CHARACTERIZATION OF TRACE ELEMENT EMISSIONS FROM A PILOT-SCALE COAL COMBUSTION UNIT

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INTRODUCTION

The flue gas cleanup projects in the in-house research program at the Pittsburgh Energy Technology Center range from laboratory-scale work to testing with the combustion products of coal at a scale equivalent to about 0.75 MW of electric power generation. The largest unit is a 500-pound-per-hour coal combustor, complete with ductwork, spray dryer, baghouse, and ancillary equipment. Over the past year, tests to investigate the distribution and fate of trace elements have been conducted with this pilot unit.

These investigations are an integral component of the Air Toxics and Fine Particulate Control subprogrammatic area of the AR&ET Power Systems Program. The overall effort of this area focuses on the improvement of existing technologies and the development of new technologies for the control of hazardous air pollutants and fine particulates associated with coal combustion. A major endeavor within the subprogram is the characterization of trace elements in flue gas from coal combustion, including a special emphasis on mercury speciation. The study described in this paper examined the results from an investigation on the pilot unit: the distribution of trace elements in the ash streams and flue gas stream, material recoveries for the system, baghouse removal efficiencies, and enrichment of ash particulate. Also, a preliminary comparison between the results from the pilot unit and a full-scale utility that burned coal from the same coal batch is provided.

PILOT UNIT AND TEST DESCRIPTION

The combustor is a wall-fired, dry-bottom furnace that burns pulverized coal at a nominal rate of up to 500 pounds per hour. A complete description and diagram of the pilot unit has been provided in previous papers [1, 2].

Sampling was conducted simultaneously over four consecutive days at two points in the flue gas stream: at the inlet to the baghouse and at the stack. An EPA Draft Method 29 train was used at the inlet for total particulate loading and trace elements. This train was modified by incorporating a cyclade (i.e., a series of cyclones) between the nozzle and filter box to allow analysis of trace elements by particle size. The nominal particle size ranges were > 7, 3.5 to 7, 1.5 to 3.5, and < 1.5 microns. At the stack, sampling for particulate loading and trace elements was conducted using a standard Method 29 train. Sampling for halogens using a Method 26A train was also conducted at the stack location. In addition, particle size distribution was measured at both the baghouse inlet and the stack using Anderson cascade impactors. These impactors size-fractionated the particulate into eight size ranges from about 0.5 to 14 microns. The flue gas sampling was conducted by a team from TRC under subcontract to Battelle-Columbus Laboratory. Battelle was responsible for analysis of the samples recovered from each of the trains.

While the flue gas sampling was conducted, hourly samples of pulverized coal were obtained. Equal amounts of each hourly sample were riffled in the PETC in-house laboratory and composited to produce a single pulverized coal sample for each day of flue gas sampling. Battelle was responsible for analysis of the pulverized coal samples for proximate, ultimate, major/minor elements, trace elements, and halogens. The coal used in testing was a low-sulfur bituminous coal from Kentucky and was from the same coal batch that was fired in a full-scale utility during air toxics testing [3]. A comparison of the average coal analysis for the pilot unit and the full-scale testing is provided in Table 1.

Ash samples were obtained from a number of locations both during and after testing. Bottom ash and baghouse ash were collected each day, weighed, and sampled. After the unit cooled to ambient temperature at the end of the test, deposits on the furnace interior walls and roof were collected, weighed, crushed, and sampled. Finally, ash deposits in the dust duct and preheater were also collected, weighed, and sampled. Since these latter three components of the ash deposits could not be obtained on a daily basis, the total amount collected over the test period was apportioned to each day on the basis of the amount of coal burned each day. All of the ash samples were analyzed for moisture, carbon, sulfur, halogens, major/minor elements, and trace elements by two separate laboratories under contract to the PETC in-house laboratory. On-line analysis of flue gas for major gas species was obtained at the furnace exit.

PILOT UNIT TEST RESULTS AND DISCUSSION

Flue gas composition at the furnace exit, averaged over the four days of testing, was 4.2% O_2, 14% CO_2, 540 parts per million by volume (vppm) NOx, 640 vppm SO_2, and 24 vppm CO. The average coal feed rate was 350 pounds per hour (lb/hr) and the percent excess air was 23%. While these parameters were fairly consistent from day to day, there were variations throughout each day as a direct result of instantaneous fluctuations in coal feed rate due to the practice of pulverizing coal on-line [2]. Also, process upsets occurred that caused flame-outs during the testing period. Every effort was made to minimize the effects of process upsets on flue gas sampling by notifying the flue gas sampling teams to discontinue sampling until steady-state conditions were re-established. However, it was not possible to completely eliminate the effects on flue gas sampling or on the composition of ash deposits collected for each day of testing.

Baghouse Removal Efficiency

The four-day average results of flue gas sampling at the baghouse inlet and at the stack are provided in Table 2, along with baghouse removal efficiencies based on these flue gas measurements. The baghouse operated at an air-to-cloth ratio of about 4:1. Cleaning was by pulse-jet set to maintain a pressure drop of 3 inches of water. The average baghouse temperature was about 255° F. These conditions were consistent for each day of testing. Most of the elements show removal efficiencies similar to that obtained for the total particulate matter. Noted exceptions are boron and mercury, which are predominantly in the vapor phase at the sampling location temperatures (277° F at the inlet and 238° F at the stack).

Mercury Speciation

A more detailed comparison of mercury concentration in the flue gas is shown in Table 3. This table shows the daily and four-day average vapor/particulate phase concentration, as well as the speciation (elemental vs. oxidized), as measured by Method 29. It was necessary to show each day's result here because of the variability of the results from day to day, especially for the stack concentrations. At the baghouse inlet, vapor/particulate ratio varied from 66:34 to 84:16 and averaged 75:25. This is somewhat lower than has been seen in other studies [4,5], where vapor-phase mercury has generally been greater

than 90% of total flue gas mercury. The higher level of particulate phase mercury is probably due to the high level of unburned carbon in the fly ash at the inlet to the baghouse. The carbon in fly ash varied from 6.9 to 11.2% and averaged 8.8% [6].

With regard to speciation, the mercury was predominantly captured in the permanganate impingers at the baghouse inlet (inferred to be elemental mercury). The percentage of elemental mercury in the vapor phase ranged from 75 to 94% with an average of 88%. At the stack, there was no apparent trend in speciation, with elemental mercury percentage of total vapor mercury ranging from 20 to almost 100%. The vapor/particulate ratio at the stack was very high (from 97:3 to 100:0) as might be expected with high particulate removals from a baghouse. However, the mercury removals suggested in Table 3 cannot be accounted for simply by removal of the particulate phase mercury. The average particulate phase mercury at the baghouse inlet was 25% of the total mercury, but the observed mercury removal shown in Table 2 was about 60%. Therefore, there was apparently more adsorption of vapor-phase mercury onto the particulate in the baghouse than on the filter in the sampling train. This difference may be attributed to the use of the cyclade on the sampling train at the inlet. This possible adsorption is supported by the material balance for mercury.

Material Balances

Material balances for all elements and halogens for the four-day testing period are provided in Table 4. The values shown are the averages of the material balances calculated for each day of testing. The total ash balance for the testing period was 107.1%. As can be seen from the table, the material balances of major and minor elements were reasonable except for aluminum, magnesium, potassium, and sodium. The poor balances for these elements may be attributed to the fact that coal analyses were performed by one laboratory and the ash analyses for these elements were performed by another [2].

With respect to trace elements and halogens, a number of elements showed low recoveries (antimony, boron, and cadmium) and these results must be examined in more detail. The recoveries for molybdenum and selenium are marginal. The recoveries for lead and fluorine were high; barium is extremely high. The recovery for mercury is in an acceptable range and lends confidence to the mercury removals seen across the baghouse.

Elements by Particle Size and Physical State

A graph of elements by particle size fraction and vapor/solid phase in flue gas is shown in Figure 1 for the baghouse inlet sampling location. The major and minor elements were predominantly in the particulate phase, as expected, and the distribution by particle size was similar to the particle size distribution of the total ash. The trace elements were also predominantly in the solid phase, with the exception of mercury. There were also significant levels of selenium and boron in the vapor phase. Antimony and arsenic showed the highest level of enrichment in the smallest size fraction. Boron, lead, and chromium showed lower but still significant enrichment in the < 1.5 micron size fraction. Cadmium, selenium, and nickel showed slight but measurable levels of enrichment. The relative enrichment for these trace elements is consistent with their relative volatilities.

PILOT-SCALE RESULTS VERSUS FULL-SCALE RESULTS

A comparison of the flue gas concentrations for total particulate and elements measured at the inlet to the particulate control equipment at the pilot unit and the full-scale utility is shown in Table 5. The particulate loading at the pilot unit was almost 30% lower than the loading found at the full-scale utility. Removal of a portion of the ash (about 13% of total ash in the coal) in the duct of the pilot unit between the furnace exit and baghouse inlet can partially explain this. In addition, the daily variability in particulate

loading, as evidenced by the standard deviation shown in the table, can account for some of the difference shown.

The flue gas concentration values for titanium, chromium, cobalt and nickel are similar for the pilot unit and full-scale utility and are consistent with the flue gas concentrations expected based on the coal analyses shown in Table 1. While the concentration values for aluminum are also similar for both units, the coal analyses indicate that the pilot-scale unit should have had lower flue gas concentrations than the full-scale utility. However, low analytical recoveries for aluminum in coal, noted in the pilot unit study, may explain the resulting similarity in flue gas concentrations. The values for manganese are directionally consistent with the coal analysis and, considering the variability in the coal and flue gas sample analyses, the differences in flue gas concentrations are not significant. The comparison for silicon shows a much higher value in the flue gas for the pilot unit, but the high standard deviation for the pilot unit value suggests that the values are not statistically different at the 95% confidence level.

The flue gas concentration values for arsenic, beryllium, and selenium appear to be somewhat lower in the pilot unit than the full-scale utility. This difference may be due to the lower particulate loading in the pilot unit, combined with variability in the analytical results for the daily samples. The discrepancy between the two units for cadmium in the flue gas may be due to the coal analysis, but poor detection limits in the full-scale test do not allow a direct comparison. For antimony, the difference in flue gas concentrations is not consistent with the difference in coal analysis. Poor analytical recoveries of antimony (<60%) in a standard fly ash were noted in quality control samples for the pilot unit study and this could partially explain the difference. The reason for the difference in flue gas concentrations of lead is not clear but it appears that the baghouse inlet concentration value for lead may be biased low.

For mercury, the high variability in the flue gas sample results from the full-scale unit resulted in a relatively high standard deviation. Therefore, the values for the two units are not statistically different. In addition, there may be a high bias in the analysis of the flue gas samples for the full-scale unit, since the coal concentration indicates that the mercury concentration in the flue gas should have been lower (about 10 ug/Nm^3).

SUMMARY

The characterization for certain air toxics from a pilot-scale utility while burning a low-sulfur bituminous coal from Kentucky has been performed. Using EPA sampling methodology at the inlet to the baghouse and at the stack, results indicate that the vast majority of elements were removed across the baghouse, except for the more volatile ones such as mercury and boron. Regarding mercury, this element was found predominantly in the vapor phase. The average mercury speciation numbers at both sampling locations would indicate that the mercury would be primarily in the elemental form as compared to the oxidized form. Although some discrepancies in the material recoveries of certain elements were experienced, the overall recovery for mercury lends confidence in continuing work on mercury sampling and control methods with the 500-lb/hr combustion unit. Evidence exists for enrichment on the smaller particulate size fraction with the semi-volatile trace elements.

Of the elements measured at both the pilot unit and the full-scale utility, some show excellent agreement in flue gas concentration at the inlet to the respective particulate control devices. Differences for the rest of the elements can be explained by a combination of sample variability and/or differences in coal analysis.

REFERENCES

[1] Hargis, R.A., and H.W. Pennline, Experimental Plan for the Assessment of Air Toxic Emissions from a Pilot-Scale Combustion Unit. Proceedings of 12th Annual International Pittsburgh Coal Conference, pp. 997-1002, September 1995. [
2] Hargis, R.A., and H.W. Pennline, Assessment of Air Toxic Emissions from a Pilot-Scale Combustion Unit. Paper presented at 1st Joint Power & Fuel Systems Contractors Conference, July 1996.
[3] Battelle, Characterization of Toxic Emissions From Two Coal-Fired Utility Boilers Operating at Different Combustion Intensities. Final Topical Report, U.S. DOE Contract No. DE-AC22-91PC90366, May 1996.
[4] Burns and Roe Services Corporation, Summary of Air Toxics Emissions Testing at Sixteen Utility Power Plants. U.S. DOE Contract No. DE-AC22-94PC92100, June 1996.
[5] Laudal, D.L., M.K. Heidt, T.D. Brown, B.R. Nott, and E.P. Prestbo, Mercury Speciation: A Comparison Between EPA Method 29 and Other Sampling Methods. Presented at 89th Annual Meeting of the Air & Waste Management Association, Nashville, TN, June 1996.
[6] Battelle, Assessment of Air Toxic Emissions From a Pilot-Scale Combustion Unit Burning Uncleaned and Clean Coal. Final Topical Report, U.S. DOE Contract No. DE-AC22-91PC90366, May 1996.

DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement by the U.S. Department of Energy.

TABLE 1 **AVERAGE COAL ANALYSIS FOR TEST PERIOD**		
	PILOT UNIT	FULL-SCALE UTILITY
ULTIMATE (%, dry)		
Carbon	74	74
Hydrogen	4.9	4.6
Nitrogen	1.4	1.4
Oxygen	6.4	6.9
Sulfur	0.89	0.88
Ash	12.7	12.1
Btu/lb (dry)	12,950	13,000
MAJOR/MINOR ELEMENTS (ug/g, as received)		

Aluminum	8100	19000
Silicon	27000	22000
Iron	4900	NR[1]
Calcium	1600	NR
Magnesium	530	NR
Potassium	1800	NR
Sodium	200	NR
Titanium	1200	1200
TRACE ELEMENTS (ug/g, as received)		
Antimony	0.90	<0.57
Arsenic	2.4	1.5
Barium	16	NR
Beryllium	2.0	1.7
Boron	1000	NR
Cadmium	0.67	<2.0
Chromium	40	27
Cobalt	8.3	11
Copper	19	NR
Lead	6.5	7.2
Manganese	250	5.9
Mercury	0.095	0.085

Molybdenum	4.8	NR
Nickel	24	27
Selenium	5.0	5.0
Vanadium	43	NR
ANIONS (ug/g, dry)		
Chloride	1200	1000
Fluoride	63	64

NR[1] = Not Reported

- **TABLE 2**
  PARTICULATES AND ELEMENTS IN FLUE GAS [6]
  AND BAGHOUSE REMOVAL EFFICIENCY

	BAGHOUSE INLET (ug/Nm^3)[1]	STACK (ug/Nm^3)[1]	REMOVAL EFFICIENCY (%)
TOTAL PARTICULATE	5700000	6300	99.86
MAJOR/MINOR ELEMENTS			
Aluminum	53000	500	98.97
Silicon	870000	1200	99.86
Iron	130000	1600	98.63
Calcium	4200	260	93.03
Magnesium	630	37	93.39
Potassium	59000	<4.3	>99.99

Sodium	5500	270	94.73
Titanium	36000	23	99.93
TRACE			
Antimony	20	0.15	99.25
Arsenic	78	0.39	99.46
Barium	1100	0.53	99.95
Beryllium	65	0.052	99.91
Boron	3800	2000	44.29
Cadmium	18	0.67	95.86
Chromium	1800	7.4	99.58
Cobalt	420	0.28	99.93
Copper	800	2.2	99.71
Lead	180	0.22	99.88
Manganese	5600	16	99.68
Mercury	9.2	3.5	59.69
Molybdenum	110	<0.05	>99.98
Nickel	1300	5.4	99.54
Selenium	180	2.8	98.34
Vanadium	1600	0.78	99.95

1 - Units are micrograms per Normal cubic meter; Normal conditions are dry, 0o C, 1 atmosphere,

and corrected to 3% oxygen.

TABLE 3 DISTRIBUTION AND SPECIATION OF MERCURY IN FLUE GAS [6] (ug/Nm^3)^3					
BAGHOUSE INLET	DAY 1	DAY 2	DAY 3	DAY 4	AVG.
Particulate	1.73	2.80	3.10	1.42	2.26
Vapor (II)[1]	0.80	1.36	0.69	0.41	0.82
Vapor (0)[2]	7.28	4.13	6.01	7.03	6.11
Total	9.81	8.29	9.80	8.85	9.19
STACK					
Particulate	0.12	0.013	0.013	0.006	0.038
Vapor (II)[1]	1.40	<0.02	0.91	1.04	0.84
Vapor (0)[2]	3.12	7.10	0.27	0.25	2.68
Total	4.64	7.12	1.19	1.30	3.56

1 - Mercury vapor captured in peroxide impingers of Method 29 train, inferred to be oxidized Mercury
2 - Mercury vapor captured in permanganate impingers of Method 29 train, inferred to be elemental Mercury
3 - Units are micrograms per Normal cubic meter; Normal conditions are dry, 0o C, 1 atmosphere, and corrected to 3% oxygen.

TABLE 4 PILOT UNIT MATERIAL BALANCES FOR TESTING PERIOD MAJOR, MINOR, AND TRACE ELEMENTS AND HALOGENS (OUT/IN, %)			
Aluminum	286.1	Magnesium	142.8
Silicon	117.7	Potassium	158.5
Iron	128.9	Sodium	146.9
Calcium	119.6	Titanium	114.3
Antimony	16.8	Copper	134.0
Arsenic	104.2	Lead	196.6
Barium	507.4	Manganese	146.8
Beryllium	105.4	Mercury	82.8
Boron	3.4	Molybdenum	65.1
Cadmium	3.1	Nickel	119.1
Chromium	109.1	Selenium	61.1
Cobalt	108.2	Vanadium	116.1
Chlorine	110.4	Fluorine	165.3

TABLE 5 PARTICULATES AND ELEMENTS IN FLUE GAS AT INLET TO PARTICULATE CONTROL DEVICE FOR PILOT PLANT AND FULL-SCALE UNIT				
	PILOT UNIT BAGHOUSE INLET (ug/Nm^3)[1]		FULL-SCALE UTILITY ESP INLET (ug/Nm^3)[1]	
	AVG.	S.D.	AVG.	S.D.
TOTAL PARTICULATE	5700000	1700000	8000000	1900000
ELEMENTS				
Aluminum	53000	25000	57000	15000

Silicon	870000	460000	220000	130000
Titanium	36000	10000	43000	1100
Antimony	20	4.1	55	4.1
Arsenic	78	20	210	70
Beryllium	65	18	110	28
Cadmium	18	5.8	8.1	2.5
Chromium	1800	1100	600	380
Cobalt	420	100	600	140
Lead	180	48	720	130
Manganese	5600	2400	440	140
Mercury	9.2	0.75	13	4.4
Nickel	1300	160	1100	300
Selenium	180	120	340	140

1 - Units are micrograms per Normal cubic meter; Normal conditions are dry, 0° C, 1 atmosphere, and corrected to 3% oxygen.

Proceedings of the 13th Annual Pittsburgh Coal Conference, pp. 1362-1368, September 1996.