rate until the solid disappears, but B and Tl may depend on variables such as active site concentrations. Boron, beryllium and thallium would all be better understood with further study.

### The Influence of Spoil

Experiments with spoil were conducted in both Series A and B. The Series B study used 25g, 50g, and 75g of sandstone or shale with 100g of either FBC ash or PCF ash. Only three cycles were run, so any evaluation of the effect of the spoil material is limited to early release behavior. Blank sandstone and shale extractions with the mine water were also conducted. Given the lack of duplicates, conclusions about effects in Series B are more tentative than for Series A, which was conducted in duplicate. Series A was less ambitious than Series B. Only samples of PCF with 50g of shale or sandstone were run.

Series B was conducted using a constant mass of ash (100g), the above amounts of spoil and a varying amount of mine water in order to maintain a v/m of 10 (Table 2). The results from the previous section using only the ash material, show that except for boron, thallium and beryllium, the constituents all scale as extracting volume, indication concentration based processes. Scaling the volumes will allow certain comparisons to be made.



Series A used two solution volumes, 1L and 1.5L, for each trial. Solid masses of 100g or 150g (ash plus spoil) were used. The v/m ratios ranged from 0.67 (150g:1L) to 1.5 (100g:1.5L) (Table 1).

Pure Spoil Blanks

Spoil analyses (Table 24) reveal that sandstone and shale contain the same

	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>S</b>	<b>Sb</b>	<b>As</b>	<b>B</b>
<b>Sandstone</b>	183	34	1624	586	2.8	112	<0.0035	<0.0047	<0.0014
<b>Shale</b>	579	32	2785	2013	10.2	51	<0.0035	<0.0047	<0.0014
	<b>Ba</b>	<b>Be</b>	<b>Cd</b>	<b>Cr</b>	<b>Pb</b>	<b>Hg</b>	<b>Se</b>	<b>Ag</b>	<b>Cu</b>
<b>Sandstone</b>	2.3	0.023	0.03	0.96	4.4	ND	0.063	0.95	0.96
<b>Shale</b>	7.1	0.145	0.04	3.0	6.3	ND	<0.0045	0.72	3.0
	<b>Ni</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>					
<b>Sandstone</b>	0.6	5.4	0.11	1.4					
<b>Shale</b>	2.0	4.2	2.9	5.9					

constituents as ash (Table 3). Both the shale and sandstone were weathered; few easily extracted constituents should remain. Excavated spoil in coal mine also would be exposed to precipitation. MWLP extractions of pure shale and sandstone were stopped after one cycle in Series A, but underwent three cycles in Series B. The one cycle concentrations and reproducibility for Series A (Table 25) reveal an acidity close to that of the original mine water (Table 4) and a pH that is 0.18 unit higher, which accounts for the large removal of Fe from the solution. The relative standard deviations are similar to those for the first cycle of the PCF as (Table 9), with Mn and Ba being substantially better. The first cycle of the Series B extractions (Table 26) are different in many respects that the Series A results. As with ash, difficulties with different technicians or use different zones of an inhomogeneous solid may be responsible. Aside from the difference in values, the reproducibility is generally poorer. The two shale samples run in Series B were performed as blanks for the PCF and FBC trials respectively; they were not run specifically as duplicates. Efforts to treat the mixed spoil and ash trials in Series B quantitatively will be complicated by the relatively poor results for the blank shale. Use of the blank values for Series A will be used with more confidence.

**Table 25. Mean of Duplicate Shale MWLP Extractions, Series A, 100g, 1000mL**

	<b>pH<sup>1</sup></b>	<b>A<sub>c</sub><sup>2</sup></b>	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>SO<sub>4</sub><sup>-</sup></b>	<b>Sb</b>
Conc., mg/L	2.72	522	39	155	18	67	1.8	1048	<0.035
Rel. Avg. Dev.	2.0%	4.2%	1.3%	2.2%	9.8%	1.4%	2.2%	0.2%	
	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Hg</b>
Conc., mg/L	0.088	0.62	0.073	0.019	<0.014	0.024	0.20	<0.032	<0.0001
Rel. Avg. Dev.	17.7%	2.8%	1.4%	2.7%		4.2%	3.2%		
	<b>Ni</b>	<b>Se</b>	<b>Ag</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>			
Conc., mg/L	0.34	<0.045	<0.045	0.12	<0.011	0.98			
Rel. Avg. Dev.	6.6%			13.7%		3.9%			

1 pH units.

2 Calculated acidity, as mg/L CaCO<sub>3</sub>

**Table 26. Mean of Duplicate Shale MWLP Extractions, Series B, 100g, 1000mL**

	<b>pH<sup>1</sup></b>	<b>A<sub>c</sub><sup>2</sup></b>	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>SO<sub>4</sub><sup>-</sup></b>	<b>Sb</b>
Conc., mg/L	3.3	323	52	340	1.5	41	2.3	1135	<.001
Rel. Avg. Dev.	9.1%	4.4%	3.6%	22.8%	15.8%	10.4%	4.4%	4.8%	
	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Cd</b>	<b>Cr<sup>3</sup></b>	<b>Cu<sup>3</sup></b>	<b>Pb<sup>3</sup></b>	<b>Hg</b>
Conc., mg/L	<.005	0.90	<.05	0.014	<.10	0.39	0.002	0.026	0.29
Rel. Avg. Dev.		9.3%		0.0%					3.4%
	<b>Ni</b>	<b>Se</b>	<b>Ag</b>	<b>Tl</b>	<b>V<sup>3</sup></b>	<b>Zn</b>			
Conc., mg/L	<.01	<.002	<.01	<.10	0.001	0.12			
Rel. Avg. Dev.						16.7%			

1 pH units.

2 Calculated acidity, as mg/L CaCO<sub>3</sub>

3-One measurable value

Series A extractions of shale also used 1500 mL. A comparison of the results of the 1000 mL extraction and the 1500 mL extraction (Table 27) reveals a good consistency, reaffirming that most of the constituents are concentration dependent. Iron, arsenic and thallium are most problematic, but iron is removed, so the great majority is now in the precipitate and thallium has only one measurement rather near its limit of detection (although thallium was unusual for ash as well, Table 23). Arsenic requires more study. When the values in

**Table 27. Comparison of 1.0L and 1.5L Extraction of 100g of Shale, Series A**

	pH <sup>1</sup>	Ac <sup>2</sup>	Mg	Ca	Fe	Al	Mn	SO <sub>4</sub> <sup>=</sup>	Sb
1.0L, mg/L	2.72	522	39	155	18	67	1.8	1048	<0.035
1.5L, mg/L	2.72	515	37	163	30	60	1.6	1059	<0.035
	As	B	Ba	Be	Cd	Cr	Cu	Pb	Hg
1.0L, mg/L	0.088	0.62	0.073	0.019	<0.014	0.024	0.20	<0.032	<0.0001
1.5L, mg/L	0.026	0.62	0.092	0.018	<0.014	0.026	0.21	0.0165	<0.0001
	Ni	Se	Ag	Tl	V	Zn			
1.0L, mg/L	0.34	<0.045	<0.045	0.12	<0.011	0.98			
1.5L, mg/L	0.39	<0.045	<0.045	<0.04	<0.011	1.04			

1 pH units.  
2 Calculated acidity, as mg/L CaCO<sub>3</sub>

**Table 28. Comparison of 1.0L and 1.5L Mass Extraction of 100g of Shale, Series A**

	Mg	Ca	Fe	Al	Mn	SO <sub>4</sub> <sup>=</sup>	B	Ba	Be
1.0L, mg	2.5	106.41	-150.78	28.16	0.15	-481	0.369	0.063	0.0095
1.5L, mg	0.7875	171.788	-207.56	32.2	0.59	-705	0.55	0.123	0.0135
	Cr	Cu	Ni	Zn					
1.0L, mg	0.018	0.0175	0.1505	0.258					
1.5L, mg	0.0293	0.04425	0.30675	0.307					

Table 26 are normalized (Table 28) and expressed as mass changes, by subtracting out the concentrations in the mine drainage (Table 4), the iron anomaly disappears. Constituents which were not measurable (such as Se) are excluded. Other difficult results appear, notably for Mg. In this instance the subtraction for 1.5 L lowers the Mg value to precariously near zero, thus the mass is low. The concentration values (Table 26) are 39 and 37 mg/L. The mine drainage originally contained 36.6 mg/L. In the case of Mg, no Mg is added and small variations of concentration result in large variations in mass. Manganese behaves similarly. Many of the mass ratios are near 1.5. As with ash, calcium is added and sulfate removed. Gypsum is supersaturated with a ratio of 1.69 for the one liter extraction and 1.8 for the 1.5L extraction. These values compare to the lowest supersaturation values for PCF ash (Table 10). Exact use of ionic strength values could lower the ratio. The Series B extractions, using the mean values for Ca and sulfate from Table 24 yield a supersaturation value of 4.0.

The equivalent results for sandstone (Table 29 for Series A and Table 30 for Series B), show that the two spoil materials behave similarly in the MWLP test.

**Table 29. Mean of Duplicate Sandstone MWLP Extractions, Series A, 100g, 1000mL**

	<b>pH<sup>1</sup></b>	<b>A<sub>c</sub><sup>2</sup></b>	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>SO<sub>4</sub><sup>=</sup></b>	<b>Sb</b>
Conc., mg/L	2.81	488	46	178	40	49	1.8	1043	<0.035
Rel. Avg. Dev.	0.5%	3.9%	0.5%	5.4%	5.8%	2.4%	0.8%	0.7%	
	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Hg</b>
Conc., mg/L	<0.047	0.56	0.05	0.01	<0.014	0.02	0.13	<0.032	<0.0001
Rel. Avg. Dev.		1.9%	0.04	7.7%		2.0%	7.8%		
	<b>Ni</b>	<b>Se</b>	<b>Ag</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>			
Conc., mg/L	0.38	<0.045	<0.045	0.02	<0.011	0.94			
Rel. Avg. Dev.	5.5%			0.0%		4.6%			

1 pH units.

2 Calculated acidity, as mg/L CaCO<sub>3</sub>

Sandstone in Series A has marginally higher pH, lower acidity, more nickel and less thallium than shale. The other differences are small, most are within the limits of the deviations. Series B sandstone has a lower acidity, more calcium, less iron, far less chromium and more nickel than Series A sandstone. The two materials are not substantially different.

Sandstone shows the equal concentration regardless of volume relationship seen for shale and the ashes. None of the Series A extractions went beyond one cycle, so constituent depletion was not seen, as was, for example, the case for thallium in PCF ash. Extraction at differing v/m ratios for Series A (Table 31) generated results consistent with concentration dependent process control, as with shale and most constituents for the PCF ash.

### Mixtures of Ash and Spoil

The critical question in the ash/spoil mixtures is whether, and possibly how, spoil influences the ash constituent release or accumulation. The answers and the ability to derive them are intricately bound within the chemistry and reproducibility of the MWLP extractions of both the spoil and the ash.

Series A conducted trials using 50g of sandstone or shale with PCF ash in duplicate using v/m ratios of 6.7 (1000 mL/150g) and 10 (1500 mL/150g). Series B had no replicates, but added shale and sandstone in varying amounts at constant v/m (10).

The reproducibility of the Series A v/m = 10 shale mix (Table 32) and sandstone mix (Table 33), as well as the first cycle results can be compared to the pure ash

**Table 30. Mean of Duplicate Sandstone MWLP Extractions, Series B, 100g, 1000mL**

	<b>pH<sup>1</sup></b>	<b>A<sub>c</sub><sup>2</sup></b>	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>SO<sub>4</sub><sup>-</sup></b>	<b>Sb</b>
Conc., mg/L	3.33	239	43.4	342	6.11	46	2.11	1080	<0.005
Rel. Avg. Dev.		9.5%	18.9%	20.2%	5.4%	7.3%	5.2%	1.9%	
	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu<sup>3</sup></b>	<b>Pb<sup>3</sup></b>	<b>Hg<sup>3</sup></b>
Conc., mg/L	<0.005	0.80	<0.1	0.011	<0.1	<0.1	0.05	0.001	0.0002
Rel. Avg. Dev.		8.3%		4.8%					
	<b>Ni<sup>3</sup></b>	<b>Se</b>	<b>Ag</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>			
Conc., mg/L	0.18	<0.002	<0.01	<0.1	<0.1	0.44			
Rel. Avg. Dev.						91.0%			

1 pH units. One obviously bad result (7.41) was rejected.

2 Calculated acidity, as mg/L CaCO<sub>3</sub>

3-One measurable value

**Table 31. Comparison of 1.0L and 1.5L Extraction of 100g of Sandstone, Series A**

	<b>pH<sup>1</sup></b>	<b>A<sub>c</sub><sup>2</sup></b>	<b>Mg</b>	<b>Ca</b>	<b>Fe</b>	<b>Al</b>	<b>Mn</b>	<b>SO<sub>4</sub><sup>-</sup></b>	<b>Sb</b>
<b>1.0L, mg/L</b>	2.81	488	46	178	40	49	1.8	1043	<0.035
<b>1.5L, mg/L</b>	2.78	494	45	182	51	44	1.8	1066	<0.035
	<b>As</b>	<b>B</b>	<b>Ba</b>	<b>Be</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Pb</b>	<b>Hg</b>
<b>1.0L, mg/L</b>	<0.047	0.56	0.05	0.01	<0.014	0.02	0.13	<0.032	<0.0001
<b>1.5L, mg/L</b>	<0.047	0.48	0.03	0.01	<0.014	0.02	0.13	0.02	<0.0001
	<b>Ni</b>	<b>Se</b>	<b>Ag</b>	<b>Tl</b>	<b>V</b>	<b>Zn</b>			
<b>1.0L, mg/L</b>	0.38	<0.045	<0.045	0.02	<0.011	0.94			
<b>1.5L, mg/L</b>	0.34	<0.045	<0.045	0.03	<0.011	0.83			

1 pH units.

2 Calculated acidity, as mg/L CaCO<sub>3</sub>

results (Table 8). The initial pH is lower for both systems with added spoil than for the pure material by 0.86 pH units (sandstone) and 1.49 units (shale). All trials are conducted at v/m of 10 using a volume of 1.5L. The pH is similar to the pH found for the v/m = 15 (Table 18). No conclusion can be drawn based on the data as to whether the v/m ratio or addition of spoil, the results of Ziemkiewicz and Knox (3) at v/m = 200 do not approach pH=0. Neither the pure sandstone

**Table 32. Mean of Duplicate PCF Ash (100g)-Shale (50g) MWLP Extractions, Series A, 1st Cycle,1500mL**

	pH <sup>1</sup>	A <sub>c</sub> <sup>2</sup>	Mg	Ca	Fe	Al	Mn	SO <sub>4</sub> <sup>=</sup>	Sb
Conc., mg/L	5.09	13.0	73	627	<0.1	1.6	2.1	1523	<0.035
Rel. Avg. Dev.	0.8%	10.3%	0.08%	13.7%		15.0%	0.2%	0.5%	
	As	B	Ba	Be	Cd	Cr	Cu	Pb	Hg
Conc., mg/L	<0.047	6.1	0.032	<0.011	0.016	0.019	<0.015	<0.032	<0.0001
Rel. Avg. Dev.		2.2%	4.8%		3.2%	2.7%			
	Ni	Se	Ag	Tl	V	Zn			
Conc., mg/L	0.35	<0.045	<0.045	0.097	0.16	0.34			
Rel. Avg. Dev.	2.5%			3.6%	8.3%	0.7%			

1 pH units.

2 Calculated acidity, as mg/L CaCO<sub>3</sub>

**Table 33. Mean of Duplicate PCF Ash (100g)-Sandstone (50g) MWLP Extractions, Series A, 1st Cycle,1500mL**

	pH <sup>1</sup>	A <sub>c</sub> <sup>2</sup>	Mg	Ca	Fe	Al	Mn	SO <sub>4</sub> <sup>=</sup>	Sb <sup>3</sup>
Conc., mg/L	5.72	4.5	74	620	<0.1	0.17	1.9	1603	0.02
Rel. Avg. Dev.	0.5%	4.8%	0	5.6%		11.8%	2.9%	0.8%	
	As	B	Ba	Be	Cd	Cr	Cu	Pb	Hg <sup>3</sup>
Conc., mg/L	<0.047	6.0	0.025	<0.011	<0.014	0.028	<0.015	<0.032	0.0001
Rel. Avg. Dev.		1.7%	8.0%			7.1%			
	Ni	Se	Ag	Tl <sup>3</sup>	V	Zn			
Conc., mg/L	0.36	<0.045	<0.045	0.041	0.20	0.12			
Rel. Avg. Dev.	3.2%				0.3%	52.2%			

1 pH units.

2 Calculated acidity, as mg/L CaCO<sub>3</sub>

3 Only one value

nor shale are alkaline to any degree (Tables 25 and 29), but they raise the pH of the extraction solution. The calculated acidities of the spoil attenuated samples track well with pH, as expected, since iron is not measurable detectable and the aluminum concentration is small.

The calcium and magnesium release from the ash-spoil mixture is substantially smaller than for pure ash (Table 34). The largest relative average deviation is for

**Table 34. Ca, Mg and Sulfate Release<sup>1</sup> from Series A PCF Ash, Ash-Spoil Mixtures and Pure Spoil.**

	<b>PCF Ash</b>	<b>Ash-Sandstone<sup>2</sup></b>	<b>Ash-Shale<sup>2</sup></b>	<b>Pure Sandstone<sup>3</sup></b>	<b>Pure Shale<sup>3</sup></b>
Calcium, mg/L	702	620	627	178	155
Magnesium, mg/L	77	74	73	46	39
Sulfate, mg/L	1915	1603	1523	1043	1048
Supersaturation	14	10.4	9.95	1.9	1.7

1 All are v/m = 10, first cycle

2 100g ash, 50 g spoil

3 100g spoil

the ash-shale mixture (13.7%). One deviation brings that value close to the value for pure ash, but the small relative deviation for pure ash (1.4%) still causes the value to still lie outside those of either mixture. The lowering of the calcium release may be significant. At the least, calcium release is not the linear sum of the two mixture components (ash-shale should be 779 mg/L Ca if that were true).

The calcium in the system is probably controlled by gypsum solubility, as discussed earlier (Table 34 and see Table 10), however the system appears to be significantly supersaturated in all trials. If gypsum were in equilibrium, the calcium and sulfate concentrations would be equal in all solutions, since the concentrations would be controlled by the solid gypsum. The degree of supersaturation scales roughly as the fraction of ash in the mixture, pure ash has a supersaturation value of 14, whereas the 2/3 ash mixtures have values around 10. Series B for PCF does not demonstrate the same trend (Figure 16), although for 75g of added sandstone supersaturation is lower. The degree of supersaturation for the pure ash is much lower than in Series A. Shale has an anomalous Ca value for pure ash, but also shows a decrease of supersaturation at higher values of added shale (Figure 17). The FBC ash with added shale maintains a high supersaturation at all added sandstone levels. Sandstone behaves similarly with a bit smaller supersaturation value.

FBC ash is extremely alkaline and overwhelms the added spoil to completely control the sulfate-calcium system in the extractions. PCF has far less alkalinity and whatever physical aspect of spoil causes the supersaturation to diminish, it has a much greater effect on PCF than FBC.

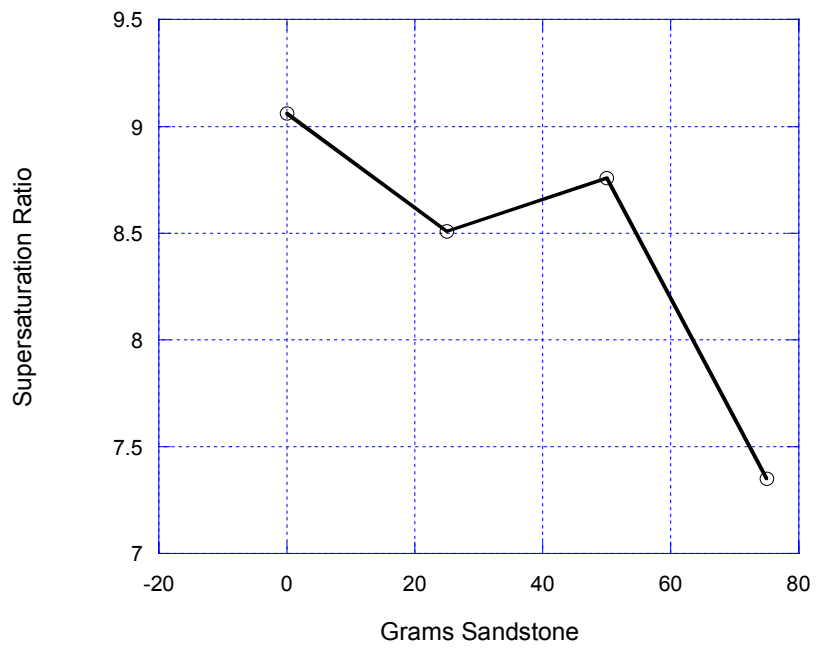


Figure 16. Change of gypsum supersaturation ratio with added sandstone. Series B, 100g PCF.

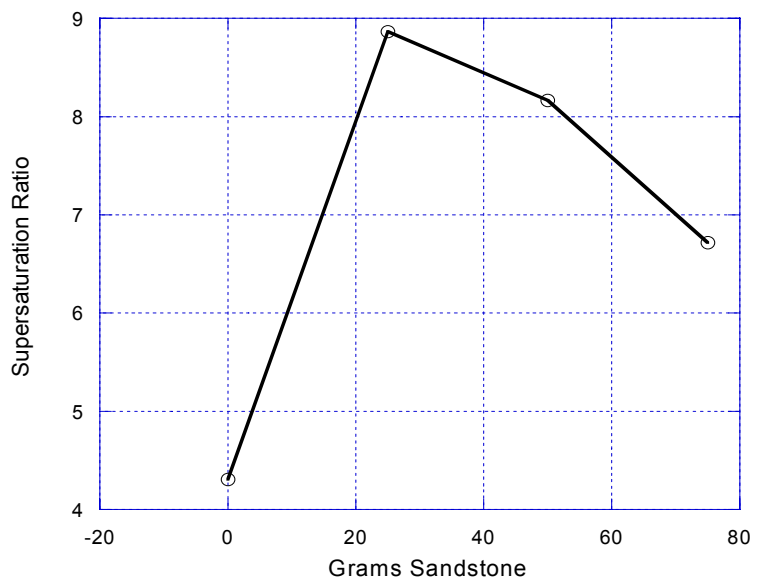


Figure 17. Change of gypsum supersaturation ratio with added shale. Series B, 100g PCF



Magnesium in Series A behaves as if it were controlled by some solubility process. If Mg just leached with independent control for each substance, the amount of Mg would expect to be additive. The concentration of magnesium in Series A is independent of added spoil. This trend is also true for Series B Mg with PCF (Figure 18) (although the Mg concentration is near 60 mg/L rather than 74 mg/L). FBC ash in Series B shows a constant magnesium concentration versus spoil added, but the Mg concentration is near 1 mg/L because it is controlled by precipitation of magnesium hydroxide at the high pH of the FBC trials (pH near 10).

The release of the Ca, Mg and the removal of sulfate over the cycles (Table 35) for Series A reiterates the response from Table 36, but shows a general

**Table 35. Ca, Mg and SO<sub>4</sub><sup>=</sup> Versus Cycle for PCF-Spoil Mixtures, Series A**

AMD <sup>1</sup>	Ca			Mg			SO <sub>4</sub> <sup>=</sup>		
	Ash	SS <sup>2</sup>	SH <sup>3</sup>	Ash	SS <sup>2</sup>	SH <sup>3</sup>	Ash	SS <sup>2</sup>	SH <sup>3</sup>
	702	620	627	77.2	74.1	73.3	1915	1603	1523
1	332	280	282	53.9	49.2	48.2	955	956	951
2	168	140	151	31.9	30.6	32.4	922	936	912
3	193	175	174	36.8	34.6	33.3	965	928	896
4	226	233	238	39.5	42.8	43.4	1004	973	979
5	186	210	145	39.3	46.8	35.9	1151	1094	1080
6	159	151	184	36.8	34.6	41.2	1052	1055	1028
7									
Total, mg	1588	2200	2189	64.1	84.9	77.5	-2728	-4738	-5002

1 Concentration in mine drainage in mg/L  
2 Ash– Sandstone  
3 Ash- Shale  
4 Total mass over 7 cycles, mg.

equalization of concentration for Ca in later cycles. As the pH decreases with increasing cycle, the supersaturation difference between pure ash and ash-spoil mixture disappears. The calcium mass release conforms to the 1:1.5 volume ratio for ash versus mixture. Magnesium has a surge in cycle 1 for all cases, which then decreases in subsequent runs to approximately the value of the original water. Apparently very little, if any, Mg is released although large amounts still were found in the ash (Table 3) and the spoil (Table 24). The mass released for Mg is variable because of the bounce around zero when the drainage concentration is subtracted. As a result, the mass does not conform to the 1.5 ratio and is overly influenced by the surge in Cycle 1.

Sulfate is removed from solution and conforms to the 1.5: 1 ratio, although an argument can be made that sandstone is less efficient than shale. To state that with certainty would require further study. Sulfate exemplifies the behavior of all constituents that are removed from solution. Beyond the contribution of alkalinity to the solution, the processes responsible for removal all are related to precipitation or some physical process. Iron is removed completely and is not influenced by the addition of sandstone or shale.

Of the constituents removed from solution only manganese has enough data to evaluate quantitatively. Manganese conforms to the 1.5:1 mass ration. The ash loses 2.7 mg, the ash-sandstone loses 4.0 mg and ash-shale lose 4.3 mg. The concentration of Mn in the first cycle of the mixtures (see Tables 32 and 33) greatly exceeds the concentration in the first cycle of the ash extraction (0.5 mg/L). This may be a pH effect. Manganese may be lost more quickly to the higher pH pure ash system, which is perfectly compatible with metal ion chemistry.

The other removed constituents, Sb, Cd, Cu, Pb, Se, Ag and Zn are either completely removed from solution in one or more of the trials or present in small, sub-mg/L amounts. Spoil should not affect their removal other than to attenuate it, which is difficult to prove with the available data. The ability of solid spoil to adsorb ions is sometimes considered, but nothing in the data indicates this pathway. The FBC ash behaved in exactly the same way, although removal tended to be complete in all samples, since the pH was near 10 rather than 6 and below.

The first cycle concentrations and full extraction mass losses for the constituents that are added to solution from the solids (Table 36). The results are similar to those discussed for Table 22. The addition of spoil lowers the initial release of all of the elements except aluminum, barium, vanadium, perhaps thallium and trivially beryllium. These elements are likely controlled by solubility or some concentration dependent release mechanism. Aluminum should be less soluble in the higher pH ash solution. Its mass release conform to the 1.5:1 ration, indicating a normal release behavior. Barium approaches the 1.5:1 ratio of the extraction volume for the mass release; the low value of 0.15 is easily affected by the reproducibility, which is low at that concentration (Table 9, recognizing that only seven, not eight cycles are used here). The apparent divergence of vanadium from the 1.5:1 ration is the result of numerous measurements that were below the analytical detection limit. Those values were taken to be zero in the mass calculation, so any actual measurements are artificially veremphasized. Beryllium behaves as in the pure ash case; enough of the total Be in the ash is released to skew the ratio lower. Thallium may have an outlier analytical result; nothing about shale would suggest such a large value. The mass result for TI is like the result found in Table 23. Like Be, TI has a large fraction of its total released to the solution, which makes the ratio of released masses nearer a ratio of one.

**Table 36. Constituents Added to Solutions from PCF Ash/Spoil Mixes, Series A**

<b>First Cycle Concentrations, mg/l</b>								
	<b>Al</b>	<b>Ba</b>	<b>Be</b>	<b>B</b>	<b>Cr</b>	<b>Ni</b>	<b>Tl</b>	<b>V</b>
Ash	0.27	0.022	0	7.76	0.092	0.088	0.046	0.22
Ash/SS	0.17	0.025	<0.011	6.0	0.028	0.36	0.041	0.20
Ash/SH	1.6	0.032	<0.011	6.1	0.019	0.35	0.097	0.16
<b>Total Mass Release, Seven Cycles</b>								
	<b>Al</b>	<b>Ba</b>	<b>Be<sup>2</sup></b>	<b>B</b>	<b>Cr<sup>2</sup></b>	<b>Ni</b>	<b>Tl<sup>2</sup></b>	<b>V<sup>1</sup></b>
Ash, mg	81	0.15	0.062	12.5	0.23	1.22	0.53	0.20
Ash/SS, mg/L	133	0.31	0.077	13.7	0.42	1.75	0.47	0.27
Ash/SH, mg/L	133	0.34	0.079	13.9	0.39	1.70	0.66	0.20
1 Many measurements below the detection limit								
2 Occasional measurement below detection limit								

The reduction of the release of Ni, B and Cr in the first cycle with the addition spoil has no obvious explanation. Nickel and chromium do, after the seven cycles, have a mass release relationship of 1.5, which indicates that the release readjusts after the first cycle inhibition. Boron, as noted above, is exhausted from the ash and has a mass ratio of one. The presence of spoil would seem to merely postpone its release.

## Conclusions

The Mine Water Leaching Procedure successfully leaches major and trace species from fly and fluidized bed combustor ash. The method provides a template for generating the data to meet the requirements of regulators and address the uncertainties of the national Academy of Sciences panel. The conundrum is that the panel had concerns about long term behavior, yet all short term field behavior is acceptable. The panel worried about circumstances that cannot yet be tested in the field. In the absence of long term field data, the only mechanism by which information can be gleaned about extended behavior is to extrapolate laboratory and short term field data based on sound scientific principles. The most realistic laboratory test is the MWLP, although the final, best method is yet to be developed.

If the objective of the MWLP is to provide legitimate predictive insights regarding the fate of CCBs in mines, then the method has requirements beyond those for a TCLP or SPLP. One requirement is reproducibility. The disagreement between

Series A and B, which used nominally the same acid water and ash, must be removed, whether the result of inconsistent method application, lack of homogeneity in the ash, or deterioration of the mine water. Intra-series reproducibility was good, but the method must be able to be reproduced between laboratories, which means inter-series reproducibility must be improved. The inability to distinguish differences in mean values due to poor series to series reproducibility inhibits data evaluation. Studies should be conducted to determine the sources of the error in order to eliminate it.

The volume of extracting solution is immaterial, within limits. Only constituents that were depleted in the solid material, notably boron and thallium, behaved in a mass limited way. Other constituents maintained the same concentration in solution regardless of volume used. Certain ions (iron, sulfate) are removed from the drainage solution via precipitation. Some metals (zinc) appear to be removed from solution due to co-precipitation. Most of the trace metals are present in such low concentrations that meaningful analysis is difficult. Studies using spiked mine drainage are recommended if in-depth chemical behavior of the trace elements is desired.

Sulfate is removed from the mine water via precipitation with calcium (as gypsum) and to a much lesser degree barium (as barite). Calcium and barium are added to solution from the solid ash or mine spoil. Calcium is presumably added as CaO, i.e. alkalinity. In every instance gypsum is supersaturated in the extracting solutions. The degree of supersaturation is greatest at higher pH and in the absence of spoil. The influence of the supersaturated solution on downstream ash or mine drainage is unknown.

Spoil has minimal effect on the leaching of the ash. Where spoil does have an effect, usually at early cycles, it has no longer term effect. Although spoil when subjected to the MWLP leaches the same substances as the ash, mixtures of spoil and ash do not undergo additive leachings. The elements behave as if controlled by their ash content or some solubility-like mechanism where the amount of solid present is immaterial.

The continuing major difference in the measured and calculated acidities must be addressed. Long term predictions require accurate knowledge of the pH and acidity of the incoming and treated water. Whether the field water behavior is reflected in the measured acidity or the calculated acidity is unknown. Acidity has traditionally been used as an indicator of certain properties of the water; its use in prediction is uncommon.

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