Mass Release of Trace Elements
from Coal Combustion By-Products

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ABSTRACT

More than 100 million short tons of coal combustion by-products (CCB) are generated annually. More stringent environmental regulations and increasing costs will discourage placement in landfills, encouraging increased utilization and the development of new uses for CCB. However, the potential release of trace elements from CCB is a continuing environmental concern. A study at the Federal Energy Technology Center is quantifying the release of trace elements from CCB's in a series of column leaching tests. A one kg fly ash sample is placed in each of seven 5-cm by 1-m acrylic columns. The material is leached at a nominal rate of 130 mL/d for 60 days. Leachants include deionized water, synthetic groundwater, synthetic precipitation, and 0.1 N solutions of acetic acid, sodium carbonate, sulfuric acid, and ferric chloride. The leachate is analyzed for antimony, arsenic, barium, boron, cadmium, chromium, cobalt, copper, lead, nickel, selenium, and zinc. Data, as the mass extracted with respect to the concentration in the solid, have been evaluated for 20 fly ash samples. In deionized water, the total amount of each trace element in the leachate was less than 1 per cent of the amount in the 1 kg sample. In the acidic solutions, the amount of trace element released increased at the lower pH. Only arsenic was released at greater than 1 per cent in the alkaline leaching solutions. Although there were general solubility trends, there was significant variation in the amount of a trace element released for individual CCB samples.

INTRODUCTION

Approximately 80 pct of the coal produced annually in the U.S. is used to generate electric power. Between 10 and 15 % of this amount is recovered as coal combustion by-products (CCB). Forty-nine million short tons (st) of CCB were produced in 1990, 82 million st in 1992, and 105 million st in 1997.[1] Of all coal combustion by-products (fly ash, bottom ash, boiler slag and flue gas desulfurization sludge) produced annually, between 25 and 30 pct is utilized, primarily in cement and concrete, structural fills and for waste stabilization. The remaining material, approximately 76 million st in 1997, was placed in landfills and ponds. Due to the large quantity of CCB generated annually and the escalating cost of landfills, there is increased interest in finding new and profitable uses for this material. However, a continuing concern is the potential release of trace elements when the CCB is exposed to environmental fluids such as acid rain, groundwater or acid mine drainage.

In 1988, the Environmental Protection Agency (EPA) published a Report to Congress[2] on wastes from the combustion of coal by electric utility power plants. EPA concluded in 1993 that regulation of such wastes under Subtitle C of RCRA was not warranted. However, the original report did not include wastes generated by utilities burning fossil fuels other than coal and wastes from non-utility boilers. In March of 1999, EPA published a Report to Congress[3] on these remaining wastes and will issue a regulatory determination by October 1, 1999. In addition to other fossil fuels, mixtures of coal and other materials, (biomass, fluidized bed combustion) are considered in this category. EPA has tentatively concluded to retain the exemption for these wastes. However, the agency is considering limiting the mixed waste and also utility CCB in some agricultural applications, due to concerns with arsenic exposure. They also reviewed CCB use in mine reclamation, but noted that the agency had insufficient information to assess potential risks of groundwater contamination due to mine backfills. In its comments on EPA's report to Congress, the U.S. Department of Energy (DOE) summarized empirical data that supported retention of the exemption for such beneficial uses. The results of the leaching tests discussed in this paper indicate that the risk of trace element mobility, including arsenic, is relatively small.

PROCEDURE

The DOE column leaching system is a continuous flow system that includes seven leachant solutions for simultaneous leaching of four different CCB samples.[4] Leachate samples, collected at 2 to 3 day intervals, are analyzed for pH, acidity and/or alkalinity, ferrous iron, total iron, aluminum, manganese, magnesium, calcium, sodium, potassium, sulfate and the heavy metals arsenic, barium, beryllium, cadmium, cobalt, chromium, copper, nickel, lead, antimony and zinc.

The leachants for the column leaching test are: Sulfuric acid (H2SO4), pH = 1.2; Ferric Chloride (FeCl3 with HCl), pH = 1.95; Synthetic Precipitation(SP)[5], pH = 4.2; Synthetic Ground Water[6] (SGW), pH = 6.7; either Ammonium Hydroxide (NH4OH), pH = 11.1 or sodium carbonate (Na2CO3), pH = 12.1; Acetic Acid (HAc), pH = 2.88; deionized water (H2O), pH = 6.

Although the system is designed to leach any CCB, the samples tested to date include 31 fly ashes and 1 steel slag. The discussion in this paper is limited to the 20 samples, 17 power plant fly ashes, 2 non-utility boiler fly ashes and the steel slag. The trace element concentration of these samples is given in Table 1.

RESULTS

The release of trace elements from fly ash varies with the sample. It is related to the leachant solution, but is not a simple function of pH. Averaged for the 20 samples, barium is the most soluble element, and it is most soluble in ferric chloride, acetic acid, water and synthetic precipitation (Fig. 1). It is slightly soluble in the basic solution, and even less soluble in synthetic groundwater. In sulfuric acid, barium dissolved from the fly ash would probably form insoluble barium sulfate. Arsenic is most soluble in a basic solution and is only sparingly soluble in all other solutions. The average release of beryllium, cadmium, cobalt, lead, antimony and selenium is 2 mg/kg or less in all leaching solutions. Chromium, copper and nickel are most soluble in the acid solutions, acetic and sulfuric, but the total amount leached is still less than 10

mg/kg. Zinc is also soluble in acetic and sulfuric acids, as well as the ferric chloride solution.

Table 1. Concentration of trace elements in CCB (fly ash) samples, mg/kg

FA#	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Se	Zn
2[1]	<100	95	<5	<25	<50	<50	<25	<50	<50	2.3	11
3[1]	<100	76	9	<25	<50	<50	51	59	<50	90.7	43
4	<100	121	<5	<25	<50	<50	<25	<50	<50	5	16
5	<100	155	<5	<25	<50	<50	<25	<50	<50	4.4	23
6	171	1140	11	<10	41	175	114	107	90	4.8	201
7	166	1090	10	<10	39	170	105	107	64	4.8	191
8	67	855	8	<10	31	171	74	1040	59	2.8	135
9[2]	<40	321	<2	<10	<20	5970	95	710	29	2.1	75
10	<200	3310	<10	<10	<100	<100	50	<100	<100	7.3	65
11	<200	859	<10	10	<100	173	115	<100	113	11	202
12	<200	893	<10	<10	<100	165	119	<100	112	9.6	207
13	<200	866	<10	<10	<100	164	112	<100	109	11.6	188
14	<100	456	12	15	40	184	93	124	71	7.6	175
15	229	844	14	15	42	185	158	106	124	8.5	235
16	301	1160	13	15	42	170	139	109	121	7.8	204
17	<100	471	<5	<15	<25	132	72	71	81	17.7	204
18	77	529	2	<1	11	97	76	85	<1	1.4	124
19	125	511	6	<1	16	111	76	92	<1	1.8	155
20	277	1380	10	<1	44	110	155	135	<1	1.6	197
21	148	849	12	<1	31	92	122	125	<1	1.9	128

[1] Non utility fly ash
[2] Steel slag fines

The mass release was also determined relative to the concentration of an element in the fly ash for each sample. If the concentration in the solid was below the detection limit, it was estimated as half of the detection limit.   When averaged for all samples, less than 10 pct of arsenic is released in all leaching solutions except the base (Figure 2). In the ammonium hydroxide or sodium carbonate, the average amount of arsenic leached is over 25 pct. Although the amount of barium released was higher than other trace elements, it constituted 12 pct or less of the average amount in the samples. On average, less than 10 pct of the cadmium, chromium, and lead was leached by all solutions. Between 10 and 20 pct of the beryllium, copper, selenium and zinc is released in the 0.1 N solution of sulfuric acid. Beryllium, selenium and zinc are also released by the ferric chloride solution. Considering the average values for this suite of 20 fly ash samples, the solubility of all the trace elements in all leaching solutions is relatively low.
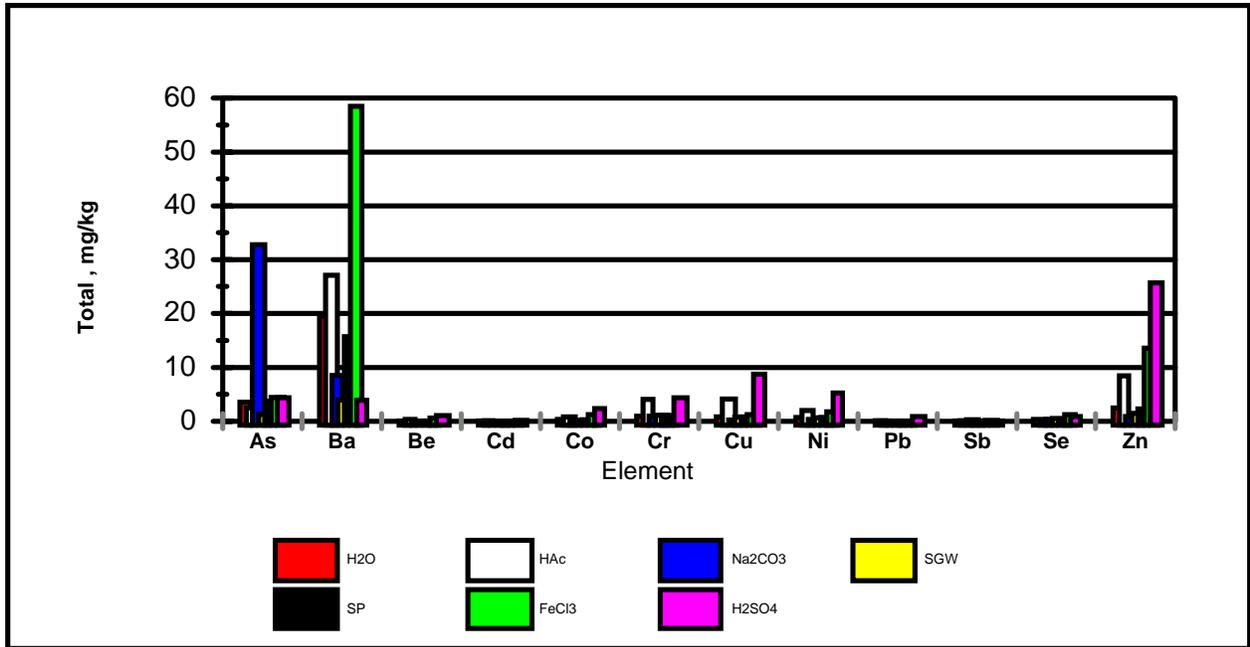
Figure 1 Average release of trace elements from fly ash samples.
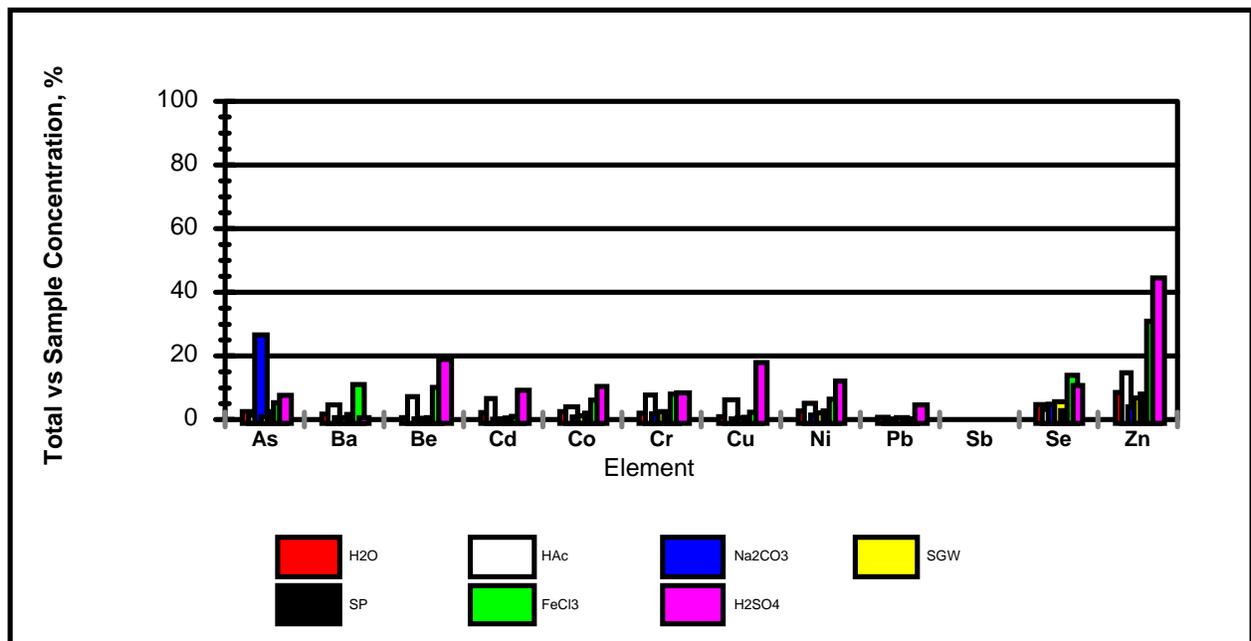

Figure 2 Average relative release of trace elements from fly ash samples, %.

If individual samples are considered, the release of a trace element is leachant specific and exhibits some correlation with the concentration in the fly ash. For example, the amount of arsenic leached from the samples is greater than 25 mg/kg only in sodium carbonate (Fig. 3) and
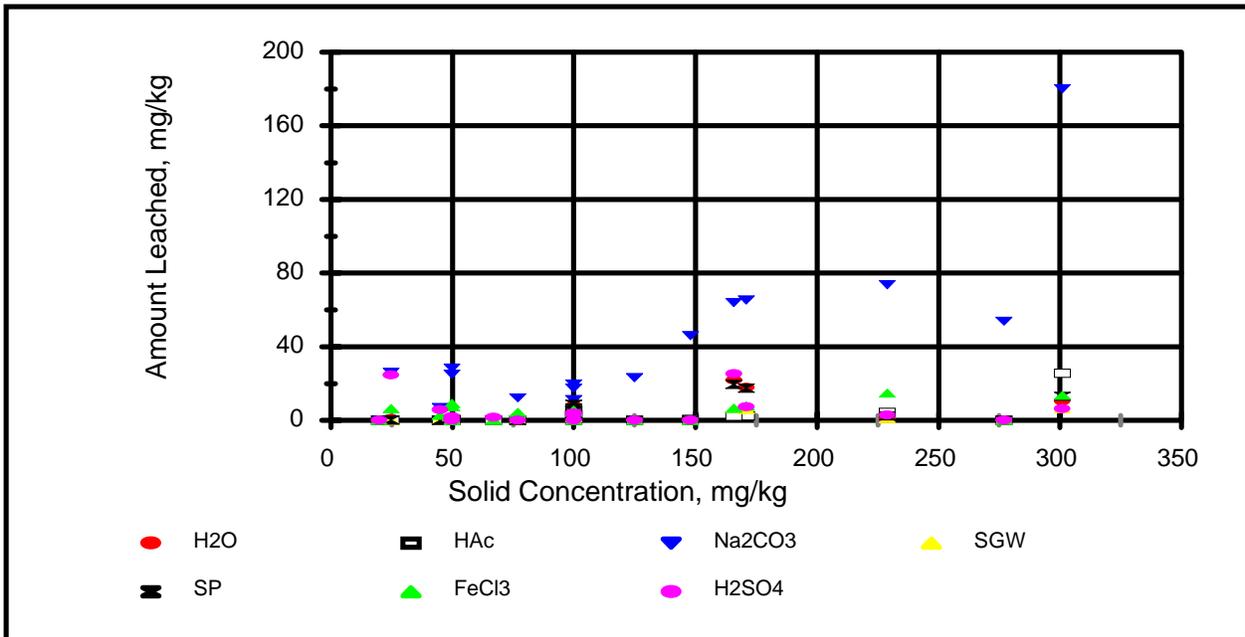
Figure 3 Release of arsenic by various leachants versus concentration in fly ash.

increases directly with increase solid concentration ($R^2 = .64$). Based on the samples with the concentration above the detection limit, the relative amount of arsenic leached is between 20 and 40 pct.

Zinc concentrations in the fly ash samples were between 25 and 250 mg/kg; all values were above the detection limit. The amounts leached were negligible in water, sodium carbonate, synthetic groundwater and synthetic precipitation solutions (Figure 4). Total zinc leached varied
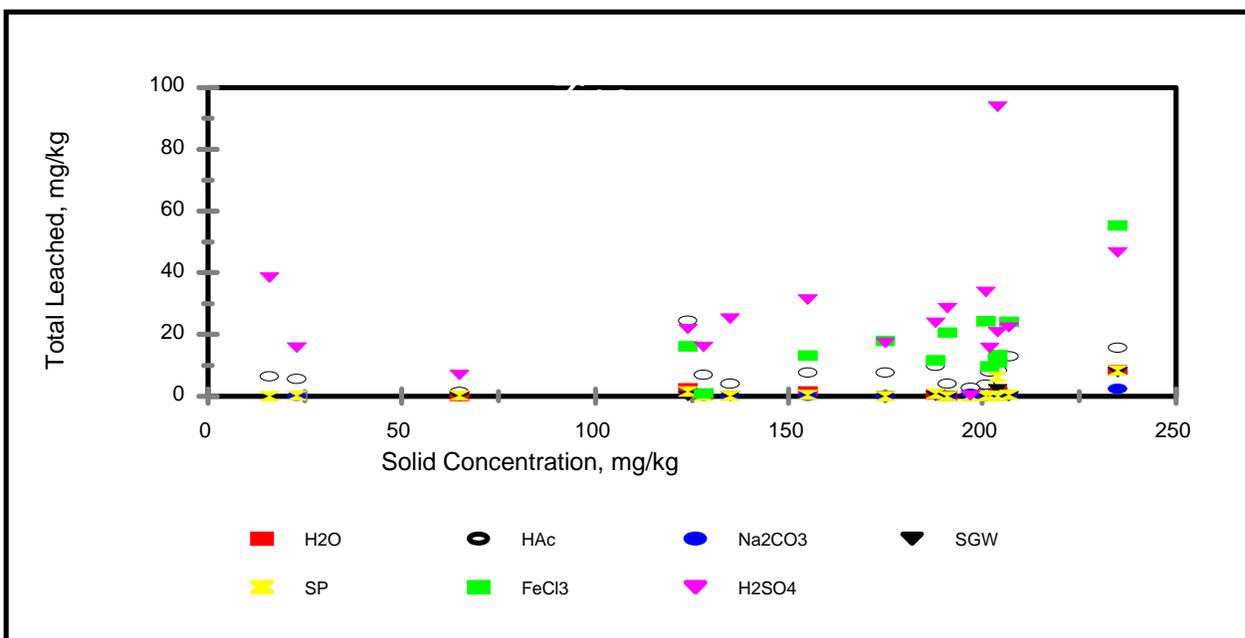

Figure 4 Release of zinc by various leachants versus concentration in fly ash.

between 0 and 30 mg/kg in the acetic acid solution, and was between 20 and 100 mg/kg in the ferric chloride and sulfuric acid solutions. On a relative basis, the percentage leached was higher at lower concentrations in the solid. If the concentration was above 100 mg/kg, the amount leached was less than 50 pct, even in the ferric chloride and sulfuric acid solutions.

Using a gravity flow system, the leachant flow rate was variable (Figure 5). The mass solubility, mg of element per kg of sample, also varied on a daily basis, but the slope of the cumulative curve could generally be approximated by a linear relationship. Plotting the cumulative release
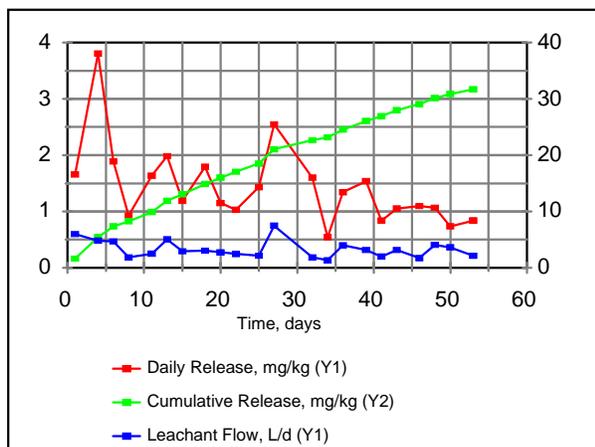
Figure 5 Daily release and cumulative release of zinc from FA-7 in sulfuric acid with daily flow rate.
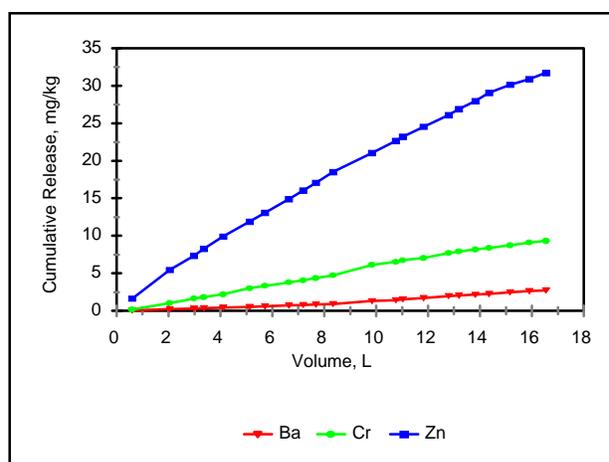
Figure 6 Cumulative release of trace elements as a function of leachant volume.

of an element versus the leachant volume produced an even more linear relationship (Figure 8). The slope was calculated for all points; the average slope was considered an index of solubility. An average of the volumetric solubility was calculated for each element in each leachant solution, and converted to a molar value. The average molar solubility (Table 2) in, micro moles per kilogram per liter (µmol/kg/L), shows a predominant solute/solvent pair that may indicate the primary type of solubility reaction for each element.

With the leachants used in this experiment, the leaching reactions may be classified as acidic, caustic or oxidizing. The elements (antimony and cadmium) that have a molar solubility of less than 1 µmol/kg/L in all leachants are considered relatively insoluble. The dissolution of arsenic seems to be a primarily caustic reaction. Beryllium and zinc appear to be released from the CCB by acidic leaching reactions. The solubility of the elements barium, chromium, copper, lead, nickel and zinc may be due to an oxidation reaction.

When the molar solubility is plotted against time, the average slope of the curve (Table 3) indicates how solubility will change over time. If the slope is positive, solubility increases with time. If the slope is negative, the solubility of an element will decrease with time, and if the slope is 0, solubility is constant with time. For example, the rate of the caustic leaching of arsenic is positive, indicating that the arsenic released from CCB may be initially low, but increase with time. In acid solutions, the slope for the dissolution of zinc is negative, indicating that most zinc is released during the initial leaching period. The slope of the molar solubility

with time for nickel is 0, indicating that it's release from fly ash occurs at a constant rate.

Table 2. Average Molar Solubility, µmol/kg/L

	H_2O	HAc	Base	SGW	SP	$FeCl_3$	H_2SO_4
As	6.4	3.2	65.2	3.1	7.3	8.2	5.0
Ba	24.2	20.4	11.4	5.5	18.8	71.7	4.2
Be	0.4	3.7	0.3	0.6	0.3	8.8	11.5
Cd	0.0	0.1	0.0	0.0	0.0	0.3	0.2
Cr	1.5	6.6	2.6	3.0	2.3	37.0	8.5
Co	0.7	0.8	0.0	0.5	0.3	4.4	3.9
Cu	0.9	7.4	1.2	3.6	2.1	38.2	15.4
Pb	0.0	0.0	0.0	0.0	0.0	1.9	0.3
Ni	1.0	2.8	0.7	2.0	1.1	19.3	9.9
Sb	0.1	0.1	0.3	0.1	0.1	0.1	0.1
Se	0.6	0.3	0.9	2.3	0.3	2.4	1.5
Zn	4.0	14.7	1.0	4.7	3.7	44.8	53.3

Table 3. Average Molar solubility as a function of time, µmol/kg/L/d

	H_2O	HAc	Base	SGW	SP	$FeCl_3$	H_2SO_4
As	0.26	-0.64	1.48	0.08	0.22	0.26	-0.05
Ba	-0.39	-1.60	-1.09	0.01	-0.74	0.37	0.04
Be	-0.04	-0.29	-0.04	0.06	-0.05	0.40	0.09
Cd	0.00	-0.03	0.00	0.00	0.00	0.02	-0.01
Cr	-0.07	-0.22	-0.10	-0.01	-0.10	0.11	-0.15
Co	0.05	-1.10	0.04	0.10	0.02	1.48	0.26
Cu	-0.02	-1.93	-0.01	0.40	-0.02	2.29	-0.07
Pb	-0.07	-0.84	-0.16	0.00	-0.19	0.77	-0.38
Ni	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Sb	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Se	0.01	-0.13	0.04	0.16	0.03	-0.18	0.03
Zn	-0.35	-2.75	-0.47	0.10	-0.45	2.04	-1.50

The average solubility and solubility rate give an indication of the predominant solubility reaction and whether solubility will increase or decrease with time for each of the trace elements. However, variables for the individual samples may be significantly different from the average. For arsenic, the molar solubility is between 45 and 70 for the majority of the samples, and the molar solubility rate is positive (Figure 7). For zinc (Figure 8), the average molar solubility rate is negative due to a discrete number of samples that are very negative and other samples that have a value that is zero or slightly positive.

SUMMARY

The leaching system described in this paper generates an extensive data set. Each test includes at least 10 sampling events for 7 leachant solutions and 4 CCB samples. Each leachate analysis includes data on 12 trace elements, and data for 20 samples has been summarized. The data

indicate some general trends in trace element solubility and when maximum solubility may occur. However, the data strongly indicate that the release of each trace element is controlled by a unique set of chemical, thermodynamic and kinetic factors. It is also apparent that these trace element factors are not the same in all fly ash samples. Factors that may contribute to the solubility of a particular element are the pH, the ionic activity of the solution, and the mineralogy of various compounds in the fly ash. The leaching tests are intended to involve at least 50 samples including bottom ash, FBC residues and FGD sludge. Determination of the ratio of amorphous to crystalline material and of the predominant mineral species in selected samples,
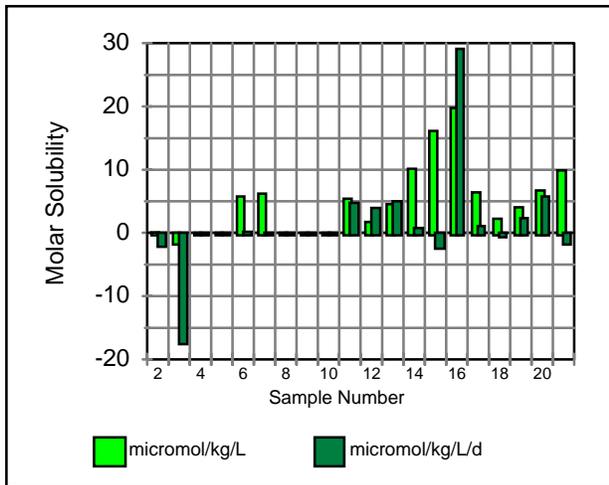

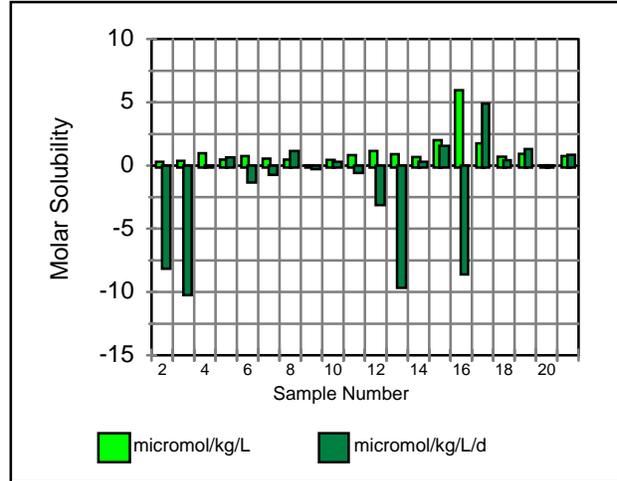**Figure 7** Arsenic - sample average molar solubility and molar solubility rate.

Figure 8 Zinc - sample average molar solubility and molar solubility rate.

with the data from the leaching tests, may be used to estimate the potential for the release of trace elements from CCB materials.

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