

1981

Evaluation of Fly Ash Leachability Using Batch Leaching Procedures

W. A. Sack
West Virginia University

B. A. Boomer
Midwest Research Institute

J. T. Tarantino
NUS Corporation

G. b. Keefer
University of Nebraska at Omaha

R. K. Seals
Louisiana State University

See next page for additional authors

Follow this and additional works at: <http://digitalcommons.unl.edu/civilengfacpub>

Sack, W. A.; Boomer, B. A.; Tarantino, J. T.; Keefer, G. b.; Seals, R. K.; and Miller, M., "Evaluation of Fly Ash Leachability Using Batch Leaching Procedures" (1981). *Civil Engineering Faculty Publications*. 79.
<http://digitalcommons.unl.edu/civilengfacpub/79>

This Article is brought to you for free and open access by the Civil Engineering at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Civil Engineering Faculty Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors

W. A. Sack, B. A. Boomer, J. T. Tarantino, G. b. Keefer, R. K. Seals, and M. Miller

W. A. Sack,¹ B. A. Boomer,² J. T. Tarantino,³ G. B. Keefer,⁴
R. K. Seals,⁵ and M. Miller⁶

Evaluation of Fly Ash Leachability Using Batch Leaching Procedures

REFERENCE: Sack, W. A., Boomer, B. A., Tarantino, J. T., Keefer, G. B., Seals, R. K., and Miller, M., "Evaluation of Fly Ash Leachability Using Batch Leaching Procedures," *Hazardous Solid Waste Testing: First Conference, ASTM STP 760*, R. A. Conway and B. C. Malloy, Eds., American Society for Testing and Materials, 1981, pp. 61-82.

ABSTRACT: The leachability of two fly ashes was evaluated using two different proposed procedures Environmental Protection Agency-Extraction Procedure (EPA-EP) and American Society for Testing and Materials method (ASTM). The EP test was also run to study the influence of contact time and the presence of dissolved oxygen. Finally, a modified EP was carried out with repeated extraction of the same ash with fresh leachate and repeated contact of the same leachate with fresh ash. Both acid and deionized water extractions were used.

The EP test was found to extract more material than the ASTM procedure on a milligrams per kilogram of ash basis, although the ASTM test gave higher concentrations. For the contact times studies (2 to 48 h), no one elution time could be chosen which would allow equilibrium for all parameters. Although certain elements evidenced sensitivity to the presence or absence of oxygen, no general pattern was found. Release during repeated extraction of the same ash with fresh leachate was found to be highly pH dependent. Most of the mobilization tended to occur in the first two extractions for the acid test, while release occurred more gradually for 5 to 7 elutions using deionized water.

KEY WORDS: leachate, fly ash, extraction, leaching tests, landfills, hazardous solid waste

A number of procedures [1-8]⁷ have been proposed and evaluated for the leaching of solids via batch or sequential batch methods. All such procedures have a predictive element in that they seek to assess the leaching potential of

¹ Professor of civil engineering, Department of Civil Engineering, West Virginia University, Morgantown, W. Va. 26505.

² Midwest Research Institute, Kansas City, Mo. 64110.

³ NUS Corporation, Pittsburgh, Pa. 15220.

⁴ Department of civil engineering, University of Nebraska, Omaha, Nebr. 68108.

⁵ Department of civil engineering, Louisiana State University, Baton Rouge, La. 70803.

⁶ American Electric Power Service Corporation, Canton, Ohio 44701.

⁷ The italic numbers in brackets refer to the list of references appended to this paper.

the waste based on a given set of presuppositions and test conditions. The testing program may be designed simply to assess leachate characteristics via a rapid standardized test, or may involve detailed studies to show the influence of a number of variables on pollutant mobilization or attenuation, or both.

The latter, more comprehensive, approach to testing should reduce the degree of uncertainty in application of laboratory test results to estimate actual field behavior. Major variables to be considered in a comprehensive leaching evaluation include extractant composition, solid-to-liquid ratio, contact time, number of elutions, and agitation method.

This paper reports the results of batch leaching studies carried out on two fly ashes. Testing was divided into five major parts, as follows: (1) a comparison of proposed American Society for Testing and Materials (ASTM) and Environmental Protection Agency-Extraction Procedure (EPA-EP) extraction methods; (2) an examination of the effect of contact time; (3) a determination of the mass available for leaching upon repeated extraction of the same ash with fresh leachant; (4) a comparison of leaching under aerobic and anaerobic conditions; and (5) an investigation of leachate concentrations attained after repeated extraction of fresh ash with the same leachant. In Parts 2 to 5, only the EP was used.

Procedure

Fly Ash

Two fly ashes (Ashes A and C) were selected for use in this study. Both ashes were generated from eastern bituminous coals and had similar physical properties. For example, both ashes had a specific gravity of 2.3, a loss on ignition of 1.2 percent, and showed between 89 and 91 percent passing a No. 200 sieve. While physical properties of the ashes were similar, the ashes were quite different chemically, with Ash A being acidic and Ash C quite alkaline. A large enough specimen of ash was secured initially, to serve for the entire study reported here.

Batch Leaching Tests

Two basic batch leaching procedures were used: ASTM [9] and EPA-EP [10]. The proposed ASTM procedures [9] included both the water shake (Method A) and acid shake (Method B) extractions. In brief, the ASTM procedure used 350 g of ash in 1400 ml of water with a specified contact time of 48 h. A reciprocating platform shaker operating at 65 one-inch strokes per minute provided agitation. The acid shake was at pH 4.5 using an acetic acid-sodium acetate buffer. The EPA-EP used was that proposed on 18 Dec. 1978 [10], which calls for a 24-h extraction at pH 5.0 using acetic acid and a final liquid-to-solid ratio of 20:1. The procedure was modified to include a deion-

ized water extraction. A 175-g specimen of ash was used unless otherwise noted. Extraction was performed in a 4-litre glass beaker, using a plastic-coated two-paddle stirring device operated at 50 rpm.

Leachate Analysis

After extraction, leachate was separated from the solids by vacuum filtration through 0.45 μm filters. Leachate tests were divided into two groups, termed chemical and elemental tests. In the chemical test series, analysis was performed for total dissolved solids (TDS), hardness, acidity (to pH 8.3), alkalinity (to pH 3.7), pH, and sulfate. All chemical tests were performed in accordance with standard methods [11]. The elemental series included aluminum, arsenic, boron, barium, cadmium, chromium, copper, iron, lead, manganese, molybdenum, nickel, selenium, and zinc. Boron was determined according to standard methods [11], while arsenic and selenium analysis was by hydride [12]. All other trace elements were determined via atomic absorption according to EPA recommended methods [13].

Results and Discussion

Comparison of ASTM and EPA-EP Extraction Procedures

The ASTM and EPA-EP leaching tests were compared using both acid and deionized water (DI) extractions. Replicate and duplicate tests were run on both Ashes A and C. Replicates refer to the results of two identical leaching tests run on specimens of the same ash at the same time to estimate reproducibility of entire test protocol. Duplicates refer to different portions of the liquid from a given leachate test. Comparison of duplicates allows evaluation of the reproducibility of the analytical methods.

ASTM Extraction—Results of the analysis of the leachate generated by the ASTM test are found in Table 1. It may be seen that “adjusted” values are listed for TDS, acidity, and alkalinity in the ASTM acid test. Tests run on a “blank” specimen of ASTM sodium acetate-acetic acid buffer solution indicated that the buffer itself would contribute a TDS of 3700 mg/l, an acidity of 2015 mg/l, and an alkalinity of 1550 mg/l. These parameters, as shown in Table 1 for the acid test, therefore have been adjusted using the preceding values in an attempt to indicate only the portion actually contributed by the ash.

Examining the DI leachate of Ash C shows an alkaline ash (pH about 12). TDS, alkalinity, and hardness are in the general range of 1000 to 1300 mg/l, while sulfate concentration is about 200 mg/l. As would be expected from the high pH level, the elemental values are relatively low, with only boron achieving a concentration of over 0.1 mg/l. The addition of acid to Ash C created a set of chemical data with significantly higher concentrations than in the DI

TABLE 1—ASTM leach test results: Fly Ashes A and C, mg/l except pH.

Specimen	Test	pH	TDS	Hardness	Alkalinity or Acidity	Sulfate	Cu	Mn	Zn	Fe	Al	Cd	Cr	B	Se
Ash A															
1	DI ^a	3.5	480	160	90	320	0.91	0.13	0.26	1.50	12.0	0.009	0.50	3.90	0.05
2	DI	3.8	442	156	90	350	0.95	0.12	0.23	1.96	13.3	0.009	0.57	3.80	ND ^c
1D	acid	4.5	356 ^b	216	985 ^b	280	0.87	0.21	0.33	0.44	8.7	0.016	<0.30	4.70	ND
1D	acid	4.5	228 ^b	216	...	280	0.87	0.20	0.33	0.41	8.7	0.017	<0.30	3.15	ND
2D	acid	4.5	254 ^b	212	1 255 ^b	275	0.87	0.20	0.29	0.61	10.8	0.012	<0.30	3.15	ND
2D	acid	4.5	184 ^b	208	...	260	0.83	0.20	0.29	0.59	10.8	0.012	<0.30	3.15	ND
Ash C															
1D	DI	11.9	1 292	1 140	810	200	ND	0.01	0.02	0.08	0.1	<0.002	<0.3	0.40	0.07
1D	DI	11.9	1 248	1 130	820	200	0.01	0.01	0.01	0.08	ND	<0.002	<0.3	0.50	0.07
2D	DI	12.0	1 356	1 330	1 190	200	ND	0.01	0.02	0.07	ND	<0.002	<0.3	0.50	ND
2D	DI	12.0	1 348	1 320	1 200	200	ND	0.01	0.02	0.04	ND	<0.002	<0.3	0.60	ND
1D	acid	5.5	4 700 ^b	2 520	2 700 ^b	300	0.35	0.47	0.44	0.10	1.1	...	0.87	0.60	ND
1D	acid	5.5	4 568 ^b	2 500	2 700 ^b	300	0.34	0.45	0.45	0.10	1.1	0.011	0.87	0.55	ND
2D	acid	5.6	5 220 ^b	2 870	2 970 ^b	350	0.41	0.48	0.17	0.12	1.2	0.010	1.0	0.60	ND
2D	acid	5.6	5 415 ^b	2 890	2 970 ^b	350	0.41	0.49	0.16	0.10	1.2	0.008	1.0	0.60	ND

NOTE—Numbers 1 and 2 are replicate specimens, while D indicates duplicate specimens.

^aDI indicates Deionized water.

^bAdjusted for contribution of the ASTM buffer.

^cND = not determined.

test. Specimen alkalinity was so large that the initial buffered pH of 4.5 rose to 5.5 at the end of the 48-h test period. The lower pH resulted in increased mobilization of almost all elements determined. For example, two elements, chromium and aluminum, reached or exceeded the 1.0 mg/l level (Table 1).

The Ash A DI leachate was very different in chemical composition, with a low pH (less than 4) and a low acidity of 90 mg/l. As would be expected for an acidic ash, sulfate was higher (average 335 mg/l) and hardness was much lower (average 158 mg/l) than that of the Ash C DI leachate. Additionally, the Ash A TDS level (average 461 ml/l) was about three times that of the hardness, indicating a markedly different pattern than that of the alkaline Ash C.

Addition of the ASTM buffer for the Ash A acid test actually raised the pH from less than 4 to 4.5. The acid test produced chemical data quite similar to the DI test except for a large increase in acidity. For the most part, Ash A DI leachate had significantly higher trace element concentrations than Ash C DI. The lower pH of the Ash A DI test leached a number of metals to a concentration of greater than 0.1 mg/l, including copper, manganese, zinc, iron, chromium, boron, and aluminum. Because of the low pH of the Ash A DI test, a number of the trace element concentrations were higher in the DI extraction than in the corresponding acid extraction of Ash A.

EPA-EP Extraction—Table 2 presents the results of the EPA-EP run on the two ashes. Since the pH of Ash A was less than 5 in DI water, an acid test was not run on this ash. Once again, the Ash C DI leachate was strongly basic with high alkalinity, TDS, and hardness values, while the Ash A DI specimen was acidic with low acidity, hardness, and TDS values. The acetic acid required to control the pH of the acid Ash C specimen to about 5 provided an environment which mobilized a much higher level of TDS, hardness, alkalinity, and sulfate than the comparable DI specimen. Examination of the trace element values in Table 2 shows a similar pattern to that observed for the ASTM leaching, with pH playing a major determinant role.

Comparing the results of the ASTM (Table 1) and EP (Table 2) procedures shows that the ASTM concentrations were significantly higher in almost every instance. This result is readily understood by considering that the 20:1 liquid-to-solid ratio used in the EP test provides a much greater dilution than the 4:1 ratio specified by ASTM. In Table 3, the mass fraction leached of each element is shown expressed as milligrams per kilogram of ash. On this basis, it may be seen that a larger mass of material was mobilized in almost every case by the EP extraction. The ratio of the EP mass fraction released to ASTM mass fraction released varied from 0.7 to 15.7, with most values in the 2 to 4 range. Thus, the EP method was in general, 2 to 4 times more efficient in leaching the constituents measured than the ASTM procedure. Bause and McGregor [2] observed the same general trend of higher concentrations with the ASTM extraction and higher mass fractions via the EP. Their investigation included the leach testing of seven different energy process wastes. The higher leaching ability of the EPA test can be attributed to solubility and agitation

TABLE 2—EPA-EP leach test results: Fly Ashes A and C. mg/l except pH.

Specimen	Test	pH	TDS	Hardness	Alkalinity or Acidity	Sulfate	Cu	Mn	Zn	Fe	Al	Cd	Cr	B	Se
Ash A															
					Acidity										
1D	DI ^a	4.2	204	85	20	100	0.5	0.09	0.16	0.25	3.5	0.010	<0.1	0.5	<0.02
1D	DI	4.2	204	85	20	100	0.5	0.06	0.15	0.26	3.4	0.009	<0.1	0.7	<0.02
2D	DI	3.6	210	80	30	100	0.2	0.05	0.10	<0.2	<0.4	0.008	<0.1	0.5	ND ^b
2D	DI	3.6	200	75	30	100	0.2	0.05	0.11	<0.2	<0.4	0.007	<0.1	0.6	ND
Ash C															
					Alkalinity										
1D	DI	12.1	765	650	570	50	0.02	0.01	<0.01	<0.2	<0.2	<0.002	0.1	<0.5	<0.02
1D	DI	12.1	760	640	570	50	0.01	0.01	<0.01	<0.2	<0.2	<0.002	0.1	<0.5	<0.02
2D	DI	11.7	700	600	470	135	0.02	<0.01	<0.01	<0.2	<0.2	<0.002	0.1	<0.5	ND
2D	DI	11.7	685	600	470	135	0.02	0.01	<0.01	<0.2	<0.2	<0.002	0.1	<0.5	ND
1D	acid	4.9	2 900	1 570	970	225	0.21	0.37	0.12	0.06	4.2	0.005	0.7	0.9	0.34
1D	acid	4.9	2 885	1 570	980	225	0.22	0.36	0.12	0.12	4.2	0.004	0.6	0.9	0.14
2D	acid	5.1	3 275	1 715	1 336	250	0.18	0.46	0.12	0.05	3.0	0.007	0.7	2.5	ND
2D	acid	5.1	3 260	1 715	1 318	250	0.18	0.47	0.12	0.02	3.0	0.008	0.7	2.5	ND

Note—Numbers 1 and 2 are replicate specimens, while D indicates duplicate specimens.

^aDI indicates Deionized water.

^bND = not determined.

TABLE 3—Comparison of mass fractions released in the ASTM and EPA tests.

	Ash C, Acid				Ash C, DI				Ash A, DI			
	Ash, mg/kg		Ash, mg/kg		Ash, mg/kg		Ash, mg/kg		Ash, mg/kg		Ash, mg/kg	
	ASTM	EP	EP/ASTM	ASTM	EP	EP/ASTM	ASTM	EP	EP/ASTM	ASTM	EP	EP/ASTM
Cu	1.51	3.95	2.6	0.04	0.36	9.0	3.72	7.00	1.9			
Mn	1.88	8.40	4.5	0.04	0.20	5.0	0.50	1.26	2.5			
Zn	1.24	2.40	1.9	0.08	0.98	2.60	2.7			
Fe	0.44	1.25	2.8	0.27	6.92	5.10	0.7			
Cr	3.76	13.60	3.6	2.0			
Al	4.6	72.00	15.7	0.40	50.4	69.0	1.4			
B	2.36	34.00	14.4	2.0	15.4	11.6	0.8			
Sc	...	6.80	...	0.28			
Cd	0.039	0.122	3.1	0.036	0.162	4.5			
TDS	19 900	61 600	3.1	5 244	14 560	2.8	1 844	4 100	2.2			
Hardness	10 780	32 860	3.0	4 920	12 460	2.5	632	1 620	2.6			
Alkalinity	17 540	23 020	1.3	4 020	10 400	2.6			
Acidity	360	500	1.4			
Sulfate	1 300	4 760	3.7	800	1 860	2.3	1 340	2 000	1.5			

factors. Since the concentration of fly ash was lower in the EP test, more material could be dissolved before saturation of any species was reached. In addition, the shaking rate specified by ASTM did not adequately keep the fly ash in suspension, allowing it to form a solid layer on the bottom of the bottle. Quite the opposite, the stirring device used in the EP kept the fly ash in total suspension and may even have caused ash deterioration due to abrasion.

Part of the purpose of this segment of the testing protocol was to examine reproducibility of test results. Referring to Tables 1 and 2 shows that the duplicate specimens (different portions of the same leachate) generally gave close results, indicating satisfactory analytical procedure. To compare replicate specimens (specimens of the same ash leached separately), the percent variation for each parameter was estimated (Table 4). It may be seen that the average percent variation ranged from 7.3 to 22.5 percent for the entire test series. Overall, the ASTM test showed lower variability than the EPA procedure in 65 percent of the cases where comparison could be made. The better agreement of replicate data in the ASTM test was probably due to the larger amount of ash used (350 g) as compared to 175 g in the EP. The larger amount of ash tends to minimize differences resulting from ash nonhomogeneity. In addition, the higher concentrations produced in the ASTM test tend to improve analytical reproducibility.

In a study which compared the reproducibility of the ASTM, the EP, and the carbonic acid extraction (CAE) tests [2], it was reported that the EP always gave lower precision than the other two methods. Interestingly, the CAE, which uses an intermediate solid-to-liquid ratio of 10:1, showed a precision in-

TABLE 4—Calculation of average variability.

	Σ % Variability	n	Average % Variability
Ash A, DI, ASTM	103.3	14	7.3
Ash A, DI, EPA	225.2	10	22.5
Ash A, acid, ASTM	180.5	11	16.4
Ash C, DI, ASTM	148.9	10	14.9
Ash C, DI, EPA	67.7	6	11.2
Ash C, acid, ASTM	147.6	12	12.3
Ash C, acid, EPA	242.8	12	20.2

NOTE— Σ % Variability = total of variability values in each test from Tables 1 and 2.

n = number of values for each test (including zeros).

$$\% \text{ Variation} = \frac{(\text{Rep}_1 - \text{Rep}_2)}{\frac{\text{Rep}_1 + \text{Rep}_2}{2}} \times 100 \quad (\text{Rep} = \text{replicate}).$$

Duplicates were averaged. Values noted as "less than" were not included.

intermediate between the other two methods. A more wide-ranging eighteen-laboratory testing program, sponsored jointly by ASTM and the Department of Energy (DOE) [7], concluded that concentrations of heavy metals leached by the ASTM and EP procedures could not be shown to be statistically different.

Investigation of the Effect of Contact Time

Ham, Anderson, Stegmann, and Stanforth [3] studied release patterns for a number of wastes, and concluded that their systems did not appear to reach equilibrium at contact times of 24 to 72 h. Lee and Plum [14] leached taconite tailings, using low solid-to-liquid ratios, for up to 500 days. They reported that for some parameters, a series of reactions took place with rising and falling concentrations. In two other studies, it was reported [15] that 60 min of mixing was adequate to arrive at a steady state concentration, and that 30 min of shaking [1] was adequate to reach maximum contaminant concentration.

Various leaching contact times were utilized to determine if short-term equilibrium values would be reached using Ash C. The EP procedure was used for both a DI and acid extraction, with contact times of 2, 4, 12, 24, 36, and 48 h. A separate specimen was used for each of the different extraction times. The data are presented in Table 5.

Chemical parameters for the deionized water extraction are shown in Fig. 1, while selected elemental values are presented in Fig. 2. The pH is seen to vary from 11.6 to 12.0. Chemical parameters peak at 4 h (except for sulfate), and then fall off, suggesting precipitation or adsorption back onto the ash. Sulfate increased slightly, up to 36 h. Selected trace elements are plotted in Fig. 2, exemplifying three general patterns. Certain elements, such as chromium, tended to increase with time. Arsenic decreased with leaching time, while a number of elements, such as barium, showed no trend or were below detection limits.

The acid extraction resulted in a markedly different time-leaching pattern than the DI test. As shown in Fig. 3 for the chemical parameters, most of the extraction took place in the first 12 h, followed by relatively stable levels for the remainder of the test period. Figure 4 presents the variation with time for arsenic, manganese, copper, and nickel again showing several time-leaching patterns. Certain elements increased and then stabilized, such as manganese and copper. Others, such as nickel, were fairly stable for the entire period or showed no trend. Arsenic again decreased over the entire 48 h period. The influence of the acid was twofold. First, a greater mass of most pollutants was mobilized, as compared to the DI system. Second, the acid tended to stabilize more of the contaminants in solution after leaching, in contrast to the DI leach, where decrease in concentration with time occurred in a number of cases. However, there was no one elution time which would allow equilibrium for all parameters at the short elution times studied.

TABLE 5—Investigation of effect of contact time using the EP, Ash C.

Time, h	pH	TDS	Hardness	Alkalinity	Sulfate	Acid Used, ml						
			Ash C—DI—Chemical Data									
2	11.9	575	640	560	65	...						
4	12.0	870	730	620	79	...						
12	11.6	400	520	590	80	...						
24	11.9	727	623	520	93	...						
36	11.8	600	460	370	100	...						
48	11.6	545	470	350	67	...						
			Ash C—Acid—Chemical Data									
2	5.0	2 345	1 390	1 050	180	250						
4	5.0	2 440	1 350	990	223	325						
12	5.0	3 115	1 780	1 190	223	325						
24	5.0	3 081	1 645	1 151	238	350						
36	5.0	3 005	1 810	1 360	250	350						
48	5.0	3 135	1 750	850	223	350						
Time, h	Al	As	Ba	B	Cr	Cu	Fe	Mn	Mo	Ni	Sc	Zn
							Ash C—DI—Trace Element Data					
2	<0.5	0.016	0.63	<0.5	0.06	<0.01	<0.01	<0.02	<0.1	<0.01	<0.005	<0.005
4	<0.5	0.005	0.87	<0.5	0.08	<0.01	0.02	<0.02	<0.1	<0.01	0.012	<0.005
12	<0.5	0.005	0.63	<0.5	0.09	<0.01	<0.01	<0.02	<0.1	<0.01	0.062	<0.005
24	<0.5	<0.02	<1	<0.5	0.10	0.02	<0.2	0.01	<1	<0.1	<0.02	<0.01
36	<0.5	0.003	0.82	<0.5	0.14	0.03	0.02	<0.02	<0.1	<0.01	0.010	0.010
48	<0.5	0.002	0.74	<0.5	0.11	0.02	0.03	<0.02	<0.1	<0.01	<0.005	<0.005
							Ash C—Acid—Trace Element Data					
2	0.8	0.66	0.60	1.4	0.52	0.16	0.02	0.19	0.16	0.08	0.400	0.07
4	1.0	0.63	0.48	2.5	0.57	0.24	0.02	0.28	0.16	0.09	0.320	0.09
12	3.0	0.32	0.60	2.6	0.60	0.24	0.07	0.40	0.14	0.06	0.410	0.13
24	3.6	0.14	<1	1.7	0.70	0.20	0.06	0.42	<1	<0.1	0.34	0.12
36	3.5	0.11	0.58	2.6	0.53	0.21	0.04	0.38	0.14	0.07	0.310	0.10
48	6.0	0.07	0.60	2.6	0.57	0.25	0.05	0.37	0.14	0.07	0.280	0.13

NOTE—All values in mg/l except pH or as noted. The 24-h values were taken from Table 2 (average).

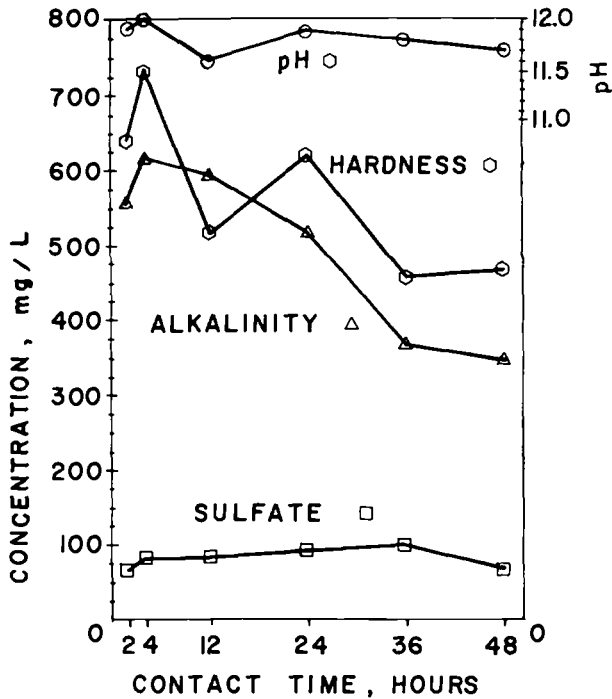


FIG. 1—Influence of contact time on chemical parameters: Ash C. DI.

Determination of Mass Available for Leaching upon Repeated Extraction with Fresh Leachate

Extraction tests (EP) were run in order to determine the mass of pollutants that might be mobilized by multiple (10) extractions with fresh leachant. The results should be useful to estimate what might occur over an extended period of time as rainwater or groundwater percolated through a certain unit mass of fly ash fill. Ash C (175 g) was leached using both deionized water and acid extractions. For each of the 10 extractions, fresh water was added as required to maintain pH. The acid extraction required 335 ml and 50 ml of acid for elutions 1 and 2, respectively, and then less than 5 ml for each of the remaining elutions. TDS and pH were run for each elution, while specimens were taken for elemental analysis at elutions numbers 1, 2, 4, 7, and 10. Results are presented in Table 6 and in Figs. 5 and 6.

The data show that pH and TDS (DI series) leveled off at about 10 and 60 mg/l, respectively, after about 5 or 6 extractions (Fig. 5). If the cumulative mass of TDS leached after 10 extractions is designated $R_T - 10$, it may be seen (Table 6) that 80 percent of this value had been removed after only 5 extractions. A very different pattern was observed for the acid extraction of Ash C, where 81 percent of the $R_T - 10$ value was removed after only one extrac-

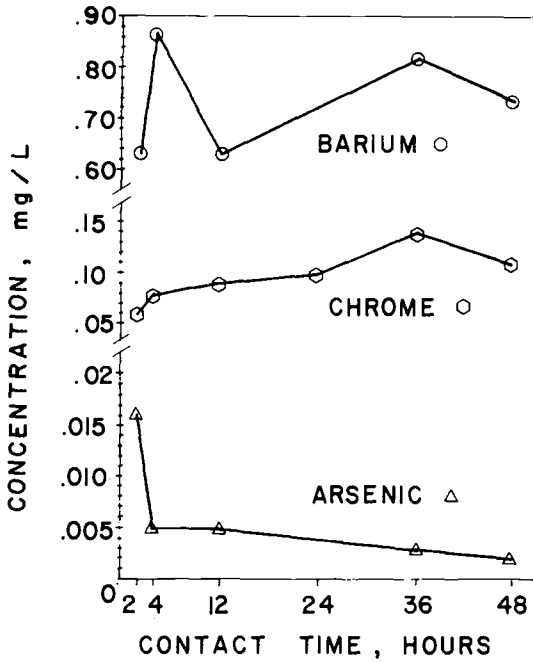


FIG. 2—Influence of contact time on arsenic, barium, and chromium: Ash C. DI.

tion. It is also interesting to note that the acid mobilized about 2.5 times more TDS in the 10 elutions than did the DI water.

The acid series showed all trace elements except iron to decrease in concentration with increasing elution. Arsenic and zinc are shown in Fig. 5 as examples. It may be seen that most of the mobilization occurred in the first two elutions for these elements. In the DI series, a number of the elements again tended to decrease in concentration with elution (Table 6). However, certain elements (iron, selenium, and aluminum) showed no regular pattern, while the concentration of arsenic actually increased with elution, and zinc remained nearly constant (Fig. 6).

Comparison of Aerobic and Anaerobic Leaching Conditions

A number of leaching procedures [4,8] make provision for leachate generation in the absence of oxygen, and anaerobic conditions may be expected to occur in some fly ash fills. Therefore, it was decided to run a modified EP leaching test (both DI and acid) under anaerobic conditions to see if significant differences in leachate quality would be observed. Since the stirring apparatus normally used could not be readily sealed, a reciprocating shaker was used. The specimens were placed in bottles and shaken at 90 cpm using a 3-in. stroke. Specimens were purged with nitrogen gas for 1-h, 1 ml of sodium

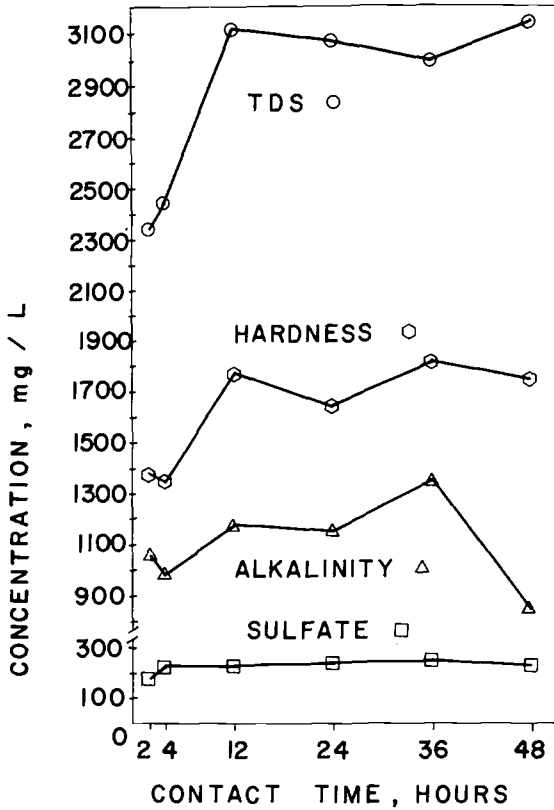


FIG. 3—Influence of contact time on chemical parameters: Ash C. acid.

sulfite (1 *N*) was added, and the bottles securely stoppered to retain a nitrogen blanket within the bottle. For the acid test, all of the acetic acid required to control the pH at 5 was added initially based on estimates, since the bottles could not be opened during the test. A 65-g specimen of ash with a total liquid volume of 1300 ml was used. Dissolved oxygen tests were performed at the end of the test period on the anaerobic specimens to verify that oxygen did not leak into the bottles.

An aerobic specimen and two anaerobic replicates were tested for both Ash A and Ash C. The results are shown in Table 7. A comparison ratio of aerobic to the mean of the anaerobic data for each parameter is listed. Examination of Table 7 shows relatively little difference between aerobic and anaerobic leachate quality in most cases. Cases where the aerobic to anaerobic ratio is less than 0.75 or greater than 1.25 (denoted by an asterisk) are felt (arbitrarily) to suggest a significant difference. Out of 40 possible cases (not including the "less-than values"), 11 fall in this category. Certain of the elements, such as arsenic and zinc, evidence considerable sensitivity, with two or more cases

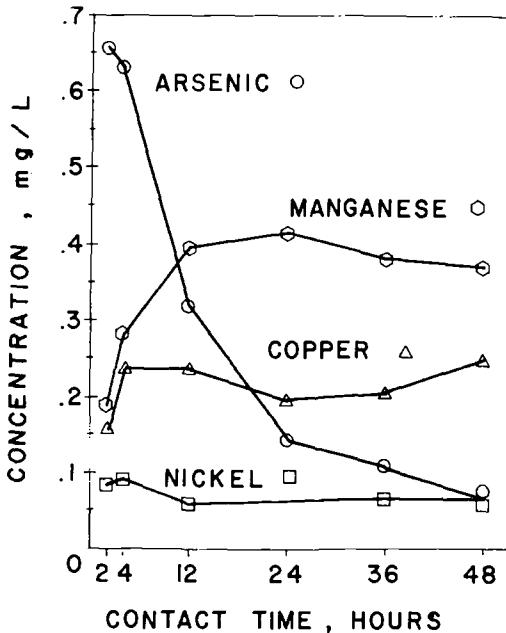


FIG. 4—Influence of contact time on arsenic, copper, manganese, and nickel: Ash C. acid.

showing large ratios. For the 11 cases noted previously, 5 had higher values when leached aerobically, and 6 had higher values when leached anaerobically. Thus, while it appears that a lack of oxygen can have a strong influence on a specific trace element concentration, no general pattern was found.

Serial Extraction of Fresh Ash Using the Same Leachate

Leachate was repeatedly contacted with fresh ash in order to determine if equilibrium concentrations would be reached for the chemical and elemental parameters measured. This type of test protocol was designed to simulate changes in contaminant concentration with length or depth of water percolation through a large mass of the waste. Five separate elutions were made with a solid-to-liquid ratio of 1:20 maintained throughout. At the end of each 24-h period, the liquid portion was filtered, a portion set aside for analysis, and the appropriate amount of ash added to begin another leaching cycle.

Leachate quality for this series is presented in Tables 8 and 9 and Figs. 7 and 8. It may be seen that the concentration (C_i) of TDS, alkalinity, hardness, and sulfate all increased as expected with repeated extraction. For Ash C, the release from each elution (R_i) fell off markedly, showing a major decrease even at the second contact. Contrariwise, release of TDS per contact for Ash A was undiminished through the fourth elution. This is not surprising since the TDS

TABLE 6—Repeated extraction using fresh leachate: EP, Ash C. All values in mg/l except pH, R_1 and R_T .

Elution	pH	TDS												
		C_i	R_i	R_T	Al	As	Cr	Cu	Fe	Mn	Mo	Ni	Sc	Zn
1	11.9	685	13.15	13.15	<0.5	0.005	0.09	<0.01	0.03	<0.02	0.11	0.025	0.013	0.010
2	11.4	205	3.94	17.09	2.3	0.031	0.08	<0.01	<0.01	<0.02	<0.1	<0.01	0.066	0.008
3	10.7	125	2.40	19.49										
4	10.1	110	2.11	21.60	3.2	0.092	<0.05	<0.01	<0.01	<0.02	<0.1	<0.01	0.17	0.011
5	10.1	95	1.82	23.42										
6	10.0	86	1.65	25.08										
7	10.0	50	0.96	26.04	1.8	0.170	<0.05	<0.01	0.02	<0.02	<0.1	<0.01	0.053	0.007
8	10.1	60	1.15	27.19										
9	9.9	60	1.15	28.34										
10	9.9	59	1.13	29.47	1.0	0.180	<0.05	<0.01	0.02	<0.02	<0.1	<0.01	0.022	<0.009
1	5.0	3150	59.40	59.40	3.2	0.116	0.70	0.18	0.02	0.37	0.19	0.062	0.270	0.100
2	5.0	390	7.35	66.75	1.3	0.031	<0.05	0.04	0.04	0.14	<0.1	0.032	0.055	0.031
3	4.7	165	3.11	69.87										
4	5.0	45	0.85	70.71	<0.5	0.011	<0.05	0.01	0.03	0.04	<0.1	<0.01	0.018	0.018
5	5.0	45	0.85	71.56										
6	5.1	15	0.28	71.85										
7	5.0	27	0.51	72.35	<0.5	0.007	<0.05	<0.01	0.04	0.02	<0.1	<0.01	0.012	0.012
8	5.1	28	0.53	72.88										
9	5.1	17	0.32	73.20										
10	5.0	20	0.38	73.58	<0.5	0.004	<0.05	<0.01	0.06	<0.02	<0.1	<0.01	0.005	0.011

where

$$\text{Elution 1: } R_1 = \frac{C_1 L_1}{W}$$

$$\text{Elution 2: } R_2 = \frac{C_2 L_2}{W}$$

C_i = concentration of leachate after i th elution, mg/l,
 L_i = volume of leachate withdrawn after i th elution, litres,

W = weight of ash used in each elution, g, and

R_i = release from i th elution, mg/g, R_T = cumulative release, mg/g.

$$R_T = \frac{C_1 L_1 + C_2 L_2}{W}$$

$$R_T = \frac{C_1 L_1}{W}$$

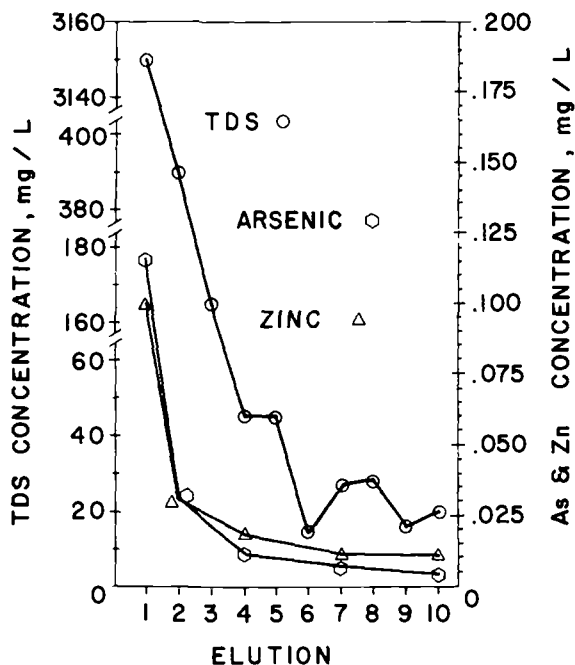


FIG. 5—Repeated extraction with fresh leachate, Ash C: acid, concentration.

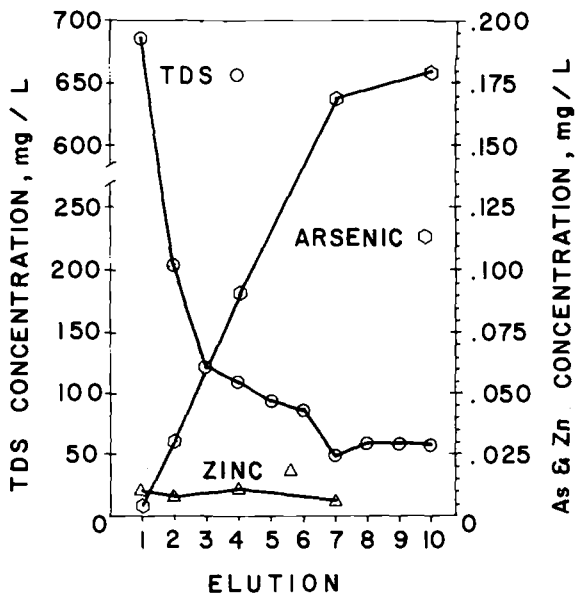


FIG. 6—Repeated extraction with fresh leachate, Ash C: DI, concentration.

TABLE 7—Aerobic-anaerobic shake comparison tests.^a

Test	pH	TDS	Hardness	Sulfate	Al	As	Cr	Cu	Mn	Ni	Sc	Zn
Aerobic	4.7	130	60	54	Ash A—Acid 0.94	0.005	0.03	0.052	0.050	0.063	<0.005	0.410
Anaerobic No. 1	4.5	164	90	50	1.01	0.006	0.03	0.052	0.050	0.050	<0.005	0.270
Anaerobic No. 2	4.5	156	90	50	1.15	0.007	0.04	0.055	0.048	0.058	<0.005	0.168
AER/ANAER ^b	1.04	0.81	0.67 ^c	1.08	0.87	0.77	0.86	0.97	1.02	1.17	...	1.87 ^c
Aerobic	6.5	126	55	63	Ash A—DI <0.1	0.004	<0.03	<0.01	0.021	0.038	0.007	0.012
Anaerobic No. 1	6.5	136	60	65	<0.1	0.004	<0.03	<0.01	0.020	0.038	0.006	0.013
Anaerobic No. 2	6.2	110	60	60	<0.1	0.002	<0.03	<0.01	0.020	0.038	0.005	0.022
AER/ANAER ^b	1.02	1.02	0.92	1.01	...	1.33 ^c	1.05	1.00	1.27 ^c	0.69 ^c
Aerobic	4.8	2392	1440	156	Ash C—Acid 2.57	0.371	0.46	0.134	0.171	0.070	0.243	0.183
Anaerobic No. 1	5.0	2994	1760	200	2.11	0.371	0.66	0.200	0.314	0.070	0.320	0.271
Anaerobic No. 2	5.0	2844	1690	200	1.86	0.337	0.51	0.195	0.263	0.070	0.330	0.286
AER/ANAER ^b	0.96	0.82	0.84	0.78	1.29 ^c	1.13	0.79	0.68 ^c	0.59 ^c	1.00	0.75	0.66 ^c
Aerobic	11.9	796	870	115	Ash C—DI <0.1	0.006	0.16	<0.01	<0.02	0.032	<0.005	0.015
Anaerobic No. 1	11.8	730	750	120	<0.1	0.009	0.11	<0.01	<0.02	0.032	0.007	0.025
Anaerobic No. 2	11.9	737	810	107	<0.1	0.009	0.11	<0.01	<0.02	0.030	<0.005	0.010
AER/ANAER ^b	1.00	1.09	1.12	1.01	...	0.67 ^c	1.45 ^c	1.03	...	0.86

^aAll values in mg/l except pH.

^bAerobic data divided by the mean of the anaerobic data.

^cDenotes ratio less than 0.75 or greater than 1.25.

^dDI = detonized water.

TABLE 8—Repeated DI water extraction of fresh ash using the same leachate: chemical test data.

Elution	pH	TDS		Alkalinity, Ash C; Acidity, Ash A		Hardness		Sulfate				
		C_i , mg/l	R_i , mg/g	R_T , mg/g	C_i , mg/l	R_i , mg/g	R_T , mg/g	C_i , mg/l	R_i , mg/g	R_T , mg/g		
Ash C												
1	11.9	685	13.70	13.70	420	8.40	8.40	440	8.80	100	2.00	2.00
2	12.0	1 135	9.00	11.67	1 060	10.39	13.80	1 130	11.07	200	2.00	2.00
3	12.0	1 365	4.60	9.73	1 290	8.86	5.20	1 390	9.51	252	1.04	1.75
4	12.1	1 705	6.80	9.25	1 560	8.30	5.80	1 680	8.91	320	1.36	1.68
5	12.1	1 960	5.10	8.84	1 710	7.77	7.40	2 050	8.76	390	1.40	1.65
Ash A												
1	5.1	117	2.34	2.34	50	1.00	1.20	60	1.20	125	2.50	2.50
2	4.8	220	2.06	2.21	50	0.55	1.20	120	1.20	200	1.50	2.05
3	4.8	343	2.46	2.28	100	1.00	0.70	130	0.94	240	0.80	1.72
4	4.8	510	3.34	2.45	120	0.40	1.80	220	1.08	295	1.10	1.62
5	4.8	547	0.74	2.28	140	0.40	1.60	330	1.13	345	1.00	1.55

NOTE—Elution 1: $R_1 = \frac{C_1 L_1}{W_1}$ Elution 2: $R_2 = \frac{(C_2 - C_1) L_2}{W_2}$

$$R_T = \frac{C_1 L_1}{W_1} \quad R_T = \frac{C_1 L_1 + (C_2 - C_1) L_2}{W_1 + W_2}$$

where

- C_i = concentration of leachate after i th elution, mg/l,
- L_i = volume of leachate withdrawn after i th elution, litres,
- R_i = release from i th elution, mg/g,
- R_T = cumulative release, mg/g, and
- W_i = weight of ash used in i th elution, g.

TABLE 9—Repeated DI water extraction of fresh ash using the same leachate: trace element data. Values in mg/l.

Elution	Al	As	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sc	Zn
1	<0.50	0.004	<0.018	0.20	<0.036	Ash C 0.110	<0.072	<0.36	0.082	<0.18	0.022	0.018
2	<0.50	0.006	<0.018	0.30	<0.036	0.044	<0.072	0.36	0.036	<0.18	0.029	0.036
3	<0.50	0.003	<0.018	0.43	<0.036	<0.036	<0.072	0.54	0.036	<0.18	0.005	<0.018
4	<0.50	0.003	<0.018	0.47	<0.036	0.044	<0.072	0.69	0.040	<0.18	0.050	<0.018
5	<0.50	<0.002	<0.018	0.58	<0.036	0.044	<0.072	0.83	0.054	<0.18	0.072	<0.018
1	0.20	<0.002	<0.005	<0.03	0.035	Ash A 0.035	0.040	<0.10	0.053	<0.05	0.007	0.075
2	0.10	0.002	<0.005	<0.03	0.026	0.052	0.071	<0.10	0.087	<0.05	0.005	0.109
3	0.10	0.003	0.005	0.03	0.010	0.024	0.100	0.12	0.099	<0.05	0.006	0.087
4	0.35	0.006	0.008	0.03	0.029	0.040	0.120	<0.10	0.135	<0.05	0.007	0.126
5	0.20	0.005	0.010	0.03	0.020	0.040	0.150	<0.10	0.160	<0.05	0.006	0.145

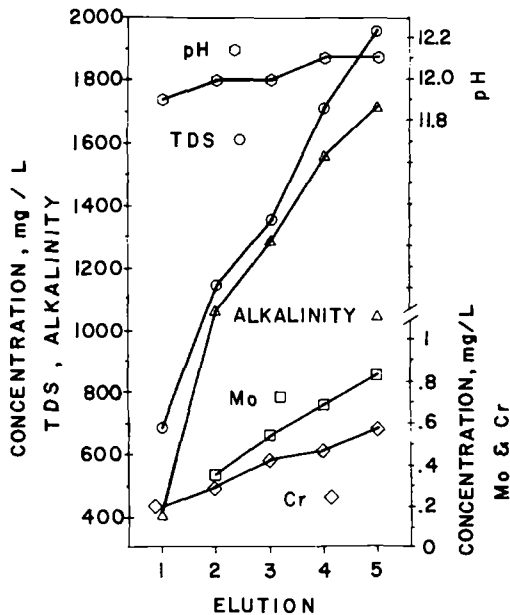


FIG. 7—Repeated DI extraction of fresh ash using the same leachate: Ash C.

of Ash A after four contacts (510 mg/l) was less than that of Ash C after only one contact (685 mg/l), and of course, the pH was much lower.

The trace element concentrations (Table 9) showed a variety of release patterns reflecting the continually changing ionic composition of the leachate. For Ash C, chromium and molybdenum increased as a function of extraction number (Fig. 7), while other elements either appeared to reach an equilibrium level (arsenic, iron) or showed no trend. The relatively high TDS level and high pH appear to have reduced the "effective" solubility of a number of elements. For Ash A, however, the lower pH and TDS allowed a steady increase with repeated extraction for nickel, zinc (Fig. 8), arsenic, cadmium, and manganese. Other elements, such as chromium and selenium, appeared to reach an equilibrium, or to behave in an irregular manner.

Conclusions

Based on the testing of two markedly different fly ashes, the ASTM leaching test showed higher leachate concentrations than the EPA-EP test in almost every case, due to the difference in the solid-to-liquid ratios used. However, the EP generally mobilized 2 to 4 times more of a given constituent on a mass fraction basis (milligrams per kilogram of ash). The ASTM test showed lower

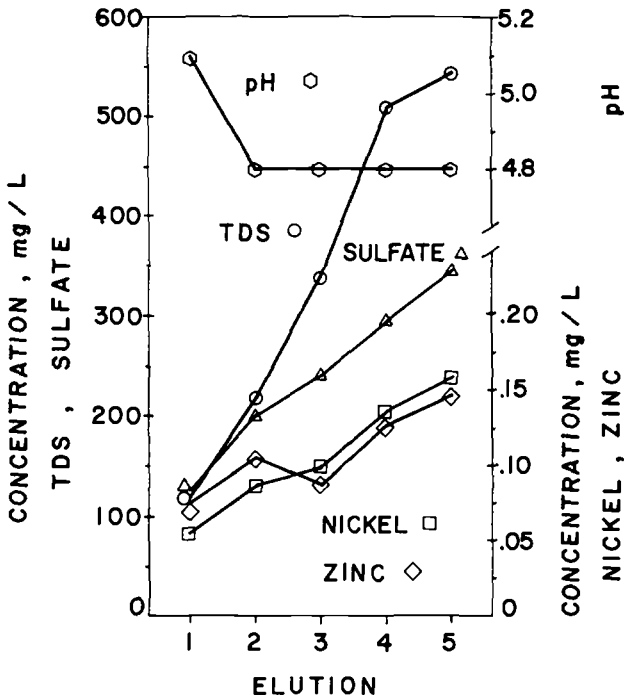


FIG. 8—Repeated DI extraction of fresh ash using the same leachate: Ash A.

variability between replicate tests than the EP in 65 percent of the cases examined. For the contact times studied (2 to 48 h), no one elution time could be chosen which would allow equilibrium for all parameters. However, more parameters tended to be stable with time in the acid leaching test as compared to the DI test where a decrease in concentration with time occurred in a number of instances.

Release during repeated extraction of the same ash with fresh leachant was found to be highly pH-dependent. Most of the mobilization tended to occur in the first two extractions for the acid test, while release occurred more gradually for 5 to 7 deionized water elutions. When comparing the results of leaching under aerobic and anaerobic conditions, it was found that while certain elements such as arsenic and zinc evidenced considerable sensitivity to the presence or absence of oxygen, no general pattern was found. Finally, during repeated DI extraction of fresh ash with the same leachate, it was found that the chemical parameters increased with extraction for both Ashes A and C. For Ash A (low pH and TDS) most trace elements also increased with extraction. However, for Ash C (high pH and TDS), many of the trace elements levelled off or actually decreased with increasing extraction number.

Acknowledgment

The authors would like to acknowledge the American Electric Power Service Corporation for support of this work and for permission to publish this account.

References

- [1] Thompson, D. W., "Elutriate Test Evaluation of Chemically Stabilized Waste Materials," EPA-600/2-79-154, U.S. Environmental Protection Agency, MERL, Cincinnati, Ohio, July 1979.
- [2] Bause, D. E. and McGregor, K. T., "Comparison of Four Leachate Generation Procedures for Solid Waste Characterization in Environmental Assessment Programs," EPA-600/7-80-118, U.S. Environmental Protection Agency, IERL, Research Triangle Park, N.C., May 1980.
- [3] Ham, R. K., Anderson, M. A., Stegmann, R., and Stanforth, R., "Background Study on the Development of a Standard Leaching Test," EPA-600/2-79-109, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1979.
- [4] Ham, R. K., Anderson, M. A., Stegmann, R., and Stanforth, R., "Comparison of Three Waste Leaching Tests," EPA-600/2-79-071, U.S. Environmental Protection Agency, MERL, Cincinnati, Ohio, July 1979.
- [5] Lowenbach, W., "Compilation and Evaluation of Leaching Test Methods," EPA-600/2-78-095, U.S. Environmental Protection Agency, MERL, Cincinnati, Ohio, May 1978.
- [6] Gullidge, W. P. and Webster, W. C., "ASTM Leachate Test Evaluation Program," EPRI FP-1183, RP 1260-6, Electric Power Research Institute, Sept. 1979.
- [7] Weaver, V. E. and Jackson, L. P., "Analysis of Selected Trace Metals in Leachate from Selected Fossil Energy Materials," U.S. Department of Energy and American Society for Testing Materials, Jan. 1980.
- [8] *California Assessment Manual for Hazardous Wastes*, California Department of Health Services, Hazardous Materials Management Section, Sacramento, Calif., Aug. 1979.
- [9] *Annual Book of ASTM Standards*, Part 31, American Society for Testing and Materials, 1979.
- [10] "Hazardous Waste Guidelines and Regulations," proposed by the U.S. Environmental Protection Agency, *Federal Register*, Part IV, Dec. 18, 1978.
- [11] *Standard Methods for the Examination of Water and Wastewater*, 14th ed., American Public Health Association, New York, N.Y., 1975.
- [12] "Methods for Chemical Analysis of Water and Wastes," EPA-500/4-79-020, U.S. Environmental Protection Agency, Cincinnati, Ohio, March 1979.
- [13] *MHS-10 Hydride System Manual*, Perkin-Elmer Corp., Norwalk, Connecticut, Feb. 1979.
- [14] Lee, G. F. and Plumb, R. H., "Literature Review on Research Study for the Development of Dredged Material Disposal Criteria," Contract Report D-74-1, Office of Dredged Material Research, U.S. Army Engineers Waterways Experiment Station, Vicksburg, Miss., 1974.
- [15] Wecter, D. W. and Niece, J. E., *Proceedings*, 29th Industrial Waste Conference, Purdue University, Lafayette, Ind., May 1974, p. 420.