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Removal of Leachable Metals and Recovery of Alumina From Utility Coal Ash

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UNITED STATES DEPARTMENT OF THE INTERIOR

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REMOVAL OF LEACHABLE METALS AND RECOVERY OF ALUMINA FROM UTILITY COAL ASH

By Robert C. Gabler, Jr.,[1] and Robert L. Stoll[2]

ABSTRACT

The extraction of metals from coal ash was investigated by the Bureau of Mines in an effort to produce a more environmentally acceptable waste and offset waste disposal costs with recovered metal values. The research was conducted in two steps: determination of the parameters that affect extraction of metals from coal ash and development of extraction-recovery procedures. Data obtained indicate that the major parameter affecting the extraction of metals from coal ash is the calcium content of the ash. Other parameters such as furnace type and operating temperature had much smaller effects on metal extraction. Two procedures were studied for metal extraction: an acid leach procedure for high-calcium ashes and a lime sinter-acid leach procedure for low-calcium ashes. An alumina product was recovered that, with sufficient washing, meets Hall cell specifications. The leach residues pass the EPA EP Toxicity Test and are thus nonhazardous wastes available for a variety of uses.

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INTRODUCTION

Approximately 75 million tons of coal ash were produced in the United States in 1979 with increasing amounts expected in succeeding years. Previous investigations of the extraction of metals from coal ash focused upon the economics of recovering valuable metals. With the classification of coal ash as a "special waste" by the Environmental Protection Agency (EPA), this voluminous byproduct of coal-fired powerplants stimulated questions concerning its environmental impact. Both industry and government face possible high-cost disposal problems that are magnified by the large volume of coal ash produced.

As part of the Federal Bureau of Mines program to convert waste materials from a disposal problem into secondary resources, studies were undertaken to determine if elements of environmental concern (12-13)[3] could be removed from coal ash while recovering alumina as a byproduct. This alumina recovery-leachable metal study conducted by the Bureau had the following objectives:

1. Develop a process that can provide an environmentally acceptable residue and also recover the available alumina.

2. Establish operating parameters for efficient leaching and subsequent precipitation of metals and for production of a Hall cell grade alumina product.

3. Evaluate the response of a large number of coal ash materials to this process.

4. Determine the properties of coal ash that significantly affect process efficiency and the extent of their effect.

According to Bureau of Mines statistics, the projected U.S. demand for alumina in 1979 was 6.6 million tons (metal content). The alumina discarded in that same year in coal ash was estimated to be more than 7.9 million tons (metal content). Based on these estimates, there is sufficient Al_2O_3 in coal ash to meet domestic needs. However, because of economic and supply considerations, the alumina from coal ash could undoubtedly serve only as a supplement to bauxite and potential domestic sources such as kaolin clays and anorthosite because of the more localized large volumes of the latter materials.

Interest in the extraction of aluminum from coal ash has increased along with the magnitude of the disposal problem. Eisele and Bauer reviewed the literature through 1976 on the technology for recovery of alumina from coal ash (10). They noted that three main routes to aluminum extraction have been studied; acid leach, lime-sinter alkaline leach, and dry chlorination. After their review, publications summarizing results on HCl leaching (2), sodium hydroxide pretreatment-acid leach (3, 6-7), and NaCl-$NaCO_3$ sinter-sulfuric acid leach (23) were published. Reports in the literature reexamining techniques studied earlier covered the lime-sinter process (6, 8, 19), the lime-soda-sinter process (11), and the chlorination processes (6, 20, 22).

Until recently, research on the extractability of aluminum from coal ash was limited to the possible economic benefits of recovering alumina. Designation of coal ash as a special waste (i.e., a large-volume waste with unknown hazard potential) by EPA (12) redirected research in this area. This study explored two methods that would render the ash residue more environmentally acceptable, while offsetting the cost by recovery of alumina.

Investigations most closely related to the studies in this report are the

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

sulfuric acid leach (16), the Calsinter process (1, 5, 9, 18), the lime-sinter-sulfuric acid leach (2), and the cement kiln dust (CKD) sinter technique (4). The Calsinter method (1, 5, 9, 18) developed at Oak Ridge National Laboratories (ORNL) is a lime-sinter, sulfuric-acid-leach process using flue gas scrubber sludge ($CaSO_4$, $CaSO_3$, and $CaCO_3$) as the sintering agent. A lime sinter process using CKD (4) in a standard lime-sinter, carbonate-leach technique was reported by the Department of Energy (DOE) Ames (Iowa) Laboratory.

The major difference between this extraction investigation and those reported in the literature is that in this study the acid leach procedure was tried on a large number of ash materials. The ash types included fly, bottom, slag, and cinder ash. The ash samples came from three types of furnaces: traveling grate, pulverized coal, and cyclone. The coals burned came from East, Central, and Western U.S. coalbeds and represented a range in calcium concentrations from 0.5 to 13.5 wt-pct.

TABLE 1. - Sources of ash materials

Company and power station	Furnace[1]				Coal source		Ash produced	
	Size, Mw	No.	Type	Operating temperature, ° F	State	pct	Type	tpy
Baltimore Gas & Electric Co., Wagner, Baltimore, Md.	1,000	3	I[2]..	2,200-2,500	West Virginia	100	Fly, bottom	50,500
Delmarva Power: Indian River, Del	340	NA	I[3]..	2,700	Pennsylvania.	100	...do..	95,000
Northern States Power Co., Twin Cities, Minn:								
A. S. King.....	600	NA	II..	2,800	Montana...... Illinois..... (4).........	75 22 3	Fly, slag.	120,000
Black Dog......	485	NA	I...	2,500	Montana...... Illinois.....	75 25	Fly, bottom	55,000
High Bridge....	400	NA	I...	2,500	Montana...... Illinois.....	75 25	...do..	50,000
Riverside......	380	6	I...	2,500	Montana...... (4).........	88 12	...do..	110,000
		8	II..	2,800	Montana...... (4).........	88 12	Fly, slag.	
Third Street...	(5)	NA	III.	1,800	Montana...... Illinois.....	75 25	Cinder.	4,500
Potomac Electric Power:								
Chalk Point, Md..	NA	NA	I...	2,500	Maryland..... Pennsylvania.	50 50	Fly, bottom	NA
Dickerson........	800	NA	I...	2,500	Maryland..... Pennsylvania. West Virginia	33 33 33	...do..	NA
Virginia Electric Power:								
Bremo Bluff, Va..	250	3	I[3]..	2,200	Kentucky..... West Virginia	50 50	...do..	51,300
		4	I[3]..	2,200	Kentucky..... West Virginia	50 50	...do..	
Chesterfield, Va.	1,470	NA	I[2]..	2,400	Kentucky.....	100	...do..	NA
Mount Storm, W. Va...........	1,600	NA	I[2]..	2,000	West Virginia Maryland.....	90 10	...do..	1,117,400

NA Not available. [1] Furnace key: I, pulverized coal; II, cyclone; III, traveling grate.

[2] Wet bottom. [3] Dry bottom. [4] Petroleum coke. [5] Heating steam.

TABLE 2. - Composition of ash samples used for screening tests

Code	Material	Concentration, wt-pct																	
		Al	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Si	Sr	Ti	Zn	CODE
	Baltimore G&E:																			
BGEFA	Fly ash.........	13.0	1.24	0.004	.0040	0.028	0.025	3.34	1.28	0.013	0.28	0.010	0.35	0.019	0.019	24.0	0.062	1.57	0.021	BGEFA
BGEBA	Bottom ash......	12.1	.76	.0003	.0098	.023	.012	5.42	1.64	.013	.42	.025	1.00	.028	.0040	24.4	.037	1.28	.0065	BGEBA
	Indian River:																			
IRFA.	Fly ash.........	12.8	.72	.0004	.010	.018	.017	8.36	1.93	.018	.30	.0097	.26	.014	.0076	22.3	.019	1.33	.019	.IRFA
IRBA.	Bottom ash......	12.3	.60	.0004	.011	.019	.013	14.5	1.70	.014	.41	.018	.46	.014	.0074	22.2	.026	1.14	.011	.IRBA
	A.S. King:																			
ASKFA	Fly ash.........	7.60	9.70	.0028	.020	.014	.015	6.43	.85	.0083	1.83	.091	.94	.016	.018	19.2	.21	1.30	.051	ASKFA
ASKS.	Slag............	9.01	8.60	.0018	.016	.0087	.0036	7.58	.51	.0074	1.41	.095	.557	.0094	ND	23.5	.16	1.09	.0037	.ASKS
BDFA.	Black Dog:																			.BDFA
	Fly ash.........	10.23	8.02	ND	.0046	.013	.0081	8.25	.60	.0069	2.25	.095	.91	.0081	.0092	21.7	ND	NA	.025	
BDBA.	Bottom ash......	8.58	7.75	ND	.0039	.013	.0069	12.13	.54	.0039	1.63	.078	1.48	.0059	.0059	23.1	ND	NA	.018	.BDBA
	High Bridge:																			
HBFA.	Fly ash.........	8.28	8.64	ND	.018	.0094	.0064	6.84	.69	.0085	1.44	.080	1.13	.0075	.0073	21.9	.16	1.09	.020	.HBFA
HBBA.	Bottom ash......	7.70	8.29	ND	.014	.0083	.0095	11.2	.39	.0059	1.18	.090	.52	.0075	.0037	21.7	.13	1.02	.012	.HBBA
	Riverside No. 6:																			
R6FA.	Fly ash.........	7.92	10.5	.0022	.014	.0080	.0063	3.93	.45	.0086	1.49	.086	1.23	.030	.0079	21.1	.19	1.03	.0064	.R6FA
R6BA.	Bottom ash......	7.84	9.26	ND	.014	.0066	.0045	8.84	.22	.0073	1.41	.086	.68	.030	.0036	23.2	.19	.96	.0030	.R6BA
	Riverside No. 8:																			
R8FA.	Fly ash.........	7.29	13.5	.0003	.0029	.0012	.015	3.92	.31	.0061	2.20	.10	1.48	.052	.011	18.0	.27	.81	.013	.R8FA
R8S..	Slag............	10.50	9.78	ND	.0039	.011	.0048	5.71	.40	.0077	2.32	.089	1.39	.022	.0039	26.1	ND	NA	.0068	..R8S
3SC..	Third St cinders	8.30	7.60	ND	.0048	.014	.0064	6.56	.63	.0056	1.70	.070	.84	.0080	.0040	22.2	ND	NA	.0072	..3SC
	Chalk Point:																			
CPFA.	Fly ash.........	10.31	1.07	.0005	.013	.0001	.015	9.55	1.23	.012	.27	.014	.16	.024	.010	23.0	.074	1.29	.023	.CPFA
CPBA.	Bottom ash......	11.39	.75	ND	.013	.0002	.0099	13.4	1.30	.011	.35	.017	.22	.016	.081	22.5	.058	1.47	.0058	.CPBA
	Dickerson:																			
DFA..	Fly ash.........	13.2	1.01	.0005	.0085	.019	.013	6.36	1.77	.013	.42	.017	.48	.014	.0072	21.0	.035	1.17	.029	..DFA
DBA..	Bottom ash......	13.0	.63	.0006	.012	.017	.0096	9.81	1.82	.012	.37	.018	.20	.015	.0049	22.0	.028	1.21	.010	..DBA
	Bremo Bluff No. 3:																			
BB3FA	Fly ash.........	12.6	.70	.0005	.0081	.014	.016	3.19	2.09	.012	.43	.0082	.27	.012	.0084	22.6	.041	1.27	.0091	BB3FA
BB3BA	Bottom ash......	10.2	.52	.0005	.0072	.018	.017	9.44	1.65	.010	.48	.048	.43	.011	.0047	22.6	.024	1.01	.0052	BB3BA
	Bremo Bluff No. 4:																			
BB4FA	Fly ash.........	12.8	.79	.0003	.0063	.016	.010	4.07	2.58	.012	.52	.011	.33	.0099	.0054	22.8	.045	1.27	.0069	BB4FA
BB4BA	Bottom ash......	13.0	.69	.0006	.0070	.020	.015	6.06	2.03	.013	.45	.025	.35	.011	.0019	26.2	.031	1.27	.0057	BB4BA
	Chesterfield:																			
CFA..	Fly ash.........	12.3	1.01	.0011	.0054	.015	.014	3.81	1.65	.011	.39	.012	.21	.026	.0027	22.9	.028	.84	.011	..CFA
CBA..	Bottom ash......	8.97	.54	.0007	.0086	.017	.014	6.89	2.20	.015	.53	.020	.25	.028	.0074	16.1	.041	1.08	.015	..CBA
	Mt. Storm:																			
MSFA.	Fly ash.........	12.4	.82	.0004	.0077	.020	.0082	7.56	2.05	.013	.41	.010	.40	.0094	.0070	24.3	.026	1.23	.021	.MSFA
MSBA.	Bottom ash......	13.3	.55	.0004	.0083	.020	.0089	9.19	1.95	.014	.35	.015	.21	.0089	.0040	23.5	.020	1.30	.067	.MSBA

NA Not available. ND Not detected.

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SAMPLES

For this study, 5- to 10-lb quantities of 27 ash samples were obtained that represented 14 furnaces at 12 power stations. Ash type, furnace operating temperature, furnace type, and fuel source are summarized in table 1. The ash types included fly ash, bottom ash, cyclone furnace slag, and one low-temperature furnace cinder ash. The furnace types were traveling grate; pulverized coal, both dry- and wet-bottom; and cyclone. Operating temperatures ranged from 1,800° to 2,800° F. The fuel sources were Eastern, Central, and Western U.S. coalfields.

The elemental composition of the 27 5- to 10-lb ash samples is given in table 2. Some of the trace elements of concern are at or near the limit of detection listed in table 3 for the atomic absorption analytical procedure used in this study.

Two 50-lb samples of fly ash were obtained for the bench-scale extraction procedure tests: one from the No. 8 furnace of the Riverside Generating Station, Northern States Power Co., Twin Cities, Minn., and the other from the No. 3 furnace of the Wagner Generating Station, Baltimore Gas & Electric Co., Baltimore, Md. A 50-lb sample of dry CKD for the sintering tests was provided by the Alpha Cement Company, Lime Kiln, Md. Analyses of these three samples are listed in table 4. The analyses of the two fly ash samples are similar to those for samples collected 1 year previously and listed in table 2.

TABLE 3. - Limit of detection by atomic absorption analysis

Element	Detection limit, wt-pct[1]	Element	Detection limit, wt-pct[1]
Aluminum......	0.01	Magnesium.....	0.0005
Calcium.......	.001	Manganese.....	.0005
Cadmium.......	.0003	Nickel........	.0005
Chromium......	.0003	Potassium.....	.0007
Cobalt........	.0006	Sodium........	.0005
Copper........	.001	Strontium.....	.001
Iron..........	.002	Titanium......	.06
Lead..........	.0003	Zinc..........	.0002
Lithium.......	.0003		

[1] Detection limits for ash and residue samples dried at 110° C.

TABLE 4. - Composition of materials for bench-scale tests

Element	Concentration, wt-pct			Element	Concentration, wt-pct		
	R8FA	BGEFA	ACKD		R8FA	BGEFA	ACKD
Aluminum..	6.65	13.0	1.54	Magnesium...	2.27	0.28	1.94
Calcium...	7.00	1.24	29.65	Manganese...	.103	.010	.014
Cadmium...	.0005	.004	.0005	Nickel......	.071	.019	.0033
Chromium..	.0083	.028	.0036	Potassium...	.213	1.28	.73
Cobalt....	.0028	.016	.0005	Silicon.....	18.5	23.97	6.56
Copper....	.0174	.025	.0020	Sodium......	.322	.35	.10
Iron......	4.50	3.34	1.03	Strontium...	.250	.062	.29
Lead......	.0475	.011	.0034	Titanium....	1.86	1.57	.22
Lithium...	.0065	.013	.0023	Zinc........	.0052	.021	.0040

ANALYSIS

All determinations except those for calcium and silicon were done by atomic absorption spectrophotometry. Calcium and silicon were determined by a borax fusion-X-ray spectrographic procedure similar to that of Pella (21) but without the heavy absorber. All other determinations were made by chemical dissolution-atomic absorption spectrophotometry. Limits of detection for the atomic absorption procedure are given in table 3.

All ash and ash residue samples were ignited to 1,000° C for 1 hr to remove carbon; treated with hydrofluoric acid to remove silica and with nitric and perchloric acids to form soluble compounds; and then fumed to near dryness. The solids residue was dissolved in a hydrochloric-nitric acid mixture. The final solution, approximately 0.6N hydrochloric acid, was taken to a known volume with 0.6N hydrochloric acid for atomic absorption analysis. These solutions were analyzed promptly as upon standing for several days, calcium and strontium may precipitate out of solution.

Leach solutions were diluted to a volume that corresponded to 4.5N sulfuric acid; subsequent dilutions were made with 4.5N sulfuric acid. Analyses were then performed by atomic absorption spectrophotometry, using standards prepared in 4.5N sulfuric acid to minimize systematic analytical errors.

The filtrates from the precipitation of aluminum and from the precipitation of metal hydroxides were first acidified with hydrochloric acid, then diluted by a factor of two to minimize differences in viscosity. Necessary subsequent dilutions for atomic absorption spectrophotometry were made with 0.6N hydrochloric acid.

Analyses of the starting ash or CKD-sinter material and the leach residue were used to determine the percent of each element extracted. Several problems appeared with this method of calculation. As the limit of detection is approached, the analytical uncertainty becomes larger leading to unreliable extraction calculations. Also, there was some problem with the limited solubility of elements such as Ca, Pb, and Sr in sulfate solution. Therefore, extraction data listed in this report are limited to those elements and samples where the analytical values were acceptable in precision and accuracy. The atomic absorption procedure is considered to be reliable from ±2 to ±3 pct for major constituents such as aluminum down to ±10 pct for elements present at four times the limit of detection.

EXTRACTION

The leach procedure used in the initial phases of this study was a modification of the procedure used for a related study of the extraction of metals and phosphorus from incinerated municipal sewage sludge ash (15). This procedure was chosen for the study because of its success in treating sewage sludge ash. Most of the initial extraction tests were limited to a two-stage consecutive leach to save time. This avoided the three-stage countercurrent leach used in the previous study that had to go through 8 to 10 samples in order to reach an equilibrium after approximately 24 to 30 leaches. Two stages, each with fresh reagent-grade sulfuric acid, provided an extraction that gave equivalent results to a three-stage countercurrent leach. Once the process parameters were experimentally established with the two-stage leach, final data were collected using the more commercially viable three-stage countercurrent leach to be discussed later.

Two hundred grams of coal ash was leached with 1,500 ml of 9N (36.7 wt-pct) sulfuric acid in the first-stage leach at the acid's boiling point, about 110° C, for a 2-hr period. The leach solution was cooled, diluted with 1,000 ml of water, filtered, and the filtrate taken to a 3,000-ml volume. The residue was reacted with a fresh 1,000-ml batch of 9N sulfuric acid, at the boiling point for 2 hr. Five hundred milliliters of water was added to cool and dilute the leach solution. This solution was also filtered and the residue washed with about 100 ml of water. The filtrate and washings were taken to a 2,000-ml volume. A 50-ml sample was taken from both the first- and second-stage solutions for analysis. The leach residue was dried and ignited at 550° C to remove any residual sulfuric acid in preparation for analysis.

Six hundred milliliters of first-stage leach solution and 400 ml of second-stage leach solution were mixed and treated with 360 ml of 50 pct sodium hydroxide to precipitate metal hydroxides and hold aluminum in solution as sodium aluminate. This precipitate was filtered off after allowing sufficient time for late-forming iron hydroxides to precipitate, and the slurry was washed several times to remove entrained soluble materials. The washings were added to the filtrate and the volume brought to 1,500 ml. The metal precipitate was dried, ignited at 550° C, and weighed.

The 1,500-ml volume of combined filtrate and washings was treated with carbon dioxide injection to precipitate the aluminum as a filterable product. The aluminum precipitate was slurry washed two times to remove entrained sodium and other soluble metals, then dried and ignited at 550° C.

PARAMETERS AFFECTING EXTRACTION

The next series of studies used the 27 coal ash samples to evaluate the factors that affected the extraction of metals and aluminum from coal ash. The standard leach procedure described in the preceding section was used on all samples. The parameters examined were as follows: calcium content, furnace operating temperatures and furnace type, particle size, leach time, and ratio of acid to ash.

Calcium Content of Coal Ash

Calcium content of the ash samples fell into two ranges: 0.52 to 1.24 and 7.60 to 13.5 pct. Leach test data listed in table 5 show a trend towards higher metals extraction with increasing calcium content of the ash. Figures 1 and 2 show this effect graphically for the extraction of aluminum and chromium. These two elements are used as examples,

TABLE 5. - Typical extraction data with increasing calcium content

Ash	Calcium content, pct	Extraction, pct								
		Al	Ca	Cd	Co	Cr	Cu	Fe	K	Li
BB3BA.	0.52	11	48	32	21	32	56	69	VAR	20
IRBA..	.60	8	32	6	23	18	15	48	VAR	7
BB3FA.	.70	15	62	23	13	28	35	60	8	29
IRFA..	.72	13	61	NR	30	30	31	73	6	17
CPBA..	.76	21	SP	NR	21	NR	27	35	14	17
BGEBA.	.76	12	43	NR	20	41	33	61	2	19
CPFA..	1.07	19	70	NR	40	NR	63	76	17	37
BGEFA.	1.24	24	76	24	44	55	46	60	4	38
BDBA..	7.76	61	21	NR	58	61	51	54	23	36
BDFA..	8.02	60	27	NR	66	76	81	77	45	54
R8S...	8.99	87	19	NR	81	~100	67	88	81	~100
R8FA..	13.5	86	21	NR	85	64	82	89	67	86
		Mg	Mn	Na	Ni	Pb	Sr	Ti	Zn	
BB3BA.	.52	30	87	62	43	SP	33	11	65	
IRBA..	.60	26	50	37	21	7	21	5	52	
BB3FA.	.70	28	60	11	33	12	50	6	33	
IRFA..	.72	37	62	38	37	20	56	5	67	
CPBA..	.76	VAR	27	VAR	36	16	SP	28	10	
BGEBA.	.76	33	80	75	61	SP	22	12	57	
CPFA..	1.07	3	56	11	59	7	41	22	43	
BGEFA.	1.24	29	70	39	39	SP	43	18	67	
BDBA..	7.76	68	60	61	64	14	19	41	48	
BDFA..	8.02	72	85	66	81	48	19	58	63	
R8S...	8.99	78	91	91	89	40	SP	81	76	
R8FA..	13.5	89	86	71	98	27	31	84	94	

NR Not reported owing to values at or below limit of detection.
SP Not reported owing to solubility problem (see "Analysis" section).
VAR Element varies in the sample making a calculation impossible.
Samples are heterogeneous with respect to these elements.

aluminum because of its economic value and chromium for its environmental importance.

Mullite, a high-temperature aluminum silicate, is essentially insoluble in 9N sulfuric acid. In a lime-sinter process with sufficient calcium, mullite is converted to dicalcium silicate and samples. The parameters examined were calcium-aluminum oxides. During burning of high-calcium coals, calcium-aluminum oxides are formed preferentially, thus resulting in the observed increase in alumina extraction. The presence of mullite in low-calcium ash materials has been demonstrated by Hurlett and Weinberger (17) using a special hydrofluoric acid surface leach procedure.

This dependence of aluminum extractability on calcium concentration is one of the most important findings in this study. Some previous studies using acid extraction that were not optimistic for aluminum recovery may have been based on low-calcium-content ashes.

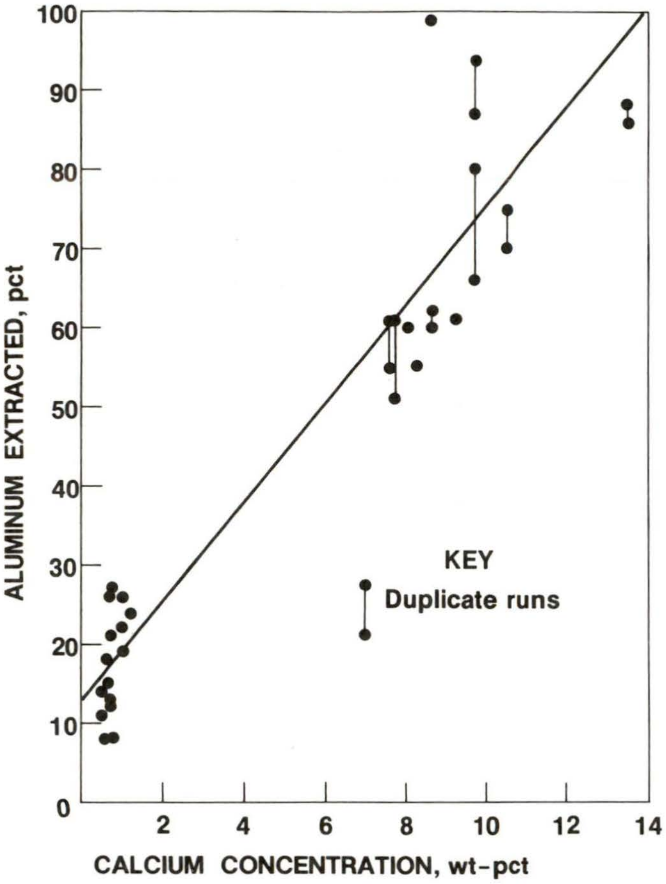

FIGURE 1. - Aluminum extraction versus calcium content.

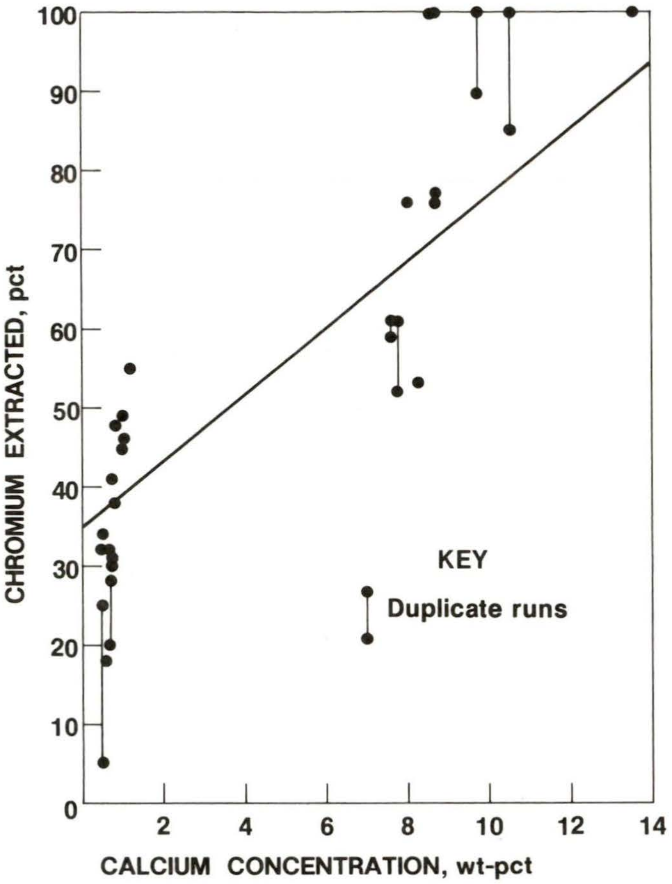

FIGURE 2. - Chromium extraction versus calcium content.

Furnace Operating Temperature and Furnace Type

Two sample sets were available that used the same coal feed in each set with different furnaces operating at several temperatures (see table 1). Set one used a mixture of 75 pct Montana subbituminous coal and 25 pct southern Illinois bituminous coal in a traveling grate furnace (1,800° F), in pulverized coal furnaces (2,500° F), and in a cyclone furnace (2,800° F). In the second set, a mixture of 88 pct Montana subbituminous coal was burned with 12 pct petroleum coke in a pulverized coal furnace (2,500° F) and in a cyclone furnace (2,800° F). The data for the first set indicate an increase in average extractability from 64 to 90 pct in going from the traveling grate furnace to the cyclone furnace, with the slag from the cyclone furnace giving the highest average extraction for aluminum, over 90 pct. In the second set, the cyclone furnace again gave the higher extraction, an average of 85 pct versus 65 pct for the pulverized coal furnace. The effect of temperature could not be separated from the furnace type in this study because furnace type controls the burning temperature.

Type of Ash

For most furnaces, the fly ash leached better than the bottom ash, averaging around 70 pct versus 50 pct for the bottom ash. However, in the cyclone furnace the bottom slag generally leached better than the fly ash, averaging around 90 pct versus 80 pct.

Particle Size

Samples of bottom ash and slag (minus 10 mesh) were leached as received and again after being ground to minus 100 mesh. The leach results show an average of about 5 pct increased extractability of aluminum for the ground material as compared to the as-received material studied. This small gain could not be justified economically because of the energy needed for grinding and screening the material.

Leach Time

As stated earlier, the preliminary tests used a 2-hr leach time; the next step was to determine if a shorter time was acceptable. Two high-calcium ash materials, A. S. King fly ash (ASKFA) and Riverside No. 8 furnace fly ash (R8FA), were leached over a range of times at temperature from 5 min to 2 hr.

TABLE 6. - Extraction data versus leach time

Time, min	Extraction, pct					
	Al	Fe	K	Mg	Na	Ti
ASKFA						
5...	58	63	67	63	40	41
10...	60	65	68	66	46	50
15...	59	66	66	64	49	50
30...	65	71	69	69	50	56
45...	63	73	70	71	60	52
60...	66	73	70	73	59	54
90...	66	75	69	73	55	54
120...	64	74	70	71	56	50
R8FA						
10...	68	70	67	67	70	47
20...	71	74	70	71	74	52
30...	74	77	69	73	75	74
40...	77	79	73	78	77	62
60...	72	77	70	72	75	53
120...	70	76	69	69	74	49

Table 6 shows that the amount extracted essentially reached a plateau within 30 min, with peak aluminum extraction for sample ASKFA of 66 pct at 60 min, and for sample R8FA of 77 pct at 40 min. Both ash materials experienced a drop in percent extracted after peak extraction, possibly owing to coprecipitation with insoluble sulfates such as calcium. When R8FA was used for the three-stage countercurrent leach tests, a leach time of 30 min was chosen.

Acid-to-Ash Ratio

Early experiments indicated that at solid-to-liquid ratios above 200 g/l, the mixture frequently turned to a jellylike sludge that could not be stirred. In order to avoid this sludge formation, acid-to-ash ratio was varied by changing concentration rather than changing the volume of solution.

The optimum acid requirement for this leach process is based on the primary requirement to use up most of the acid during the leaching operation as was done in prior work on the leaching of incinerated municipal sewage sludge ash (15).

Low acid concentrations were tested to reduce costs and to reach an optimum acid level where most of the acid would be consumed during the leach. Calculations of the amount of acid needed to dissolve the leachable elements in R8FA and convert the calcium to calcium sulfate indicated that 3N sulfuric acid would leave only a slight excess of acid over that required for the leach. Single-stage leach tests with 3N sulfuric acid gave leached values comparable to single-stage leaches with 9N sulfuric acid. However, when 3N sulfuric acid was tried later in the three-stage countercurrent leach procedure, the residues were extremely difficult to filter. On standing, an alumina and silica gel material formed in the clear leach solution. Additional tests of the three-stage countercurrent leach procedure using 4.5N and 6N sulfuric acid produced similar results. When the concentration was raised to 9N sulfuric acid, the problem disappeared. samp, the problem disappeared. Apparently the high efficiency of the three-stage countercurrent leach leads to greater acid depletion, and, at low acid levels, solubilization of silica occurs. This solubilized silica forms a gel that clogs the filters.

In another approach to use up the acid, the same 9N sulfuric acid leach solution was used sequentially to leach and confirmed that when the acid was depleted the silica problem arose. Table 7 lists the results of this test. In addition to the silica problem and

TABLE 7. - Elements extracted from multiple samples of ash using the same 9N sulfuric acid leach solution

Sample	Extraction, pct					
	Al	Fe	K	Mg	Na	Ti
1.....	84	87	77	86	83	69
2.....	82	83	75	84	82	64
3.....	81	80	75	82	81	54
4.....	77	58	68	78	77	20

poor filtration, the percentage leached decreased for the fourth leach.

Based on these results, high-calcium ash samples were tested in a three-stage countercurrent leach procedure using a 200-g sample with 1,000 ml of 9N sulfuric acid, even though the excess acid must subsequently be neutralized with caustic.

EXTRACTION PARAMETERS FOR SINTERED CKD-ASH

Lime sintering, prior to leaching, is one of several possible methods for extending the sulfuric acid procedure to low-calcium coal ash and improving extraction of alumina. This procedure breaks down unreactive mullite to form dicalcium silicate and calcium aluminate thus facilitating the leaching process. Cement kiln dust (CKD) was used as a lime reagent because it is inexpensive, readily obtainable, and is also a waste product containing extractable metals (table 4).

For this procedure, 1,000 g of ash and 1,500 g of CKD were thoroughly mixed in a twin-shell blender. Fifty-gram portions of the mixture were placed in a plastic container and 4.5 ml of water added. The container was capped and mixed on a Mixer-mill[4] for 5 min. The mixture was split into three parts and pelletized in a 1-in-idam die at 8,000 psi for 2 min. The pressed damp pellets had good physical stability and were easily handled for transfer from the die to silica dishes for drying at 150° C for 2 hr. The physically stable pellets were then sintered in a muffle furnace at 1,100° C for 2 hr, and then were removed from the furnace and allowed to cool. The sintered pellets were quite hard and required mechanical grinding in a cone mill to reduce them to minus 100 mesh for leaching. The crushed pellet material was again blended and stored until needed for extraction tests. The blended material showed no tendency to pick up moisture or carbon dioxide.

CKD-to-Ash Ratio

Various 100-g mixtures having CKD-to-ash ratios ranging from 0.5:1 to 3:1 were prepared using CKD from Alpha Cement Co. Owing to CO_2 loss during sintering, the final prepared sample weight ranged from 60 to 86 g. Three ash materials were studied--BGEBA, BB4BA, and MSBA. The leaches were conducted using the procedure developed for the high-calcium ash, except 60 to 86 g of the sinter material was leached in 750 ml of 9N sulfuric acid.

Table 8 shows the most elements essentially reached a plateau for single-stage extraction at a 1.5:1 CKD-ash ratio. Above this ratio no significantly higher extractions were achieved. Therefore, to minimize acid consumption, the 1.5:1 ratio was chosen as optimum.

This is a lower lime-to-ash ratio than used in most lime sinter procedures. The lower ratio is possible because this procedure uses an acid leach where most studies of the lime sinter technique have used an alkaline leach. The alkaline leach is quite sensitive to CaO-to-SiO_2 and CaO-to-Al_2O_3 ratios, whereas the acid leach procedure appears only to require the partial breakdown of mullite. Complete conversion to dicalcium silicate ($2\ CaO \cdot SiO_2$) and calcium aluminate ($5\ CaO \cdot 3\ Al_2O_3$), as specified by Chou (8) is not necessary for the acid leach. To reach the specified ratio for an alkaline leach would require about 10 parts CKD to each part

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[4] Reference to manufacturers or specific brands does not imply endorsement by the Bureau of Mines.

TABLE 8. - Element extraction with 9*N* sulfuric acid versus CKD-ash ratio in sintered material

CKD-ash ratio	Extraction, pct						
	Al	Cr	Cu	Fe	Mn	Ni	Ti
BGEBA							
0:1......	9	40	0	19	57	37	19
0.5:1....	80	68	52	73	67	54	88
1.5:1....	83	80	80	74	80	80	85
2.0:1....	73	80	80	75	80	80	84
2.45:1...	89	90	90	78	80	80	91
3.00:1...	87	80	90	82	90	90	90
BB4BA							
0:1......	9	20	0	5	40	0	14
1:1......	52	75	32	21	67	70	61
1.5:1....	82	70	70	49	83	70	80
2.0:1....	85	70	90	63	87	80	84
2.45:1...	83	70	70	56	80	90	79
3.00:1	84	80	80	(1)	85	80	88
MSBA							
0:1......	6	13	0	26	30	0	58
0.5:1....	71	69	59	50	83	0	83
1:1......	68	85	80	67	75	70	81
1.5:1....	88	70	90	67	90	80	81
2.0:1....	64	80	50	67	85	90	81
2.45:1...	82	70	90	75	90	90	83

[1] Value not reported owing to contamination of the residue with rust.

ash, diluting the alumina content to about 2.5 pct. If this quantity of calcium were needed for the acid leach, about 30 lb of sulfuric acid would be required for every 1 lb of aluminum recovered. Thus, the use of a 1.5:1 ratio of CKD to ash is a significant improvement over most lime sintering techniques and gives an aluminum recovery of better than 80 pct in a one-stage leach.

Sintering Temperature

A sintering temperature of 1,200° C is reported for the Calsinter process (*1*, *5*, *9*, *18*, *23*). Sintering temperatures in the range from 900° to 1,200° C were studied using the same bottom ash samples and leach procedures as used in the previous section. It was found that mixtures with the selected CKD-ash ratio of 1.5:1 melted above 1,180° C; therefore, lower sintering temperatures were studied for optimum extraction. A series of 1.5:1 CKD-ash ratios of ash samples BGEBA, BB4BA, and MSBA was sintered at 900°, 1,000°, and 1,100° C.

The sintered pellets were crushed and leached as usual. The results of the leach tests are listed in table 9. Aluminum extractability increased, in general, with increasing sintering temperature. The results for all the other elements studied were variable. Because aluminum is the primary element for recovery, 1,100° C was chosen as the sintering temperature to provide an ample margin below the melting point of the pellets and to achieve good aluminum recovery.

Leach Time

Optimum leach times were determined for the CKD sintered ash, using the same acid-ash ratios as for high-calcium ash. A 1,500-g portion of sintered pellets was prepared as described previously, consisting of 1 part fly ash from the Wagner Plant, Baltimore Gas & Electric

TABLE 9. - Effect of sintering temperature on extraction

Temperature, ° C	Extraction, pct						
	Al	Cr	Cu	Fe	Mn	Ni	Ti
			BGEBA				
900.........	55	53	90	78	89	88	81
1,000.........	52	44	83	70	86	90	71
1,100.........	71	71	83	84	86	80	81
			BB4BA				
900.........	61	58	88	60	79	78	78
1,000.........	70	38	82	60	77	88	68
1,100.........	79	69	86	70	82	56	93
			MSBA				
900.........	58	60	83	62	86	91	81
1,000.........	66	50	75	68	91	92	63
1,100.........	78	55	89	64	86	78	93

Co., Baltimore, Md.; 1.5 parts CKD from the Alpha Cement Co., Lime Kiln, Md.; and 0.225 part demineralized water. Each leach test used 100 g of sintered material, and 750 ml of 9*N* sulfuric acid. Leach times at the boiling point of the solution were varied from 10 min to 2 hr. At the end of the leach time the solutions were quenched with cold water, filtered, washed, and taken to a 1,500-ml volume. The data for the tests listed in table 10 indicate that 30 min in a three-stage countercurrent leach will be sufficient time for extraction.

TABLE 10. - Element extraction with time from CKD-ash sintered material

Time, min	Extraction, pct					
	Al	Fe	K	Mg	Na	Ti
10.....	52	41	69	57	59	21
30.....	68	63	68	69	55	56
60.....	67	62	64	68	60	59
90.....	62	53	58	63	53	52
120.....	70	67	76	67	58	58

THREE-STAGE COUNTERCURRENT EXTRACTION TESTS

Procedure

The more commercially viable three-stage countercurrent leach process using 9N sulfuric acid was tested for the high-calcium ash direct leach and the sintered CKD-ash leach. Cement kiln dust from the Alpha Cement Co., Lime Kiln, Md., was sintered with fly ash (BGEFA) from the Wagner Plant in a blend of 1,200 g of BGEFA and 1,800 g Alpha CKD for the data presented in this section. Fifty-gram portions of the mixture were mixed with 4.5 ml of water and then pressed in a 1-in-diam die at 8,000 psi to form three pellets. The pellets were then dried at 150° C for 2 hr prior to sintering in silica dishes at 1,100° C for 2 hr in a muffle furnace. After cooling, the pellets were crushed to minus 100 mesh in a cone mill and blended. One hundred-gram samples of this material were used for all subsequent leach tests of sintered material.

These initial pelletizing and sintering steps were not necessary for the high-calcium ash materials, where 200-g samples of fly ash from the No. 8 furnance of the Riverside Power Station (R8FA) of Northern States Power Co. were used directly for testing. This material came from a cyclone furnace operating at 2,800° F.

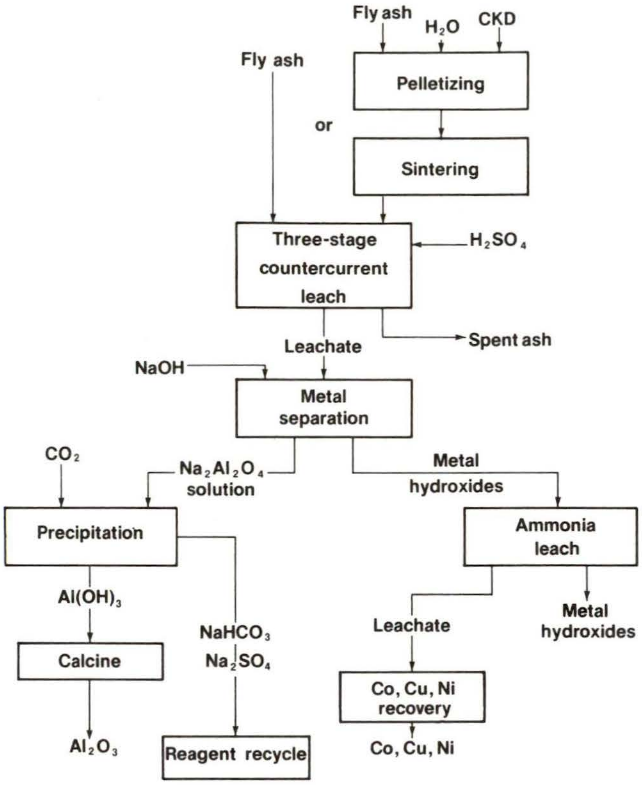

FIGURE 3. - Flowsheet for recovery of metal values from coal ash by an acid leach procedure.

The procedure for the high-calcium ash materials and the sintered CKD-low calcium ash materials is identical beginning the the three-stage countercurrent leach as shown in figure 3. The ash material was placed in a reaction kettle, 1,125 ml of water was added and mixed with solids, followed by the slow addition of 375 ml of concentrated sulfuric acid. The kettle was sealed and the solution maintained at its boiling point (110° C) for 30 min. A 30-min boiling period was used for each stage of the extraction. The third-stage residue of the three-stage countercurrent extraction procedure was filtered from the leach solution and washed with 500 ml of water. The wash was added to the leach solution. The loaded leach solution was filtered off the first-stage residue and treated with sufficient 50 pct sodium hydroxide solution to precipitate the metals and leave aluminum in solution as sodium aluminate ($Na_2Al_2O_4$). The solution was treated with carbon dioxide to precipitate the aluminum as described previously. The bayerite precipitate was washed by reslurrying and refiltering, and then calcined to alumina.

The wet metal hydroxide precipitate was leached with 0.8M ammonium hydroxide-0.6M ammonium sulfate solution for 2 hr at the solution boiling point. The metal hydroxides were then filtered from the leach solution for disposal, and the leach solution saved for Cu, Co, and Ni recovery.

TABLE 11. - Extraction achieved with three-stage countercurrent leach

Stage	Extraction, pct												
	Al	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Ti	Zn
	LOW-CALCIUM ASH SINTERED WITH CKD												
1.........	96	66	95	83	85	94	97	89	89	83	0	91	96
2.........	1	3	0	2	5	2	1	2	2	0	5	6	2
3.........	2	0	0	3	4	2	0	0	0	1	36	0	0
Total	99	69	95	88	94	98	98	91	91	84	41	97	98
	HIGH-CALCIUM ASH												
1..........	72	42	68	70	78	59	75	78	66	69	80	86	73
2..........	6	20	1	6	7	1	6	5	4	5	0	4	11
3..........	2	0	0	5	4	0	3	3	2	3	0	1	0
Total	80	62	69	81	89	60	84	86	72	77	80	91	84

Results

The extraction efficiencies of the three-stage countercurrent leach for 13 elements from the two kinds of ash are listed in table 11. The data show that most of the extractable material is recovered in the first-stage leach, while only smaller amounts are extracted in the second and third stages. The compositions of typical leach residues ("spent ash" in fig. 3) are listed in table 12 along with the composition of the starting ash. The levels of all elements are lower in the residues than in the starting ash except for calcium and several minor elements. Attempts at further leaching indicate that all leachable elements have been extracted.

The residues had pH values of 2 to 3 when slurried with water. Several residues were treated with lime (produced by calcining CKD at 950° C) until the pH was approximately 9. The solids were then evaluated as hazardous wastes using the Environmental Protection Agency EP Toxicity Test (13). None of the residues examined gave detectable levels of the eight criteria elements in the leachate, and would therefore not be classified as hazardous wastes. This material could be used in such applications as soil conditioning or landfill without the restrictions imposed on hazardous wastes.

TABLE 12. - Typical leach residues and starting materials from acid leach procedure, weight-percent

Element	High-calcium		Low-calcium		Element	High-calcium		Low-calcium	
	Residue	Starting ash	Residue	Starting CKD-ash		Residue	Starting ash	Residue	Starting CKD-ash
Aluminum	1.84	6.65	0.080	6.71	Magnesium	.50	2.27	0.019	1.41
Calcium.	8.81	7.00	Major	Major	Manganese	.019	.10	.0009	.014
Cadmium.	.0004	.0005	.0004	.0012	Nickel...	.022	.071	.0016	.011
Chromium	.0045	.0083	.0016	.016	Potassium	.120	.21	.052	1.99
Cobalt..	ND	.0028	.0006	.0073	Silicon..	Major	Major	Major	Major
Copper..	.0045	.017	.0018	.013	Sodium...	.124	.32	.051	.46
Iron....	.68	4.50	.21	3.07	Strontium	.303	.25	.067	.12
Lead....	.021	.048	.0073	.0095	Titanium.	.35	1.86	.053	1.10
Lithium.	.0029	.0065	ND	.0073	Zinc.....	.0028	.0052	.0005	.021

ND Not detected.

TABLE 13. - Typical leach solutions from acid leach procedure

Element	Leach solution concentration, gpl		Element	Leach solution concentration, gpl	
	High-calcium ash	CKD sintered low-calcium ash		High-calcium ash	CKD sintered low-calcium ash
Aluminum.	3.55	2.21	Copper.....	0.0095	0.0037
Iron.....	2.67	.962	Strontium..	.0045	.0050
Magnesium	1.27	.46	Chromium...	.0038	.0049
Titanium.	1.13	.36	Lithium....	.0029	.0024
Sodium...	.16	.14	Zinc.......	.0029	.0070
Calcium..	.15	.20	Cobalt.....	.0005	.0023
Potassium	.085	.65	Cadmium....	.0002	.0003
Manganese	.060	.0042	Lead.......	.0002	.0002
Nickel...	.037	.0034			

The compositions of typical pregnant leach solutions are listed in table 13. As would be expected from the composition of the starting ash, Al, Fe, Mg, and Ti are the major constituents present with minor amounts of Na, Ca, and K.

The metal-separation step in figure 3, using sodium hydroxide precipitation of the metals while holding aluminum in solution, was successful. All metals except Al, Ni, Zn, and the alkalis reported at greater than 95 pct in the metal precipitate. Aluminum is more than 90 pct contained in the filtrate, nickel 10 to 20 pct, and zinc 60 to 100 pct depending on the thoroughness of the reslurry-refilter washing technique. The compositions of typical metal hydroxide precipitates are listed in table 14. This precipitate, containing the extractable portions of the heavy metals, amounts to only about 8 to 12 pct of the original ash depending on the thoroughness of the wash to remove entrained soluble sodium and aluminum.

TABLE 14. - Composition of metal hydroxide precipitates from acid leach procedure, weight-percent

Element	High-calcium ash	CKD-sintered ash	Element	High-calcium ash	CKD-sintered ash
Aluminum..	5.66	6.44	Magnesium.	5.56	5.95
Calcium...	1.12	5.99	Manganese.	.72	.17
Cadmium...	.002	.002	Nickel....	.45	.11
Chromium..	.042	.13	Potassium.	.042	.080
Cobalt....	.006	.021	Sodium....	14.1	2.75
Copper....	.11	.12	Strontium.	.040	.036
Iron......	30.9	32.0	Titanium..	7.93	11.4
Lead......	.005	.007	Zinc......	.019	.026
Lithium...	.006	.004			

TABLE 15. Comparison of trace metals in a typical alumina product and in the thoroughly washed alumina product with Hall cell specifications, weight-percent

Element	Alumina product		Hall cell specification[1]	Element	Alumina product		Hall cell specification[1]
	Typical	Well washed			Typical	Well washed	
Calcium...	0.016	ND	0.03	Nickel....	0.003	0.008	0.004
Cadmium...	.0007	0.0003	None	Phosphorus	ND	ND	.0004
Chromium..	.0009	.0001	.001	Potassium.	.008	ND	.004
Cobalt....	.001	.0008	None	Silicon...	ND	ND	.007
Copper....	.003	.004	.008	Sodium....	18.0	.34	.30
Iron......	.027	.01	.010	Strontium.	ND	ND	None
Lead......	.001	ND	None	Titanium..	ND	ND	.001
Lithium...	.002	ND	None	Vanadium..	ND	ND	.001
Magnesium.	.003	.02	None	Zinc......	.016	.006	.008
Manganese.	.001	.003	.002				

ND Not detected.

[1] Target specifications from a subcommittee of the Bureau of Mines-Industry Alumina Miniplant Steering Committee.

BYPRODUCT RECOVERY

To recover metal values, leach solutions were treated with sufficient sodium hydroxide to precipitate iron and the other metals and leave aluminum in solution as sodium aluminate. The iron precipitate (red mud) was filtered off, washed, and dried.

The ammonia-ammonium sulfate extraction of elements from the metal hydroxide precipitate as listed in table 13 was not successful. The ammonia complex-forming elements were extracted only in small percentages with the extraction of nickel and zinc showing the greatest promise for success. However, this approach is not recommended for the recovery of elements such as Co, Cu, and Ni from coal ash.

The filtrate from the hydroxide precipitation was treated by carbon dioxide injection to precipitate the aluminum as bayerite, a crystalline aluminum hydroxide that is readily filtered. These alumina products can be washed to minimize contamination with sodium and other soluble metals (15) thus making the product acceptable as Hall cell alumina. Alumina from DBA, CPFA, and ASKS were well washed and their sodium levels are within specifications for Hall cell alumina as listed in table 15.

SUMMARY AND RECOMMENDATIONS

A three-stage countercurrent acid procedure was developed that removes leachable metal constituents from coal ash and provides a Hall cell grade alumina as a byproduct. High-calcium ashes are leached directly; whereas another waste product, CKD, is added prior to sintering to low-calcium ashes.

The most significant finding of this study of 27 ash materials is that the calcium content of the ash material is the principal variable controlling leachability of the metals. This observation probably answers the question raised by Eisele and Bauer (10) concerning the variable extractabilities obtained on alumina from coal ash with sulfuric acid by various researchers.

During the study of acid extraction on a large number of ash samples and the studies for optimization of extraction parameters, a number of significant factors were observed.

1. When acid levels are depleted, silica is dissolved leading to significant filtration problems. This problem can be resolved by going to higher acid concentrations.

2. Alumina extraction with a CKD-to-ash ratio of 1.5:1 is a significant improvement over the lime sinter process criteria which require a 10:1 ratio. This lower ratio results in reduced acid and lime consumption.

3. Extraction of alumina was highest from cyclone furnace ash (2,800° F), with pulverized coal furnace ash (2,500° F) somewhat lower, and traveling grate furnace ash (1,800° F) lowest. The relationship between furnace type and temperature could not be separated because furnace type controls burning temperature.

4. Fly ash generally leaches better than bottom ash except for cyclone furnace ash where the glassy slag leaches better than the fly ash.

5. Extraction efficiency for minus 100-mesh ash is approximately 5 pct greater than for as-received ash at minus 10 mesh. However, this small improvement may not justify additional costs for grinding and sizing.

6. Metal extraction with this acid leach procedure is rapid with optimum leaching occurring in 30 min.

The process is technically feasible but probably not economically competitive with the present sources of aluminum. One of the disadvantages of the process is the requirement for large amounts of NaOH per unit of Al_2O_3 produced. Further research may provide methods of lowering the quantity of NaOH required, perhaps through partial neutralization with lime, followed by metal and aluminum separation with NaOH. Recycled NaOH from $NaHCO_3$ after Al_2O_3 precipitation should also lower the cost of this reagent. However, if coal ash is named a "hazardous waste," with disposal costs rising significantly, the lower disposal costs of the leached residue would provide an economic incentive to the process.

The effects on extraction of intermediate-level calcium concentration (1.5 to 7.5 wt-pct) (14) would be useful. Also, the feasibility of using small CKD additions to high-calcium ashes with the sinter procedure to effect metal extractions in the 90-pct range should be investigated. Reagent recycle studies would furnish the required final data to make an effective economic evaluation.

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