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Pathways of Thirty-seven Trace Elements Through Coal-Fired Power Plant

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Coal, fly ash, slag, and combustion gases from a large cyclone-fed power plant 870 MW(e) were analyzed for a suite of elements. Mass balance calculations show that the sampling and analyses were generally adequate to describe the flows of these elements through the plant. Most Hg, some Se, and probably most Cl and Br were discharged to the atmosphere as gases. As, Cd, Cu, Ga, Mo, Pb, Sb, Se, and Zn were quite concentrated in fly ash compared to the slag, and were more concentrated in the ash discharged through the stack than in that collected by the precipitator. Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti show little preferential partitioning between the slag and the collected or discharged fly ash. Cr, Sc, Na, Ni, U, and V exhibit behavior intermediate between the latter two groups.

Annual world coal consumption approaches 3×10^9 tons. On combustion, the trace elements in coal are transferred to slag, fly ash, or gases, and are discharged to the environment. The data given by Bertine and Goldberg (1) show that the total quantities of trace elements involved in coal combustion are large, being roughly comparable to the quantities annually mobilized by the natural process of weathering of crustal rocks. Bertine and Goldberg suggest that for most elements about 5% of the amount in the coal is discharged to the atmosphere, but they propose that selective volatility may lead to a greater atmospheric discharge of As, Hg, Cd, Sn, Sb, Pb, Zn, Tl, Ag, and Bi. The present study was undertaken to determine the fate of trace elements during coal combustion.

Most coal consumed in this country is burned at central power plants where the elements entering the boiler in the coal stream are partitioned between a bottom ash (or slag) stream, and a flue gas stream containing suspended fly ash and the vapors of volatile elements or compounds. A further partitioning of the flue gas stream takes place in the particulate emission control devices—electrostatic precipitators or scrubbers—that efficiently remove larger fly ash particles but are less efficient for vapors and finer particles. Ash from the boiler and ash removed by the precipitators are flushed with water to ash ponds, where elements may be leached from the ash and enter the aquatic environment in runoff. Small particles and vapors are discharged to the atmosphere and enter the terrestrial and aquatic environment by wet or dry deposition.

The flow of trace elements through a plant may be conveniently presented as input-output mass balances. Mass balance data for 15 elements have been presented by Kaakinen and Jorden (2), and two groups (3, 4) have reported Hg balances. This paper reports mass balance data for 37 elements around the T. A. Allen Steam Plant in Memphis, Tenn., a part of the Tennessee Valley Authority (TVA) electrical generating system.

A thorough description of the plant and of the sampling and analytical procedures is given by Bolton et al. (5, 6); this information is summarized briefly below.

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Plant Description

The Allen plant has a peak capacity of 290 MW(e) from each of three cyclone fed boilers. Ash produced in the cyclone-fed boilers is distributed about equally between slag and fly ash, in contrast to the more common pulverized coal boilers, where as much as 90% of the total ash is fly ash. Figure 1 is a block flow diagram of the Allen plant. Each unit consumes about 110 tons of coal per hour at peak load, and discharges flue gas through its own electrostatic precipitator and 400-ft stack. Most of the coal burned at Allen is from Southern Illinois or Western Kentucky mines. Proximate analysis of the coal composites by TVA for coal burned during our sampling activities gave the following results (as fired basis, 1972 results first then 1973 results): moisture, 13.4%, 11.1%; volatile matter, 34.7%, 35.7%; fixed carbon, 40.5%, 42.8%; ash, 11.4%, 10.4%; sulfur, 3.4%, 3.1%, Btu, 10,740 and 11,390. For this study the central unit of the plant was sampled. This unit was selected because of the recent installation of a new high-efficiency electrostatic precipitator. Thus, the results of this work describe atmospheric discharges when the best available technology for particulate pollution abatement is employed.

Sampling

Preliminary results showed that adequate mass balances could be obtained by sampling only the coal, slag, and precipitator inlet flue gas streams. Thus input air and slurry-ing water, for example, do not contribute (within experimental error) to the trace element flows through the plant. The precipitator outlet flue gas stream was also sampled to evaluate precipitator efficiency for various elements and thereby to provide a measure of atmospheric discharges. For balance calculations, the data required are the concentrations of the elements in each stream and the total flow rate of each stream. Two sets of samples were collected, one in January 1972, when the unit was operating at 240 MW(e), and the other in August 1973, when operating at 280 MW(e). Each set represented several days of plant operation.

The flue gas streams were sampled by the ASTM method (7). The ASTM train was modified for the 8/73 runs to include a set of five impinger solutions (two 5% Na_2CO_3 solutions to trap acid mists, a 5% $\text{NaC}_2\text{H}_3\text{O}_2$ solution for Se and other volatiles, and two 10% ICl solutions for Hg). For each run, flue gas samples were collected isokinetically at 24 points in the precipitator inlet ducts and at 16 points in the outlet ducts. About 4–5 hr were required for sample collection for each run, and each set of samples includes at least three runs.

Coal samples for analysis were composites of coals grab sampled from the cyclone conveyor system at 15-min intervals over the period when the flue gases were being sampled. Truly representative slag samples could not be collected since the slag initially accumulates in a hopper beneath the boiler and is flushed periodically (about every 4 hr at peak load) to the ash pond. Grab samples of slag were collected during the flushing operation, but these samples cannot correspond exactly to the coal collected at 15-min intervals, or to the suspended fly ash and volatiles collected continuously.

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The coal feed rate was obtained from the plant metering system and corrected to dry weight. The flue gas sampling provided data to calculate the mass of fly ash per volume of flue gas, and Pitot tube measurements of gas velocity gave the volume flow rate of the flue gas. The flow rate of the slag could not be measured accurately because of the intermittent nature of this flow. In earlier reports (5, 6), the slag flow was calculated from the ash content of the coal as determined in the laboratory and from the measured flows of coal and fly ash. The product formed by ashing coal in the laboratory is qualitatively and quantitatively different from that formed in the boiler because of the rapid movements of the coal through the high-temperature combustion zone of the boiler. Therefore, this method of calculation gave a false (low) estimate of the slag flow. For this paper the slag flow is obtained by imposing a mass balance for one of the major elements, namely, Al.

It is assumed that the aluminum flux in the coal stream equals the sum of the aluminum fluxes in the slag stream plus the fly ash stream. The following equation utilizes the three measured concentrations and the two measured flows to obtain the required slag flow:

$$\frac{\text{g coal}}{\text{min}} \times \frac{\text{g Al}}{\text{g coal}} = \frac{\text{g fly ash}}{\text{min}} \times \frac{\text{g Al}}{\text{g fly ash}} + \frac{\text{g slag}}{\text{min}} \times \frac{\text{g Al}}{\text{g slag}}$$

The flow rates are given in Table I. Coal flow was greater in the 1973 runs, corresponding to the higher power level. A relatively greater flow of inlet fly ash was also observed in the 1973 runs. At least in part this is because such intermittent cleaning operations as blowing soot from the air heaters and boilers were operating essentially continuously during the 1973 runs and were not operating during the 1972 runs; these operations add to the fly ash loadings. Removal of fly ash by the precipitator was considerably better in 1973 than in 1972, but there is no obvious explanation for this observation.

Analysis

Most elements were determined by nondestructive instrumented neutron activation analysis (NAA). Cd, Pb, and Zn were determined by isotope dilution spark source mass spectroscopy (IDSSMS), and Hg was determined by

flameless atomic absorption (AA) following wet ashing with $\text{HNO}_3\text{--HClO}_4$. Details on these methods have been reported previously (5, 6). The Se analyses were done by a newly developed method, gas chromatography with microwave emission spectrometric detector (GCMS) (8). Cu, Ga, Ni, and Sr were determined by a new absolute, high-sensitivity X-ray fluorescence (XRF) technique using monochromatic X rays for excitation (9). Some elements were determined by several methods. Mercury, for example, was checked by AA, IDSSMS, and NAA followed by chemical separation. Agreement was excellent between all three methods.

In Table II results obtained using these various analytical techniques are reported for National Bureau of Standards Standard Reference Materials, 1632 coal and 1633 fly ash. Also tabulated for comparison are the NBS results which have been reported for these materials and the averaged results of a four laboratory intercomparison reported recently by Ondov et al. (10). In general, the ORNL results are in good agreement (differences less than 10%) with the NBS and Ondov results.

Mass Balance

Table III gives the element flows for the two sets of runs. Serious negative imbalances occur for Br and Cl. The impinging solutions were not analyzed for these elements. Serious positive imbalances are present for Cr and V; perhaps some excess of these elements in the fly ash is due to corrosion of the boiler tubes. The 1972 results for arsenic gave a large negative imbalance whereas those obtained from the 1973 samples gave an equally large positive imbalance. Inasmuch as no appreciable arsenic was found in any of the

Table I. Mass Flow Rates

Run	Coal, g/min	Slag, g/min	Inlet fly ash, g/min	Outlet fly ash, g/min	Flue gas, SCF/min
1/72	1.24×10^6	1.33×10^5	5.50×10^4	1900	5.30×10^5
8/73	1.47×10^6	8.43×10^4	7.39×10^4	370	6.21×10^5

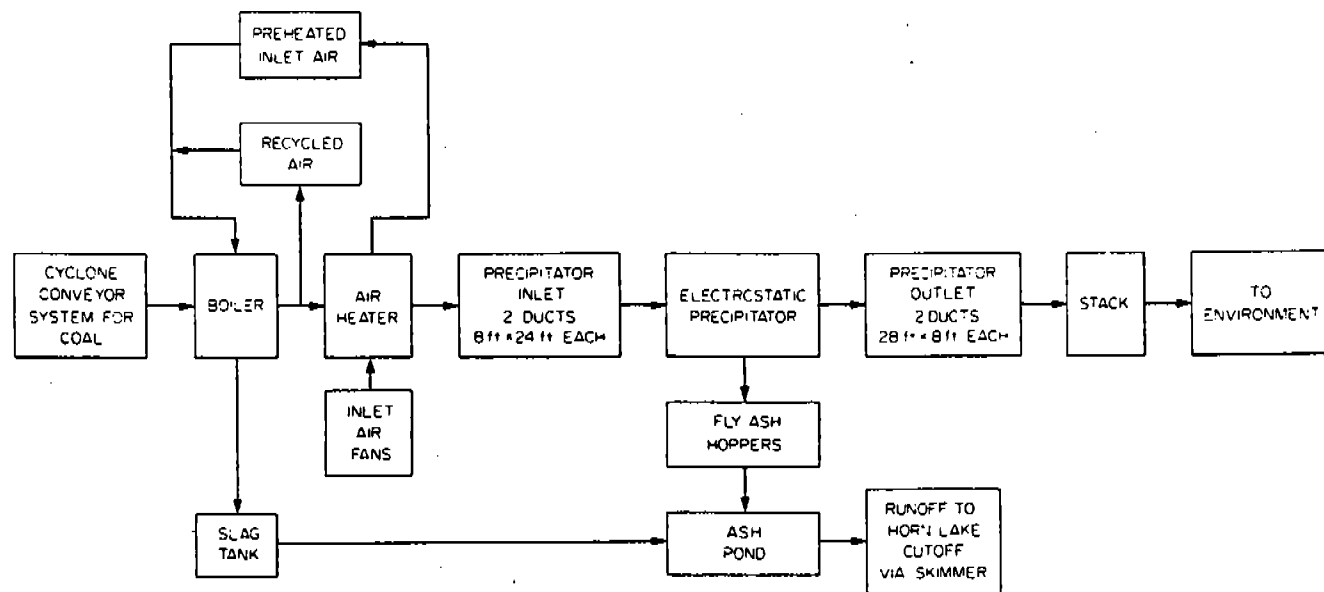


Figure 1. Block diagram indicating flow through Allen Steam Plant

impinger solutions, our tentative conclusion is that very little of the arsenic is in the vapor phase. Thus, the imbalance is probably due to sampling or analytical difficulties. Excepting these five elements no bias in the mass balances was observed, and the standard deviation from balance was 15%.

Element Partitioning

Concentrations of the trace elements in the various streams are given in Table IV, together with ratios of concentrations which reflect partitioning. Three classes of partitioning behavior are observable:

Class I. Twenty elements—Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti—are readily incorporated into the slag ($[X] \text{ slag}/[X] \text{ coal} \geq 6.6$).

These elements are partitioned about equally between the inlet fly ash and slag ($[X] \text{ inlet}/[X] \text{ slag} = 1.2$, $S = 0.3$). There is no apparent tendency to concentrate in the outlet fly ash ($[X] \text{ outlet}/[X] \text{ inlet} = 1.3$, $S = 0.5$).

Class II. Nine elements—As, Cd, Cu, Ga, Pb, Sb, Se, XX, and Zn—are poorly incorporated into slag ($[X] \text{ slag}/[X] \text{ coal} \leq 3.6$). These elements are concentrated in the inlet fly ash compared to the slag ($[X] \text{ inlet}/[X] \text{ slag} \geq 6$) and in the outlet fly ash compared to the inlet fly ash ($[X] \text{ outlet}/[X] \text{ inlet} \geq 3.5$).

Class III. Hg, Cl, and Br remain essentially completely in the gas phase.

The other elements—Cr, Cs, Na, Ni, U, and V—cannot be definitely assigned to a class based on our data but appear intermediate between Classes I and II.

Table II. Comparison of ORNL Results for NBS Standard Reference Material Coal and Fly Ash to Results Reported by NBS and by Ondov et al. (10)

	NBS coal standard, SRM #1632			NBS fly ash standard, SRM #1633		
	ORNL	NBS	Ondov et al. (10)	ORNL	NBS	Ondov et al. (10)
Al%	1.90		1.85 ± 0.13	12.5		12.7 ± 0.5
As	5.5	5.9 ± 0.6	6.5 ± 1.4	54	61 ± 6	58 ± 4
Ba	405		352 ± 30	2780		2700 ± 200
Br	14.2			6.0		12 ± 4
Ca%	0.44		0.43 ± 0.05	4.34		4.7 ± 0.6
Cd IDSSMS	0.31	0.19 ± 0.03		1.85	1.45 ± 0.06	
Ce	18.5		19.5 ± 1.0			146 ± 15
Cl	1000		890 ± 125			42 ± 10
Co	5.9	6 (in)	5.7 ± 0.4	46	38 (in)	41.5 ± 1.2
Cr	21 ± 2	20.2 ± 0.5	19.7 ± 0.9	138	131 ± 2	127 ± 6
Cs	1.4		1.4 ± 0.1			8.6 ± 1.1
Cu XRF	18	18 ± 2		133	120	
Eu	0.21		0.33 ± 0.04	2.86		2.5 ± 0.4
Fe, %	0.84	0.87 ± 0.03	0.84 ± 0.04	6.37		6.2 ± 0.3
Ga XRF	8.5			49		
Hf	0.95		0.96 ± 0.05	10.8		
In	0.07		0.20 ± 0.12			
Hg AA	0.088 ± 6%	0.12 ± 0.02		0.127 ± 2.2%	0.14 ± 0.01	
K, %	0.290		0.28 ± 0.03	1.8		1.61 ± 0.15
La	10.5		10.7 ± 1.2	82		82 ± 2
Mg, %	0.248		0.20 ± 0.05		1.98	1.8 ± 0.4
Mn	46 ± 3	40 ± 3	43 ± 4	460	493 ± 7	496 ± 19
Mo	3.4					
Na	390		414 ± 20		3070	3200 ± 400
Ni XRF	14.5	15 ± 1	18 ± 4	109	98 ± 3	98 ± 9
Pb IDSSMS	29.4	30 ± 9		78 ± 4	70 ± 4	75 ± 5
Rb XRF	24		21 ± 2	120	112 (in)	125 ± 10
NAA	19.5					
Sb	4.45		3.9 ± 1.3	7.8		6.9 ± 0.6
Sc	4.5		3.7 ± 0.3	32		27 ± 1
Se NAA	3.05	2.9 ± 0.3	3.4 ± 0.2		9.4 ± 0.5	10.2 ± 1.4
GMES	2.86 ± 0.13			9.35 ± 0.03		
Sr		3.2 (in)				21 ± 2
Sr			1.7 ± 0.2	15		12.4 ± 0.9
Sr	144		161 ± 16	1301	1380	1700 ± 300
NAA	123					
Ta	0.17		0.24 ± 0.04	1.6		1.8 ± 0.3
Tb	3.0	3.0 (in)	3.2 ± 0.2	26	24 (in)	24.8 ± 2.2
Ti	930	800 (in)	1100 ± 100	6420		7400 ± 300
U IDSSMS	1.21	1.4 ± 0.1	1.41 ± 0.07	11.8	11.6 ± 0.2	12.0 ± 0.5
NAA	1.26					
V	40 ± 3	35 ± 3	36 ± 3	240	214 ± 8	235 ± 13
Zn XRF	34	37 ± 4	30 ± 10	208	210 ± 20	216 ± 25
Zr	45					301 ± 20

* The symbol (in) after certain NBS values indicates that these are information values not certified values. All values reported are in ppm unless otherwise indicated. All ORNL results were obtained by instrumented neutron activation analysis unless otherwise indicated.

Table III. Trace Element Flows Through a Coal-Fired Power Plant^a

Element		Element flow, g/min				Imbalance, ^b %	Atmospheric discharge, g/min
		Coal	Slag	Inlet fly ash	Inlet gas		
Al	72	14,000	10,400	3,600		0	0
Al	73	15,340	8,620	6,720		0	0
As	72	5.3	0.5	1.8		-57	0.2
As	73	6.5	1.5	8.1	<0.1	+48	0.2
Ba	73	96	42	55		+1	0.3
Br	73	5.4	0.2	0.3		-90	0
Ca	72	5,200	4,000	1,000		-4	20
Ca	73	6,380	3,880	2,360		-2	10
Cd	72	0.58	0.42	0.30		+24	0.01
Cd	73	0.69	0.09	0.59	<0.05	-1	0.02
Ce	73	12.1	7.1	6.2		+10	0.04
Cl	73	1340	8	15		-98	~1,300
Co	72	4.9	2.7	2.1		-2	0.04
Co	73	4.3	1.8	2.9		+9	0.02
Cr	72	27.5	21.2	14.0		+28	
Cr	73	26	13	22		+33	0.3
Cs	72	1.9	1.1	0.9		+5	
Cs	73	1.6	0.6	1.0		0	0.01
Cu	73	12.2	1.7	10.3		-2	
Eu	72	0.30	0.15	0.10		-17	
Eu	73	0.15	0.09	0.09		+20	0.0005
Fe	72	19,700	14,800	6,100		+6	200
Fe	73	15,950	9,440	8,940		+16	60
Ga	73	6.6	0.4	6.0		-3	
Hf	73	0.59	0.39	0.30		+17	0.002
Hg	73	0.18	0.002	0.004	0.17	0	0.1 (gas only)
K	72	2,700	1,550	850		-11	20
K	73	2,260	1,330	1,480		+24	9
La	72	6.5	5.5	1.8		+12	0.04
La	73	5.6	3.5	3.0		+16	0.02
Mg	72	2,000	1,400	620		+1	50
Mg	73	1,780	1,040	780		+2	
Mn	72	66	56	18		+12	0.8
Mn	73	49.7	24.9	22.0		-6	0.2
Na	72	840	420	320		-12	8
Na	73	1,020	420	750		+15	4
Ni	73	23	7	16		0	
Pb	72	9.2	0.6	7.8		-9	0.2
Pb	73	7.2	0.5	5.9	<0.1	-11	0.2
Rb	73	22.8	8.6	11.5		-12	0.07
Sb	73	0.74	0.05	0.89	<0.1	+27	0.2
Sc	72	4.2	2.8	1.5		+2	0.2
Sc	73	3.2	1.8	1.9		+16	0.01
Se	73	3.2	0.0	1.8	0.53	-22	0.4
Si	73	33,960	19,300	14,480		-1	
Sm	73	1.47	0.69	0.78		0	0.003
Sr	73	34	14	18		-6	
Ta	73	0.16	0.08	0.10		+12	0.0007
Th	73	3.1	1.3	1.5		-10	0.01
Ti	72	680	390	230		-9	6
Ti	73	740	340	440		+5	4
U	72	3.0	2.0	1.1		+3	0.02
U	73	3.20	1.26	2.22		+8	
V	72	46	34	23		+24	0.8
V	73	41.9	21.9	32.5		+30	0.4
Zn	72	120	3	78		-35	2
Zn	73	68	8.4	55	<1.0	-7	2

^a All analytical data by NAA except: Cu, Ga, Ni and Sr by XRF; Hg by AA; Se by GC/MES and Cd, Pb and Zn by IDSSMS; values for As (73) and Rb are averages of NAA and XRF. ^b Imbalance = (Slag Flow + Fly Ash Flow + Gas Flow - Coal Flow)/(Coal Flow).

This classification correlates well with the results of Natusch et al. (11), who have studied the relationship between trace element concentration and particle size in fly ash. They report that, of elements studied at Allen, As, Cd, Cr, Ni, Pb, Sb, Se, and Zn show a clear inverse relationship between concentration and particle size. Except for Cr and Ni (in the intermediate group), these elements are in Class II. Natusch et al. report no trend or poorly defined trends for Al, Ca, Co, Cu, Fe, K, Mg, Mn, Si, Ti, and V; of these elements Cu is in Class II and V is in the intermediate group, but the other nine are in Class I. A volatilization-condensation or adsorption mechanism is proposed by Natusch to account for the size-concentration behavior. Those elements which accumulate on the smaller fly ash particles are assumed to be volatile at the temperature of combustion (1300-1600°C); as the flue gas cools, the volatiles condense or adsorb on the fly ash. Since condensation and adsorption are surface phenomena, the concentration of condensed elements should be inversely proportional to particle size. Those elements not volatile in the combustion zone form the fly ash particles upon which the volatiles con-

dense. Natusch points out that the elements that are enriched on the smaller particles usually have boiling points comparable to or less than the temperature of the combustion zone.

This proposed volatilization-condensation or adsorption mechanism can be modified to rationalize the classes of behavior at the Allen plant:

Class I. These elements are not volatilized in the combustion zone, but instead form a melt of rather uniform composition that becomes both fly ash and slag. The slag is removed directly and quickly from the combustion zone, while the fly ash remains in contact with the cooling flue gas. The Class I elements remain in the condensed state, and hence show minimal partitioning between slag, inlet fly ash, and outlet fly ash.

Class II. These elements are volatilized on combustion. Since the slag is removed from the combustion zone, they have no opportunity to condense on the slag. They do, however, condense or become adsorbed on the fly ash as the flue gas cools. These elements are thus preferentially depleted from the slag (volatility effect), and preferentially

Table IV. Concentrations and Concentration Ratios for 1973 Runs

	Element concentration, ^a ppm				Concentration ratios		
	Coal	Slag	Inlet fly ash	Outlet fly ash	Slag/coal	(Inlet fly ash)/slag	(Outlet fly ash)/(inlet fly ash)
Al	10,440	102,300	90,900	76,000	9.8	0.9	0.8
As	4.45	18	110	440	4.05	6.1	4.0
Ba	65	500	465	750	7.7	0.9	1.6
Br	3.7	2	~4		0.5	2.0	
Ca	4,340	46,000	25,200	32,000	10.6	0.5	1.3
Cd	0.47	1.1	8.0	51	2.3	7.3	6.4
Ce	8.2	84	84	120	10.2	1.0	1.4
Cl	914	≤100	≤200		≤0.1	~1	
Co	2.9	20.8	39	65	7.2	1.9	1.7
Cr	18	152	300	900	8.4	2.0	3.0
Cs	1.1	7.7	13	27	7.0	1.7	2.1
Cu	8.3	20	140		2.4	7.0	
Eu	0.1	1.1	1.3	1.3	11.0	1.2	1.0
Fe	10,850	112,000	121,000	150,000	10.3	1.1	1.2
Ga	4.5	5	81		1.1	16.2	
Hf	0.4	4.6	4.1	5.0	11.5	0.9	1.2
Hg	0.122	0.028	0.050		0.2	1.8	
K	1,540	15,800	20,000	24,000	10.3	1.3	1.2
La	3.8	42	40	42	11.0	1.0	1.0
Mg	1,210	12,400	10,600		10.2	0.9	
Mn	33.8	295	298	430	8.7	1.0	1.4
Na	696	5,000	10,100	11,300	7.2	2.0	1.1
Ni	16	85	207		5.3	2.5	
Pb	4.9	6.2	80	650	1.3	12.9	8.1
Rb	15.5	102	155	190	6.6	1.5	1.2
Sb	0.5	0.64	12	55	1.3	18.8	4.6
Se	2.2	20.8	26	36	9.5	1.2	1.4
Si	2.2	0.80	25	88	0.0	310	3.5
Sr	23,100	229,000	196,000		9.9	0.9	
Sn	1.0	8.2	10.5	9	8.2	1.3	0.9
Sr	23	170	250		7.4	1.5	
Ta	0.11	0.95	1.4	1.8	8.6	1.5	1.3
Ti	2.1	15	20	26	7.1	1.3	1.3
Ti	506	4,100	5,980	10,000	8.1	1.5	1.7
U	2.18	14.9	30.1		6.8	2.0	
V	28.5	260	440	1,180	9.1	1.7	2.7
Zn	46	100	740	5,900	2.2	7.4	8.0

^a Analytical data by NAA except: Cu, Ga, Ni, and Sr by XRF; Hg by AA; Se by GCMS and Cd, Pb, and Zn by IDSSMS; values for As (73) and for Rb are averages of NAA and XRF.

concentrated on the outlet fly ash compared to the inlet fly ash (particle size effect).

Although most Class II and Class III elements are relatively low boiling, and most Class I elements are relatively high boiling, there are enough exceptions to make it unlikely that elemental boiling point is the major factor determining elemental partitioning. For example Ca and Cu behave as if they are low boilers, while Rb, Cs, and Mg behave as if they are high boilers. It is more probable that the state of the element in the coal determines the behavior on combustion, and the following scheme may be proposed:

(1) Trace elements in coal are present in aluminosilicates, as inorganic sulfides, or as organic complexes.

(2) On combustion the aluminosilicates are not decomposed. Rather, they melt and coalesce to form the slag and fly ash.

(3) During the initial stages of combustion, the conditions in a coal particle and within its immediate vicinity are probably reducing and under these conditions the chemical bonding between metallic elements and sulfur in sulfide mineral inclusions or between the elements and the organic matrix is broken, and these elements form volatile species. If the elements are dispersed in the coal organic matrix, they become initially dispersed in the gas stream when the coal is burned. Thus, even those elements that are not as stable as the vapor at the combustion temperature initially enter the flue gas stream as the vapor.

(4) The elements initially volatilized or dispersed in the flue gas stream may then be oxidized to form less volatile species which may then condense or be adsorbed on the fly ash as the temperature of the flue gas drops.

(5) Since the slag is in contact with the flue gas for a short time, and at a high temperature, condensation of volatiles on the slag is minimal.

Although there is no direct experimental evidence to support this proposed scheme, there is some indirect geochemical support. Elements have been classified as lithophiles or chalcophiles according to their tendency to be associated with aluminosilicate minerals (lithophiles) or sulfide minerals (chalcophiles). Presumably the lithophiles should show Class I behavior, and the chalcophiles should show Class II behavior. The Class III elements are very volatile, and may do neither. According to the classification by Mason (12), all the Class I elements are lithophiles in crustal rocks except that Co and Fe may be either lithophile or chalcophile. All the Class II elements are chalcophiles in crustal rocks, except that Cu may be either chalcophile or lithophile. Of the unclassified elements, Na, Cs, and U, and V are lithophiles and Cr and Ni may be either lithophile or chalcophile. Thus the geochemical classification of the elements yields predictions of the state of trace elements in coal, and these predictions lead to reasonable explanations of the behavior of the trace elements on combustion. A similar argument has been advanced recently by Kaakinen (13) working at the University of Colorado and Lawasani (14) at the same institution who treated Kaakinen's data.

Atmospheric Discharge

Overall precipitator efficiency at the Allen plant was different during the two sets of runs. In the 1/72 runs about 3.5% of the incoming fly ash left the precipitator in the flue gas stream while in the 8/73 runs only about 0.5% passed through. Hg and Se are discharged both in fly ash and as the vapor, but since no other metals were detected by our techniques in the impingers, other metals apparently are discharged only with the fly ash. The quantities discharged to the atmosphere are given in the last column of Table III. The atmospheric discharge data are less precise than the other data given here, partly because very little sample

could be collected for analysis and partly because the sampling ports in the outlet ducts were located in positions where the gas flow was not smooth and sampling may not have been adequate to give an accurate estimate of the outlet ash flow. Discharge data, therefore, are presented to only one significant figure.

These results, and those of Natusch et al. show that the ability of the precipitator to remove trace elements from the flue gas stream depends on the specific element as well as on precipitator design and operating conditions. With Class I elements removed more efficiently than Class II elements. The removal of most major elements, especially Al, is appreciably more complete for the 8/73 runs. In contrast, the improved overall precipitator efficiency was without effect on the percent of Cd (3%), Pb (3%), and Zn (2%) discharged to the atmosphere because these elements concentrate on the finer particles that are less efficiently collected even by a high-efficiency electrostatic precipitator. Measurements at Allen for the #2 Unit electrostatic precipitator made during our 1973 sampling trip by Southern Research Institute showed a minimum in precipitator efficiency of about 80-85% for particles 0.1-0.5 μ in diameter (15).

Hg and Se are special cases since they were observed to enter the precipitator partly in the vapor phase. About 20% of the Se passes through the precipitator, primarily as the elemental vapor (Andren et al., to be published). Selenium in both the vapor state and that in the fly ash phase appeared to be in the zero oxidation state [Andren et al. (16)]. Hg flows into the precipitator at 0.18 g/min of which 0.17 g/min is vapor. The impinger solutions on the outlet collected mercury corresponding to only 0.10 g/min, and the fly ash removed by the precipitator contained essentially no mercury. The outlet fly ash was not analyzed because of the limited amount of sample; however, to account for the balance of mercury the outlet ash would have had to contain about 200 ppm, a rather large value. In any case, not less than 60%, and probably about 90% (3, 4) of the mercury entering in the coal stream is discharged to the atmosphere as the vapor. Although data are not available to permit comparison of the 1/72 runs with the 8/73 runs, it is unlikely that the change in precipitator efficiency could have an effect on the relative quantity of these elements discharged as the vapor.

Thus, it appears that electrostatic precipitators can be made efficient for the removal of most elements, but will be less efficient for removal of those elements that concentrate on the very fine particulates, and are essentially without effect on such volatiles as Hg. Since most of the Class I and Class II elements are in the collected ashes, from which they may be removed by weathering or biological processes, the fate of the potentially toxic metals in coal will depend largely upon how the ashes are stored or disposed of. The stability of the ash under environmental conditions requires further study.

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NOTES

Improvements in Phenoldisulfonic Acid Method for Determination of NO_x

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■ The phenoldisulfonic acid method prescribed by the Environmental Protection Agency gives erratic results using the procedure outlined in the *Federal Register*. To remedy this situation, we have studied certain variables in the analysis and determined their effect on the results. By control of these variables, reproducible and accurate analyses can be carried out: Carry out the evaporation step in new unetched borosilicate dishes, discarding any samples with a precipitate and avoiding platinum; add only enough NaOH to neutralize the acidic solution of nitrates; add excess of NH₄OH prior to the spectrophotometric measurement; and read the absorbance at 405 nm. Samples of NO in N₂ analyzed by the modified phenoldisulfonic acid method and chemiluminescence agree within 1.5% on average.

The phenoldisulfonic acid method for the determination of NO_x is currently prescribed by the Environmental Protection Agency (1) for the analysis of effluents from stationary sources. Difficulties in obtaining reproducible and accurate results have been reported (2), and alternate procedures in the method have been recommended (2, 3). In our laboratory, similar problems have occurred with resulting poor precision.

The method requires sampling in an evacuated 2-liter borosilicate vessel containing 25 ml of absorbing solution (0.03% H₂O₂ in 0.1N H₂SO₄). After rapid filling with the

sample gas, the vessel is allowed to stand for 16 hr prior to analysis. The analysis: Transfer quantitatively to a borosilicate evaporating dish, add NaOH until alkaline, evaporate to dryness, add phenoldisulfonic acid to the residue, dilute with water, neutralize with NH₄OH, and measure spectrophotometrically the chromogen formed.

The method serves as the reference method for the analysis of gaseous samples containing NO and NO₂, including standard gaseous mixtures to be used in calibrating chemiluminescence analyzers. In our study, we used standard solutions of KNO₃ to eliminate gas-sampling variables and focused our attention on the steps in the analysis portion of the method.

Experiments

The first variable considered was the choice of vessel used for the evaporation step. Martens et al. (2) have reported that considerable etching and precipitate formation occurred sporadically with borosilicate vessels with resulting erratic and low results and therefore recommended platinum vessels. In our work, 1250 µg of KNO₃ as NO₂ was used and borosilicate dishes, not etched, were used as the reference. Table I shows the results for these dishes, etched dishes, and platinum dishes. Analyses in which etching occurred and precipitate formed were lower on average and had a higher standard deviation. Results with platinum dishes were also lower and had a higher standard deviation. It would appear that adsorption of the chromogen or pre-