

Relative Solubility of Cations in Class F Fly Ash

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Coal utilization byproducts (CUB), such as fly ash, contain cations that may be released during exposure to fluids such as acid rain or acid mine drainage. Researchers at the Department of Energy's National Energy Technology Laboratory (DOE/NETL) have conducted a long-term column leaching study of 32 Class F fly ash samples from pulverized coal (PC) combustion, and quantified the release of 19 cations in four leachants with a pH between 1.2 and 12. The relative solubility (M_{Lr}) of each cation was defined as the total mass leached (M_L) relative to the concentration (M_T) of that element in the fly ash sample. A frequency distribution of relative solubility values was computed with ranges defined as insoluble, slightly soluble, moderately soluble, and very soluble. On the basis of this sample set, Ba, Cd, Fe, Pb, Sb, and Se in PC fly ash are insoluble. The elements Al, Be, Ca, Co, Cr, Cu, K, Mg, Mn, Na, Ni, and Zn are slightly to moderately acid soluble. Only Ca and Na are water soluble; As and Ca are soluble in the basic solution. The results of this study indicate that the extent to which cations in Class F PC fly ash can be leached by naturally occurring fluids is very limited.

Introduction

More than 50% of the electricity generated in the United States is produced by coal-burning power plants (1). Electric power production also generates over 100 million tons of coal utilization byproducts (CUB), including 63 million tons of fly ash (2). The CUB are primarily the inorganic residue from coal; they contain a number of elements that, if released to surface water or groundwater, could affect the environment or public health. The extent to which they can be released from CUB by fluids such as acid rain or acid mine drainage impacts their suitability for various beneficial uses, such as bulk fill and mine remediation.

Researchers at the U.S. Department of Energy's National Energy Technology Laboratory (DOE/NETL) have conducted a long-term column leaching study to determine the compositional and leachant factors that control the solubility of various metals from fly ash. The column leaching experiment was designed to simulate natural flow conditions and to include a large random population of CUB samples.

The cations analyzed in this study have been selected from those for which EPA has established maximum contaminant levels and from freshwater aquatic life criteria. Several elements in these categories were excluded (Ag and Hg, for example) because their concentration in this group of fly ash samples is known to be extremely low. Major and

TABLE 1. Leachant Solutions for Column Leaching Tests of PC Fly Ashes

leachant solution	ID	pH	type	concentration, mol/L
sulfuric acid	H ₂ SO ₄	1.2	H ⁺	0.05
acetic acid	HAc	2.9	H ⁺	0.099
deionized water	H ₂ O	5.7	HOH	
sodium carbonate	Na ₂ CO ₃	11.1	OH ⁻	0.05

minor elements, such as Ca and Mg, were included because their dissolution affects the pH of the leachate which controls the solubility of several trace elements. Although fly ash contains a high percentage of quartz and amorphous silica, its concentration in the leachate was not determined because the solubility of these compounds at pH <9 is very low and because they are not regarded as aquatic contaminants.

Solubility of major, minor, and trace elements was determined as the cumulative amount leached divided by the sample weight. The relative solubility was calculated as a function of the concentration in the fly ash. Both parameters were evaluated with respect to the acid-base character of the leachant solution.

The objectives of this study were to determine the total amount of each of 19 cations leached from Class F PC fly ashes, and to assign a relative solubility class for each element based on the amount leached relative to the total amount in the sample.

Materials and Methods

To develop data that are broadly applicable to the release of cations from fly ash and to quantify the release as a function of the composition of the ash, the sample population must encompass the inherent variability of the material. Of the 48 samples used in this project, 32 were Class F fly ashes obtained from pulverized coal (PC) electric power plants. The majority of these PC plants were located in Pennsylvania and West Virginia, but samples were also obtained from plants in Florida, Maryland, and Tennessee. The relative solubility of cations from the other samples, such as bottom ash, Class C fly ash, and fly ash from fluidized bed combustion, will be addressed in future papers.

The Class F PC fly ash samples were sent to a commercial laboratory for analysis. They were dissolved by triple acid digestion in HF, HNO₃, and H₃BO₄, and analyzed by ICP-AES. The PC fly ashes are composed mainly of oxides of Si, Al, Ca, and Fe. When calculated as oxides, between 40 and 65% of the sample is SiO₂ as quartz or amorphous silica. Approximately 25% of the sample by weight is Al₂O₃, and the concentration of FeO is between 3 and 30% of the fly ash sample. Calculated as CaO, the calcium concentration averages 3% of the fly ash sample. The fly ash samples also contain variable amounts of the minor elements (Mg, Mn, K, and Na) and trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, and Zn). The composition of the samples is given in the Supporting Information, Tables S1 and S2 and Figure S1.

Leaching was carried out in a column system designed to simulate the reaction of granular materials during exposure to fluids, such as acid rain or acid mine drainage (AMD). The columns, appropriate for unconsolidated materials with a particle diameter of less than 0.5 cm, are constructed of 1-m sections of 5-cm i.d. clear PVC pipe, capped with threaded PVC pipe caps (3). Plastic pipe fittings, 6-mm i.d., are used for the leachant delivery line, a pressure relief tube, and

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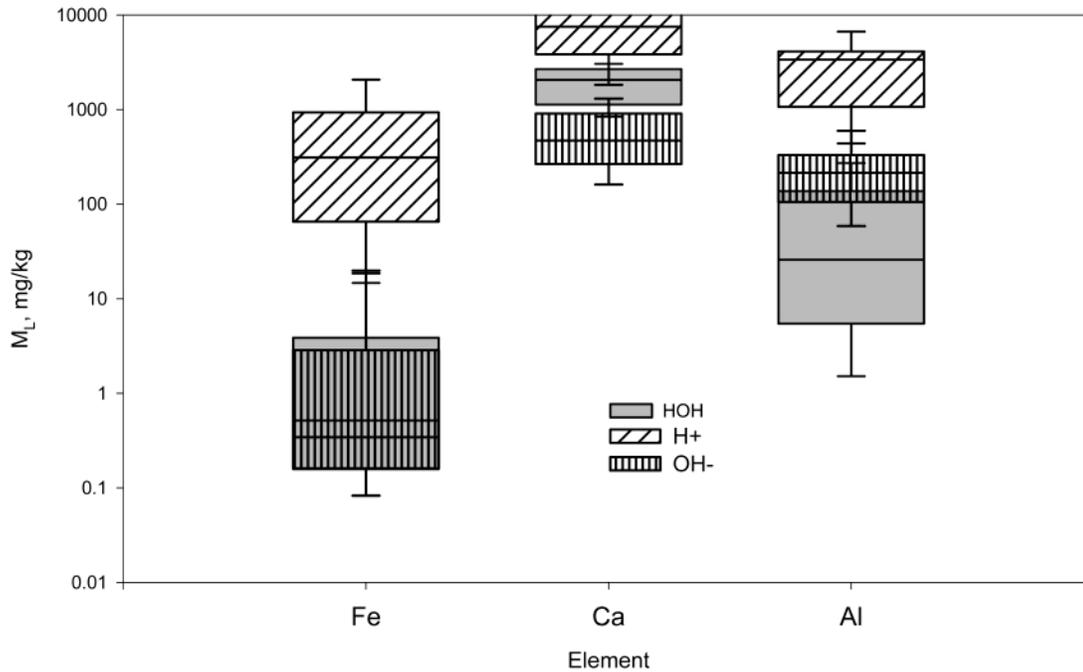


FIGURE 1. Box plot of distribution of leached mass (M_L) values for major elements in 32 Class F fly ash samples in acidic (H^+), basic (OH^-), and neutral (HOH) leachants. The box represents the 10th to 90th percentiles; the solid line within the box represents the median.

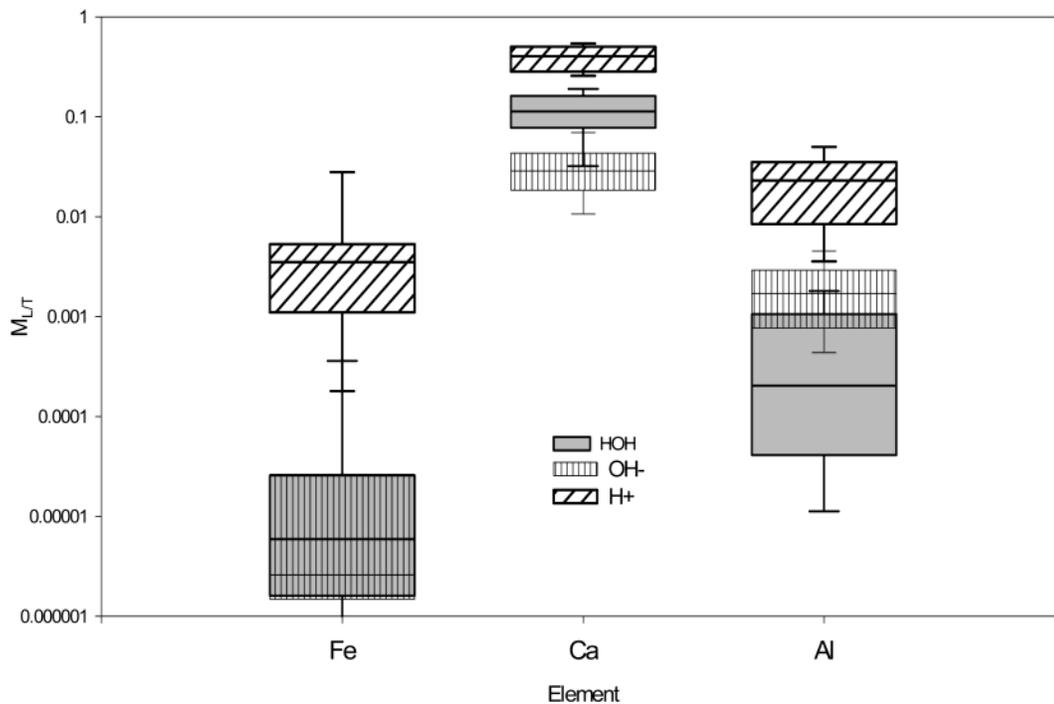


FIGURE 2. Box plot of relative solubility ($M_{L/T}$) values for major elements in 32 Class F fly ash samples in acidic (H^+), basic (OH^-), and neutral (HOH) leachants. The box represents the 10th to 90th percentiles; the solid line within the box represents the median.

leachate recovery. The columns have an approximate volume of 2 L, large enough to hold a representative 1-kg sample of Class F PC fly ash.

The leaching solutions were selected to represent the broad pH range of common fluids (Table 1). Deionized water is a neutral liquid, representative of exposure to surface water or groundwater. Acetic acid is a weak acid, and is an indicator of potential leaching during co-disposal in a municipal solid waste (MSW) landfill. Sodium carbonate is a high pH solution

for elements that are caustic soluble. Sulfuric acid is a strong acid and is a component of AMD.

The 0.1 N leachant solutions are stored in 20-L reservoirs, and a peristaltic pump delivers them to the columns at a flow rate of approximately 130 mL/d. Leachate is collected in 1-L volumetric cylinders. Samples were taken at 2- to 3-d intervals and analyzed for pH, the major elements (Al, Ca, and Fe), the minor elements (Mn, Mg, K, and Na), and the trace elements (Sb, As, Ba, Be, Cd, Co, Cr, Cu, Pb, Ni, Se, and

TABLE 2. Average Elemental Concentration (M_T) of Cations in Class F PC Fly Ash and Cumulative Amount Leached (M_L , in mg/kg) in Acids, and in Basic (OH^-) and Neutral (HOH) Leachants

element	M_T	M_L			
		OH^-	HOH	HAc	H_2SO_4
Al	130276.56	326.67	99.39	729.73	3175.80
As	115.69	34.37	3.02	2.18	6.77
Ba	887.97	5.36	15.11	24.21	4.42
Be	10.61	0.03	0.03	0.34	0.87
Ca	22520.00	630.11	2042.33	8775.96	4787.10
Cd	10.79	0.02	0.04	0.13	0.20
Co	40.61	0.08	0.12	0.64	1.98
Cr	154.06	2.57	1.38	5.29	5.28
Cu	163.03	0.70	0.92	5.01	11.55
Fe	102805.31	4.97	5.82	122.09	767.76
K	16187.81	221.40	181.66	259.35	584.49
Mg	5702.50	29.69	43.32	411.31	559.71
Mn	271.56	0.54	0.92	24.63	26.40
Na	3631.25	ND ^a	189.92	353.33	1196.05
Ni	152.64	0.58	0.43	2.07	5.87
Pb	77.13	0.00	0.07	0.02	0.43
Sb	10.92	0.34	0.07	0.06	0.02
Se	8.97	2.17	0.77	0.63	0.71
Si	229743.13	ND	ND	ND	ND
Zn	158.50	0.77	1.04	8.35	20.53

^a Not determined.

Zn). The concentration of the metals was determined by ICP-AES. Each set of samples was leached for between 30 and 90 d, depending on the natural alkalinity of the Class F fly ash samples. All tests were run at ambient temperature, averaging 21 °C with seasonal variations of ±9 °C.

Results

Leaching was assumed to have reached completion when the slope of the cumulative leached mass curve versus leachate volume approached zero (4). To determine the relative solubility of each of the measured cations, the cumulative amount leached per unit sample mass was calculated and then divided by the concentration of that element in the fly ash sample. The cumulative amount of an element leached per unit sample, M_L , is equal to the sum of

the concentrations measured in each leachate sample times the volume of leachate divided by the total weight of the sample.

$$M_L = \frac{\sum(C \cdot V)}{S} \quad (1)$$

where M_L = cumulative amount leached in mg/kg; C = concentration in the individual leachate sample (mg/L); V = volume of individual leachate sample in L; and S = sample weight in kg.

The relative solubility of each cation in the fly ash, $M_{L/T}$, was defined as the cumulative amount leached per unit sample divided by the concentration of that element in the solid fly ash.

$$M_{L/T} = \frac{M_L}{M_T}$$

where $M_{L/T}$ = mass leached relative to the total concentration in the flyash; M_L = cumulative amount leached from the ash sample in mg/kg; and M_T = total concentration of an element in the fly ash sample in mg/kg.

This calculation was performed for major, minor, and trace elements in four leachant solutions: water (H_2O), sodium carbonate (Na_2CO_3), acetic acid (HAc), and sulfuric acid (H_2SO_4).

The distribution of M_L values in water (HOH), basic (OH^-), and acidic (H^+) leachants for the major elements is shown in Figure 1. In this and subsequent figures, the box represents the values between the 10th and 90th percentiles, and the median is represented as a solid line within the box. The acid (H^+) value is the maximum amount leached for a given sample in either HAc or H_2SO_4 . For this group of samples, the pH (or more accurately the concentration of hydrogen ions) is the controlling variable regardless of the acid donor. The leached concentration in H_2SO_4 is greater than that in HAc by a factor of 2 to 10, except for Ca and Ba which form insoluble sulfates that precipitate in the columns.

The total mass of Fe leached per unit sample (M_L) was less than 10 ppm in aqueous and basic solutions; in 0.1 N acid solutions, less than 1 g/kg (1000 ppm) Fe was leached

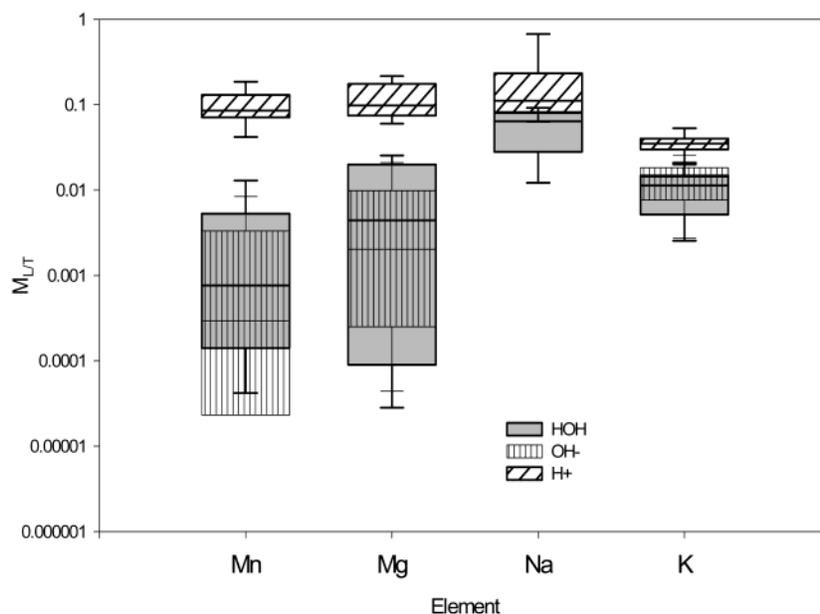


FIGURE 3. Box plot of relative solubility values for minor elements in 32 Class F PC fly ash samples in acidic (H^+), basic (OH^-), and neutral leachants. The box represents the 10th to 90th percentiles; the line within the box is the median.

TABLE 3. Frequency Distribution and Relative Frequency Distribution of Relative Solubility Values (M_{LT}) for Mg Leached from Class F Fly Ash

M_{LT} range	H ₂ O		Na ₂ CO ₃		HAc		H ₂ SO ₄	
	number of values	% of values	number of values	% of values	number of values	% of values	number of values	% of values
≤0.02	24	75	28	88	4	13	3	9
0.02 to 0.20	8	25	4	13	27	84	26	81
0.20 to 0.65	0	0	0	0	1	3	3	9
>0.65	0	0	0	0	0	0	0	0

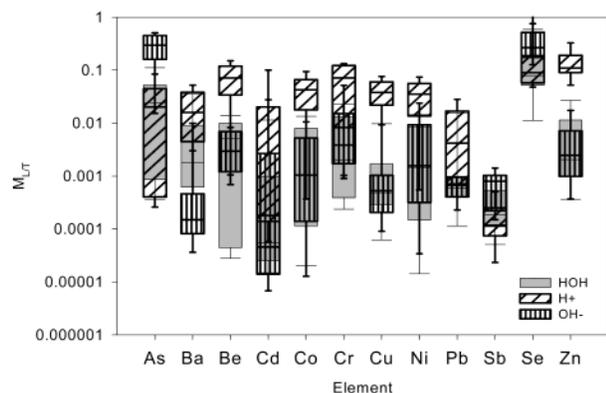


FIGURE 4. Box plot of relative solubility (M_{LT}) values for trace elements in 32 Class F PC fly ash samples in acidic (H^+), basic (OH^-), and neutral (HOH) leachants. The box represents the 10th to 90th percentiles; the solid line in the box is the median.

from the fly ash samples (Figure 1). The fraction of Fe leached relative to the concentration in the fly ash samples (M_{LT}) was less than 0.0001 in water and in the basic solution, and less than 0.01 in the acid leachant (Figure 2). Between 0.3 and 8 g/kg of Al was leached from the fly ash by the acid leachants. In all leachants, the M_{LT} values for Al were between 0.00001 and 0.1, slightly higher than those for Fe. Calcium (Ca) was the most soluble major element; in water, M_L was greater than 1 g/kg. The median acid soluble mass was 6.9 g/kg and the maximum value was 26.3 g/kg. For Ca, M_{LT} was greater than 0.01 in water and approached 1 in the acid leachant. Average values of M_L for all elements in the four leachants are given in Table 2.

On the basis of the median values, the cumulative amount of the minor elements (Mn, Mg, Na, and K) leached was less than 1 g/kg in all leachants. On a relative basis, M_{LT} values for Mn were between 0.00001 and 0.02 in water and the basic leachant, and between 0.01 and 0.2 in acidic leachants (Figure 3). The M_{LT} values for Mg were slightly higher. The leachable fraction of Na was between 0.01 and 1, and for K it was between 0.001 and 0.1.

The trace elements As, Sb, and Se, which form oxyanions, tended to be more soluble in basic solutions (M_{LT} values between 0.0001 and 1) than in water or acid (Figure 4). The other trace elements were most soluble in acidic leachants; the highest M_L value for these elements was 16 mg/kg (Zn), and M_{LT} values were between 0.01 and 0.5. In water, the relative solubility of the trace elements was less than 0.1.

Discussion

To evaluate the relative solubility of the individual cations, a frequency distribution of the M_{LT} values for this set of 32 Class F fly ash samples was calculated for each element in four leachant solutions. Four relative solubility classes, based on the mass fraction leached, were defined as: insoluble, $M_{LT} \leq 0.02$; slightly soluble, $0.02 < M_{LT} \leq 0.20$;

TABLE 4. Relative Solubility of Major, Minor, and Trace Elements in Class F PC Fly Ash Samples^a

element	H ₂ O	Na ₂ CO ₃	HAc	H ₂ SO ₄
Al	I ^b	I	I	SS ^c
As	I (72%)	MS ^d (56%)	I (63%)	I
Ba	I	I	I (63%)	I
Be	I	I	SS (68%)	SS (64%)
Ca	SS	SS (69%)	MS	MS
Cd	I	I	I	I
Co	I	I	I	SS
Cr	I	I	SS (52%)	SS (65%)
Cu	I	I	I (52%)	SS (65%)
Fe	I	I	I	I
K	I	I	I (63%)	SS
Mg	I	I	SS	SS
Mn	I	I	SS	SS
Na	SS	ND	SS	I
Ni	I	I	I	SS (69%)
Pb	I	I	I	I
Sb	I	I	I	I
Se	I	I	I	I
Zn	I	I	SS	SS

^a The number in parenthesis is the percentage of values in the dominant category if it is less than 75%. ^b Insoluble. ^c Slightly soluble. ^d Moderately soluble.

moderately soluble, $0.20 < M_{LT} \leq 0.65$; and very soluble, $M_{LT} > 0.65$. As an example, a frequency distribution for Mg is shown in Table 3. In the column labeled "number of values" under H₂O, the mass fraction of Mg leached was less than 0.02 for 24 of the 32 samples. In acetic acid, the fraction of Mg leached was between 0.02 and 0.20 for 27 of the samples. The value of M_{LT} was greater than 0.65 for none of the 32 samples in any of the leachants. From these data, a relative frequency distribution, shown in the columns labeled "% of values" in Table 3, was calculated. On the basis of a population of 32 samples, M_{LT} was <0.02 for Mg in water for 75% of the samples and between 0.02 and 0.20 for more than 80% of the samples in the acid solutions. Therefore, Mg is evaluated as insoluble in H₂O and slightly soluble in acid.

The results of the frequency distribution determined the solubility class assigned to a given cation/leachant combination. If 75% of the M_{LT} values fell within the limits of a solubility class, that class was assumed to describe the relative solubility for this set of samples. In the example given in Table 3, Mg is insoluble in water and alkaline reagents, and slightly soluble in acid solutions. One solubility class was clearly dominant for 85% of the cation/leachant combinations that met this criterion (Table 4). If less than 75% of the relative solubility values were in one category, the dominant solubility category is listed in Table 4 with the percentage of values in that category shown in parentheses. In all but 4 of these instances, the dominant category indicated higher solubility.

For this set of Class F PC fly ash samples, the cations Cd, Fe, Pb, Sb, and Se were insoluble in all types of leachant, as M_{LT} was less than 0.02 for at least 75% of the samples tested.

The elements Be, Cr, Mg, Mn, and Zn were slightly acid soluble, but insoluble in water and the high pH leachant. The cations Al, Co, Cu, K, and Ni were slightly soluble in the sulfuric acid, but were insoluble in the weaker acetic acid, water, and basic leachant. Only Ca and Na were even slightly soluble in H₂O; Ca is moderately soluble in both acids and slightly soluble at high pH. The trace element As was moderately soluble in the basic Na₂CO₃ leachant.

The solubilities determined in this study are consistent with the solubility of minerals normally found in fly ash. For example, Fe in fly ash is an insoluble oxide, either hematite or magnetite. Gypsum or anhydrite are the primary Ca compounds, which are slightly soluble in water and more soluble in acid. Aluminum in aluminosilicates, residual clay particles, is also insoluble. The solubility of As at high pH is consistent with its presence as an oxyanion. There are insufficient data on chemical or mineral distribution of minor and trace elements in fly ash to explain their solubility. Although differences in experimental conditions preclude direct comparisons, other researchers have found similar results (Table S3 in the Supporting Information) with respect to the solubility of various elements in fly ash.

Coal utilization byproducts (CUB) are a nonhomogeneous material, containing a variety of cations in different chemical or mineral matrixes. In this study, 32 Class F PC fly ash samples were leached in columns for extended periods of time at acidic, neutral, and basic pH; the leachates were analyzed for 19 cations. The results demonstrate that the degree of solubility varies for each element, and that the solubility of a given element is different in acidic, basic, and neutral leachant solutions. Although all fly ash samples may not exhibit the same solubilities, this random population of Class F PC fly ash samples indicates that most cations in fly ash are insoluble or only slightly soluble. Exposure to fluids in natural environments is unlikely to release significant amounts of the cations studied. This study supports the

beneficial use of CUB in applications such as bulk fill and mine remediation.

Acknowledgments

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Supporting Information Available

Data on the major, minor, and trace element compositions of the fly ash samples (Tables S1 and S2 and Figure S1). A summary of the results of fly ash leaching tests by other researchers (Table S3) and the maximum elemental solubility (M_L) of 19 cations in Class F PC fly ash samples (Table S4) are also included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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