

Rapid Batch Characterization of Coal Utilization By-Products

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Abstract

Many leaching methods have been used for various purposes by research groups, industries and regulators, but there is still a need for a simple yet comprehensive approach to leaching coal utilization by-products (CUB) and other granular materials. A serial batch characterization method has been developed at the National Energy Technology Laboratory that can be completed in 2-3 days to serve as a rapid screening tool. The procedure provides an indication of metals release under varying pH conditions and increasing liquid to solid ratio. The method was applied to 8 fly ashes; leachates were analyzed for 30 elements. Data is presented on leachability relative to elemental content in the ashes, and a measure of method reproducibility is given and discussed.

1. Introduction

A large number of leaching methods have been developed 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 have been regulatory driven or designed to 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 generating data that 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 role of pH as the dominant influence 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.

On-site trials provide vital data,^{2,8} and laboratory column leaching studies provide useful information,^{10,12,23} especially at low liquid to solid (L/S) ratios.²⁴ However, both of these approaches can take too long to allow timely decision making regarding the potential fate of CUB and other solid phases.^{8,17,25,26} Regulations concerning a class of materials, specific site conditions, and details of the material placement may subsequently warrant further testing.⁸

A general scheme suggested by the IAWG²⁷ is based on the extensive work of the Netherlands Energy Research Foundation (ECN)^{12,24} and was further developed by the European Standardization Organization (CEN).^{8,10,28} These collaborators have concluded that the leaching behavior of all types of solid phase by-products is systematic, and is governed by several critical factors, including specific element solubility and availability or release potential. A crucial factor in element solubility is the influence of leachant pH.^{4,11-14,24,29} Other primary factors are the major constituents of the solid phase²⁷ and their chemistry,¹³ leaching time, particle size, and solubility kinetics.^{10,30}

Detailed quantitation of the leaching behavior of a specific material at a specific location is beyond the scope and intent of this method. Among the factors suggested to contribute to such complete understanding of release behavior are: the mineralogy of solids;^{30,31} complex formation by metallic elements and either inorganic species or dissolved organic matter, and the reducing properties of the solid phase;^{10,14,29,32,33} and secondary reactions³⁴ and associated thermodynamic behavior.¹⁴ Microbial action has not been widely discussed, but can be expected to play a role in a natural setting.

The leaching protocol described here, derived from the European work, is designed for routine testing of CUB. The method is intended to quickly give information with regard to the total leachable material in an ash, and to estimate the rate at which an element can be extracted during a specified period of time in an environmental setting. Thus, one can ascertain if any hazardous components in a waste are potentially mobile under normal environmental conditions. The method has been applied to eight pulverized coal (PC) combustion fly ashes. The method includes a cumulative static pH leaching (availability) procedure and a serial batch procedure (long term) at increasing liquid to solid ratios. The availability test is a dynamic sequential batch procedure, and the long term leaching is a combination of a static batch step and a dynamic serial batch process. To demonstrate the reproducibility of the method, data from four replicates of both procedures are presented for eight ashes. The precision for each step of both parts of the method are presented as relative standard deviation (RSD) for each of the 30 elements. Data are also presented to demonstrate the leachable fraction of the 30 elements examined out of the total content in the 8 ashes by the various cumulative steps of the leaching procedure. The use of this screening method is best suited to applications involving water infiltration, removal, and replenishment in a dynamic flow scenario.

2. Experimental Method

The identification of specific manufacturers is for informational purposes only, and does not imply recommendation or endorsement by the United States Government, the U.S. Department of Energy, or the National Energy Technology Laboratory.

The Rapid Batch Characterization method consists of three discrete steps: acid/alkaline classification, availability for release, and long term estimate of release behavior. The method uses standard laboratory equipment and can be completed in 2-3 days.

Distilled, deionized (DI) water from a Millipore¹ Milli-Q reagent water system operating between 10-13 Mohm was used as a diluent and for all equipment rinsing. Reagents were nitric acid (trace metal grade – Fisher Scientific) and sodium hydroxide as an, aqueous solution (10.0N certified – Fisher Scientific), diluted as appropriate with DI water. A 1L pressure filtration device (Millipore) and cellulose ester membrane filters, 0.45 μ m pore (Millipore) were used for filtering operations. The autotitrators were obtained from Cole-Palmer. Electrochemical measurements, including pH, used equipment from Thermo Orion, Corning, and Fisher Scientific. All laboratory equipment, including mixing and other vessels, stirring bars, weighing pans, filtration devices, filters, and sample bottles were washed with laboratory detergent, rinsed thoroughly with water, rinsed with 1.0N HNO₃, and then triply rinsed with DI water. Each fly ash sample was digested according to EPA Method 3052, using a mixture of nitric, hydrofluoric, and boric acids, and analyzed for all elements of interest except mercury, using inductively coupled plasma-atomic emission spectroscopy. The Hg concentration was determined by direct mercury analyzer (DMA-80, Milestone, Inc., Monroe, CT) following EPA 7471. The ash analysis data is summarized in Table 1.

For the availability portion of this method, particle size reduction is required if less than 95% of the material passed a 300 μ m sieve. For the long-term leaching portion, 95% of the substrate would be required to pass a 4mm opening. For the 8 ashes used in this study, at least 98% of each ash passed the 300 μ m sieve, and therefore no size reduction was required. The samples were not pre-dried. In general, the liquid to solid (L/S) ratios for the long-term leaching tests and for the availability determinations should be based on dry weight, with the amounts of added leachant adjusted accordingly to include sample moisture. Separate samples of each ash were dried to constant weight at 105C. Tests on the 8 subject ashes resulted in moisture contents of 0.5% or less. These values were considered negligible, and the as-received weight of the ashes was taken as the dry weight.

The first step of the availability test was to classify the ash as alkaline or acidic. A pH measurement was made on each ash in DI water at an L/S ratio of 100, after stirring for 20 min., allowing the mixture to settle for 5 min., and monitoring for 5 min. For the purposes of this procedure, any material that demonstrated a pH equal to or greater than 8 was classified as alkaline. Those materials having a pH lower than 8 were treated as acidic substrates. Six of the ashes had a natural pH of about 11, and the two remaining ashes had natural pH values of 4-5. Alkaline materials were leached at progressively more acidic levels, and acidic ashes were leached in separate steps at more acidic pH levels and a more alkaline (near neutral) pH level. Availability data was obtained from a series of discrete, short-term leaches of the same 9.00 g ash sample in open Erlenmeyer flasks with magnetic stirring at 250 rpm. An initial volume of

450 mL DI water was added to the flask; thus, the L/S ratio for each step was 50. To maintain the static pH values of later steps, the addition of reagent by the autotitrator increased the L/S ratio by 5-15%. This increase in volume was taken into account in subsequent calculations of element release.

For the alkaline ashes, the duration of the natural pH step was 2 hrs. Initial and final pH readings were taken. The leachate was isolated by use of a pressure filtration device containing a 0.45 μ m pore membrane filter, using 50 psig N₂. No pre-filters were used, thereby avoiding trapping material in the coarse pores of such filters, which could interfere with effective leaching of the ash sample in later pH steps. All liquid and flowing solids were poured onto the filter. A portion of the filtrate was sealed with minimal headspace and stored cold for later analysis by ICP for 29 elements and by CVAA for mercury. The remainder of the filtrate was analyzed electrochemically for pH, conductivity, and oxidation-reduction potential. The filter residue and filter were returned to the flask, and the ash sample was leached at pH = 8 for 3 hrs, then at pH = 4 for 2 hrs, and finally at pH = 2 for 2 hrs, all with stirring at 250 rpm. The pH was maintained ± 0.1 unit with 0.1N HNO₃ by means of an autotitrator. After each step, the leachate was isolated and analyzed as above, with the total leachate volume noted and the filter residue and accumulating filters returned to the extraction vessel. Thus, cumulative data was obtained at each pH step, and can be examined for pH values of about 11 (for these materials); for 11 and 8; for 11, 8, and 4; or for 11, 8, 4, and 2, depending on the specific utilization or disposal scenario for the material.

For acidic ashes, the availability portion had two parts. In the first part, the material was leached at its natural pH for 3 hrs, then at pH = 4 for 2 hrs, and finally at pH = 2 for 2 hrs. The second part used a fresh ash sample and leached the ash at its natural pH for 4 hrs, and then at pH = 8 for 3 hrs. The elevated pH was maintained by use of an autotitrator and 0.1N NaOH. The total leaching time of each part for acidic ashes was 7 hours. In all cases, the filtration and analysis steps were the same as for the alkaline steps, providing two sets of cumulative data for these acidic ashes, which had natural pH values of 4-5: for natural pH, for natural and pH 4, and for natural, 4, and 2 in one set; and for natural pH, and for natural and pH 8 in the other set.

The other major piece of data required is the release of material from the waste that can be expected under normal environmental conditions over various periods of time. This was acquired by using the successive L/S ratios 2, 8, and 10 of DI water leachant on the same 45g sample of ash. The ash/water mixtures were sealed in 0.5L high-density polyethylene bottles and mixed on a bottle roller operating at 4-5 rpm. The individual step leachant volumes and their run times were 90mL and 6 hrs, 360mL and 18 hrs, and 450mL and 24 hrs, respectively. An alternative scheme for some runs was to use 90g of ash, a 1L bottle, and doubled volumes of DI water, providing identical L/S ratios at each step. At the conclusion of each step, the leachate was separated, a portion was stored and the remainder was analyzed. The filter residue and filter were returned to the extraction vessel with the appropriate amount of new leachant added, as in the availability tests. Because the same ash sample was being leached, the resultant L/S ratios are cumulative, and are treated as L/S ratios of 2, 10 (2+8) and 20 (2+8+10). A separate L/S ratio of 100 was run with 10g of ash and 1000mL DI water. The L/S ratio can be related to a leaching time scale in terms of a cumulative infiltration rate if specific details of the utilization or

disposal scenario are predicted. The experimental method steps which provide the raw leachate data are summarized by the sequence given below:

- Perform elemental analysis of substrate
- Evaluate particle size, reduce if necessary
- Measure moisture content
- Determine pH of sample
- Perform availability leaching, alkaline or acidic
- Perform long term leaching

Test section	Ashes	Leachant	L/S of Step	Cumulative L/S	Leaching time (hr)
Availability	Alkaline	Natural pH	50	50	2
		pH 8	50	100	3
		pH 4	50	150	2
		pH 2	50	200	2
	Acidic	Natural pH	50	50	3
		pH 4	50	100	2
		pH 2	50	150	2
	Acidic	Natural pH	50	50	4
		pH 8	50	100	3
	Long term	All	DI water	2	2
8				10	18
10				20	24
100				100	24
100				100	24

The type of data generated by this method can be seen in Figures 1 and 2, which depict the release of boron from FA 38 and FA 49, respectively. Cumulative availability data from this rapid characterization can be easily compared with long term release for any sample and element, and release rate data can be generated. For those elements detected in the ash, the availability to be leached can be compared to an element's content in the original ash. The raw data from the leachate analyses for the 30 target elements was in the form of ug /L of leachate, except for Ca, Na, and S, which were given as mg / L. In all cases, this data was transformed into mg of element per kg of ash. For each element and each ash, the mg / kg data from 4 replicates (except for 5 replicates for the FA 24 long term leaching sequence) were averaged, a standard deviation was determined, and a fractional expression of standard deviation divided by the mean, relative standard deviation (RSD) was calculated. In this report, RSD values are presented as decimals, rather than in the more familiar percent form.

3. Method Reproducibility

For discussion purposes, the natural pH value for the alkaline ashes will be called "pH 11." The actual range of natural pH values for the alkaline ashes was from 10.5 – 11.3. By reducing the raw leachate data of "ug of an element per L of leachate" to the RSD format, general evaluations of method reproducibility over multiple ashes can be made. The wide variability of raw leachate data between ashes and from raw data derived from different pH conditions for a given ash are so great, that they would overwhelm the relatively small differences between replicates if comparisons were attempted on unreduced data. It can be noted that the actual leached amounts detected among the 30 elements within a single leachate sample can vary over six orders of

magnitude between Ca and V, for example. When the Hg data is considered, this spread is several orders greater.

The availability data for the raw leachate show general trends with pH. For the alkaline ashes, little or no leachable quantities were detected at pH = 11 for Be, Cd, Co, Mn, Ni, P, Sb, Ti, and Tl. At pH = 8, nearly all leachates had measurable quantities of Mn and P, and one in four had detectable Ni and Sb. At pH = 4, Be, Cd, Co, and Ni were found in all samples. Not surprisingly, solubility is widespread at pH = 2, even for Pb.

The leachate pH changes little in the L/S series, with all runs at or near their natural pH for the 8 ashes. Thus, other factors, such as cumulative time, attrition, and the effects from leaching out other interacting components must play greater roles in the leachate composition in later steps of the L/S series in the absence of the effects from changing pH levels. The L/S series data includes 9 replicates at each L/S level from the 2 acidic ashes of natural pH = 4-5. The elements Be, Cd, Co, Ni, P, Ti, and Tl show detectable levels in the L/S series composite statistical data of all 8 ashes. This detection is indicated by the parenthetical values in Table 3. However, these species are present only in a small number of samples, and most cases of their detection were from the 2 acidic ashes. These elements demonstrate solubility in the pH = 4-5 range. The L/S = 100 data show fewer cases of detection for some elements than was found in the L/S series. In part, this result may be attributable to the dilution factor, where elements that are barely detectable in the L/S = 2, 8, and 10 series data fall below detection at L/S = 100.

The variations in leachability of any given element under specific conditions within replicate groupings of one ash exhibit element specific ranges. Variability within such a range was typically much smaller than the difference between ranges of separate ashes leached under the same conditions. Variability within replicate ranges was generally very much smaller than the significant differences between data from the several sample types of a given ash, within a given replicate. The RSD composite data from the two acidic ashes are based on only 8 potential data points per element for each sample type. These statistical values are considered less meaningful than the alkaline ash RSD data, which is derived from 24 potential data points, or the long term leaching data, which contains a potential pool of 32 or 33 points per element per sample type. As a general summary, relative to the alkaline ash availability RSD data, values from the acidic ashes were lower (less deviation from the mean) for Ag, Al, Be, Hg, K, Mg, Mn, Na, Pb, and S. The RSD data for the acidic ashes was higher (greater deviation) for B, Ba, Co, Cr, Cu, Mo, Ni, Sb, Si, and Tl. Values for RSD were similar from the two ash types for As, Cu, Cd, Fe, P, Se, Sr, Ti, V, and Zn.

The availability data expressed in the RSD form from 4 replicates for each sample type averaged over the 6 alkaline ashes is given in Table 2. There are 24 possible data points from each condition and 24 cumulative sums from each of the conditions after the natural pH runs. The RSD data is shown for those cumulative sums, rather than from the specific step, at pH = 8, 4, or 2, since these sums are considered more meaningful. Because the same ash particles are being leached at 4 successive pH steps, the leaching of material at pH 8 is not an isolated event. The leachate composition from pH = 8 depends not only on this pH environment, but also on what occurred during the pH = 11 step. Similarly, results from pH = 4 have a dependence on prior leachings at pH = 11 and pH = 8, and the pH = 2 leachate cannot be isolated from the leaching

processes from pH = 11, 8, and 4 for the specific ash particles. The increasingly acidic pH sequence is intended to follow the trend of an alkaline ash in a more acidic environmental setting. The dominant alkaline components will be gradually washed out, and the residual ash components will be less able to dominate the aqueous media surrounding ash particles. The ash will be exposed to progressively lower pH environments, and these more acidic conditions will result in new leaching characteristics. For both this RSD data and in the method's leachate concentration data for any given ash, values can be examined after the natural pH step, or after any cumulative step at progressively lower pH values, or higher and lower values for the acidic ashes.

The RSD data from the long term results for L/S = 8 and L/S = 10, shown in Table 3, are from the cumulative sums of L/S = 2 and L/S = 8, and from L/S = 2, L/S = 8, and L/S = 10, respectively, since the same ash particles were leached in the successive steps. There are 33 possible data points at each step for all elements except Sr, for which only 28 points are possible, due to the unavailability of Sr data from several early runs. The L/S = 100 data was obtained from separate quantities of the same 8 ashes, providing 32 possible data points from the 4 replicates of each ash. Parenthetical values in Tables 2 and 3 indicate how many analytical data entries from the replicates of the specific conditions for the 6 or 8 ashes went into the accompanying values. The reproducibility of the method is best evaluated by examining elemental data where the species are present at detectable levels for all or nearly all samples, so that data points for a given element are at or near the maximum possible. All cases of leachate results below detection limits were ignored for the determination of mean values. For cases where only one replicate of an ash had a detectable amount of an element in a given leachate step, the analyzed value was the same as its mean, and the standard deviation across those replicates was zero, as was the RSD value. When such values are entered into averages over the small number of subject ashes in this study, these resultant averages will be lowered accordingly, relative to averages comprised entirely of non-zero values. Some of the large RSD values in Tables 2 and 3 for Hg can be attributed in part to relatively large variations in very small numbers. Small variations in the percent of total ash content leached for an element such as Fe, where the amount present in ash is very large but the amount typically leachable is very small, can also produce large variations in statistical data.

4. Method Application Results

Figures 3-6 depict the high, low, and average values of the fraction leached of each analyzed element for the 6 alkaline ashes studied. The figures follow the availability test steps, such that Fig. 3 is a summary of uncontrolled natural pH (approximately 11) data, Fig. 4 adds pH 8 results, Fig. 5 combines the data from pH 11, 8, and 4, and Fig. 6 is a total after adding the pH 2 results. All data below detection was excluded; it was not used in the average depictions or for the low data points for elements. The first parenthetical entry in each pH column of Table 2 tells how many detectable values were available for use on these four figures.

Of the 30 analytes, only those elements both found in the ash and detected in the specific or a prior pH step are included in these figures. Boron is excluded because the ash analysis preparation, a triple acid microwave digestion that uses boric acid, introduces boron into the sample, although B is detected in nearly all leachates. Silver, which shows up in several alkaline ash leachates but only in one raw acidic ash and no alkaline ashes, is not included in Figs. 3-6.

Similarly, cadmium, antimony, selenium, and thallium are not included, because they were not detected in the ash analyses. Cd was detected in all pH 4 and 2 leachates, Se was found in all but one pH 11 leachate, and both Sb and Tl were detected sporadically. Nickel, lead, and titanium were omitted from Fig. 3, since they were not found in any pH 11 leachates. Lead was also not detected at pH 8, and is not on Fig. 4. One replicate from FA 38 is responsible for the point on Fig. 5 for Pb. Lead was detected in all alkaline ash samples at pH 2, and is shown on Fig. 6 to have leached, on average, 10% of its ash content at this low pH. Thus, the method is capable of revealing leachable amounts of some elements of potential concern although they were not detected in the ash. As one progresses sequentially through these four figures, it is possible for the average values for some elements to decrease. An element previously below detection for one or more ashes might be detected at a lower pH, but the amount leached could be such a low fraction of the element's content in an ash, that the average over the 6 ashes of the fraction released might drop. In an isolated case, such a decrease was observed for copper in the early L/S sequence of the long term leaching. However, a decrease was never observed in the availability results, and the average fraction leached of every element only increased with each successive drop in pH, except for cobalt remained unchanged from pH 11 to pH 8. This exception can be traced to one replicate of one ash releasing measurable Co at pH 11, and no replicates reporting Co at pH 8. The cumulative nature of this sequential batch leaching method carries such isolated data from a higher pH into the results at pH 8 and lower, as might happen in a natural setting, as alkaline material is neutralized. As seen in the parenthetical data of Table 2, detectable amounts of a number of elements are not being released in the replicates of the 6 ashes at pH 11. Upon decreasing the pH from 4 to 2, only Ag, Sb, Hg, Se, Tl, and Pb, in increasing frequency order, are not released in all replicates. Mercury is an important element of concern, which was detected in the alkaline ashes in a range of 7-264 (average value 104) ng/g ash. The average fraction leached is shown to have steadily increased from 0.001 by factors of 2, 3, and 4 through Figs. 3-6. The minimum value was unchanged, derived from 2 of 4 replicates of FA 20 at pH 11, since FA 20 released no detectable Hg at lower pH levels. The maximum Hg value increased an order of magnitude, and thus the high to low spread increased from one to two powers of 10. The highest fraction, about 2 %, was leached from the sample with the lowest Hg ash content. The actual amounts of Hg released in the cumulative data over 4 pH steps for the 6 alkaline ashes were (in ng Hg per g ash) 0.04, 0.08, 0.11, 0.13, 0.16, and 0.51, averaging 0.17. Since Hg was found in only 13 of the 96 alkaline ash availability leachate samples, the typical leachate result for Hg was "below detection limit." More commonly found was arsenic, detected in all replicate series of alkaline ash availability and in most samples at any pH step. Both the highest value and the average value of As increased by an order of magnitude from the pH 11 result to the cumulative pH 2 data. The minimum As value increased to a greater extent, and at pH 2, the data range for the fraction leached is only a factor of 4. For this discussion, 12 elements are considered major constituents of these alkaline ashes, and these elements, in decreasing order of average ash content, are Si, at 22%, Al, Fe, Ca, K, Mg, Ti, Na, S, P, Ba, and Sr, at 0.1%. It is these elements and their compounds in the ashes which determine the pH environment of the leachate and provide the inorganic matrix for complexation of other elements, thereby influencing the solubility of other ash components. The fraction of these elements leached at pH 11 in decreasing order are S, Ca, Sr, Na, Ba, K, Al, P, Mg, Si, Fe, and Ti. By pH 2, the cumulative decreasing order was S, Ca, Mg, Sr, Ba, P, Na, Al, K, Fe, Si, and Ti, with only Mg changing position appreciably in the sequence. The high to low spread for most of these major elements from pH 11 to cumulative pH 2 shows little variability, with large increases

evident only for Fe, P, Si, and Ti, which all have much greater solubility at low pH values. For phosphorus compounds, the large increase in the high to low difference from pH 11 to pH 8 can be traced to the low solubility of P species at high pH, with only 1 ash giving leachate results above detection levels. For Al, the overall pattern moves up by a factor of 4-5 with the enhanced solubility from pH 4 to pH 2, while the patterns of Mg and to a lesser extent of S move most noticeably from pH 11 to pH 8. The upward drift from Fig. 3 to Fig. 6 is more gradual for Ba and Si. In terms of average concentration in availability leachates for alkaline ashes, most prominent of the 12 major elements were Ca, followed by S, with Ti always last. At high pH the positions 3-11 in decreasing order were held by Al, Na, K, Si or Sr, Mg, Fe, and P. At pH 8, Mg and Si solubility had increased, and the order was Al, Si, Na, Mg, K, Sr, Ba, P and Fe. By pH 4, these average positions were Si, Al, Mg, Sr, K or Na, Ba, P, and Fe. Finally, at pH 2, the sequence was Al or Si, then Mg, Fe, Na, K, Ba, Sr, and P. Even in this small set of 6 ashes, these leachate concentration orders varied considerably. While Ca was first and Ti was last for every ash, the other elements could be found in any of 2-4 positions, depending on the ash. This variability is also shown in the spread between high and low data on Figs. 3-6. Although not determined in the ashes, boron was detected in all but 1 of the 96 alkaline availability leachates. For most ashes, B was found in greater concentration than many of the major ash constituents in at least the higher pH samples. Control experiments eliminated lab glassware as a source for the amounts observed in the leachates.

There are 10 elements detected in the alkaline ashes that can be considered minor constituents for this discussion. These elements in order of decreasing average ash content (ug element/g ash) are V (303 ug/g), Mn, Zn, Cr, Cu, Ni, As, Pb, Mo, and Co (41 ug/g). The set of Ag, Cd, Sb, Se, and Tl, which were not detected in the alkaline ashes, but were found in leachates for at least one ash, are classified here along with Hg, as trace elements. These minor and trace elements were found in varying numbers of alkaline ash leachates, as noted in the parenthetical data of Table 2. The leachate concentrations of a few of these lesser constituents rivaled that of the less soluble major ash constituents in some samples. The high to low spread depicted on Figs. 3-6 is among the highest for Cr, found in all 96 alkaline ash leachates, and for Hg, found rarely. The small or non-existent spreads between high and low values for Be, Co, and Cu in the alkaline and neutral samples summarized on Figs. 3-4 correspond to low or even single data points for these elements. Molybdenum was found in 11 of 24 pH 4 leachates and in all 72 of the remaining availability samples for these ashes, but in only 2 of the 6 ash substrates. The data in Figs. 3-6 are concerned only with results from these ashes where Mo was found. As the figures show, most of the Mo in these two ashes was soluble, leaching out overwhelmingly in the early pH 11 and pH 8 steps. The general trend of enhanced solubility at low pH is evident for the minor and major ash components in the figures, while Table 2 shows that the trace elements do not necessarily follow this trend. Both Cd and Tl increased solubility as pH was lowered, and Sb and Se had higher solubility at moderate or high pH values, respectively. The large variability of solubility for nearly all elements over the pH ranges of the method for even this limited set of Class F pulverized coal combustion fly ashes demonstrates how individual these materials are.

The availability leachate data for the two acidic ashes in this study, FA 24 and FA 28, were similar for corresponding steps and are combined in Figure 7. The analyses of the two substrate ashes, recorded in Table 1, demonstrate the dramatically lower Ca content of these materials, compared to the alkaline ashes. Iron and sulfur values were also found to be much lower, while

the silicon content was higher. The acidic ashes are shown to have the highest contents of Be, Co, Ti, and V, and the lowest content of Mn, but these differences are relatively minor. Of the 8 ashes studied, only FA 28 had detectable Ag or Cd. Since Cd was found in all acidic-ash availability tests, Cd values are included in Fig. 7, whereas Ag is excluded, since it was not detected in any of these leachates. Other element contents are in or very near the broad range established by the alkaline materials. The average fractions leached in the two ashes are shown in Fig. 7 for the initial and subsequent composite pH steps for both parts of the acidic availability portions of the method. The serial batch steps produce cumulative data. The figure legend indicates the final pH level included in that particular sum. In part 1, results depicted are for pH 5, for pH 5 and pH 4, and for pH 5, 4, and 2. In part 2, data is shown for pH 5 and for pH 5 and pH 8. The axis labeling, simplified for clarity, omits pH 4 of part 1 (which would be second from the front) and pH 5 of part 2 (second from back.)

Comparisons of acidic ash results on Fig. 7 and alkaline ash data from Figs. 3-6 must consider not only the limited number of ashes involved, but the number and sequence of pH steps in each version of the availability test. The average values from 2 ashes shown in Fig. 7 are within the range of results in Figs. 3-6 for nearly all elements. The exceptions are that the average data for Ba, Ca, Cu, Mg, Si, Sr, and to a lesser extent Mn and Zn are lower in Fig. 7 than the average results in Fig. 6 for these elements. The high solubility of sulfur species shown in Fig. 6 is also evident in Fig. 7, but the Ca compound solubility in the acidic ashes did not match its high values of Fig. 6. Apparently lacking the great excess of Ca typically resulting from sulfur capture technology, the greatly diminished content of Ca in the acidic ashes is present in a higher percentage as less soluble species, relative to the alkaline ashes. The enhanced solubility of As, Mo, and V at pH 2 and pH 8 over that at pH 4 or 5 is shown more clearly in Fig. 7 than in the alkaline ash availability sequence, where the prior pH 11 step and the sequence of steps obscures such a finding. The greater solubility of Ti species at pH 2 than at higher pH levels is shown in all availability figures. Although it is difficult to tell from the figures, data revealed a higher percent of Fe compounds being leached from the 2 acidic ashes after pH 2 than after pH for some alkaline ashes. For all of these leachate availability results, unique properties of the total ash matrix and interactions between various components can be expected to influence individual element results.

While the availability test provides an indication of the extent of release of the target elements under varying pH conditions, the long term leaching portion of the method is more focused on the rate at which elements will be released at their natural pH, where the major ash components determine the leachate pH environment. Data from the 6 alkaline and 2 acidic ashes are combined on Figs. 8-11. The result is that some elements exhibit very broad variation from one ash to another. This data is most comparable in terms of pH environment to that depicted in Fig. 3 and in the pH 5 data of Fig. 7. The results of Fig. 10 represent a composite L/S of 20 and a total leaching time of 48 hr, while the Fig. 11 data is from a single L/S = 100 step for 24 hr. These conditions contrast with the Fig. 3 results from 2 hr at L/S = 50 and the pH 5 data of Fig. 7 obtained from leaching at L/S = 50 for 3 or 4 hr, depending on which part of the procedure is being performed. For some elements, the portions soluble under natural pH conditions are readily soluble even at the lowest L/S level, such that the average soluble fractions depicted on Fig. 8 differ little from their corresponding values on Fig. 10 or Fig. 11. These elements are Cd, Cu, K, Na, Ni, S, and Zn. Those elements, whose soluble portion benefits the most from more

leachant and more leaching time at their natural pH, show the greatest increase from Fig. 8 to Fig. 10 or 11. This group of elements includes As, Ba, Pb, Si, Ti, and V.

5. Conclusions

A serial batch characterization method has been developed which can generate leachate data on granular materials with 2-3 days of lab work. The procedure has been applied to 8 Class F pulverized coal combustion fly ashes. The method provides an indication of leachability of target elements under varying pH conditions and increasing liquid to solid ratios, including elements not detected in routine ash analyses. The method reproducibility has been presented over this range of leaching conditions. Some high values of RSD may be attributable to instrumental variability near the detection limits, resulting in large variations in very small numbers. This method is easy to use, requires only standard lab equipment, and can readily provide data that can be applied to the evaluation of the extent and rate of release of target elements in an aqueous environment. A universally adopted approach to leaching that is judged appropriate to material generators, handlers, and regulators will enhance the utilization of these materials while addressing environmental concerns.

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REFERENCES

- [1] Wastewater Technology Centre, *Compendium of Waste Leaching Tests*, Environmental Protection Series, Report EPS 3/HA/7, Environment Canada, Ottawa, Canada, 1990.
- [2] van der Sloot, H.A., Heasman, L., Quevauviller, Ph., *Harmonization of Leaching / Extraction Tests*, 281pp, Studies in Environmental Science 70, Elsevier, Amsterdam, 1997.
- [3] Clark, L.B., *Legislation for the management of coal-use residues*, IEACR/68, IEA Coal Research, London, Mar. 1994. ISBN 92-9029-234-2.
- [4] van der Sloot, H.A., Hoede, D., and Bonouvrie, P., "Comparison of different regulatory leaching test procedures for waste materials and construction materials," Netherlands Energy Research Foundation Report ECN-C--91-082, Dec., 1991.
- [5] Sorini, S, S., "An overview of leaching methods and their application to coal combustion by-products," *Proceedings: 12th International Symposium on Coal Combustion By-Product (CCB) Management and Use*, Vol. 2, pp43.1-43.17, American Coal Ash Association, EPRI TR-107055-V2, 3176, Jan., 1997.
- [6] Kim, Ann G., "CCB leaching summary: Survey of methods and results," *Proceedings: Coal Combustion By-Products and Western Coal Mines: A Technical Interactive Forum*, Golden, CO, April 16-18, 2002, 22 pp.
- [7] Kim, Ann G., "Leaching methods applied to CUB: standard, regulatory, and other," 15th International Symposium on Management and Use of Coal Combustion Products, St. Petersburg, FL, January 27-30, 2003, pp29-1 – 29-12.
- [8] van der Sloot, H.A., "Quick techniques for evaluating the leaching properties of waste

- materials: Their relation to decisions on utilization and disposal,” *Trends in Analytical Chemistry*, Vol.17, No.5, pp298-310, 1998.
- [9] Karuppiah, Makesh, and Gupta, Gian, “Toxicity of and metals in coal combustion ash leachates,” *Journal of Hazardous Materials*, Vol. 56, pp53-58, 1997.
- [10] van der Sloot, H.A., “Developments in evaluating environmental impact from utilization of bulk inert wastes using laboratory leaching tests and field verification,” *Waste Management*, Vol. 16, No. 1-3, pp65-81, 1996.
- [11] ASTM Subcommittee D34.02, Physical and Chemical Characterization, “Standard test method for sequential batch extraction of waste with water,” D4793, Mar., 1993.
- [12] van der Sloot, H.A.. “Leaching behavior of waste and stabilized waste materials; characterization for environmental assessment purposes,” *Waste Management & Research*, Vol. 8, pp215-223, 1990.
- [13] van der Sloot, H.A., Comans, R.N.J., and.Hjelmar, O., “Similarities in the leaching behavior of trace contaminants from waste, stabilized waste, construction materials and soils,” *The Science of the Total Environment*, Vol. 178, pp111-126, 1996.
- [14] Eary, L.E., R. Dhanpat, S. V. Mattigod, and C. C. Ainsworth, “Geochemical factors Controlling the Mobilization of Inorganic Constituents from Fossil Fuel Combustion Residues: II. Review of the Minor Elements,” *Journal of Environmental Quality*, Vol. 19, April-June, 1990, pp202-214.
- [15] Duchesne, J., and Reardon, E.J., “Lime treatment of fly ash: Characterization of leachate composition and solid / water reactions,” *Waste Management* Vol. 19, pp221-231, 1999.
- [16] Praharaj, T., Powell, M.A., Hart, B.R., and Tripathy, S., “Leachability of elements from sub-bituminous coal fly ash from India,” *Environment International*, Vol. 27, pp609-615, 2002.
- [17] Wilson, D.C., and Young, P.J., “Testing methods for hazardous wastes prior to landfill disposal,” Testing Methods for Hazardous Wastes - Problems in Characterization, Ch. 8, pp69-81, Butterworth Publishers, Woburn, MA, 1983.
- [18] Eighmy, T.T., and H.A. van der Sloot, “A Unified Approach to Leaching Behavior of Waste Materials”, *Environmental Aspects of Construction with Waste Materials*, pp979-988, Elsevier Science, 1994.
- [19] Brunori, C., S. Balzamo, and R. Morabito, “Comparison between Different Leaching / Extraction Tests for the Evaluation of Metal Release from Fly Ash,” *Intern. J. Environ. Anal. Chem.*, Vol. 75(1-2), pp19-31, 1999.
- [20] Kosson, D. S., 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,” *Environmental Engineering Science*, Vol. 19, No. 3, pp159-203, 2002.
- [21] Hassett, D.J., “A Generic Test of Leachability: the Synthetic Groundwater Leaching Method,” *Proceedings: Waste Management for the Energy Industries Conference*, April 29 – May 1, 1987, University of North Dakota, Grand Forks, North Dakota, pp31-39, 1987.
- [22] Hassett, D. J., “Synthetic Groundwater Leaching Procedure,” Encyclopedia of Environmental Analysis and Remediation, R. A. Meyers, ed., pp4797-4803, John Wiley & Sons, Inc., Hoboken, NJ, 1998.
- [23] Kim, Ann G., G. Kazonich, and M. Dahlberg, “Relative solubility of cations in class F fly ash,” *Environ. Sci. & Technol.*, Vol. 37, No.19, pp4507-4511, 2003.
- [24] de Groot, G.J., Wijkstra, J., Hoede, D., and van der Sloot, H.A., “Leaching characteristics of selected elements from coal fly ash as a function of the acidity of the contact solution and the liquid/solid ratio,” pp70-183, Environmental Aspects of Stabilization and Solidification of

Hazardous and Radioactive Wastes, ASTM STP 1033, P.L. Côté and T.M. Gilliam, Eds., American Society for Testing and Materials, Philadelphia, 1989.

[25] Mudd, Gavin M., and Kodikara, Jayantha, "Field studies of the leachability of aged brown coal ash," *Journal of Hazardous Materials*, Vol. 00, pp1-34, 2000.

[26] Fytianos, K., Tsaniklidi, B., and Voudrias, E., "Leachability of heavy metals in Greek fly ash from coal combustion," *Environment International*, Vol. 24, No. 4, pp477-486, 1998.

[27] van der Sloot, H.A., Kosson, D.S., Eighmy, T.T., Comans, R.N.J., and Hjelmar, O., "Approach towards international standardization: A concise scheme for testing of granular waste leachability," pp453-466, Environmental Aspects of Construction with Waste Materials, J.J.J.M. Goumans, H.A. van der Sloot, and Th. G. Aalbers, Eds., Elsevier Science, Amsterdam, 1994. ECN-RX-94-012, ECN, Petten, The Netherlands, 1994.

[28] Quevauviller, Ph., H.A. van der Sloot, A. Ure, H. Muntau, A. Gomez, and G. Rauret, "Conclusions of the Workshop: Harmonization of Leaching/Extraction Tests for Environmental Risk Assessment," *The Science of the Total Environment*, Vol. 178, pp133-139, 1996.

[29] van der Sloot, H.A., de Groot, G.J., and Wijkstra, J., "Leaching characteristics of construction materials and stabilization products containing waste materials," pp125-149, Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes, ASTM 1033, P.L. Côté and T.M. Gilliam, Eds., American Society for Testing and Materials, Philadelphia, 1989.

[30] Fällman, A.M., "Performance and design of the availability test for measurement of potentially leachable amounts from waste materials," *Environmental Science and Technology*, Vol. 31, pp735-744, 1997.

[31] Van Herck, P., and Vandecasteele, C., "Evaluation of the use of a sequential extraction procedure for the characterization and treatment of metal-containing solid waste," *Waste Management*, Vol. 21, pp685-694, 2001.

[32] van der Sloot, H.A., D.Hoede, R.N.J. Comans, "The Influence of Reducing Properties on Leaching of Elements From Waste Materials and Construction Materials," *Environmental Aspects of Construction with Waste Materials*, pp483-490, Elsevier Science, 1994.

[33] Wang, J., A. Takaya, and A. Tomita, "Leaching of Ashes and Chars for Examining Transformations of Trace Elements During Coal Combustion and Pyrolysis," *Fuel*, Vol. 83, pp651-660, 2004.

[34] Hassett, D.J., D. F. Pflughoeft-Hassett, and G. J. McCarthy, "Ettringite Formation in Coal Ash as a Mechanism for Stabilization of Hazardous Trace Elements," *Proceedings: Eighth Annual Pittsburgh Coal Conference, Pittsburgh, PA, Oct. 14-18, 1991*, pp563-568.

Figure 1. Release of Boron from FA 38

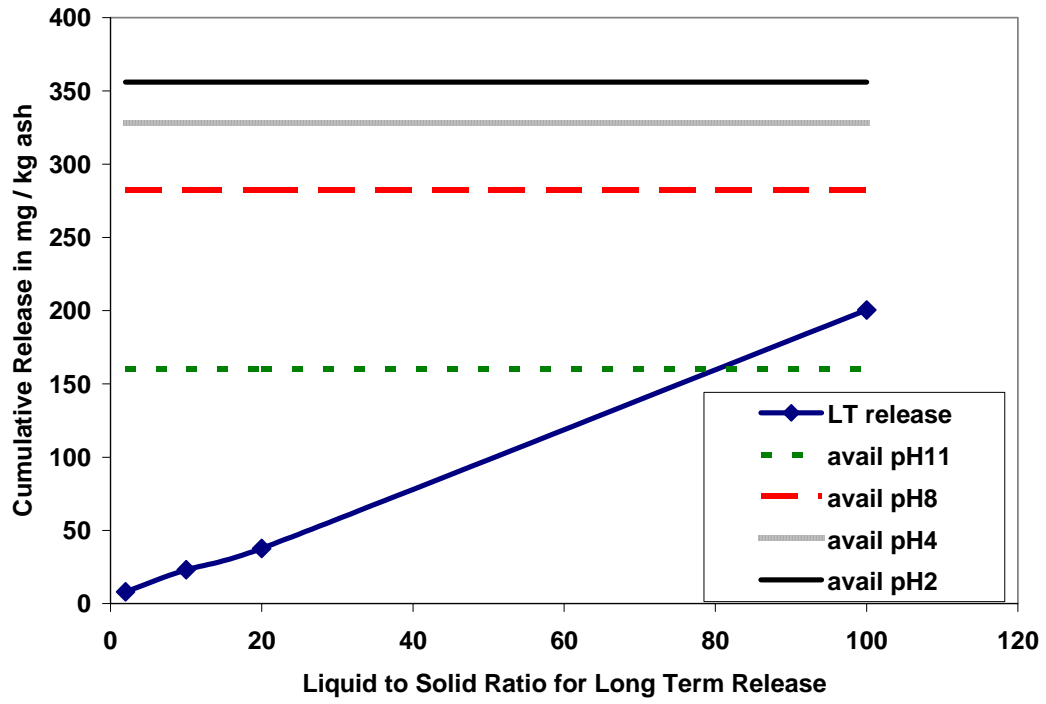


Figure 2. Release of Boron from FA 49

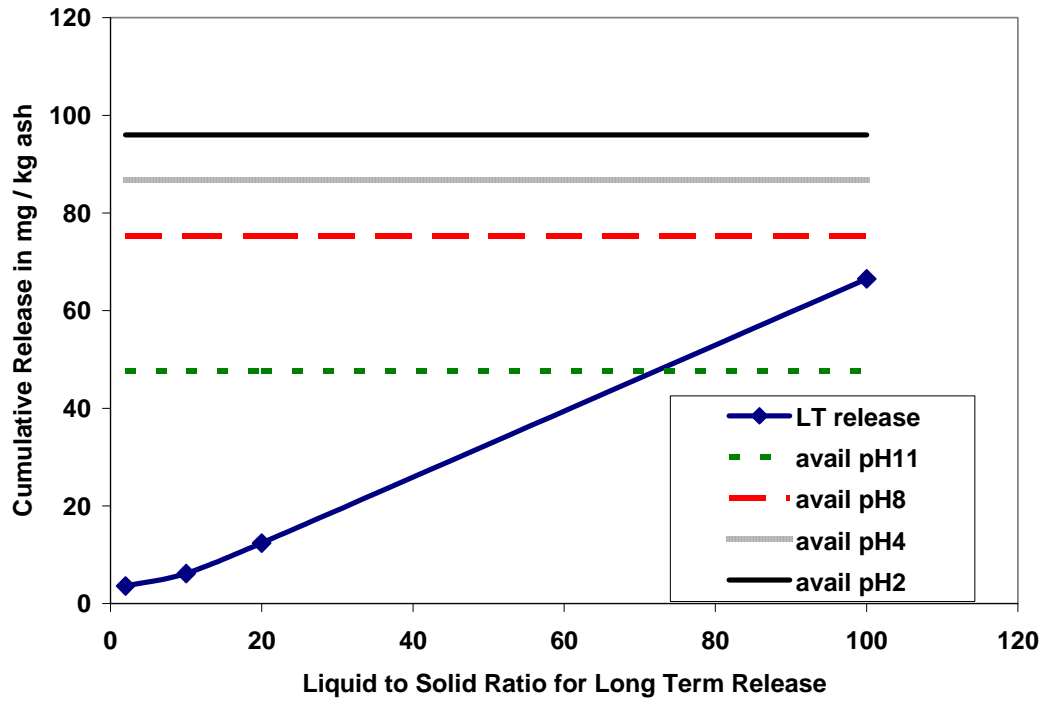


Figure 3. Alkaline Ashes pH 11

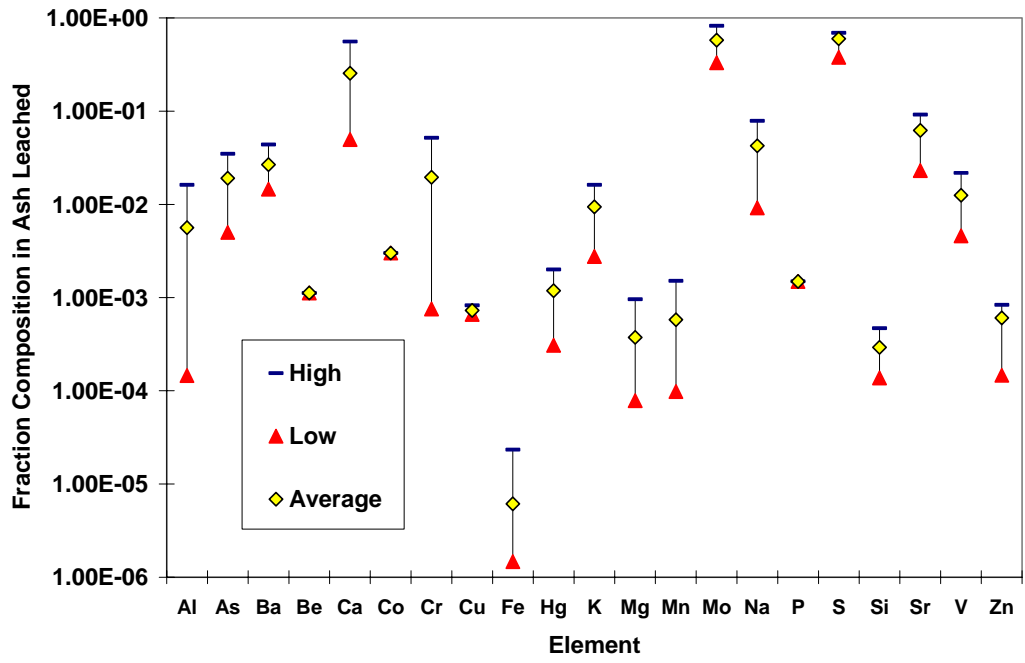


Figure 4. Alkaline Ashes pH 11 and 8

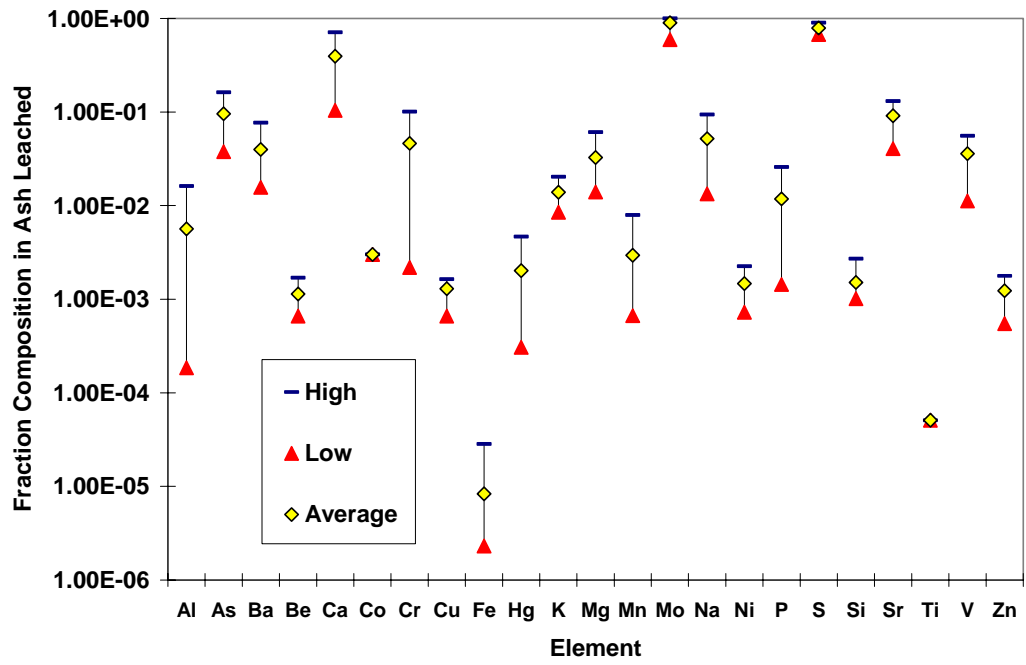


Figure 5. Alkaline Ashes Ph 11, 8, and 4

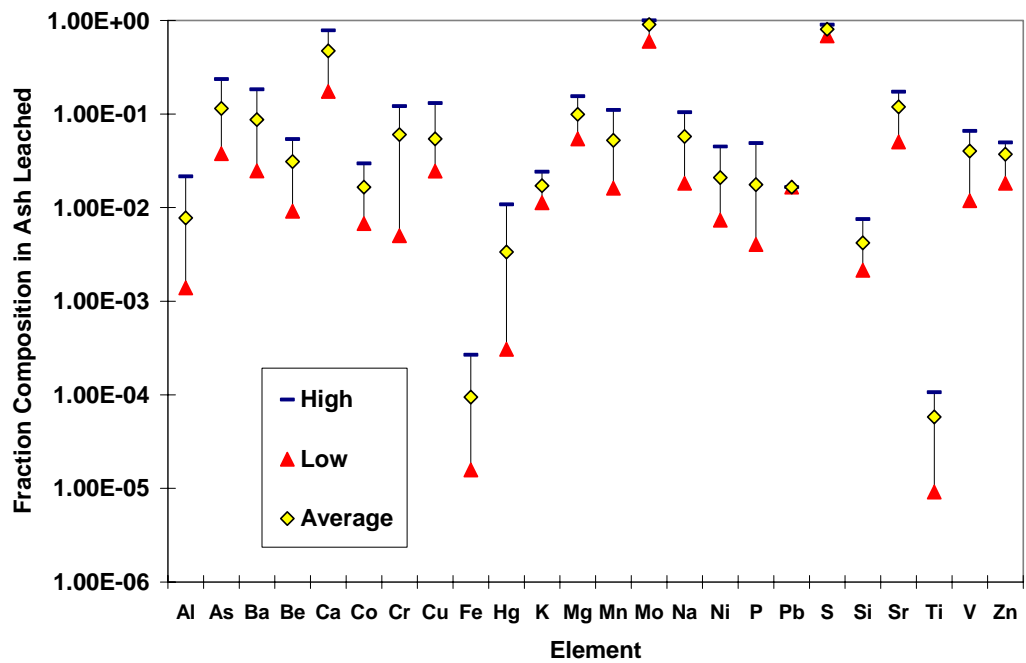


Figure 6. Alkaline Ashes pH 11, 8, 4, and 2

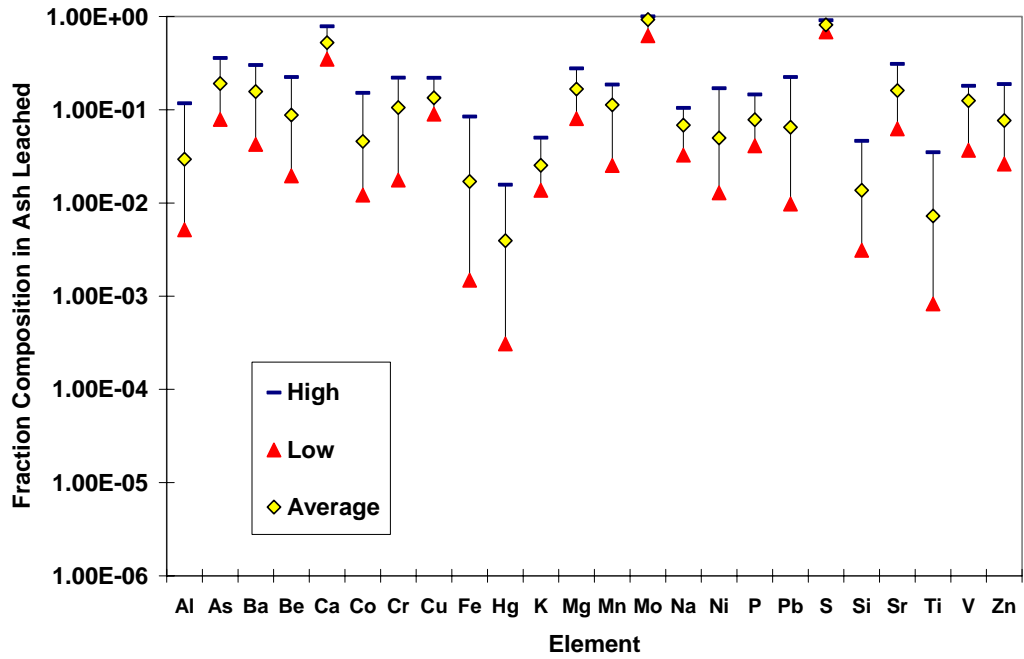


Figure 7. Leached Fraction of Ash Composition. Availability Test on Acidic Ashes

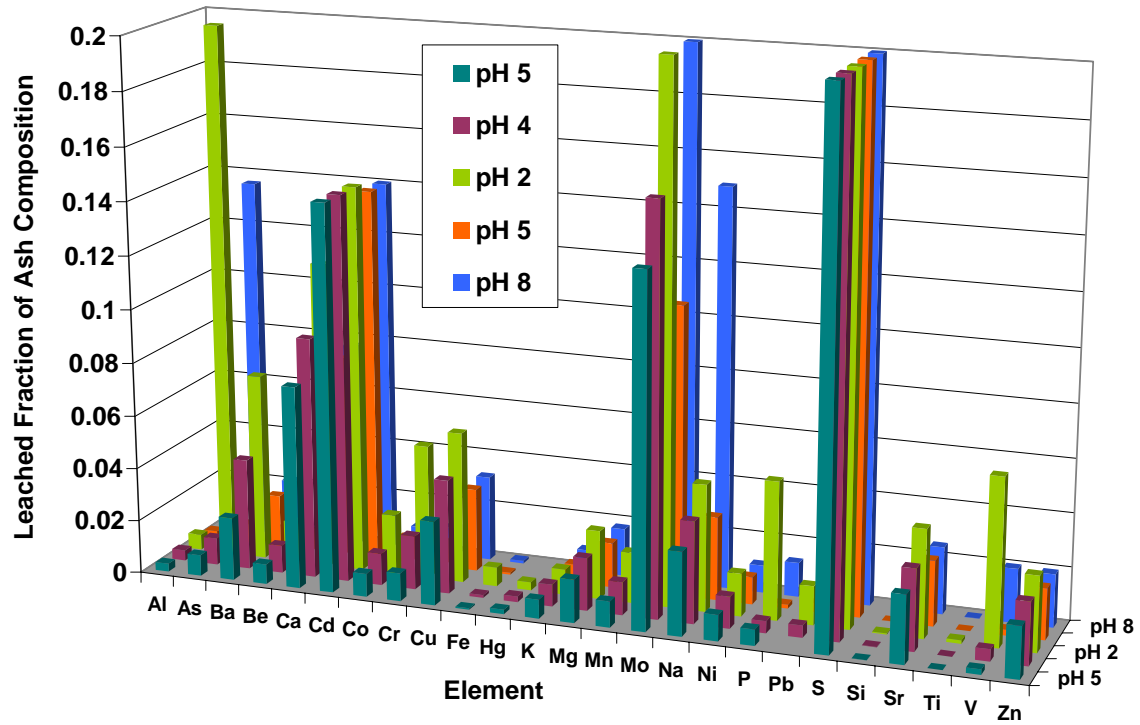


Figure 8.

L/S 2

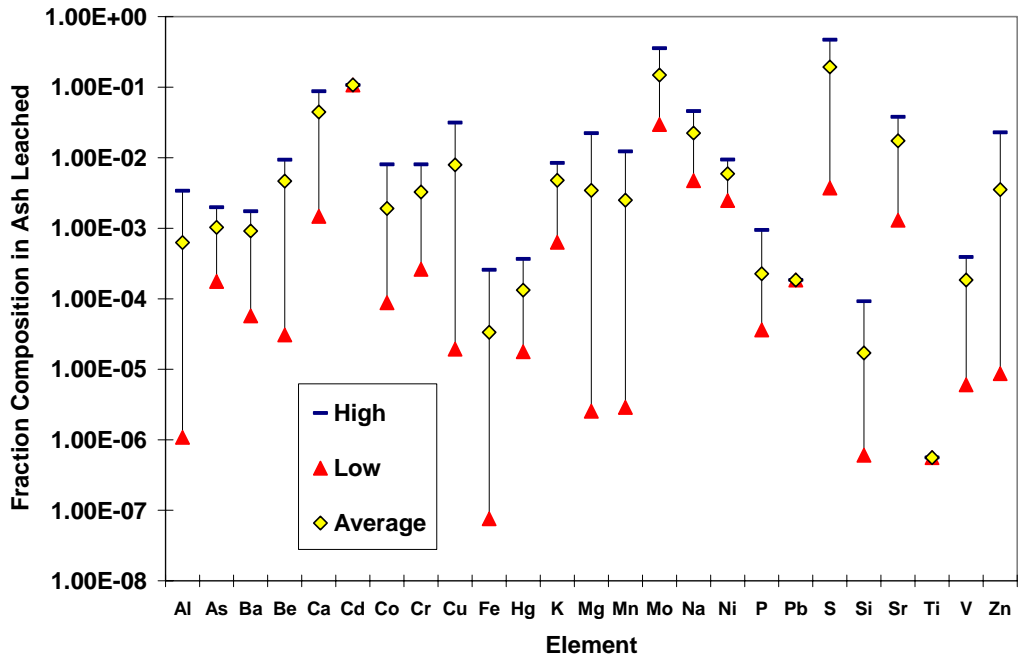


Figure 9.

L/S 2 + 8

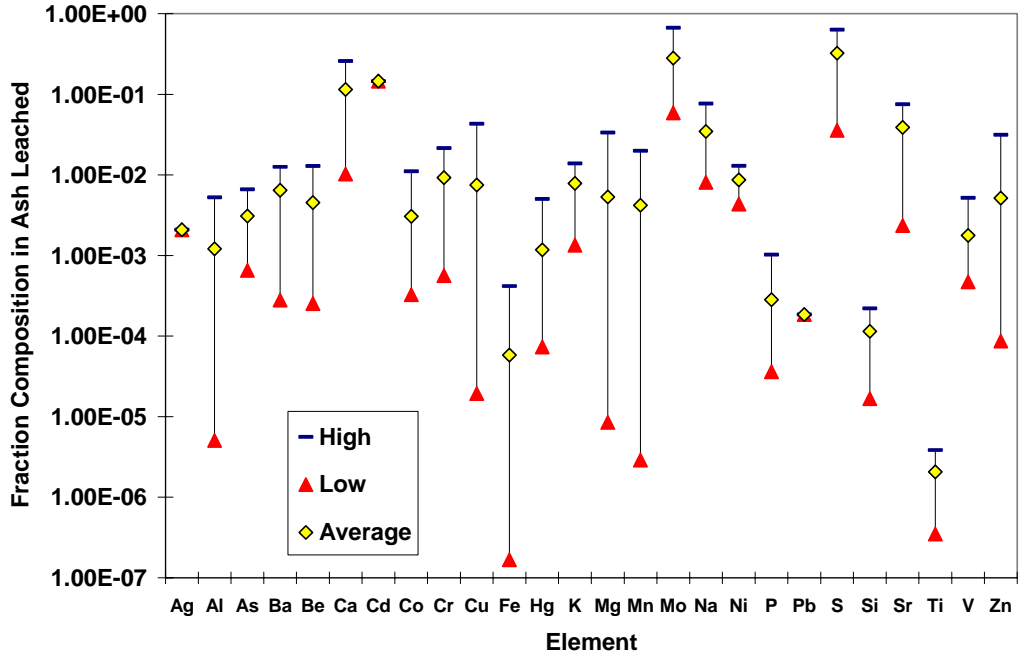


Figure 10.

L/S 2 + 8 + 10

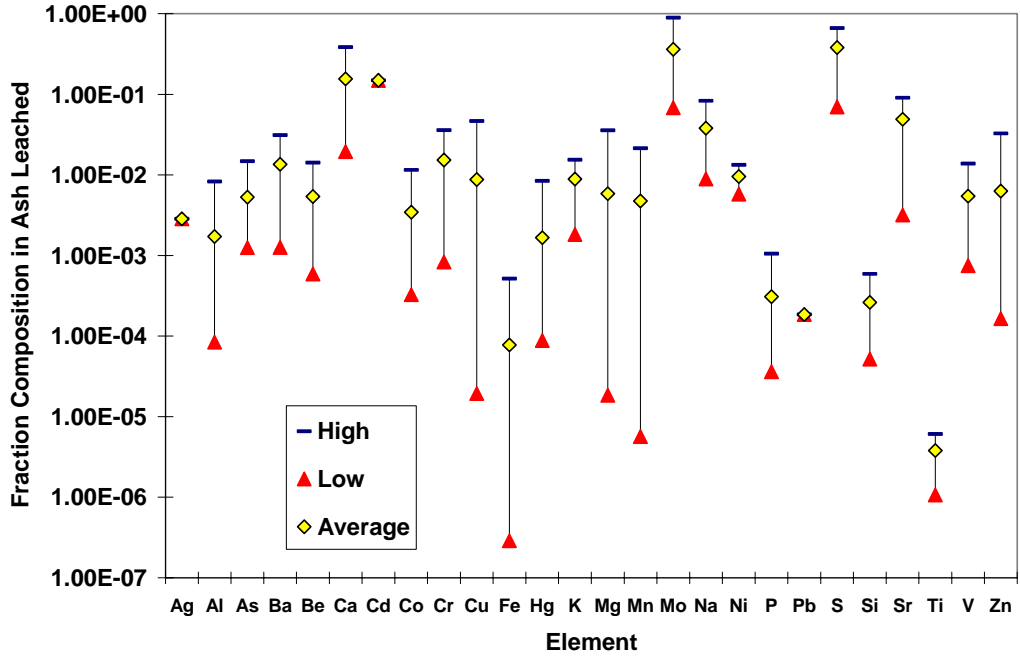


Figure 11.

L/S 100

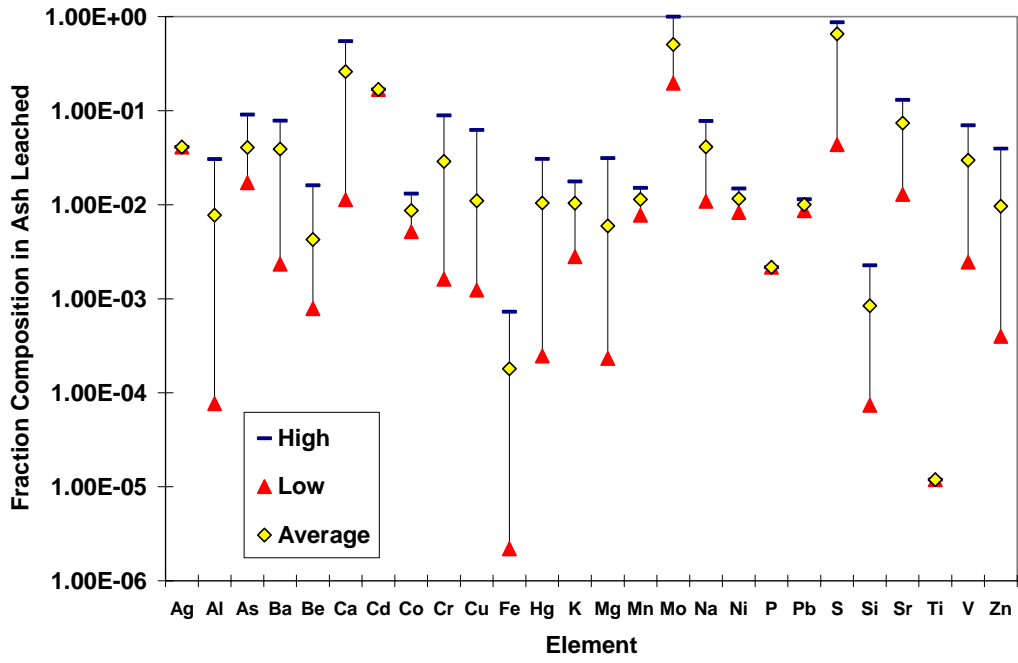


Table1. Fly Ash Composition in ug / g.^a

Element	FA 20	FA 24	FA 28	FA 32	FA 38	FA 39	FA 41	FA 49
Ag	<1	<1	5	<1	<1	<1	<1	<1
Al	112000	159000	86200	103000	122000	127000	120000	79300
As	238	43.8	62.4	62.8	63.9	136	44.4	18.4
Ba	1220	728	525	692	810	1420	4200	441
Be	12.2	15.3	20.7	8.92	7.59	10.8	9.17	4.74
Ca	27100	4290	4510	35900	33200	38600	113000	21800
Cd	<0.5	<0.5	1.4	<0.5	<0.5	<0.5	<0.5	<0.5
Co	53.4	63.6	81.5	34.9	29.8	50.1	42.8	34.2
Cr	184	180	194	178	148	167	115	106
Cu	139	150	174	61.6	64.6	170	197	25.9
Fe	88000	19900	15300	113000	93500	55000	37700	197000
Hg	0.1304	0.0513	0.0484	0.0071	0.0488	0.0817	0.2642	0.0921
K	16700	22700	19500	18800	12600	19700	9880	8800
Mg	3890	4680	2830	5410	5470	9840	22900	3390
Mn	161	99.8	158	367	201	352	169	260
Mo	5.7	6.7	18.4	47.7	<3	<3	<3	<3
Na	2430	2700	2240	8050	6880	3780	9030	2300
Ni	138	118	125	119	74.4	84	82.8	69.4
P	1740	398	775	963	1660	1190	3340	439
Pb	74.5	68.7	89.8	92.8	39.7	77.2	41.5	9.9
S	2310	859	2170	7000	4540	4300	3190	4040
Sb	<7	<7	<7	<7	<7	<7	<7	<7
Se	<8	<8	<8	<8	<8	<8	<8	<8
Si	230000	306000	295000	104100	237000	274000	270000	203000
Sr	524	542	305	310	1240	1180	2200	556
Ti	7080	8950	11000	5790	6190	8470	8740	3980
Tl	<10	<10	<10	<10	<10	<10	<10	<10
V	256	262	291	784	192	227	229	131
Zn	252	150	165	477	152	201	150	85.7

^a Fly ash numbers refer to samples in the NETL CUB inventory.

Table 2. Reproducibility from Availability Data.^b

Element	pH 11	pH 11+8	pH 11+8+4	pH 11+8+4+2
Ag	0.153(2)	0.519(1,2)	0.782(1,3)	0.329(2,4)
Al	0.174(24)	0.172(21,24)	0.126(13,24)	0.146(24,24)
As	0.0949(17)	0.116(22,22)	0.121(13,22)	0.245(24,24)
B	0.173(23)	0.0934(24,24)	0.0908(24,24)	0.116(24,24)
Ba	0.107(24)	0.110(24,24)	0.765(24,24)	0.106(24,24)
Be	0(1)	0.140(3,4)	0.0961(24,24)	0.104(24,24)
Ca	0.0455(24)	0.0520(24,24)	0.0290(24,24)	0.0604(24,24)
Cd	0(1)	0(0,1)	0.111(24,24)	0.124(24,24)
Co	0(1)	0(0,1)	0.0889(24,24)	0.200(24,24)
Cr	0.0854(24)	0.0910(24,24)	0.0881(24,24)	0.120(24,24)
Cu	0.0684(5)	0.318(3,5)	0.147(24,24)	0.106(24,24)
Fe	0.286(20)	0.370(12,20)	0.316(24,24)	0.378(24,24)
Hg	0.406(7)	0.260(2,8)	0.428(3,10)	0.464(5,13)
K	0.0832(24)	0.238(24,24)	0.213(24,24)	0.163(24,24)
Mg	0.273(23)	0.0713(24,24)	0.428(24,24)	0.0696(24,24)
Mn	0.0330(4)	0.327(22,23)	0.0658(24,24)	0.120(24,24)
Mo	0.0601(24)	0.0544(24,24)	0.0536(11,24)	0.0550(24,24)
Na	0.0881(24)	0.0911(24,24)	0.0918(24,24)	0.112(24,24)
Ni	bdl(0)	0.0455(7,7)	0.0753(24,24)	0.108(24,24)
P	0(1)	0.152(24,24)	0.136(19,24)	0.350(24,24)
Pb	bdl(0)	bdl(0,0)	0(1,1)	0.328(19,19)
S	0.0632(24)	0.0560(24,24)	0.0564(24,24)	0.0578(24,24)
Sb	0.0644(3)	0.208(7,9)	0.241(4,10)	0.328(2,10)
Se	0.200(23)	0.200(21,24)	0.216(8,24)	0.218(6,24)
Si	0.161(24)	0.0932(24,24)	0.0513(24,24)	0.117(24,24)
Sr	0.0215(24)	0.0310(24,24)	0.0205(24,24)	0.0562(24,24)
Ti	bdl(0)	0(1,1)	0.0859(3,3)	0.537(24,24)
Tl	0(1)	0(0,1)	0.0755(9,9)	0.199(12,15)
V	0.0761(24)	0.0834(24,24)	0.0781(24,24)	0.218(24,24)
Zn	0.188(10)	0.324(12,12)	0.0802(24,24)	0.0916(24,24)

^b Relative standard deviation within the replicates at each step, derived from mg / kg ash data and averaged for 6 alkaline ashes. () = No. of detected data points. First value is for the specific pH step, second is for the cumulative sum of steps. “bdl” indicates all replicates were “below detection limit.”

Table3. Reproducibility from Long Term Data.^c

Element	L/S 2	L/S 2+8	L/S 2+8+10	L/S 100
Ag	0.299(11)	0.279(10,14)	0.357(6,15)	0.381(10)
Al	0.387(29)	0.513(31,31)	0.332(31,31)	0.0801(32)
As	0.296(19)	0.247(23,25)	0.241(21,28)	0.0918(20)
B	0.335(29)	0.299(27,29)	0.218(28,29)	0.152(30)
Ba	0.247(33)	0.195(33,33)	0.174(33,33)	0.0523(32)
Be	0.255(8)	0.349(9,9)	0.288(10,10)	0.0414(11)
Ca	0.109(33)	0.132(33,33)	0.102(33,33)	0.0265(32)
Cd	0.109(16)	0.174(17,19)	0.215(15,19)	0.0655(10)
Co	0.129(14)	0.293(14,15)	0.252(11,15)	0.0620(9)
Cr	0.226(33)	0.144(33,33)	0.125(33,33)	0.0443(32)
Cu	0.0800(11)	0.225(11,14)	0.166(9,14)	0.104(17)
Fe	0.320(22)	0.336(21,23)	0.285(23,23)	0.523(31)
Hg	0.655(11)	0.733(11,12)	0.800(11,15)	0.433(14)
K	0.186(33)	0.148(33,33)	0.144(33,33)	0.0401(32)
Mg	0.309(30)	0.217(31,31)	0.162(31,31)	0.176(32)
Mn	0.130(20)	0.133(17,20)	0.270(16,21)	0.0154(8)
Mo	0.231(33)	0.189(33,33)	0.182(33,33)	0.0876(32)
Na	0.136(33)	0.121(33,33)	0.125(33,33)	0.0308(32)
Ni	0.178(9)	0.183(9,9)	0.157(9,9)	0.0753(8)
P	0.0884(10)	0.122(6,10)	0.130(3,10)	0.190(2)
Pb	0(1)	0(0,1)	0(0,1)	0.180(4)
S	0.161(33)	0.123(33,33)	0.108(33,33)	0.0677(32)
Sb	0(2)	0(2,2)	0.227(3,5)	0.180(12)
Se	0.213(33)	0.190(33,33)	0.170(30,33)	0.0823(28)
Si	0.250(31)	0.257(33,33)	0.249(33,33)	0.136(32)
Sr	0.141(28)	0.0962(28,28)	0.0861(28,28)	0.0190(32)
Ti	0.355(4)	0.178(5,6)	0.139(7,7)	0.111(4)
Tl	0.0722(4)	0.100(4,4)	0.100(0,4)	0(1)
V	0.331(27)	0.284(33,33)	0.183(33,33)	0.0629(32)
Zn	0.552(25)	0.539(18,25)	0.520(15,25)	0.0982(12)

^c Relative standard deviation within the replicates at each step, derived from mg / kg ash data and averaged for all 8 ashes. () = No. of detected data points. First value is for the specific L/S step, second is for the cumulative sum of steps. L/S =100 is a separate set.