

Inter-laboratory Comparison of Leaching Methods

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ABSTRACT

There is a recognized need for coal ash producers, handlers, and regulators to have a useful and effective characterization tool for leaching behavior of coal ashes. To address this need, an inter-laboratory study has been undertaken by five voluntary laboratories to primarily compare four leaching methods. The participants are the National Energy Technology Laboratory (NETL), the University of North Dakota Energy & Environmental Research Center (UND EERC), the University of the Western Cape Department of Chemistry, Virginia Tech Department of Crop and Soil Environmental Sciences, and the West Virginia Water Research Institute National Mine Land Reclamation Center (WVWRI). The methods being compared are those developed at NETL, WVWRI, UND EERC, and the 3-tier procedure published by Kosson, van der Sloot, Sanchez, and Garrabrants (2002, *Environ Eng Sci*, Vol. 19, No. 3, 159-204). The TCLP has been included in some laboratory comparisons. Preliminary results from applying the leaching methods to coal combustion by-products have been summarized.

1. INTRODUCTION

A large number of leaching methods have been developed and tested during the past 40 years, and many of these methods have been described in general reviews.¹⁻⁷ The initial work during the 1960s and 1970s was directed mainly to devising tests for specific purposes and scenarios.^{3,8} Some methods are regulatory driven or provide detailed characterization of a solid phase, but may not be suitable as evaluation tools for initial utilization, material reuse, or disposal and management scenarios.⁸⁻¹¹ International efforts on coal utilization by-products (CUB),^{4,10,12,13} as well as extensive work on incinerator ash and metallurgical process streams have recognized the

limitations of established regulatory methods. This situation has led to the development of a large number of tests that generate data which are difficult to correlate.^{2,4,10,14} There has been a recognized need for a single screening method that can be used for decision making, establishing leaching trends, and quality control.^{2,8,15-18}

In the past twenty years, the International Ash Working Group (IAWG) and others have made a concerted effort to devise leaching techniques that give systematic results and can be applied to a wide variety of wastes and reusable materials. A comparative study of European leaching tests supported the dominant influence of pH in determining the release behavior of metals from an ash.¹⁹ Kosson and co-authors²⁰ have recently provided a multi-tiered approach to address successively more specific leaching conditions. Hassett²¹ provided a leaching method and compared its use with results from the EPA-EP, the TCLP, and an ASTM procedure, concluding that leaching tests should be matched to field conditions. A later report by this author²² included a discussion in greater depth of the importance of matching a procedure's leaching solution to the intended future environment of a material.

In support of the continued interest in leaching methods used to characterize the release of heavy metals from coal utilization by-products (CUB) the National Energy Technology Laboratory (NETL) initiated an inter-laboratory comparison of several leaching methods. By 2003, NETL had been contacted by a number of laboratories expressing potential interest in participating in such a study. Early in 2004, NETL distributed details of this comparative evaluation of methods to interested parties, and the group of laboratories willing to be part of this informal arrangement was firmly established. The intent of the study is to determine if the various methods produce comparable data and to allow each participant to both gain information about how leaching methods relate to each other and evaluate the sensitivity, precision, time required, simplicity, and applicability of the several procedures. Section 2 lists the participating laboratories, summarizes the distributed procedures and provides some general parameters of the study. Sections 3-6 are reports from these laboratories that contain further background, lab-specific experimental details and insights from the participants.

2. PARTICIPANTS AND LEACHING METHODS

The participants are the National Energy Technology Laboratory (NETL), the University of North Dakota Energy & Environmental Research Center (UND EERC), the University of the Western Cape Department of Chemistry, Virginia Tech Department of Crop and Soil Environmental Sciences, and the West Virginia Water Research Institute National Mine Land Reclamation Center (WVWRI). The methods being compared are those developed at NETL, WVWRI, UND EERC, and the 3-tier procedure published by Kosson, van der Sloot, Sanchez, and Garrabrants (2002, *Environ Eng Sci*, (Vol. 19, No. 3, 159-204). In addition, several participants added the TCLP to the methods being compared. The method descriptions are summarized below:

Mine Water Leaching Procedure (Paul F. Ziemkiewicz, Jennifer S. Simmons, West Virginia Water Research Institute National Mine Land Reclamation Center; Anna S. Knox, Savannah River Ecology Laboratory University of Georgia) evaluates behavior of an ash in a replenishing acidic media, such as acid mine drainage.

100g sample, 2L mine water or 0.002N H₂SO₄, liquid to solid ratio (L/S) = 20, end-over-end mixing, 30 rpm for 18 hr, filter at 0.7 um, measure pH and analyze leachate, add fresh liquid to solids and repeat until leachate pH is equal to 3.

Serial Batch Leaching Procedure (Peter A. Hesbach, Steven C. Lamey, National Energy Technology Laboratory) is intended as a rapid screening procedure most applicable for granular material in an environment where there is replenishment of the leaching media.

Availability (alkaline ash) – 9 g sample, 450 mL DI H₂O, L/S = 50
magnetic stirring, 250 rpm, uncontrolled pH for 2 hr, filter at 0.45um, measure pH and analyze leachate,
add fresh liquid to solids, control pH at 8 with HNO₃, stir 3 hr, filter,
repeat, controlling pH at 4 for 2 hr, filter
repeat, controlling pH at 2 for 2 hr.

Long Term Simulation - 45g sample, 90 mL DI H₂O, L/S = 2
bottle roller for 6 hr, filter at 0.45um,
measure pH and analyze leachate,
add fresh liquid to solids, L/S = 8, roller for 18 hr, filter,
repeat, L/S = 10, roller for 24 hr.

- 10g sample, 1 L DI H₂O, L/S = 100
bottle roller for 24 hrs, filter, analyze.

Synthetic Groundwater Leaching Procedure and Long Term Leaching (David J. Hassett, University of North Dakota Energy & Environmental Research Center) was developed as a simulation of actual field conditions, and addresses the incorporation of species into insoluble molecular matrices in a more static and arid environment. SGLP - 100g sample, 2L DI H₂O, L/S = 20, end-over-end, 30 rpm, 18hr, filter at 0.45um, measure pH and analyze leachate.

LTL – repeat above for 30 and 60 days.

3-Tier Leaching Protocol (D.S. Kosson, H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants, “An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials,” 2002, Environ Eng Sci, Vol. 19, No. 3, 159-204) is an extensive examination of factors affecting leaching behavior.

Titration curve pretest – 8g sample, 800mL DI H₂O, pH 2-12.

Availability – titration curve, pH 5-9, 8g sample, 800mL 0.5M EDTA, L/S = 100, pH 7, 7.5, 8.

Leachability A – 40g sample, 400mL DI H₂O, L/S = 10,

Adjusted for target final pH, each pH unit 3-12 plus natural pH, 11 samples.

Leachability B – DI H₂O, 40g, L/S = 10; 40g, L/S = 5; 50g, L/S = 2; 100g, L/S = 1; 200g, L/S = 0.5.

For avail. L-A, L-B – end-over-end, 28 rpm, 48 hr, filter at 0.45um, measure pH and analyze leachates.

The Integrated Framework has other procedures, such as leaching of monoliths, which are not part of this comparative study, and a discussion of the possible applications of the various tiers of the method.

Toxicity Characteristic Leaching Procedure (EPA Method 1311) provides leaching data on material as would occur with co-disposal in a municipal waste landfill. pH test, then 100g sample, 2L leaching fluid (acetic acid or acetate buffer), end-over-end, 30 rpm, 18 hr, measure pH and analyze leachate.

The TCLP has procedural elements for multi-phase samples and extraction of organic samples, which are not relevant to this comparative study.

Method (Source)	Leaching Type	Total Steps	Minimum Time	Sample Per Rep	Leachants
MWLP (VWVRI)	Serial batch	Varies	Varies 1 d / cyc.	100 g	H ₂ O H ₂ SO ₄
SBLP (NETL)	Serial batch	8	2 d	65 g	H ₂ O HNO ₃
SGLP (EERC)	Batch	3	60 d	300 g	H ₂ O
3-Tier (Kosson et.al.)	Titration + Batch	2 19	2 d / run 14 d?	900 g	H ₂ O EDTA HNO ₃ KOH
TCLP (EPA)	Batch	1	1 d	100 g	HOAc NaOAc

Figure 1. Method comparison summary.

A summary of the methods is shown in Figure 1. Each run is performed in triplicate. The analytes are: aluminum (Al), arsenic (As), antimony (Sb), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), potassium (K), selenium (Se), sodium (Na), thallium (Tl), vanadium (V), and zinc (Zn).

An Eastern coal fly ash was distributed by NETL to each participant, who each agreed to perform from 2-5 leaching methods. A Western coal fly ash was distributed to several of the

labs by UND EERC for a similar examination by multiple leaching methods. A standard of trace elements obtained from NIST was distributed to each participant to allow for a comparison of the instrumental analysis of samples from the participant laboratories. The results from the standard sample will enable the study to separate variation from instrumental performance from laboratory variations in carrying out the several leaching methods. Data from leachate analyses are entered into a common spreadsheet. This spreadsheet allows for data tabulation, performs unit conversions, and carries out other operations specific to methods, such as summations or the generation of slopes of trend lines.

3. NATIONAL ENERGY TECHNOLOGY LABORATORY RESULTS

The NETL laboratory effort characterized the study ashes by all of the leaching methods described in the previous section, including the TCLP. This discussion will be limited to results from the first ash. In this section, the acronym “SGLP” will be used to refer to the combined SGLP and LTL procedure. Figure 2 depicts results from NETL on this Eastern fly ash using the four study methods and the TCLP, and includes the analysis data from the raw ash. Data are presented in units of mg of each element per kg of ash, and represent an average of 3 replicates. When an element was found in only 1 or 2 replicates, the detected sum of these replicates is still divided by three and used as the average. Where a given element was below detection for all of the replicates of a method, it is omitted from the plot for that method. A selection was made from the data generated by the several methods to be shown on Fig. 2. The SBLP data are taken from the sum of the four static pH steps of the availability portion of that method, which include a natural pH of 10.8 and steps of pH = 8, 4, and 2. The serial batch nature of this method generates data from successive leaching of the same ash sample at progressively lower pH values. Data can legitimately be examined at only the natural pH, as a sum of natural and pH = 8, from natural, pH 8 and pH 4, or as a sum of all 4 steps, as was done in Fig. 2. Because what is leachable at pH = 4 depends in part on what has already been leached at the higher pH steps, one cannot compare only the pH = 4 leachate, for example, to the 3-Tier pH = 4 step, in which the raw ash sample is only leached at that pH value. The MWLP data are a sum of the results from the first 8 steps. After the 5th step, the leachate pH had dropped below 4, and vacillated up and down among the replicates in the range of pH = 3-4 from steps 8 through 11. The leaching occurred over a pH range of about 11.5 to 3.5. Since the MWLP is also a serial batch method, individual steps are not discrete leachings of the raw ash, but rather represent additions to a cumulative result. The 3-Tier data chosen for Fig. 2 are from the 3-Tier b portion, derived from leaching in 0.05M EDTA, designed to represent availability. The pH of this leaching process was near 7.5. The TCLP provides for both an acidified and a non-acidified analysis sample from the leachate. Selection would depend on which would provide greater sample stability prior to analysis for a given element. The highest replicate average between these two samples for each element was used in Fig. 2. The extraction fluid was No. 1, and the leaching environment was close to pH 5. The SGLP and LTL procedure provides data from three leaching times. For this figure, the largest replicate average value among the three for each element was taken. Admittedly, this choice is a very conservative (worst case scenario) use of this method, and perhaps the most arbitrary selection in the figure. This leaching occurred at pH about 11. The pH environment of the leaching procedures, be it the nearly constant, but very different values of SGLP, TCLP and 3-Tier b, the static cumulative steps of SBLP, or the dynamic cumulative range of MWLP, can be expected to have a significant influence on values of some elements, and this

effect is shown in Fig. 2. A universal observation is the significant spread between ash content and any method's leachate data for nearly every element. Calcium is a notable exception, and to a lesser extent molybdenum. The high Na value for 3-Tier b arise from the EDTA solution being derived from a sodium salt, and the high Na level for TCLP is due to solution No. 1 being a sodium acetate buffer. The similarity of values from the various methods for some elements resulted in obscuring some data points. The raw ash analysis precludes this data from providing results for B. The elements As, Sb, and Se were not detected in the raw ash analysis. The SBLP availability detected all elements except Tl, as did the SGLP and LTL procedure. The MWLP did not detect Pb or Tl, while the 3-Tier b did not detect Sb or Tl. The TCLP did not detect Pb or Sb.

The data in Figure 3 is a depiction of leaching results in units of mg of each element per kg of ash per L of leachate per hour of leaching time. The use of these units allows representation of an initial rate of release of elements. For Fig. 3, the SBLP data is from the slope of the trend from the long term leaching simulation L/S series of 2, 8, and 10. The serial batch nature of this short series, in which the same ash sample is leached at progressively larger L/S ratios means that the L/S values are cumulative, and are treated as 2, 10 (2+8) and 20 (2+8+10). These leachates had final pH values above 11. The elements Be, Cd, Mn, Ni, Pb, Sb, and Tl were all below detection in these samples and are not on Fig. 3 for this method. The MWLP is also taken from the slope of a trend line, and both Pb and Tl were below detection. The SGLP data on Fig. 3 is taken from the trend of 18 hr, 30 days and 60 days of the SGLP and LTL steps. While these data are from independent leaching events, and thus not strictly comparable to the results from SBLP or MWLP, the longer times of the LTL portion of this method are appealing parts to any examination of long term behavior and attempt to estimate release rates. Data for Tl was below detection. Also absent from this method's data on Fig. 3 are results from Al, B, Ca, Mg, Mo, Sb, and Se, all of which trended downward with time. The resultant negative slope produces values that do not plot on the figure's log scale, and may be indicative of gradual incorporation of these elements into insoluble molecular matrices, as has been discussed previously.²² The TCLP data are derived from the same values used in Fig. 2, after factoring in method parameters to arrive at the same units. From TCLP, Pb and Sb were below detection. The 3-Tier L/S series data are discrete leachings of identical duration. The lowest L/S components provided little or no leachate and the remaining samples reveal more of an inherent solubility trend rather than rate, compared to the SGLP, MWLP, or even the SBLP. While the L/S results may nonetheless be arguably the better data for the Fig. 3 comparison, the chosen data for this figure was the 3-Tier b EDTA results used previously, after the application of method parameter factors to match units. In this data set, Cd, Sb, and Tl were below detection. The high initial release rates shown for Na are due to the reasons discussed for Fig. 2. Inherent solubilities, pH effects, chemical interactions between species, kinetic factors, and other method specific factors can all be expected to influence the values depicted on Fig. 3. For a serial batch process such SBLP and especially the MWLP, as more steps are included in the trend line before taking the slope, the depletion of the soluble form of an element will necessarily flatten the cumulative release relative to cumulative L/S. This flattening results in a slope trending toward zero over time, and will depress values such as those on Fig. 3.

Figure 2. Leachate Comparison with Raw Ash Content NETL SBLP Availability Sum, UND/EERC SGLP highest Step, WVVRI MWLP Sum of 8 Steps, 3-Tier b EDTA, TCLP, and Raw Ash

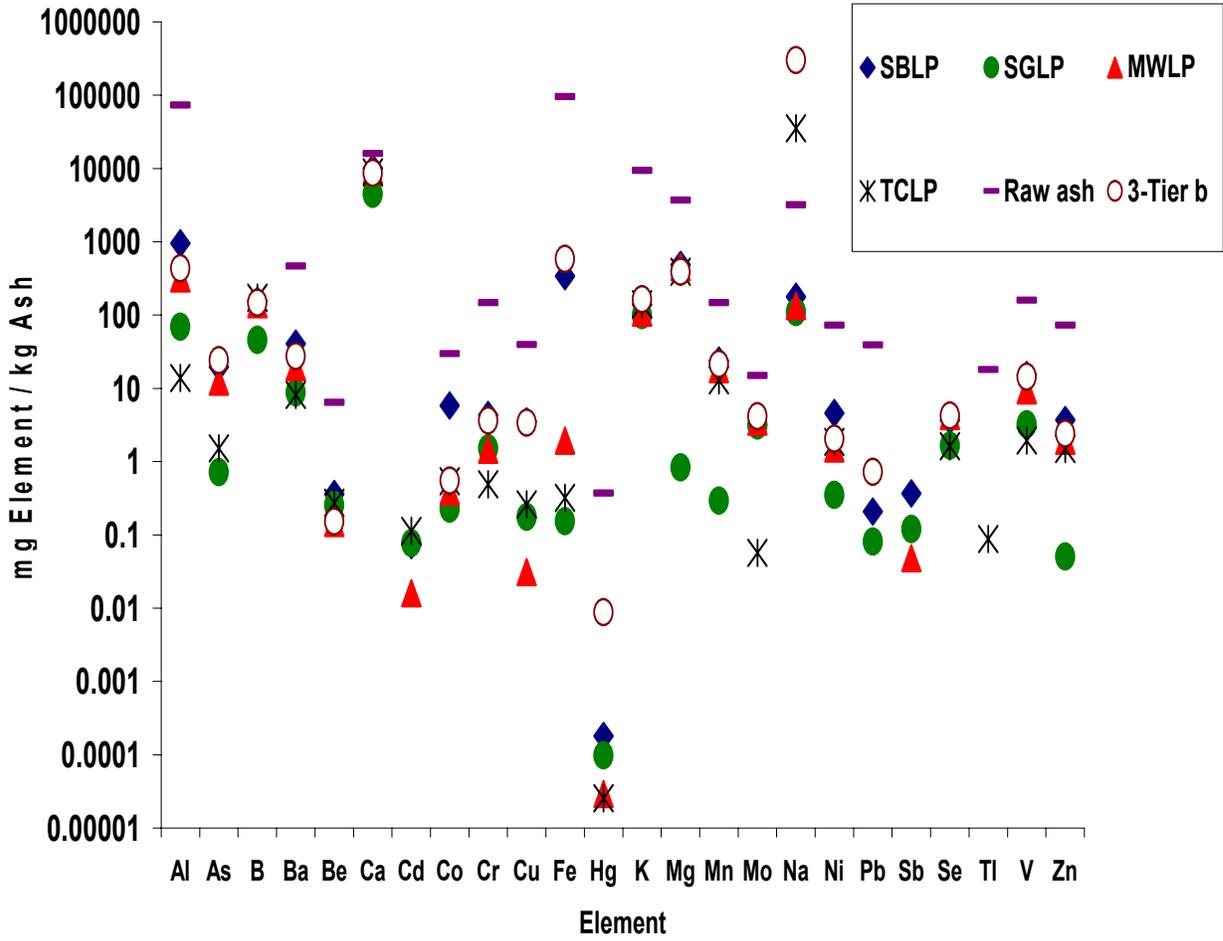
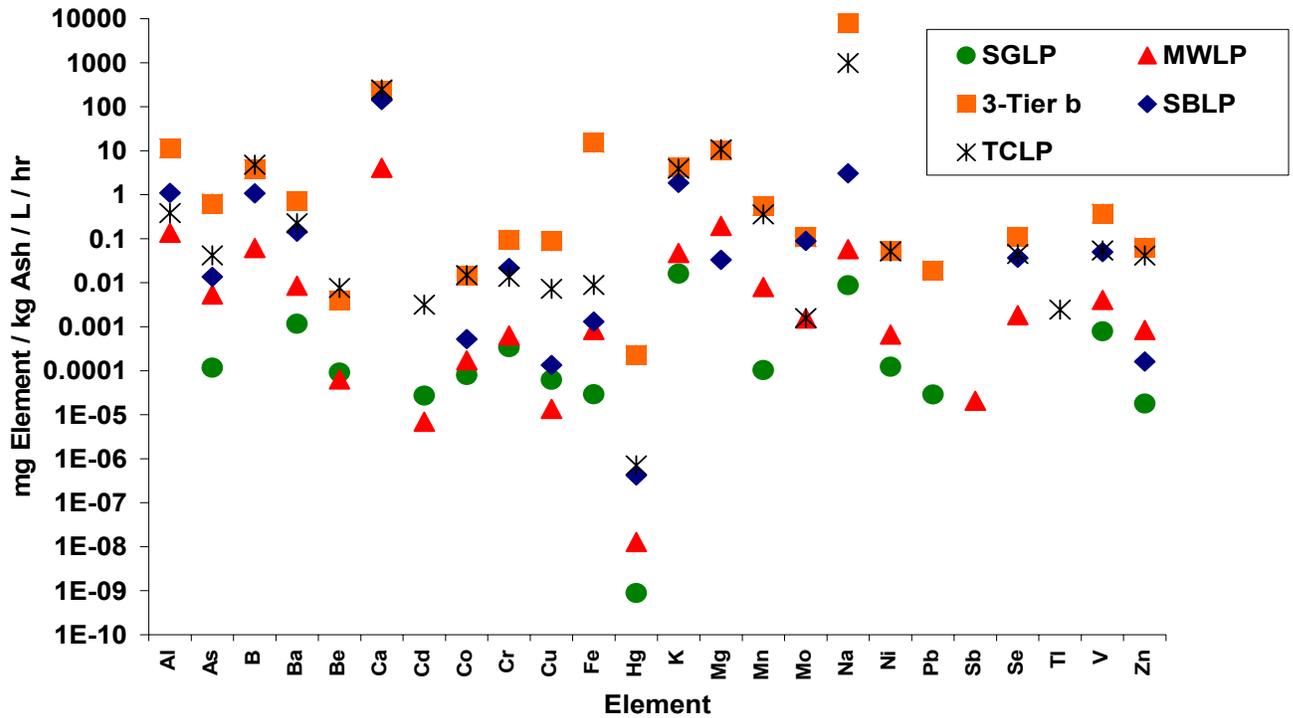


Figure 3. Comparison of Leaching Rates



4. WEST VIRGINIA WATER RESEARCH INSTITUTE RESULTS

4.1. OBJECTIVE

There are a number of laboratory leaching tests that are used to predict the leaching behavior and mobility of toxic elements associated with solid materials such as coal combustion products (CCP's). The objective of this study is to compare the performance of two leaching procedures, the Mine Water leaching Procedure (MWLP), and the combined Synthetic Groundwater Leaching Procedure (SGLP) and Long Term Leaching (LTL) Procedures, for leaching elements from a standard 100 g sample of Class F fly ash.

4.2. MINE WATER LEACHING PROCEDURE

The Mine Water Leaching Procedure (MWLP) was developed and designed to determine the long-term leaching potential of toxic elements associated with CCP's when exposed to acid mine water in saturated field environments.

One hundred grams of coal combustion fly ash from a facility in the Eastern United States was combined with 2 liters of an extraction fluid created to simulate acid mine water. The acid mine water was simulated by adding 0.002 N H₂SO₄ to 2L of deionized water in a TCLP container, to

obtain a pH of approximately 3.0. The container was then sealed with Parafilm® under the lid to ensure a tight seal. Three replicates were performed for each of twelve sequential test cycles.

The three replicate containers were secured on a rotating platform and were agitated for 18 hours at 30 rpm. Upon completion of the 18-hour agitation cycle containers were removed from the rotating platform and the entire contents of each were filtered through a stainless steel pressure filtration unit at a maximum of 20 psi using 0.7 µm acid rinsed TCLP filter paper. The filtrate was then collected in 250 ml sample bottles and the pH of the sample was measured and recorded. The filtrate was then acidified with 1 ml of nitric acid to preserve the sample for metal analysis. The solids remaining on the filter paper were then rinsed back into their corresponding containers using “fresh” liters of simulated mine water. Twelve cycle runs were required in order to deplete the alkalinity and stabilize the sample pH at 3.0. All samples were preserved and sent to Sturm Environmental Services for metal analysis.

4.3. MWLP RESULTS

The averages of the three replicates in each cycle are shown in Table 1. Element concentrations at or below that of the method detection limit are displayed in gray-scale, while values above detection limit are shown in black. Results show differential leaching rates for the various elements with a general decline in concentrations. The elements As, Ba, Mg, Mn, Pb and Zn were initially slow to leach but the rate (concentration) increased in later cycles. Low concentrations of Cr, Pb and Hg were present in the initial leachate cycle however the concentrations were near the MDL, which could be the result of analytical variability associated with these elements.

4.4. COMBINED SYNTHETIC GROUNDWATER LEACHING PROCEDURE (SGLP) AND LONG TERM LEACHING (LTL)

The SGLP and LTLP were completed using 100 grams of the same fly ash used in the previous procedure leached with 2L of DI water. The ash and water were combined in three TCLP containers and sealed with Parafilm® before tightening the lid. The containers were placed on the rotating platform and tumbled for their specified durations (18, 720(SGLP), and 1440 hours (LTLP)). Once the container completed the appropriate agitation duration, it was removed from the rotating device and its contents were then filtered through a .45 µm acid rinsed TCLP filter paper. The filtrate was collected and preserved with 1 ml of nitric acid and sent to Sturm Laboratory for analysis.

4.5. SGLP AND LTLP RESULTS

Table 2 shows results for the averages of three replicates. All metals with values above the method detection limit are displayed in black print, while values below method detection limit are shown in gray-scale. Metals leached from the coal combustion fly ash with DI water include Al, As, B, Ba, Ca, Cr, Fe, K, Mg, Mo, Na, Pb, Se, V, and Zn.

Table 1. MWLP Results.

Method	MWLP	Analytical Detection Limits											
Cycle	1	2	3	4	5	6	7	8	9	10	11	12	
Replicate	Average												
Leach Time	18	18	18	18	18	18	18	18	18	18	18	18	
Al	3.543	3.620	3.147	1.067	0.290	0.303	0.223	0.073	0.080	0.173	1.770	1.613	0.050
As	0.029	0.040	0.074	0.384	0.295	0.281	0.084	0.029	0.005	0.001	0.001	0.001	0.001
B	1.173	0.727	0.610	0.386	0.188	0.124	0.065	0.101	0.100	0.100	0.100	0.117	0.100
Ba	0.253	0.100	0.100	0.027	0.050	0.043	0.097	0.090	0.197	0.440	0.267	0.190	0.100
Be	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Ca	246.7	101.7	50.00	17.00	21.97	15.27	15.93	7.970	9.320	12.000	6.737	3.720	0.010
Cd	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Co	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
Cr	0.077	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050
Cu	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
Fe	0.157	0.050	0.067	0.050	0.050	0.050	0.100	0.050	0.050	0.050	0.053	0.050	0.050
K	5.263	0.647	0.153	0.197	0.090	0.090	0.080	0.237	0.430	0.433	0.383	0.280	0.200
Mg	0.010	0.037	0.203	3.907	4.480	2.587	2.370	2.163	2.053	1.650	0.930	0.400	0.010
Mn	0.010	0.010	0.010	0.010	0.010	0.010	0.013	0.027	0.170	0.323	0.127	0.077	0.010
Mo	0.143	0.027	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Na	4.743	0.930	0.743	0.927	1.087	0.667	1.383	0.903	0.903	0.880	1.103	0.100	0.100
Ni	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040	0.040
Pb	0.004	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001
Sb	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Se	0.023	0.014	0.014	0.035	0.011	0.004	0.002	0.003	0.002	0.002	0.002	0.002	0.002
Tl	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
V	0.100	0.133	0.143	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100
Zn	0.009	0.007	0.009	0.006	0.016	0.022	0.134	0.026	0.035	0.117	0.109	0.134	0.005
Hg	0.0003	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002

** Items in Gray-scale represent values at or below that of the detection limit.

4.6. METHOD COMPARISON

A comparison of the results of the two leaching procedures indicates that higher leachate concentrations of Al, As, B, Mg, Mn and Zn resulted from the MWLP. These elements are apparently more soluble in acidic solution. The elements Ca, Fe, K, Mo, Na, Pb, Se, and V appeared to leach at about the same concentration in both the MWLP and SGLP/LTLP. Results show that the MWLP is apparently more aggressive in leaching certain elements.

Table 2. SGLP/LTLP Results.

Method Step	SGLP 1	SGLP 2	LTLP 3	Analytical
Replicate	Average	Average	Average	Detection
Leach Time	18	720	1440	Limits
Al	2.427	0.680	2.863	0.050
As	0.038	0.008	0.013	0.001
B	0.990	0.100	0.127	0.100
Ba	0.250	0.470	0.423	0.100
Be	0.005	0.005	0.005	0.005
Ca	238.0	168.7	158.7	0.010
Cd	0.005	0.005	0.005	0.005
Co	0.100	0.100	0.100	0.100
Cr	0.050	0.050	0.057	0.050
Cu	0.020	0.020	0.020	0.020
Fe	0.130	0.050	0.035	0.050
K	5.010	6.277	6.583	0.200
Mg	0.010	0.027	0.010	0.010
Mn	0.010	0.010	0.010	0.010
Mo	0.147	0.140	0.157	0.010
Na	5.753	4.710	0.933	0.100
Ni	0.040	0.040	0.040	0.040
Pb	0.004	0.001	0.001	0.001
Sb	0.005	0.005	0.005	0.005
Se	0.025	0.003	0.009	0.002
Tl	0.001	0.001	0.001	0.001
V	0.100	0.100	0.137	0.100
Zn	0.010	0.014	0.009	0.005
Hg	0.0002	0.0002	0.0002	0.0002

** Items in Gray-scale represent value at or below method detection limit.

5. UNIVERSITY OF THE WESTERN CAPE RESULTS

A COMPARISON OF THE MINE WATER LEACHING PROCEDURE CONDUCTED AT UWC AND NETL

5.1. INTRODUCTION

The University of the Western Cape (UWC) is situated in Cape Town, South Africa and chose to be part the inter-laboratory leaching study to characterise the heavy metals released from coal utilisation by-products (CUB's). South Africa burns more than 100 million tons of coal per year. This low grade coal consists of approximately 25% inorganic material which remains as waste, largely consisting of fly ash. This fly ash is then pumped as a slurry to large waste dumps where it is left to harden and weather. There are many on-going studies in South Africa and at UWC to develop new methods of waste disposal both for the fly ash, as mine backfill or alkaline material to neutralise acid mine drainage, and for the sludges remaining after neutralisation.

A secondary aim for engaging in this study is to adopt a standard leaching method for fly ash and related wastes that is more specific than the TCL (toxicity characteristic leaching) protocol. Standard leaching methods that are adapted for uni-waste disposal sites are more accurate and cost-effective in terms of monitoring and remediation.

UWC tested 3 of the prescribed methods, namely the mine water leaching procedure (MWLP), three tier leaching protocol and the synthetic groundwater leaching (SGLP) and long term leaching (LTLP) procedures. This report compares the UWC data for the MWL procedure with the data from the National Energy Technology Laboratory (NETL).

5.2. METHOD

5.2.1. Determination of moisture content

Three masses of ash were placed in evaporating dishes and heated in an oven at 100°C. The evaporating dishes were weighed after 6 hours and again after 24 hours. The mass was slightly reduced after 6 hours but didn't decrease any more after 24 hours. The moisture content is less than 1% and was thus discounted as having no effect on any experiments.

5.2.2. MWL procedure

The MWL protocol attempts to predict the leachability of metals from CUB's when in contact with acidic water. This is achieved by the sequential addition of low molarity acid to each ash sample until all alkalinity is exhausted and the final filtrate water is similar to the unreacted acid. The method was followed according to that set out in Ziemkiewicz *et al.*, 2003 with no deviations.

5.2.3. Analytical techniques

All solutions were contained in HDPE bottles of 2L in size and were agitated on a platform shaker. Solutions were double filtered through a vacuum pump filtration system, initially using No. 1 Qualitative Whatman paper filters and then with 0.45 µm membrane filters.

All samples were then analysed with a Perkin Elmer / Sciex Elan 6000 inductively coupled plasma mass spectrometer equipped with an acid-resistant cross flow nebuliser, a Rytan™ Scott-type spray chamber and a Perkin Elmer AS 90 autosampler at the University of Cape Town.

5.3. MATERIAL

All participants used one ash derived from the combustion of a bituminous coal from the eastern United States. This ash was observed to be very dark in colour, fine grained. It was surmised to have a high Fe content as it was readily magnetised by the magnetic stirrer bars used. From x-ray diffraction analysis (Figure 4) quartz, mullite, maghemite and magnetite can be identified. It is

difficult to identify the magnetite and maghemite peaks, as there is only a small quantity of each mineral in the sample and the strong mullite and quartz peaks mask their reflections.

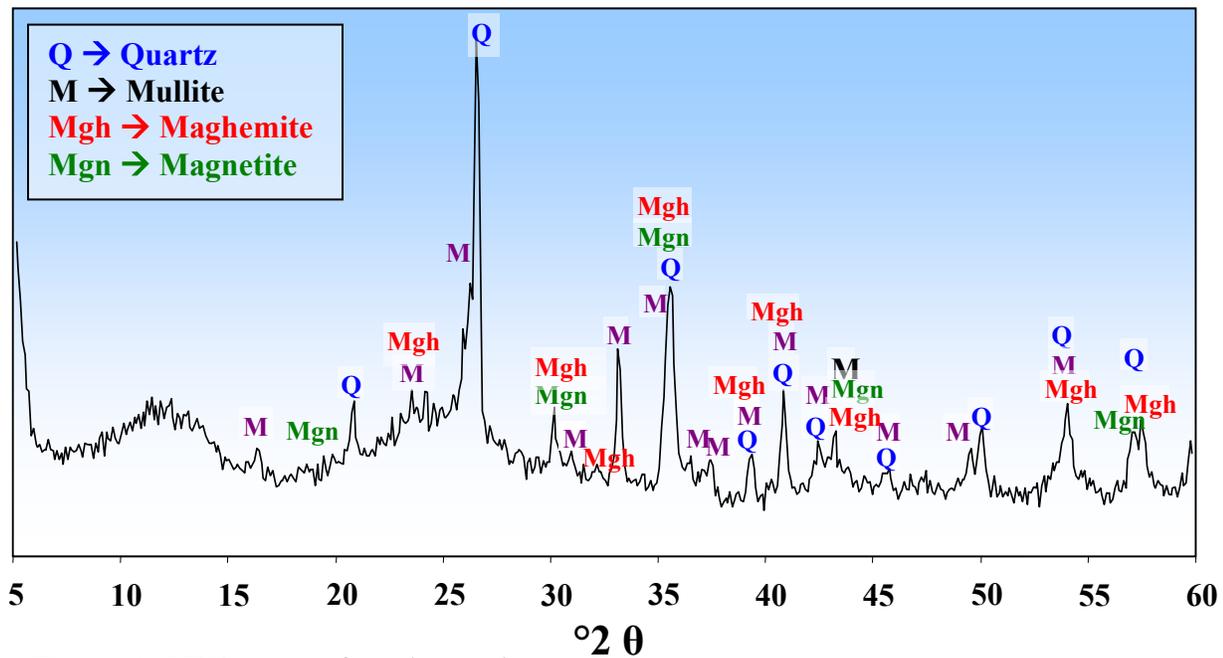


Figure 4: XRD pattern for ash sample.

5.4. RESULTS

5.4.1. Comparison of standards

In order to determine the accuracy of the data given for the ICP-MS analyses a National Institute of Standards and Technology (NIST) metal standard (1640) was analysed at the beginning of each batch of analyses. Another trace metal standard (1643) was analysed to compare NETL and UWC data. These standard analyses are presented here.

Table 3 shows the NIST-1640 analyses performed during the analysis of MWLP samples. The % Diff Cert refers to the difference between the sample analysis and the certified value given as a percentage of the certified value. The second NIST-1640 sample analysis, which was analysed along with the majority of the MWLP samples, indicates 16 samples that are greater than 10% different from the certified value. Analysis b did not achieve good accuracy. The analysis of major elements such as Al, Fe and K frequently suffer from interference problems and can be quite inaccurate. With the minor and trace elements, which are all quoted in $\mu\text{g/L}$ a small difference in values can mean a high percentage difference. For example in analysis b a difference of 27 $\mu\text{g/L}$ between the certified value and the analysed value amounts to a percentage difference of 18%.

Table 3: Standard reference material 1640a analyses compared to certified value and the difference between analysis and certified as a percentage of certified value. Values in bold indicate differences of more than 10%.

$\mu\text{g/L}$	1640a Certified	1640a Analysis	% Diff Cert a	1640a Analysis	% Diff Cert b
Al	52.00	57.27	10.1	64.65	24.3
As	26.67	26.54	0.5	29.90	12.1
B	301.1	309.8	2.9	305.3	1.4
Ba	148.0	159.2	7.5	174.9	18.2
Be	34.94	34.70	0.7	39.34	12.6
Ca	7 045	8 501	20.7	7 086	0.6
Cd	22.79	22.22	2.5	25.21	10.6
Co	20.28	20.74	2.3	23.91	17.9
Cr	38.60	38.93	0.9	43.26	12.1
Cu	85.20	86.02	1.0	94.30	10.7
Fe	34.30	21.11	38.5	50.70	47.8
K	994.0	751.8	24.4	871.6	12.3
Mg	5 819	4648	20.1	5 759	1.0
Mn	121.5	121.8	0.3	118.8	2.2
Mo	46.75	46.44	0.7	50.40	7.8
Na	29350	22 541	23.2	29 867	1.8
Ni	27.40	26.93	1.7	30.26	10.4
Pb	27.89	28.36	1.7	31.01	11.2
Sb	13.79	13.79	0.0	15.05	9.1
Se	21.96	21.36	2.7	21.59	1.7
Ti	-	11.04	100	11.26	100
V	12.99	13.87	6.8	15.61	20.2
Zn	53.20	58.73	10.4	65.02	22.2
Hg	-	4.426	100	3.805	100

Table 4 shows the analyses for the NIST reference material SRM 1643e. The major elements that give unreliable analyses are Al, B, Ca, Fe and K. The high number of elements that have a greater than 10% difference with respect to the certified values may not indicate that the ICP mass spectrometer was not functioning satisfactorily. An analysis of standard reference material 1640 (Table 5), for the batch of analyses that included the SRM 1643e sample, shows only two elements (Fe and K) to have an analysed value more than 10% different from the certified value. The difference in the accuracy of the analyses could be a result of the differences in the standards themselves. Standard 1643e has much higher concentrations of metals than 1640a. The NETL laboratories use ICP-OES for sample analysis, which is not as sensitive as ICP-MS, which is what UWC uses. The inaccuracy of the SRM 1643e analysis may be a result of mass interferences. The two different analytical methods must be taken into account as a source of discrepancy. Another reason why the sample analysis of 1643e is inaccurate could be changes in the samples en route to South Africa. Samples may have leaked or evaporated slightly.

Table 4: Comparison of analysis of NIST standard reference material 1643e and the difference given as a percentage of the certified value. Values in bold indicate differences of more than 10%.

$\mu\text{g/L}$	1643e Certified	NETL analysis	UWC analysis		% Diff Cert NETL	% Diff Cert UWC 1	% Diff Cert UWC 2
			1	2			
Al	141.8	272.0	257.9	684.7	62.9	58.1	131
As	60.45	60.90	53.72	55.39	0.7	11.8	8.7
B	157.9	557.0	844.5	839.7	112	137	137
Ba	544.2	522.0	543.2	550.0	4.2	0.2	1.1
Ca	32 300	30 800	23 728	24 493	4.8	30.6	27.5
Cd	6.568	6.300	6.074	5.795	4.2	7.8	12.5
Co	27.06	27.10	25.03	25.34	0.1	7.8	6.6
Cr	20.40	21.30	17.13	20.22	4.3	17.4	0.9
Cu	22.76	21.40	27.62	24.17	6.2	19.3	6.0
Fe	98.10	111.0	354.5	202.8	12.3	113	69.6
K	2 034	2140	16.80	2814	5.1	197	32.2
Mg	8 037	8 010	7 633	7 878	0.3	5.2	2.0
Mn	38.97	41.90	37.05	37.91	7.2	5.1	2.8
Mo	121.4	124.0	107.2	109.5	2.1	12.4	10.3
Na	20 740	21 700	16 762	17 783	4.5	21.2	15.4
Ni	62.41	65.70	55.24	77.78	5.1	12.2	21.9
Pb	19.63	19.10	16.50	16.88	2.7	17.4	15.1
Se	11.97	12.40	14.01	13.28	3.5	15.7	10.4
Sr	323.1	336.0	318.6	322.4	3.9	1.4	0.2
V	37.86	35.20	35.26	36.61	7.3	7.1	3.4
Zn	78.50	94.40	74.04	111.4	18.4	5.8	34.7

In general though ICP-MS does not produce accurate results for K or Fe. The data for Fe in Figure 5 is suspicious, as it does not follow the mobility that is expected of Fe i.e. high solubility at low pH values.

Table 5: Standard reference material 1640a analyses compared to certified value and the difference between analysis and certified as a percentage of certified value. Values in bold indicate differences of more than 10%.

µg/L	1640 Certified	UWC Analysis	% Diff Cert
Al	53.01	52.00	1.9
As	26.51	26.67	0.6
B	300.2	301.1	0.3
Ba	149.1	148.0	0.7
Ca	6907	7045	2.0
Cd	22.73	22.79	0.2
Co	20.52	20.28	1.2
Cr	37.30	38.60	3.4
Cu	84.91	85.20	0.3
Fe	27.48	34.30	19.9
K	810.4	994.0	18.5
Mg	5 862	5 819	0.7
Mn	119.9	121.5	1.3
Mo	46.06	46.75	1.5
Na	28 576	29 350	2.6
Ni	27.30	27.40	0.4
Pb	27.06	27.89	3.0
Se	21.65	21.96	1.4
Sr	4 159	4 730	0.3
V	124.5	124.2	2.8
Zn	12.63	12.99	1.3

5.4.2. Comparison of data

Graphs with no values indicate that concentrations of that element were below detectable limits.

The following section compares the elemental data of the MWLP at each incremental acid addition and hence pH. Figures 5 and 6 compare the major elements in the UWC and NETL data, respectively. More acidity was added to get the solution in the MWLP to below a pH value of three in the UWC experiment. However, pH values for the NETL data are not given so concentrations will be compared at mmol H₂SO₄ added. The elementals for each set of data show the same concentration trends. Initially a large amount of Na and Ca enter the acid solution. With the second leaching this amount decreases significantly. This sudden initial decrease between the first two leachings is probably a result of the dissolution of soluble salts. Sodium maintains a steady concentration with each successive leaching; this suggests that there is still a high amount of Na remaining on the surface of the particles. Calcium decreases from a concentration of around 100 000 µmol/kg FA (1 mol/kg FA) to around 5 000 µmol/kg FA.

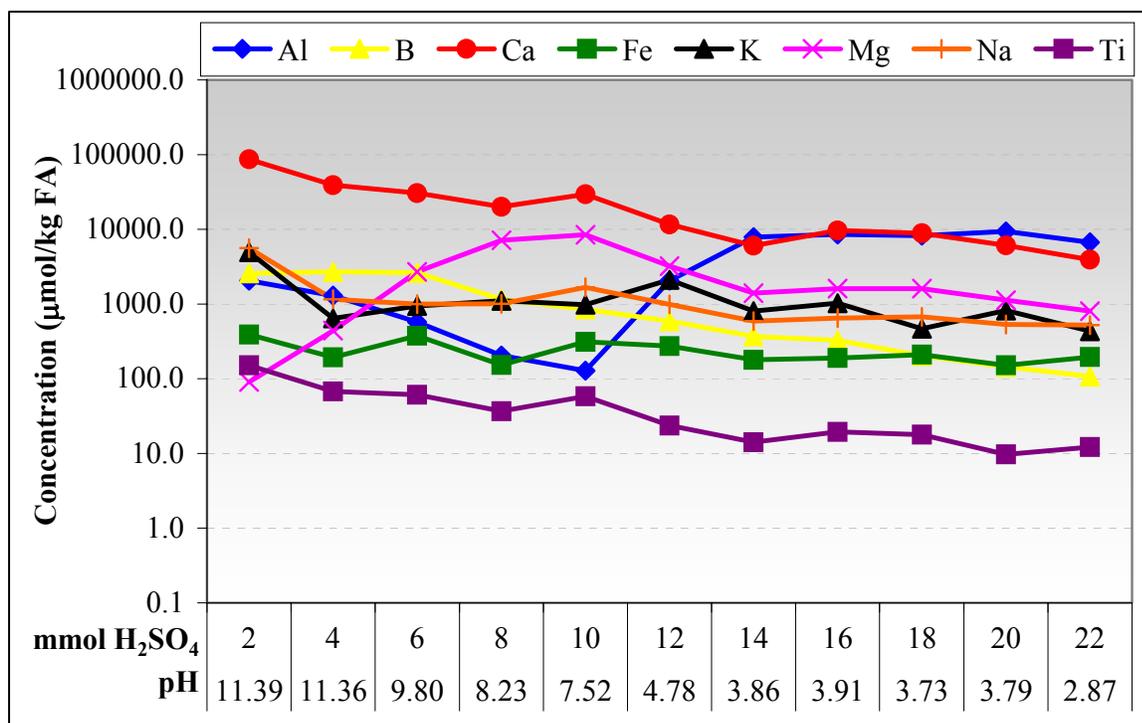


Figure 5: Major element concentration (µmol/kg FA) for UWC MWLP analyses.

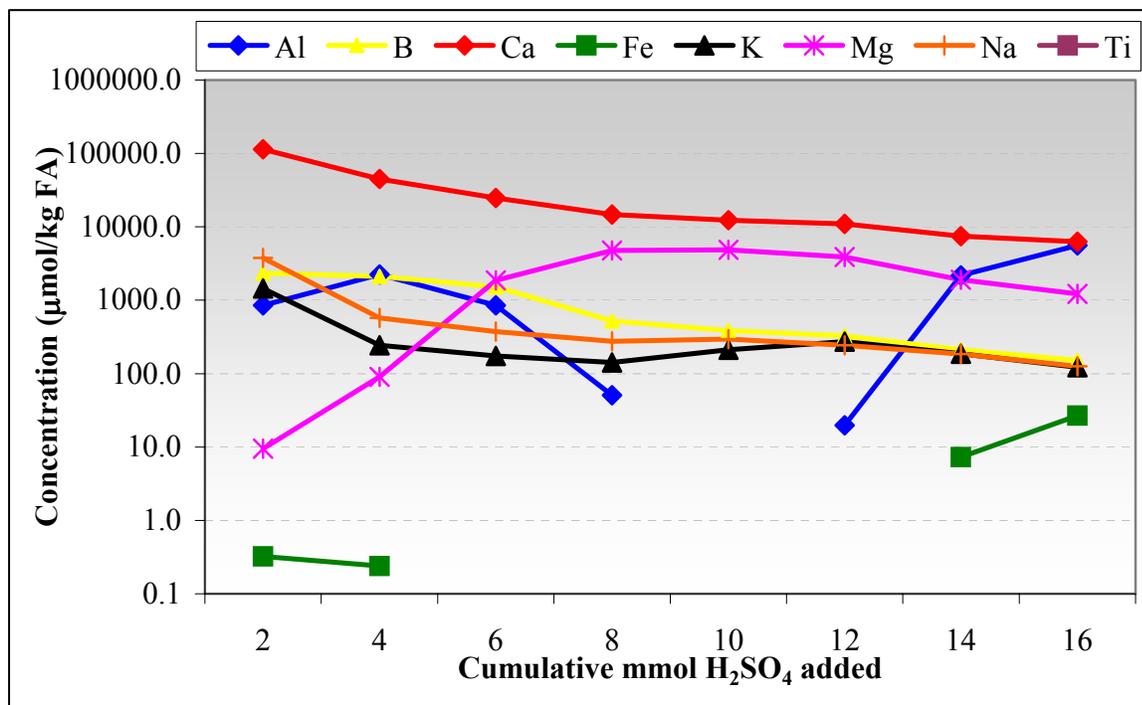


Figure 6: Major element concentration (µmol/kg FA) for NETL MWLP analyses.

There is a steady decrease in all elements with sequential addition of acid except Mg and Al (Figures 5 and 6) and As and Fe, whose concentrations remain relatively constant. The concentration of Al decreases in solution until 10 mmol of H₂SO₄ has been added or a circumneutral pH has been reached, and then increases with decreasing pH. This is a result of the mobility of Al in solution at high and low pH values. The concentration of Mg increases steadily with each acid addition, reaching a maximum concentration around 10 000 μmol/kg FA with the addition of 10 mmol H₂SO₄ or a circumneutral pH of 7.5. Thereafter the concentration of Mg decreases to around 1 000 μmol/kg FA and remains relatively constant. The discrepancies in the two sets of data from UWC and NETL may be explained by the use of different instruments for analysis. Below a certain concentration Al and Ti are not detected. Iron, which is detected by XRD, is also not detected except in small concentrations as a result of interference from the more highly concentrated elements.

Figures 7 and 8 show the minor element concentrations for the two sets of data from UWC and NETL. The mobility of elements at different pH values is well illustrated. Where elements are detectable in the NETL data, it can be seen that they follow the same trends as those in the UWC data.

The elements Ba, Be, Cu, Mn and Zn all show dramatic increases in their concentrations in solution at the pH at which they become mobile. For Ba, Be and Cu the pH at which they become mobile is around 8 or after 8 mmol H₂SO₄. For Mn and Zn the pH at which they become mobile is 10 and 5 or 6 and 12 mmol H₂SO₄, respectively.

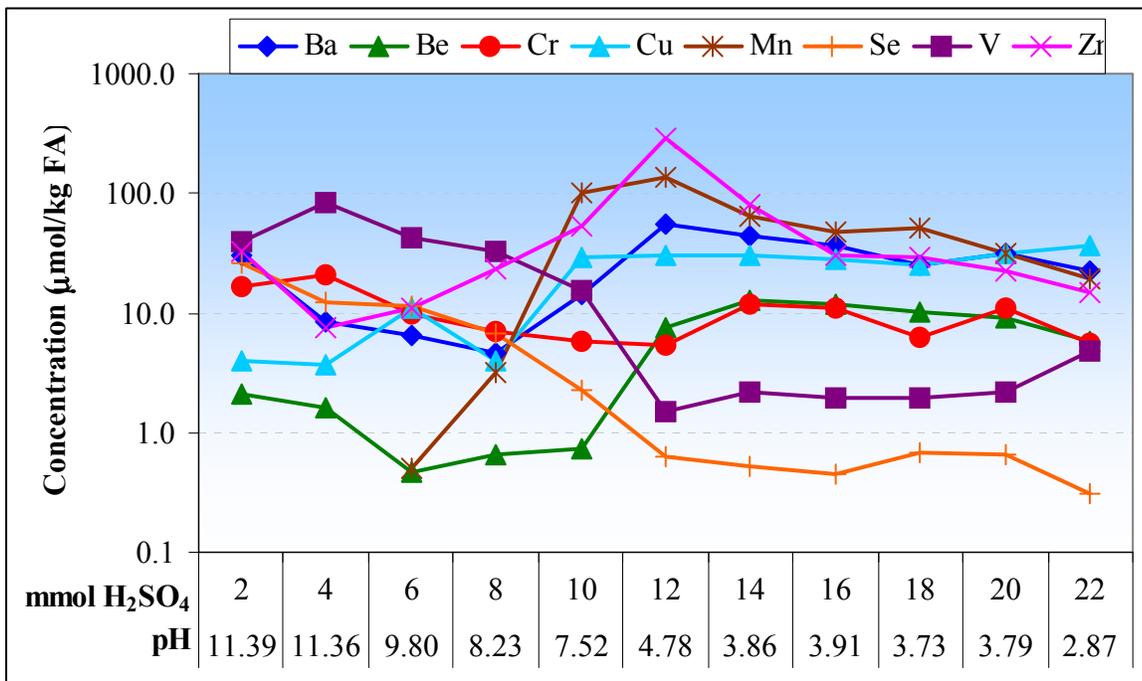


Figure 7: Minor element concentrations (μmol/kg FA) for UWC MWLP analyses.

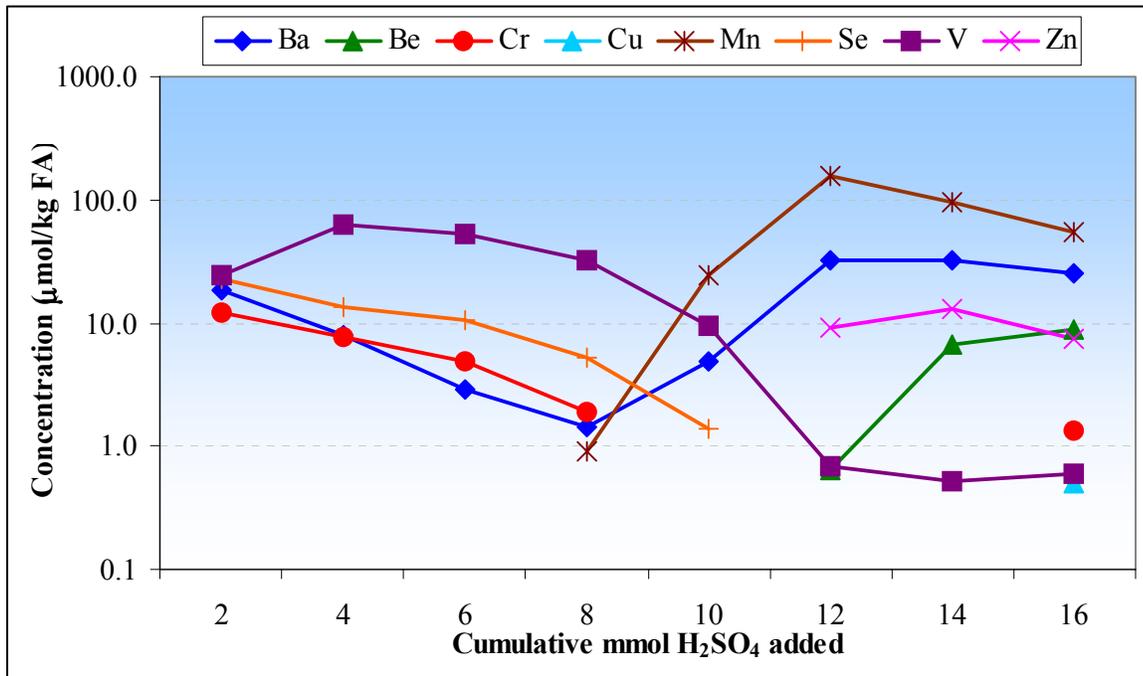


Figure 8: Minor element concentrations ($\mu\text{mol/kg FA}$) for NETL MWLP analyses.

By contrast Se and V decrease rapidly until a pH of 5 or 12 mmol H₂SO₄, whereafter the concentration in solution becomes fairly constant. The concentration of Cr decreases to below 10 $\mu\text{mol/kg FA}$ at a pH of 5 or 12 mmol H₂SO₄ and remains around a concentration of 10 $\mu\text{mol/kg FA}$.

Figures 9 and 10 show the trace metal concentrations for the MWLP samples from NETL and UWC. All trace metals concentrations are below 100 $\mu\text{mol/kg FA}$. From the elements that are detectable in NETL data As, Mo, Co and Ni show similar trends. As and Sb follow the same pattern of increasing initially and reaching a maximum with the addition of 6 mmol H₂SO₄, then decreasing with further sequential additions of acid until a pH of 5 or 12 mmol of H₂SO₄ addition.

The concentrations of Ni, Co and Cd also follow the same trend of maintaining a relatively steady concentration until 8 mmol H₂SO₄ has been added and the solution is at a pH value of around 8, then the concentration increases rapidly. These elements reach a maximum concentration at a pH of around 5 and an addition of 12 mmol H₂SO₄, thereafter decreasing in concentration.

The concentration of Pb and Hg appear not to be affected by the pH of the solution as they show alternately increasing and decreasing concentrations. The concentration of Mo decreases from very high initial values of 51.4 $\mu\text{mol/kg FA}$ to 0.05 $\mu\text{mol/kg FA}$.

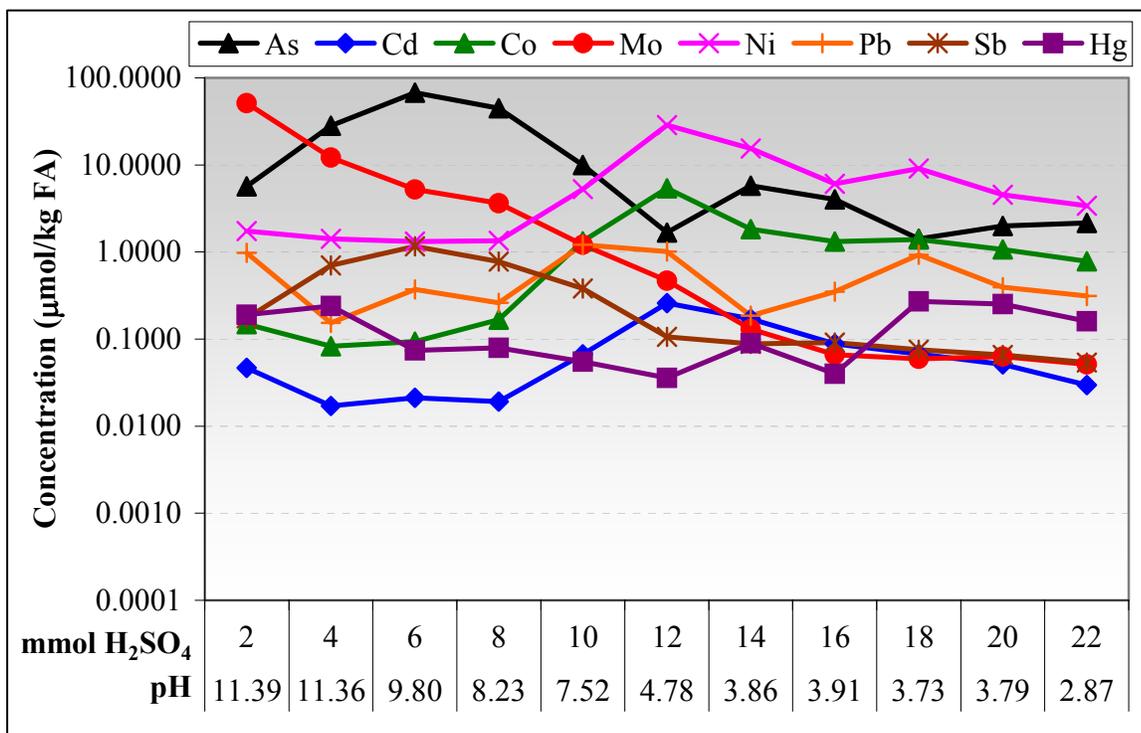


Figure 9: Trace element concentrations (µmol/kg FA) for UWC MWLP analyses.

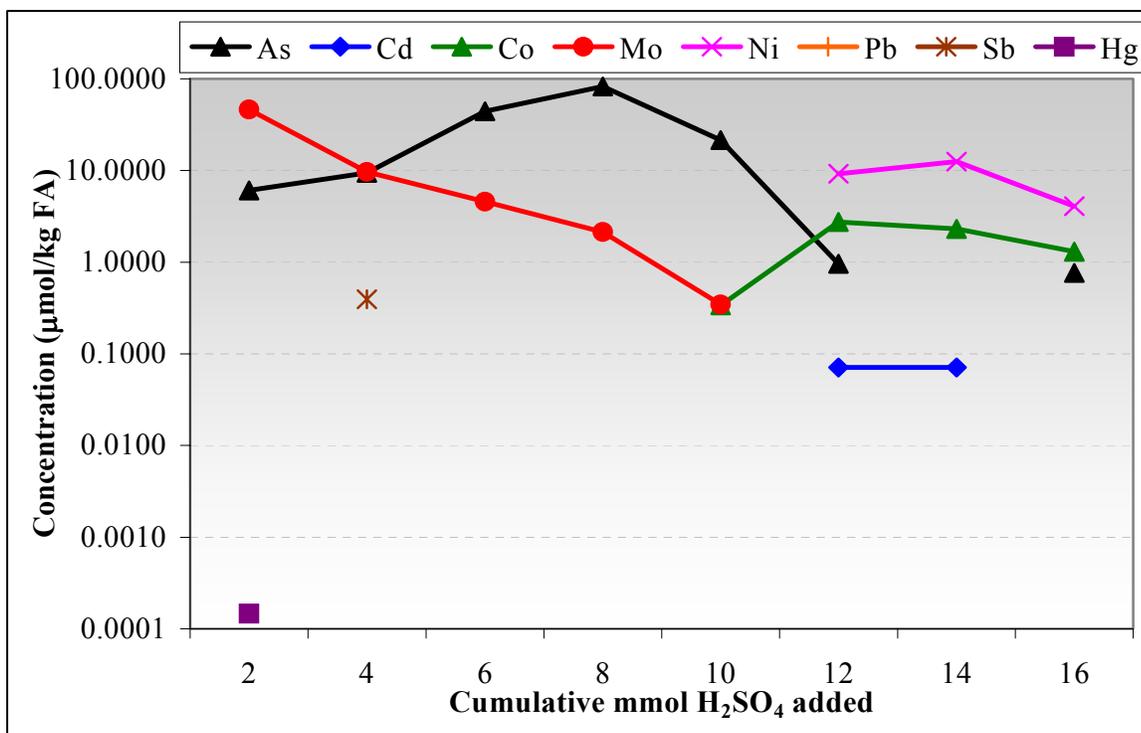


Figure 10: Trace element concentrations (µmol/kg FA) for NETL MWLP analyses.

5.5. CONCLUSIONS

- Differences in analytical instruments must be taken into consideration in the future and a standard reference material suitable for ICP-MS and ICP-OES should be compared.
- A percentage deviation from the certified standard should be accepted as being too high upon which those samples should be re-analysed.
- Extremely high concentrations of major elements may mask concentrations of minor and trace elements.
- The concentration of Ca is an order of magnitude higher than any other elements.
- The concentration of B is high enough for it to be ranked as a major element.
- From an environmental point of view fly ash should not be leached to a pH of 5 or below as that is the pH at which the most number of minor and trace metals reach their highest concentrations in solution.
- This study would benefit from using the same method with deionised water instead of dilute H₂SO₄ added sequentially until the solution reaches neutral pH values.

6. UNIVERSITY OF NORTH DAKOTA, ENERGY & ENVIRONMENTAL RESEARCH CENTER RESULTS

Synthetic Groundwater Leaching Procedure with Long-Term Leaching

6.1 INTRODUCTION

Over the last nearly 28 years, researchers at the Energy & Environmental Research Center (EERC) have leached a very large number of varying coal combustion by-products (CCBs), initially using the more common standard tests. Extraction procedure toxicity test (EP-TOX)²³ leaching was done during the first year or two. It was apparent from the beginning that this method had several weaknesses including the method of shaking and the incremental addition of the required acid. As a result, EERC researchers initiated an effort to identify a more appropriate methodology with a focus on high-calcium alkaline CCBs. Simultaneously, research on ash hydration reactions was being performed in parallel efforts. The two studies intersected suddenly with the realization that the mineral ettringite was the primary hydration phase that was always seen during the reaction of alkaline ash with water^{24,25}. This result is consistent throughout 25+ years of laboratory investigations at the EERC. At times, this mineral may exhibit poor crystallinity, but it always forms. Ettringite, which is a calcium aluminate sulfate hydroxide hydrate with the nominal composition [Ca₆Al₂(SO₄)₃(OH)₁₂·26 H₂O], can substitute other oxyanions for sulfate during formation²⁵⁻²⁷. Ettringite requires sources of calcium, aluminum, sulfate, excess water, and high pH (>11) in order to form. Variations in these requirements may play a role in the level of crystallinity of the ettringite formed. Oxyanions shown to participate in the ettringite formation include those of arsenic, boron, chromium, molybdenum, selenium, and vanadium. As a result of incorporating these elements into the ettringite structure, decreases in solution concentration of these elements can be observed in what the EERC refers to as anomalous leaching behavior.

The first example of anomalous leaching that was observed in our laboratory was seen about 25 years ago in a first-time long-term leaching experiment. We noticed a decrease in boron

concentration in a reanalysis of a large-scale leaching experiment done after about 21 days. Seeing this initial decrease in the concentration of boron and several other elements, we decided to continue the experiment and did so for over 550 days. It was eventually determined that the loss in boron concentration could be correlated specifically to an increase in the concentration of the mineral ettringite. The results of this long-term leaching procedure for boron are shown in Figure 11.

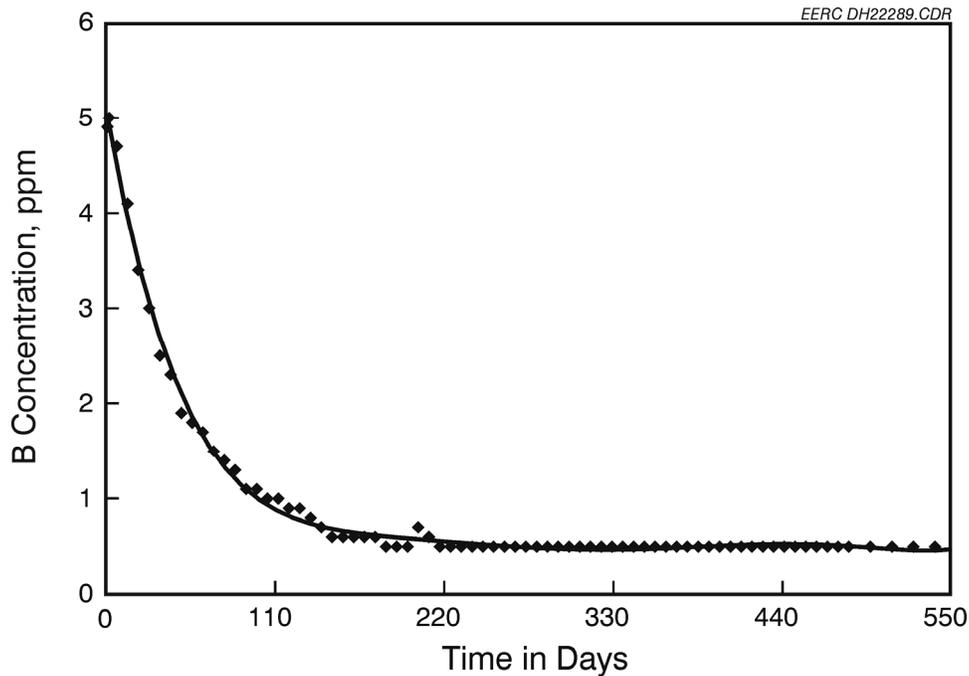


Figure 11. Long-term leaching results for boron.

The EERC developed a leaching method to allow the use of synthetic groundwater and longer leaching times. These tests came to be known as the synthetic groundwater leaching procedure (SGLP) and long-term leaching (LTL)^{21,22,28,29}. These tests have been used to evaluate numerous types of CCBs, and results indicated that the long-term leaching provides significant added data only for reactive CCBs²¹. Short-term leaching is adequate for evaluating CCBs with pH <9 because ettringite formation occurs at much higher pH levels.

The maximum equilibration time for long-term leaching could be an extremely long duration for some CCBs. It is well known that concrete can take up to years to reach its maximum strength. Some of the same hydration reactions responsible for concrete strength development are also responsible for the reduced leaching of some CCB constituents. A leaching duration of years is impractical for most purposes. The EERC proposes that long-term experiments include a time series of up to 3 months and that the resulting data be interpreted relative to the short-term leaching (18 hours) and at least two long-term data points. An evaluation of the resulting trend is part of the data interpretation. Field evaluation of high-calcium CCBs shows ettringite present in disposed masses for up to 10 years following placement^{30,31}.

6.2 EXPERIMENTAL

The SGLP batch leaching procedure is a relatively simple test that follows many of the conditions of the toxicity characteristic leaching procedure (TCLP)³². The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, and usually employs a leaching solution consisting of either water from the site, water which has been prepared in the lab similar to water likely to contact the ash, or distilled deionized water²². For the long-term component of this procedure, multiple bottles are set up and analyzed at different time intervals. A typical SGLP and LTL test might consist of 18-hour, 30-day, and 60-day equilibration times. Although 60 days is often not long enough to have achieved complete equilibrium, it is generally long enough to determine the concentration evolution of individual parameters. The most important factor when performing LTL is to have at least three equilibration times to determine a true trend. The EERC utilized 18-hour, 30-day, 60-day, and 90-day equilibration times for the SGLP and LTL component of the current interlaboratory leaching comparison study.

6.3 RESULTS AND DISCUSSION

Indirect evidence of ettringite formation can be seen in the leaching profile of the sample submitted by the EERC to the interlaboratory leaching study group using SGLP and LTL. The leachate results from the 60-day leaching period were not available at the time of this publication. Decreased concentrations are evident in the oxyanions of arsenic, boron, chromium, molybdenum, selenium, and vanadium, as shown in Figure 12. This is accompanied by an increase in the solution pH over the 90-day period. Direct evidence of ettringite formation is only achieved by using x-ray diffraction techniques to compare the initial solid sample to the hydrated solid sample after leaching.

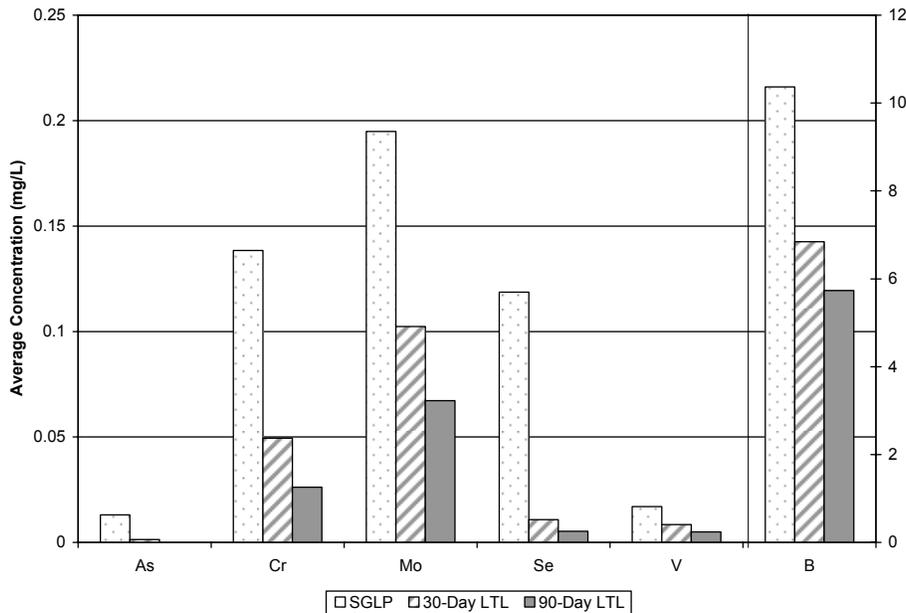


Figure 12. Indirect evidence of ettringite formation using SGLP and LTL. Boron is on a secondary axis.

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7. GENERAL CONCLUSIONS

The results presented in this report are only preliminary findings selected from the wealth of information being generated by the voluntary laboratories participating in this study. As more data becomes available and all participants have examined the data generated from the other laboratories, much more extensive comparisons of these methods will be made. It is anticipated that the result will be a significant contribution to the approach to characterizing the solid by-products of coal use.

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