

Experimental Study of Leaching of Fly Ash

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Leaching of Alaskan coal fly ash was investigated to characterize the leachate generated and identify any toxic elements released in large amounts. Pressure was used to increase the rate of leaching in the column apparatus. Effects of compaction, freezing and thawing, curing, and cement stabilization on leaching were also investigated. Results indicate that high levels of barium are released from ash when rapidly leached with distilled water, although the Environmental Protection Agency Toxicity Characteristic Leaching Procedure test method did not identify this potential hazard. Stabilization of fly ash with portland cement reduces to the maximum concentration of barium leached.

Coal fly ash has traditionally been disposed in monofills or landfills, but as a result of increasing disposal costs, reuse is being explored to relieve pressure on disposal sites and to reduce disposal costs. Low-volume uses of coal fly ash, such as lime-fly ash-aggregate road bases and fly ash concrete, have been widely used. High-volume uses continue to be investigated to use greater amounts of ash (1). Compacted fly ash road bases, containing no aggregate and little or no stabilizer, have performed adequately in demonstration projects performed in the last 15 years (2-4). The ash used in this study achieved a 28-day unconfined compressive strength (ASTM C39-88) of 7,930 kPa (1,151 psi) without the addition of portland cement as a stabilizer. With 12 percent cement added, the ash achieved a 28-day compressive strength of 30,700 kPa (4,455 psi) (Figure 1).

Because fly ash is composed of most of the noncombustible elements present in coal, a major concern in the use of coal fly ash is the potential environmental hazard due to the leaching of heavy metals from the ash. Results of other leaching studies indicate a wide range of concentrations of heavy metals in coal fly ash leachate. This variability is due in large part to differences in (a) chemical composition of the source coal, (b) coal preparation and combustion, and (c) laboratory methods. In one extensive study, Ainsworth and Rai (5) conducted Paar bomb extractions on 34 fly ash samples using pressurized water and nitric acid at 105°C. The summary in Table 1 demonstrates the range of concentrations of various metals in leachate from different fly ashes. Values of the leachate concentration for some of the metals tested (As, Cr, and Pb) exceed Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) limits (Table 2).

Other extraction studies concentrated on specific metals and obtained varying results. Moretti et al. (6) focused on immobilization of arsenic in fly ash by adding lime or gypsum and found concentrations of arsenic as high as 1.5 ppm in control samples. Arsenic concentrations decreased to 0.1 ppm in extract from samples treated with lime. Grisafe et al. (7) found elevated levels of lead (2.7 ppm), chromium (2.8 ppm), arsenic (1.2 ppm), and selenium (0.64 ppm) in fly ash extract. Lower levels of arsenic (0.05 ppm) and

lead (0.15 ppm) were found in an extraction study by Garcez and Tittlebaum (8).

Several column leaching studies on coal fly ash performed by Dudas (9) and Warren and Dudas (10) focused on describing leaching trends and mechanisms. They observed that calcium and sodium concentrations decreased while silicon, aluminum, iron, and magnesium concentrations increased during long-term leaching tests. In another study, Warren and Dudas (11) further described leaching behavior of many elements and linked minor and trace element leaching behaviors to those of major elements in the ash.

OBJECTIVES

The significant variabilities in the chemical and physical characteristics of coal ashes require investigation of ashes from individual coal sources and individual power plants. The leaching study reported herein is part of a larger study on the use of Alaskan fly ash as a road-base source material. Included in the larger study are investigations of the characteristics and strength properties of fly ashes from six power plants in interior Alaska, all burning coal from the Usibelli Coal Mine in Healy, Alaska.

This leaching study investigates the possible negative effects on the environment from the use of fly ash in road bases by accelerating the leaching of fly ash under various possible field conditions. Specifically, the objectives of the study are to (a) identify toxic elements that may be released from the ash under field conditions, (b) identify leaching trends of the major and minor elements that make up the ash, and (c) more completely describe the leachate produced.

EXPERIMENTAL WORK

Material Description

The fly ash sample used in this study was collected in August 1992 from the Golden Valley Electric Association (GVEA) power plant in Healy, Alaska. Approximately 400 kg (880 lb) of ash was collected from eight hoppers in 1 day and was combined to produce one composite sample. The power plant uses a pulverized-coal firing system and a fabric filter ash collection system. The coal burned at the plant is classified as a sub-bituminous coal with a heating value of 20,900 kJ/kg (9,000 Btu/lb), with ash and sulfur contents of 11 and 0.05 percent, respectively (12). The fly ash sample, classified as alkaline calisalic (13) met the specifications of ASTM C618-91, Specifications of Fly Ash for Use as a Mineral Admixture in Portland Cement Concrete, for a Class C Fly Ash (Table 3). The ash sample was composed primarily of the oxides of silicon, aluminum, iron, and calcium, which together make up more than 90 percent of the ash. Less than 1 percent of the ash was unburned carbon.

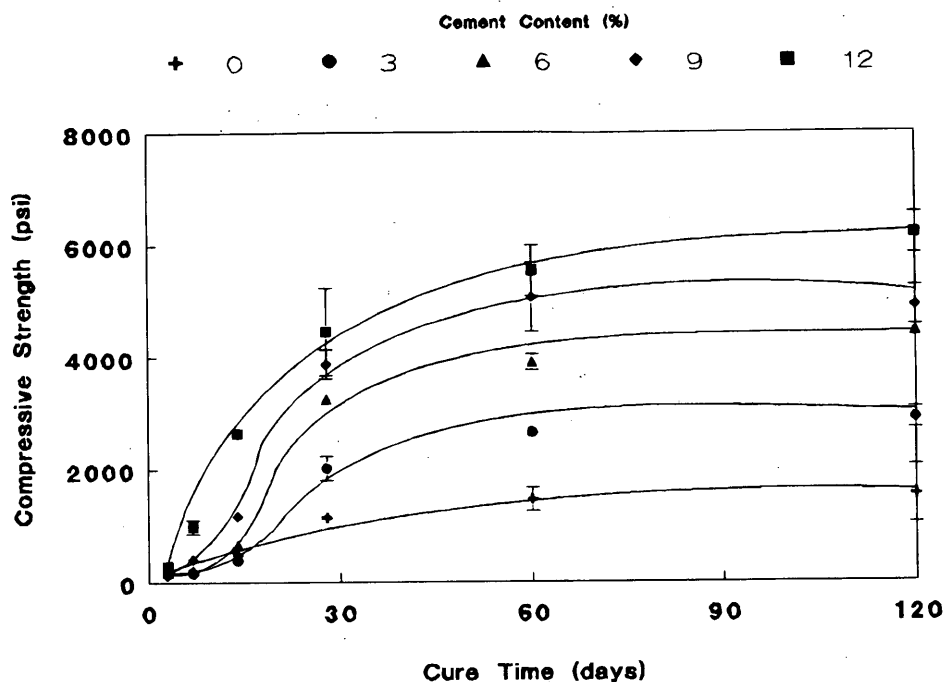


FIGURE 1 Compressive strength of compacted fly ash specimens with varying cement contents.

TABLE 1 Range of Concentrations in Leachate from 34 Fly Ash Samples (5)

Element	Concentration (mg/l)	
	Water	Acid
Al	0.123-268	50.3-423
As	<0.1-14.1	0.1-6.29
B	0.482-82.4	0.128-18.7
Ba	0.045-2.99	0.254-24.4
Ca	61.5-634	14.1-879
Cd	<0.002-0.792	0.002-0.134
Cr	<0.01-5.32	0.068-1.47
Cu	<0.004-61.6	0.06-6.44
F ⁻	<0.1-4.25	-- ^a
K	0.715-307	1.73-39
Mg	0.039-118	2.39-184
Mn	<0.001-2.07	0.164-4.57
Mo	0.036-1.86	0.039-0.737
Na	1.87-2008	1.14-329
Ni	<0.01-8.52	0.064-1.08
Pb	<0.06-3.76	<0.06-9.16
SO ₄ ²⁻	32.1-4600	--
Sb	<0.05-0.752	<0.05-0.715
Si	<0.05-9.8	0.107-7.95
Sr	0.034-23.7	0.285-27.3
Zn	0.01-121.2	0.116-12.8

^a no data available for dashed entries

TABLE 2 Maximum Allowable Concentrations of Metal Contaminants in Leachate from TCLP Test (19)

Element	Maximum (mg/l)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

Fly ash particles are typically hollow or solid spheres that form from molten residues in the boiler. Amorphous and rounded vesicular particles form when temperatures are insufficient to melt the ash matrix. Amorphous particles resemble precombustion particles, and rounded particles are partially combusted and typically contain vesicles of exhaust gases and unburned carbon (14). The particles range in size from less than 1 μm to greater than 100 μm (15). Seventy-eight percent of the particles in the ash sample used in this study passed the No. 325 sieve (45 μm).

Experimental Design

A column leaching apparatus was chosen over an extraction apparatus to better simulate leaching of fly ash under field conditions. Laboratory conditions differed from field conditions in two important ways: (a) laboratory influent pressures were increased to accelerate leaching and (b) laboratory temperatures, 21°C (70°F), are significantly higher than average field leaching temperatures.

Columns were constructed of 4-in.-diameter Plexiglas tubing with attached end plates fitted with couplings for influent solution and effluent leachate. Porous stones and filter paper were placed in the bottom of each column before the ash was compacted or placed (uncompacted) in the column. Distilled, deionized water was used for the leaching solution and was supplied to the cylinders via a pressurized metal tank equipped with a rubber bladder. The rubber bladder prevented the metal tank from contaminating the leaching solution. Because of the low hydraulic conductivity of the ash samples, pressure was used to force the solution through the samples to obtain sufficient volumes and to simulate long-term leaching (Figure 2). The influent pressure head was increased incrementally from 70 to 200 kPa (10 to 30 psi) during the study to maintain leachate volumes at levels sufficient for analysis.

TABLE 3 Results of ASTM C618-91, Specifications of Fly Ash for Use as Mineral Admixture in Portland Cement Concrete

Chemical Composition(%):		Specifications Class C Fly Ash	
Silicon Dioxide	40.71		
Aluminum Oxide	16.31		
Iron Oxide	6.95		
Total		63.97	50.0 Min
Sulfur Trioxide		0.44	5.0 Max
Calcium Oxide		27.90	
Moisture Content		0.06	3.0 Max
Loss on Ignition		0.40	6.0 Max
Sodium Oxide	0.37		
Potassium Oxide	0.55		
Available Alkalies (as Na ₂ O)		0.73	1.5 Max
<u>Physical Test Results:</u>			
Fineness			
Retained on #325 sieve, (%)	22.10		34 Max
Strength Activity Index			
With Portland Cement, (%)			
Ratio to Control at 7 days	75.3		
Ratio to Control at 28 days	85.3		75 Min
Pozzolanic Activity Index			
With Lime at 7 days (psi)	1170		No Limit
Water Requirement, % of Control	93.4		105 Max
Soundness			
Autoclave Expansion (%)	0.057		0.8 Max
Drying Shrinkage			
Increase at 28 days (%)	-0.004		0.03 Max
Specific Gravity	2.52		

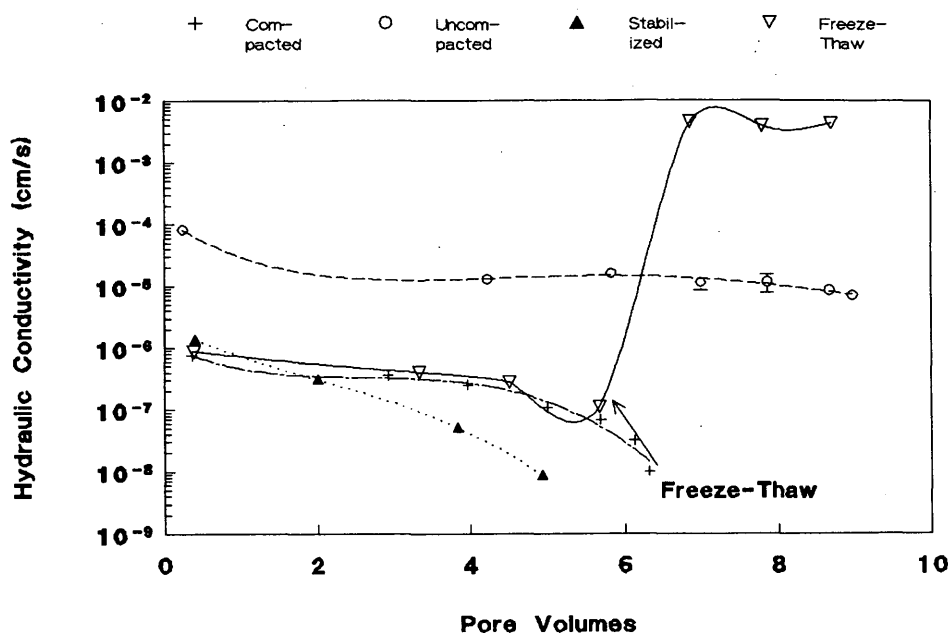


FIGURE 2 Variations in hydraulic conductivity of fly ash specimens.

Six groups of triplicate specimens were prepared to investigate leaching of fly ash under differing field conditions: compaction, curing, freeze-thaw, and cement stabilization (Table 4). Three groups of compacted specimens were prepared, each containing 2.8 kg (6.2 lb) of ash, with a dry density of 1700 kg/m^3 (106 pcf). Group A, the control group, was leached continuously for 8 weeks. Groups B and C were leached continuously for 4 weeks, and then Group B was allowed to cure under saturated conditions for 4 weeks while the specimens in Group C were subjected to 12 freeze-thaw cycles. Each freeze-thaw cycle consisted of 24 hr at -18°C (0°F) followed by 24 hr in a moist room at 21°C (70°F). Groups B and C were then leached for 4 more weeks. Groups D and E consisted of uncompacted ash, 2.8 kg (6.2 lb) and 2.1 kg (4.6 lb), respectively, with a dry density of 1280 kg/m^3 (80 pcf). The leaching solution was not pressurized for Groups D and E because the hydraulic conductivity of these specimens was greater than the compacted specimens, and sufficient leachate volumes could be obtained from a 1-m influent elevation head. Groups D and E were leached continuously for 8 weeks. Group F contained compacted fly ash with 3 percent portland cement by dry weight of fly ash, for a combined weight of 2.8

kg (6.2 lb), with a dry density of 1700 kg/m^3 (106 pcf). Group F was leached continuously for 4 weeks.

The compacted ash specimens were compacted in accordance with ASTM D1557-78 (modified Proctor), which produced specimens 20 cm (8 in.) high with a density of 1700 kg/m^3 (106 pcf). The specimens were compacted at the optimum moisture content of 15 percent.

Leachate samples were taken after the first 24 hr of leaching and then at intervals of 1 week thereafter. The pH of the samples was measured and the samples were weighed and acidified before the chemical analysis was conducted. The leachate was analyzed by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES) for 15 elements (Al, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Si, Sr, Ti, and V) and analyzed for mercury by cold vapor atomic absorption spectrophotometry. The leachate from Group F was analyzed only for barium using ICP-AES.

This experimental procedure was designed to create a worst-case scenario leaching of fly ash under various field conditions. The column setup was similar to that of Dudas (9) and Warren and Dudas (10) with several exceptions. This study included compacted ash

TABLE 4 Summary of Experimental Design and Treatment of Specimen Groups

Group	Weight (kg)	Compaction	Stabilizer	Freeze-Thaw
A	2.8	Compacted	None	None
B	2.8	Compacted	None	None
C	2.8	Compacted	None	12 Cycles
D	2.8	Uncompacted	None	None
E	2.1	Uncompacted	None	None
F	2.8	Compacted	3% Cement	None

TABLE 5 Averages of Concentrations of Calcium, Sodium, and Potassium in Fly Ash Leachate

Group	Days	Calcium		Sodium		Potassium	
		average	SD	average	SD	average	SD
A	1	630	3.05	798	27.6	220	4.91
A	7	836	17.0	117	6.34	53.6	3.06
A	14	407	2.46	397	18.3	423	17.4
A	21	344	2.14	385	8.08	450	14.8
A	28	298	7.66	415	15.6	492	18.7
A	35	242	11.5	431	12.3	513	17.0
A	42	189	22.4	504	4.06	609	6.81
A	49	110	26.4	693	9.23	864	14.4
B	1	637	5.96	786	30.0	216	3.36
B	7	843	24.4	110	13.7	59.9	11.4
B	14	394	35.0	427	152	381	68.3
B	21	352	18.9	370	22.5	427	22.7
B	28	311	25.6	394	33.9	468	37.5
C	1	627	27.0	780	15.9	206	8.40
C	7	865	2.21	97.3	4.35	59.8	3.84
C	14	436	16.6	365	21.9	386	25.8
C	21	368	14.1	357	21.7	403	26.1
C	28	337	22.3	366	35.0	435	37.7
C	65	245	54.3	309	21.1	378	24.1
C	77	78.2	65.0	265	167	342	230
C	92	51.2	62.0	260	453	336	73.3
D	1	587	32.4	2050	189	547	54.2
D	7	773	15.5	76.9	2.03	40.5	16.8
D	14	467	16.4	282	29.1	281	31.1
D	21	407	5.56	272	34.1	299	42.2
D	28	355	20.4	337	52.7	386	64.2
D	35	303	9.84	345	75.1	389	84.5
D	42	291	31.1	362	57.2	415	80.3
D	49	247	27.8	450	78.7	541	97.7
E	1	598	39.7	1570	205	414	54.8
E	7	776	15.6	74.4	5.07	32.8	3.92
E	14	468	56.4	213	16.4	208	9.82
E	21	378	24.8	246	34.1	257	44.2
E	28	346	30.8	325	43.4	358	49.8
E	35	282	31.2	339	47.0	381	58.0
E	42	277	21.6	340	26.5	391	32.9
E	49	228	18.4	407	40.9	487	50.8

Values presented in ppm followed by standard deviations.

specimens and used pressure to increase the production of leachate in a relatively short time. No other studies were found in the literature using compacted ash in a column apparatus.

The EPA method of classifying wastes as toxic or nontoxic is TCLP, an extraction procedure using a distilled water leaching solution adjusted to pH 3 or 5 with acetic acid. The solid waste is added to the solution at a ratio of 1:20 and agitated in a zero headspace extractor for 18 hr. This method was designed to identify possible toxic elements that may be released from a waste under typical land-fill conditions (16).

The results of numerous TCLP tests of fly ashes from interior Alaska power plants show that the fly ash consistently passed the TCLP test. Dissolved metal concentrations were typically below 10

percent of the maximum allowable levels. The procedure used in this study was developed to better simulate possible field conditions, road base, or fill material and to investigate the long-term leaching behavior of selected elements.

RESULTS AND DISCUSSION

Sufficient leachate volumes for analysis were obtained from Groups A, D, and E through Week 7 of the study. No leachate samples could be obtained from Group B after the curing period, which occurred from Week 5 through 8. Samples taken from Group C after Week 8 were obtained without pressure by introducing 500 ml of leaching

TABLE 6 Averages of Concentrations of Magnesium, Silicon, and Aluminum in Fly Ash Leachate

Group	Days	Magnesium		Silicon		Aluminum	
		average	SD	average	SD	average	SD
A	1	0.200	0.020	0.466	0.412	0.955	0.063
A	7	0.512	0.011	0.000	0.000	2.14	0.044
A	14	0.453	0.003	0.000	0.000	4.49	0.682
A	21	0.181	0.014	0.553	0.019	5.16	0.421
A	28	0.134	0.032	1.07	0.187	5.01	0.948
A	35	0.166	0.014	0.904	0.012	5.45	1.04
A	42	0.140	0.012	0.822	0.251	5.97	2.35
A	49	0.342	0.040	2.48	1.08	8.17	3.33
B	1	0.244	0.001	0.220	0.197	1.01	0.131
B	7	0.526	0.023	0.000	0.000	2.09	0.106
B	14	0.478	0.034	0.000	0.000	4.85	0.089
B	21	0.201	0.006	0.488	0.022	5.49	0.220
B	28	0.144	0.027	1.08	0.183	5.69	0.119
C	1	0.250	0.014	0.000	0.000	1.03	0.063
C	7	0.494	0.024	0.000	0.000	1.91	0.097
C	14	0.430	0.022	0.000	0.000	4.54	0.297
C	21	0.169	0.013	0.287	0.042	5.40	0.267
C	28	0.160	0.008	0.981	0.047	5.90	0.197
C	65	0.227	0.043	1.27	0.240	5.52	0.178
C	77	0.187	0.032	1.07	0.064	5.44	1.35
C	92	0.085	0.015	1.45	0.458	5.74	0.961
D	1	0.559	0.118	0.961	0.069	2.46	0.226
D	7	0.496	0.007	0.000	0.000	2.61	0.017
D	14	0.437	0.021	0.000	0.000	3.86	0.099
D	21	0.176	0.005	0.214	0.137	5.23	0.058
D	28	0.146	0.013	0.795	0.224	5.20	0.511
D	35	0.154	0.026	0.720	0.246	5.25	0.391
D	42	0.155	0.009	0.245	0.108	5.66	0.245
D	49	0.809	1.07	1.15	0.177	6.08	0.378
E	1	0.615	0.009	0.715	0.140	2.27	0.168
E	7	0.499	0.017	0.000	0.000	2.88	0.070
E	14	0.385	0.044	0.000	0.000	3.50	0.336
E	21	0.191	0.028	0.097	0.058	4.35	0.617
E	28	0.158	0.005	0.779	0.042	4.86	0.122
E	35	0.175	0.033	0.602	0.078	5.15	0.349
E	42	0.150	0.005	1.04	0.084	5.49	0.262
E	49	0.181	0.011	1.21	0.050	6.35	0.250

Values presented in ppm followed by standard deviations.

solution each week. The leachate samples from Groups A through E were analyzed for concentrations of 16 elements. Of these, the concentrations of six elements (Cr, Co, Cu, Fe, Mn, and V) in the leachate were near or below the detection limit. Thus, no results for these elements are reported. A mercury analysis was performed on a random group of 26 leachate samples. The maximum concentration of mercury in the leachate was found to be less than 2 ppb. The concentrations of the other nine elements (Al, Ba, Ca, K, Mg, Na, Si, Sr, and Ti) are presented in Tables 5, 6, and 7. The leachate samples from Group F (Table 8) were analyzed only for barium to investigate the effect of cement stabilization on barium leaching.

The leaching behavior of these nine elements may be classified in one of four groups:

- An initial increase in concentration followed by a gradual decrease, demonstrated by Ca, Ba, and Sr (Figure 3);
- An initial decrease followed by a gradual and then sharp increase, demonstrated by Na and K (Figure 4);
- A gradual increase with a more pronounced increase near the end of the study, demonstrated by Si and Al (Figure 5); and
- No distinct leaching trend, demonstrated by Mg and Ti.

A decrease in dissolved metals was observed for the specimens of Group C after they were subjected to 12 freeze-thaw cycles. This decrease is most likely the result of the increase in hydraulic conductivity of the specimens due to visible cracks that developed during freezing and thawing. As a result of the increased hydraulic conductivity, the contact time between the leaching solution and

TABLE 7 Averages of Concentrations of Titanium, Barium, and Strontium in Fly Ash Leachate

Group	Days	Titanium		Barium		Strontium	
		average	SD	average	SD	average	SD
A	1	0.023	0.002	136	2.14	302	3.36
A	7	0.043	0.001	542	15.3	516	9.78
A	14	0.034	0.001	401	6.11	280	7.94
A	21	0.012	0.001	209	2.31	165	2.85
A	28	0.006	0.001	75.0	1.64	101	4.03
A	35	0.017	0.005	34.5	1.40	73.7	4.99
A	42	0.010	0.000	16.5	1.15	48.6	3.64
A	49	0.024	0.004	4.46	0.19	26.9	3.24
B	1	0.028	0.001	141	2.94	310	5.71
B	7	0.043	0.002	541	1.46	511	32.7
B	14	0.036	0.003	373	43.2	256	34.6
B	21	0.015	0.001	207	8.87	161	3.30
B	28	0.008	0.001	74.1	3.67	96.5	3.67
C	1	0.029	0.001	138	1.77	0.0	5.29
C	7	0.041	0.002	529	7.33	477	19.5
C	14	0.033	0.001	407	5.06	267	7.44
C	21	0.013	0.002	212	2.00	158	6.91
C	28	0.009	0.001	78.6	2.43	96.1	4.24
C	65	0.016	0.006	7.05	5.13	13.3	5.65
C	77	0.012	0.002	0.00	0.00	2.8	2.24
C	92	0.007	0.001	0.00	0.00	6.5	9.26
D	1	0.050	0.006	0.15	0.20	0.0	21.6
D	7	0.040	0.001	329	79.7	254	61.5
D	14	0.034	0.002	456	27.5	314	9.56
D	21	0.013	0.001	258	11.6	179	29.2
D	28	0.009	0.000	91.3	4.54	107	11.8
D	35	0.013	0.003	38.9	2.03	77.7	10.7
D	42	0.012	0.001	24.2	3.16	66.9	2.90
D	49	0.013	0.001	12.8	1.51	48.2	0.83
E	1	0.056	0.001	0.00	0.00	0.0	2.21
E	7	0.042	0.001	360	17.4	260	6.38
E	14	0.030	0.002	415	40.2	276	8.30
E	21	0.013	0.001	226	27.4	136	29.1
E	28	0.010	0.001	90.0	2.88	92.4	7.43
E	35	0.011	0.001	38.0	1.75	70.9	3.75
E	42	0.011	0.001	31.5	6.17	88.3	10.6
E	49	0.011	0.000	11.9	1.37	51.9	108

Values presented in ppm followed by standard deviations.

the ash was greatly reduced. The ash surface area in contact with the solution was also greatly reduced because the solution passed through cracks in the material instead of permeating the specimen.

As observed in the specimens of Group C, the hydraulic conductivity of the material can have a great effect on the leaching of metals from the ash. Specimens of Groups D and E, uncompacted, had higher hydraulic conductivity than those of Groups A, B, and C (before freeze thaw). The leaching trends in Groups D and E were similar to the compacted specimens but differed in magnitude. Higher concentrations of sodium and potassium were initially observed in the leachate from the uncompacted specimens (Groups D and E).

The hydraulic conductivity decreased in all specimens that were not subjected to freeze thaw. During the time period of the study, the decrease was approximately two orders of magnitude in the compacted specimens, from 8×10^{-7} to 1×10^{-8} cm/sec, and one order of magnitude in the uncompacted specimens, from 8×10^{-5} to 8×10^{-6} cm/sec. The change in hydraulic conductivity of fly ash can be attributed to the pozzolanic reactions that occur in high-calcium fly ashes such as the one used in this study.

Portland cement was added to Group F specimens as a source of sulfate to precipitate barium as barium sulfate and reduce the leaching of barium. Portland cement was chosen as a source of sulfate because it increases the strength of the compacted material and is therefore likely to be used as a stabilizer in road bases. With the

TABLE 8 Averages of Barium Concentrations in Cement-Stabilized Fly Ash Leachate

Group	Days	Concentration (mg/l)
F	1	61.7 ± 5.37
F	7	190 ± 23.5
F	14	323 ± 38.0
F	21	287 ± 14.1 ^a
F	28	63.7 ± 17.1 ^a

^a represents average of two samples

addition of 3 percent cement to the ash, the peak barium concentration (average of three samples) in the leachate was reduced by about 40 percent. The authors hypothesize that additional cement would further immobilize barium (Figure 6).

The leaching behavior of many of the elements analyzed in this study (Ca, Mg, Sr, Na, K, Si, and Al) were similar to those described by Dudas (9) and Warren and Dudas (10,11). Other elements, most notably barium, behaved differently than described by these researchers. Barium was not readily leached in a study by Warren and Dudas (11). They attributed this behavior to the presence of sulfate in the leaching solution from sulfuric acid that was used to adjust the pH. Warren and Dudas predicted that in the absence of sulfate, barium would exhibit a leaching behavior similar to calcium, as was observed in this study.

Of the metals with maximum concentration limits (MCL) specified in the EPA TCLP, only barium was observed in the leachate in levels exceeding the MCL (100 ppm). The maximum concentration of barium observed in this study was 542 ppm (the average for Group A, Week 1). The TCLP test was performed on the ash sample used in this study, and the concentration of barium in the leachate was found to be 2.1 ppm, equivalent to a release of 0.042

mg per gram of dry ash. The maximum release of barium from the ash in this column leaching study was 0.35 mg per gram of dry ash, nearly 10 times the release of barium in the TCLP.

The factors controlling the solubility of barium in the column and TCLP tests cannot be easily identified from these results. In the TCLP, barium may not have reached equilibrium. In an extraction study performed as part of this study, barium concentrations were still increasing in samples after 24 hr of agitation. The length of time required to reach equilibrium in an extraction study may be due to the heterogeneity of the ash particles. Certain elements are concentrated in the highly soluble outer layer of the particle; others are concentrated in the interior glass matrix (17). The availability of elements will therefore change as the particle surface dissolves. No chemical species can be identified from the results to explain the solubility of barium in the column leaching test. Barium carbonate and barium sulfate have low solubilities: solubility products 2.58×10^{-9} and 1.07×10^{-10} , respectively (18). Sulfate and carbonate must therefore have been greatly limited in the leaching column. If sulfate or carbonate were available, barium would precipitate as barium sulfate or barium carbonate and would not be present in the leachate in the high concentrations observed.

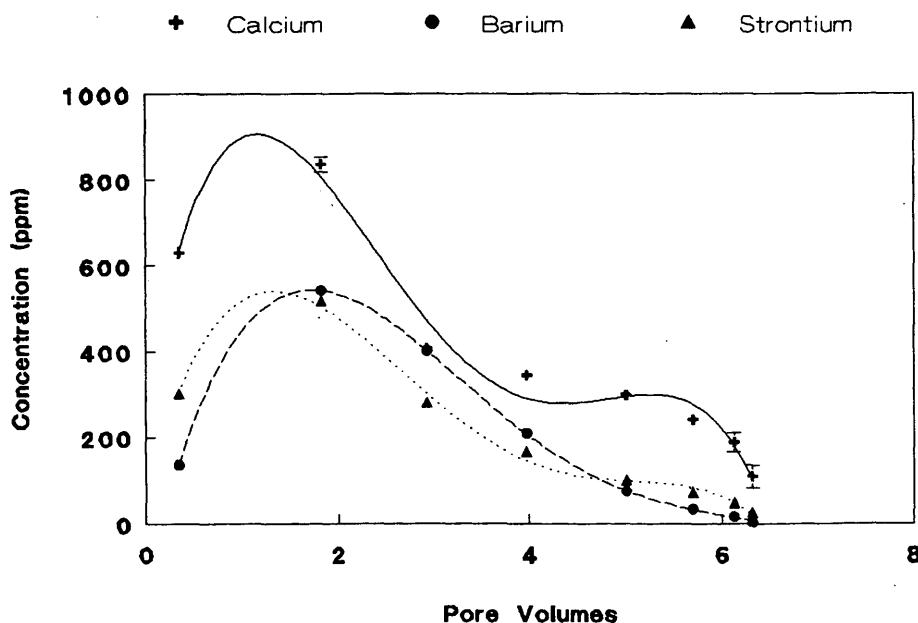


FIGURE 3 Variation of concentrations of calcium, barium, and strontium in Group A leachate.

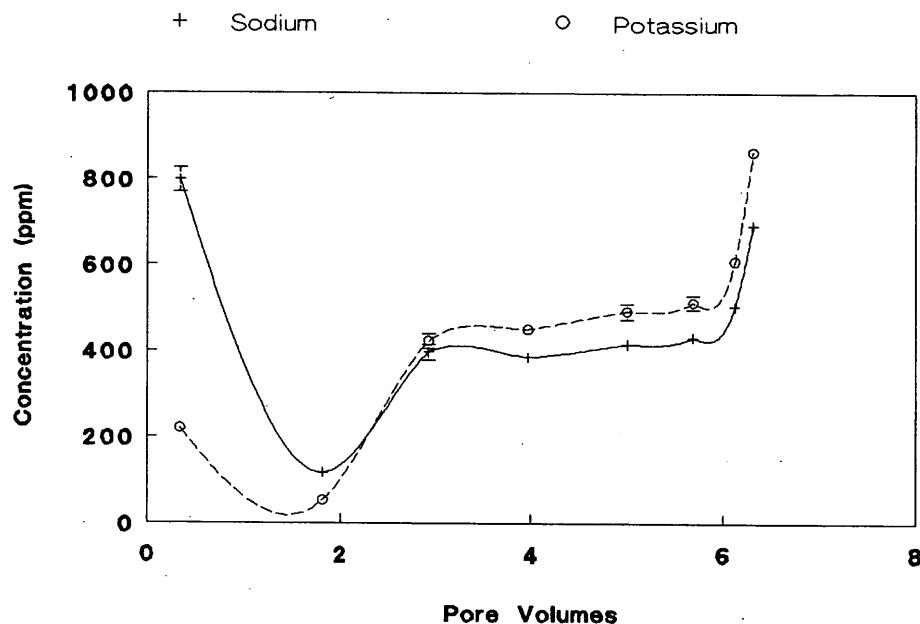


FIGURE 4 Variation of concentrations of sodium and potassium in Group A leachate.

SUMMARY AND CONCLUSIONS

Although fly ashes generally pass the TCLP, this test may not accurately predict worst-case field leaching. As observed in this study, barium leaching occurred to a much greater extent in the column study using distilled water than in the TCLP test, an extraction procedure using distilled water and acetic acid. Leaching of fly ashes containing barium may result in large releases of dissolved barium when sulfate and carbonate are unavailable. The addition of 3 percent portland cement to the ash as a source of sulfate reduced the

peak concentration of barium in the leachate by about 40 percent. Increasing the cement content may further immobilize barium in the ash.

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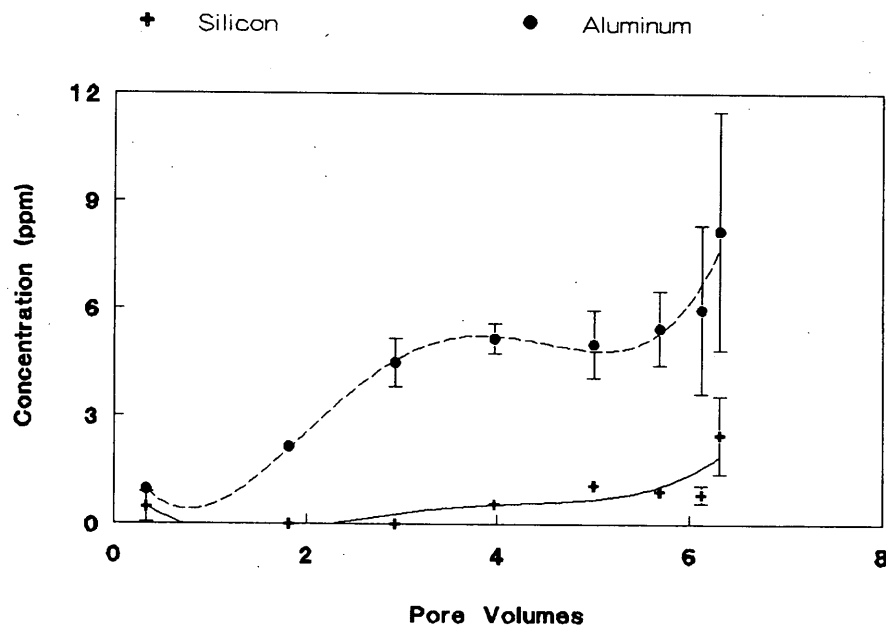


FIGURE 5 Variation of concentrations of silicon and aluminum in Group A leachate.

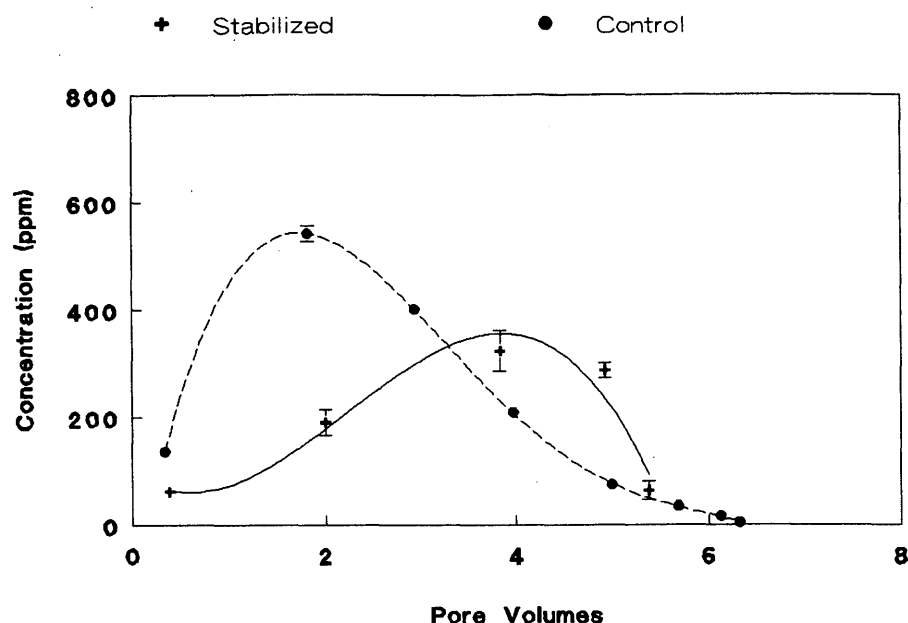


FIGURE 6 Variation of concentration of barium in compacted unstabilized (Group A) and stabilized (Group F) specimens.

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