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BUREAU OF MINES TECHNICAL PROGRESS REPORT

FATE OF TRACE MERCURY IN THE COMBUSTION OF COAL

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by

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and Pollution Program

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FATE OF TRACE MERCURY IN THE COMBUSTION OF COAL

by

R. C. Diehl,[1] E. A. Hoffman,[1] H. Schultz,[2] and R. J. Horen[3]

ABSTRACT

Coal, fly ash, and flue gas samples were analyzed for mercury (Hg) by double gold amalgamation-flameless atomic absorption spectrophotometry. The purpose of the study was to elucidate the fate of the trace mercury in the coal when the coal is burned. Samples were collected from a bench-scale 100-g/hr combustor, a 500-lb/hr combustor, and three coal-burning powerplants. In all cases mercury was found in the fly ash. The amounts ranged from about 9 to about 70 percent of the mercury in the coal that was burned.

INTRODUCTION

The potentially detrimental effects of trace metal emissions on both the environment and public health have recently been the subject of much concern (2-3).[4] One possible source of such emissions is coal, which is known to contain trace amounts of a number of metals (1, 8). Among the metals whose presence in the environment is of concern, mercury stands out owing to its volatility and known toxicity (5). While coal is known to contain only small amounts of mercury (0.01 to 1 μg Hg/g coal) (7, 10-11), the amount of coal consumed is large. World production of coal exceeds 3×10^9 tons, and coal consumption in the United States alone exceeds 500×10^6 tons (4). The approximately 300×10^6 tons of coal burned annually in the United States for electrical power generation (4) could possibly release as much as 300 tons of mercury to the environment.

Recent publications concerning mercury emissions from coal combustion have assumed that all the mercury present in coal is released to the environment as a gaseous emission (2-3, 7). However, some of the mercury could be combined with the fly ash and be removed from the stack gas and thus eliminated as a source of atmosphere contamination. The purpose of the present work is to determine this distribution of mercury between the fly ash and the flue gases.

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[1]Research chemist.
[2]Research supervisor.
[3]Chemical engineering technician.
[4]Underlined numbers in parentheses refer to items in the references at the end of this report.

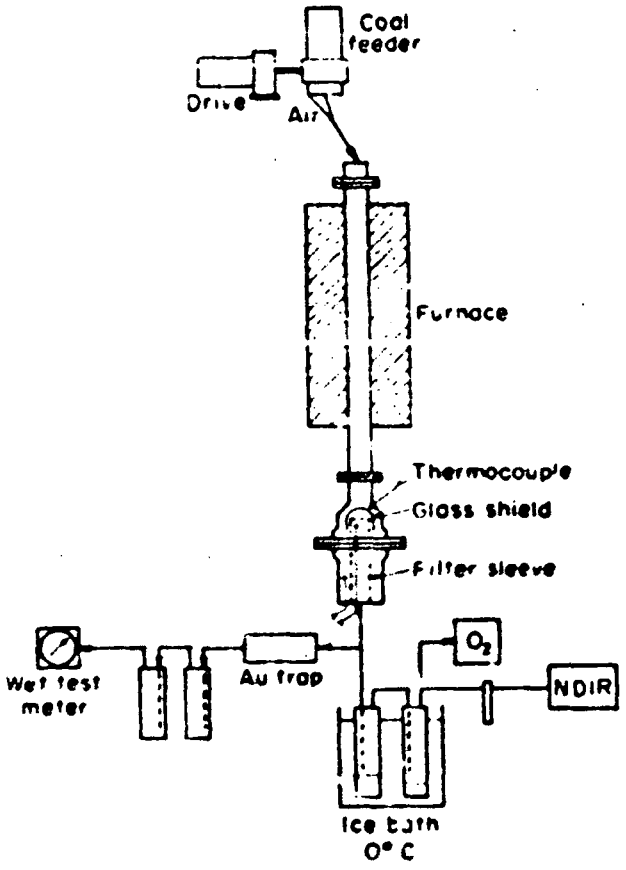

FIGURE 1. - Schematic Flow Diagram of Trace Element Unit.

For the initial studies a bench-scale pulverized-coal combustor was employed. The use of a small-scale combustor allowed for better control. The coal feed rates and airflow rates could be measured with a fair degree of accuracy. The coal associated with the effluents could be more readily identified than would be possible with a powerplant, and attempts at material balances were thus feasible. As part of the study, analyses were performed on coal, trapped fly ash, and flue gas from the bench-scale combustor. Some analyses were performed on samples of coal and fly ash from an experimental 500-lb/hr pulverized-coal combustor. Samples of fly ash from large powerplants were collected and analyzed for purposes of comparison.

EXPERIMENTAL WORK

100-g/hr Pulverized Coal Combustor

A flow diagram of the bench-scale pulverized-coal-fired combustion unit and the trace-metal recovery system are shown in figure 1. Prior to being charged to the feeder hopper, the coal, 100 to 200 mesh, is dried for 2 hours at 110° C and then weighed. The coal combustor is a 2-inch-ID by 36-inch-long alumina tube that is heated to about 1,200° C by a three-zone electric furnace. Platinum versus platinum-10 percent rhodium thermocouples monitor the temperature of the combustor. Airflow transports the coal into the combustor. The residence time of the coal in the combustor is increased by interrupting the vertical descent of the coal by a deflector. Coal at a feed rate of 100 g/hr is burned with about 1.3 m^3/hr of air at an excess air level of 20 to 25 percent. Carbon combustion efficiencies are greater than 95 percent.

The fly ash and combustion gas effluent continue through the ceramic combustor and into a glass recovery system. The fly ash is entrapped at 150° to 177° C using a 6-inch-long by 2-inch-diameter Nomex[3] bag filter. After exiting from the bag filter, the gas flow is divided into two unequal

[3]Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

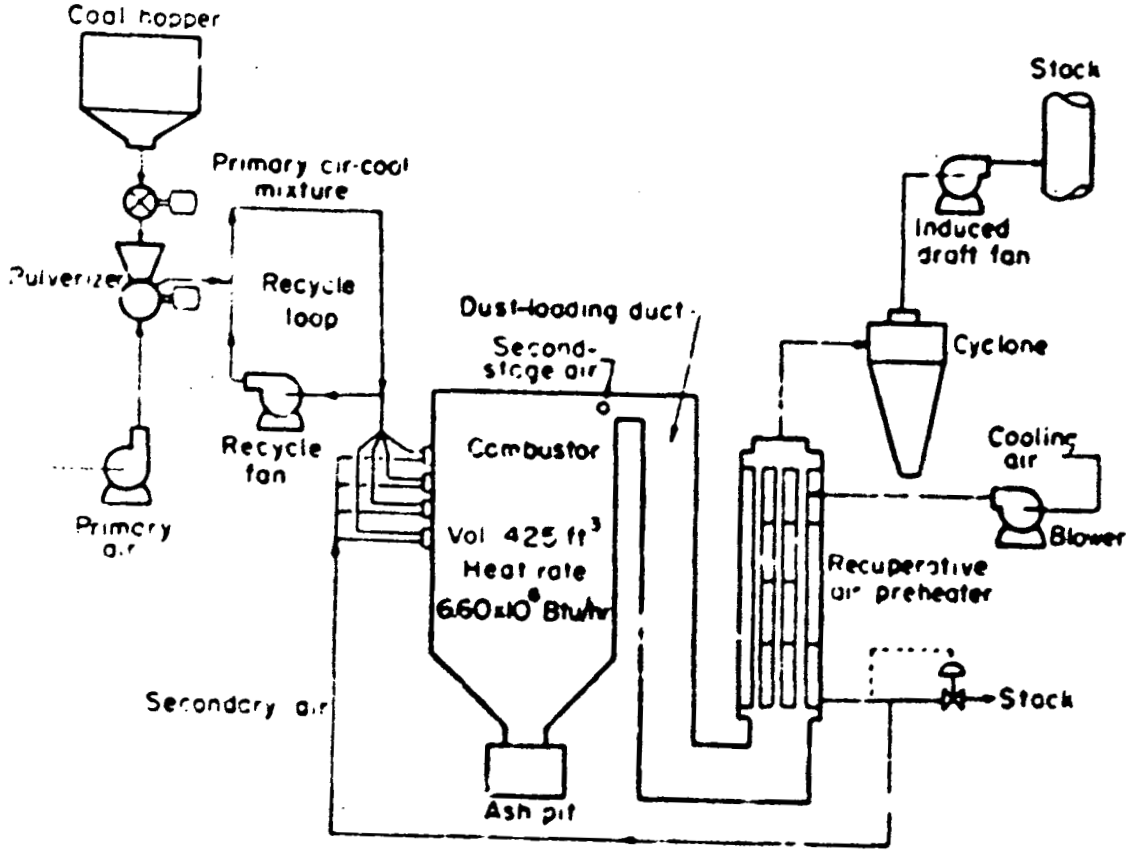

FIGURE 2. - Simplified Flowsheet of 500-lb/hr Pulverized-Fuel-Fired Furnace.

streams. The larger stream is again split, with half passing through a coulometric oxygen analyzer and half passing through a nondispersive infrared nitric oxide analyzer. The smaller stream (≈0.15 m³/hr) passes through the mercury collection equipment.

Samples of coal remaining in the feeder were removed, weighed, riffled, and analyzed for mercury. Samples of fly ash and the gold trap and bubbler solutions were also analyzed for mercury.

500-lb/hr Pulverized Coal Combustor

The 500-lb/hr pulverized coal combustor is shown in figure 2. The furnace, capable of burning 500 pounds of pulverized coal per hour, was designed to simulate the operation of a conventional wall-fired, dry-bottom unit such as those used in the utility industry. Coal is pulverized to 85 percent through 200 mesh prior to firing. Ash from pulverized-coal-fired furnaces is emitted largely in the effluent gas stream. In this furnace nearly 98 percent of the ash in the coal is emitted with the flue gas. Ash removal from the flue gas is accomplished by a single-stage cyclone collector,

with about 75-percent collection efficiency. Ash for the mercury determination study was obtained from "thief" samples of ash from the cyclone hopper. This sampling method utilizes a probe, or "thief," which extracts core samples from several positions in the hopper, thus providing a degree of representation. Flue gas temperature at the cyclone inlet was about 220° C. Coal samples used in the study were obtained by extracting a portion of the coal feed to the burners during operation, again providing a representative sample of the coal used during the combustion period.

Coals Used in 100-g/hr and 500-lb/hr Combustors

Table 1 shows the analyses of the coals used in the combustion experiments with the 100-g/hr and 500-lb/hr combustors. DRB-E is a washed, deep-mined Pittsburgh seam coal originating in Washington County, Pa. P-3 is a mixture of Tebo seam and Weir seam coals from Henry County, Mo., and MR is a Pittsburgh seam coal originating in Washington County, Pa.

TABLE 1. - Analysis of coals combusted (mf basis)

	DRB-E	P-3	MR
Proximate analysis, weight-percent:			
Volatile matter	35.8	37.8	37.7
Fixed carbon	57.3	40.6	52.2
Ash	6.9	21.6	10.1
Ultimate analysis, weight-percent:			
Hydrogen	5.1	4.4	5.0
Carbon	78.1	61.9	74.2
Nitrogen	1.6	1.0	1.5
Oxygen	7.1	5.9	7.1
Sulfur	1.2	5.2	2.1
Ash	6.9	21.6	10.1
Calorific value, Btu	13,970	11,190	13,310
Free swelling index	8	2.5	1.5

ANALYTICAL PROCEDURES

Mercury is determined on the coal, fly ash, flue gas, and scrubber solutions using a double gold amalgamation-atomic absorption procedure. The procedure is adapted from that used by Professor M. Suhr of the Pennsylvania State University.[a]

The double gold amalgamation apparatus is shown schematically in figure 3. Part A is a combined combustion and catalyst section, and parts B and C are successive gold traps. The three sections are constructed of 19-mm-OD Vycor brand tubing wound with resistance wire. The current input to each heating coil is controlled by a variable transformer. Integral 18/9 Vycor brand ball and socket joints fitted with Viton O-rings connect the three sections.

[a] A visit was made to Prof. Suhr's laboratory where the mercury analysis system was observed in operation.

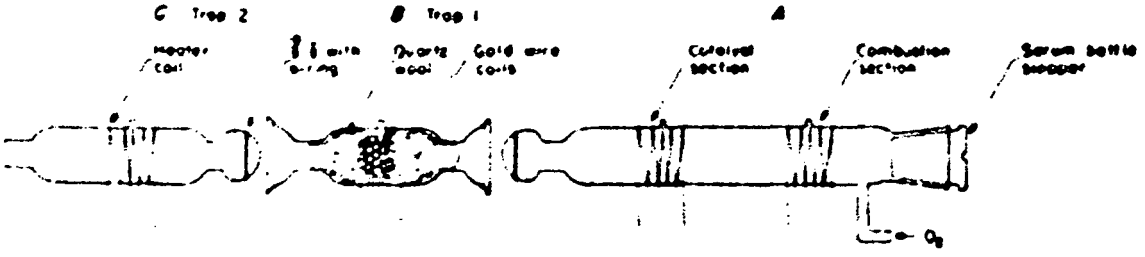

FIGURE 3. - Apparatus for Determination of Mercury by Double Gold Amalgamation.

The analysis train was designed with integral ball and socket joints so that the first gold trap could be removed from the system and used for the collection of mercury from air or flue gas. The flue gas collection train used on the 100-g/hr and the 500-lb/hr combustor was designed to accept part B. After collection of a sample, the gold trap is replaced in the analysis train and the analysis is completed by heating the trap to drive the mercury off the first gold trap and onto the second gold trap. Finally the mercury is driven off the second gold trap into the optical path of an atomic absorption spectrophotometer.

Calibration is accomplished by injecting mercury-saturated air into part A through the rubber septum at the end of part A. The calibration is periodically checked with National Bureau of Standards reference material 1630.

Mercury is volatized from the scrubber solutions by the Hatch and Ott procedure (6), passed through silica gel and magnesium perchlorate drying tubes, and amalgamated in the first gold section. It is then reamalgamated and finally measured in the atomic absorption spectrophotometer. By concentrating the mercury in this manner, the sensitivity is increased and interferences are removed.

The time required for the analysis of a 50- to 100-mg coal sample is about 15 minutes.

The sensitivity of the method was found to average about 1.5 nanograms for 1-percent absorption. Since the mercury hollow cathode tube produces a stable base line, a detection limit on the order of 0.6 nanogram is possible. (A typical calibration curve is shown in figure 4.)

RESULTS AND DISCUSSION

The results of the experiments conducted with the 100-g/hr combustor are summarized in table 2, and the results of the experiments conducted with the 500-lb/hr combustor are summarized in table 3.

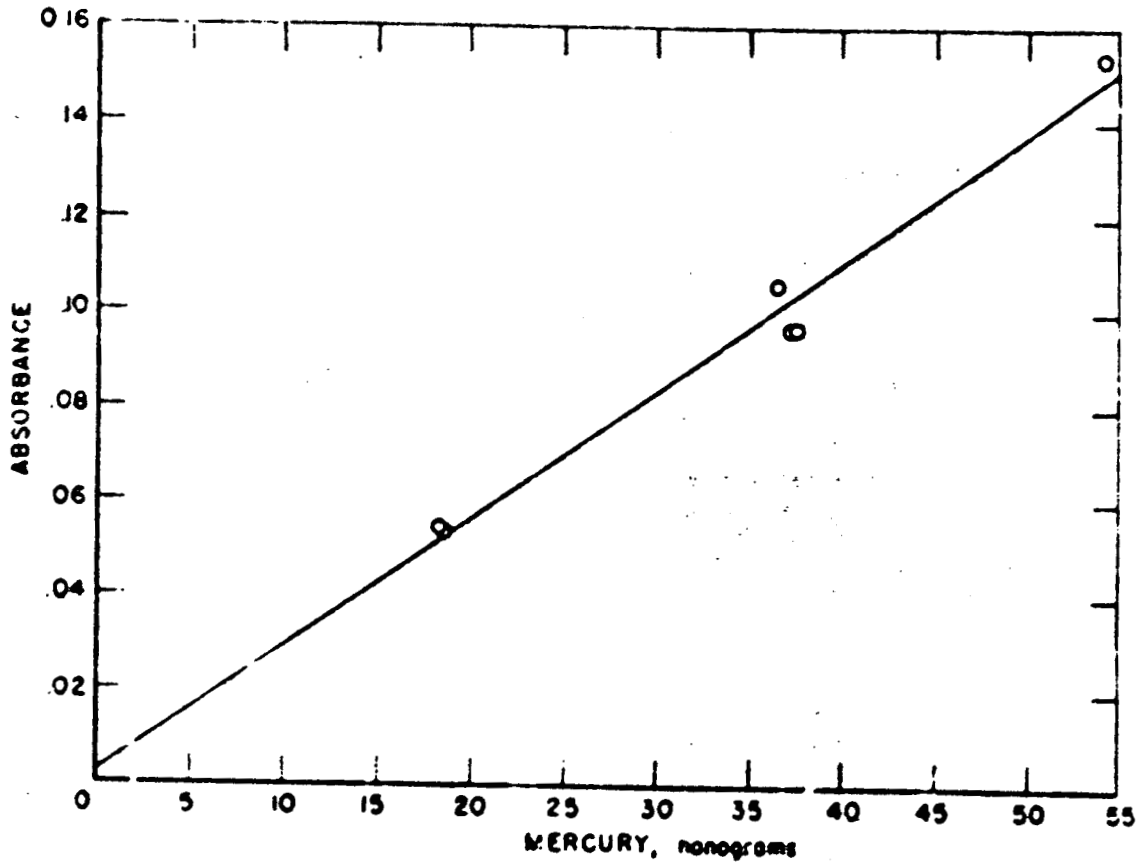

FIGURE 4. - Mercury Concentration Versus Absorbance.

TABLE 2. - 100-g/hr combustor: Summary of results

Coal	Run	Coal feed rate, g/hr	Combustion efficiency, percent	Fly ash production rate, g/hr	Mercury content (±1 standard deviation)			Percent of total mercury in fly ash	Percent of total mercury accounted for
					Coal, μg/g	Fly ash, μg/g	Flue gas, μg/m³		
DRB-E	1	98.1	97.6	9.1	[1]0.15±0.02	0.97±0.05	2.2	60	77
DRB-E	2	105.1	97.0	10.4		.83± .13	6.5	55	101
DRB-E	3	108.1	96.4	11.3		.95± .09	1.7	66	78
P-3	1	98.9	97.5	23.8	[2].24± .05	.31± .04	7.4	31	62
P-3	2	135.7	96.3	34.3		.35± .06	([3])	37	([3])
P-3	3	117.2	98.3	27.1		.37± .04	14.4	36	94

[1]Average value of 12 replicates for DRB-E
[2]Average value of 21 replicates for P-3.
[3]No flue gas sampling on this run.

TABLE 3. - 500-lb/hr combustor: Summary of results

Mercury in coal (MR).....μg Hg/g coal..	0.18±0.04
Number of replicates.....	23
Mercury in fly ash.....μg Hg/g ash...	0.22±0.04
Number of replicates.....	17
Percent of total mercury found in fly ash.....	12±3

Attempts at collecting the mercury from the flue gas have not been entirely successful. Initial attempts at using a gold trap revealed the following difficulties:

1. At trap temperatures of 100° to 150° C (high enough to prevent water condensation), the gold loses up to 15 percent of the mercury per hour.

2. At combustion efficiencies of 96 to 97 percent, sufficient combustion products condensed on the gold surface to cause occlusion of the mercury. In addition, when the gold was heated, the ultraviolet absorbing species condensed on the gold surface yielded erroneously high absorption signals at the mercury resonance line.

3. A silver trap heated to 500° C to catalyze the oxidation of the combustion products was not successful owing to the low oxygen levels (4 to 7 percent) in the flue gas.

4. A bubbler filled with 10 weight-percent nitric acid (HNO_3) did not trap all the mercury passing through the gold trap.

The next series of experiments planned will attempt to overcome the difficulties listed above by--

1. Using higher combustion efficiencies where possible.

2. Using a heated copper oxide furnace prior to the gold trap to oxidize the combustion products.

3. Using a two-bubbler system following the gold trap to increase the trapping efficiency for mercury vapor. One trap will contain acidic permanganate, and the other 10 weight-percent nitric acid.

Six separate experiments were conducted with the 100-g/hr combustor. The percentage of the original mercury found in the fly ash ranged from 31 to 66. The percentage of original mercury that could be accounted for ranged from 62 to 96. Each coal gave consistent results for the percentage of the total mercury from the coal that could be accounted for in the fly ash. It is significant that the values for the percentage of original mercury accounted for vary in approximately the same manner as the values for the amount of mercury found in the flue gas. This effect can be explained by the fact that the mercury in the flue gas was not quantitatively trapped. Therefore, the maximum quantity of mercury that could enter the environment via the flue

gas would be the amount of mercury accounted for in the analysis of the flue gas plus the mercury that was unaccounted for.

Samples of fly ash collected from three different coal-burning powerplants were analyzed for mercury. Table 4 gives descriptions of the powerplants sampled and the mercury found in the fly ashes. The first two powerplants produce about 250 megawatts and the third about 175 megawatts. All the fly ashes were found to contain mercury.

TABLE 4. - Summary of powerplant data

Type of firing	Steam conditions			Coal fired	Fly ash sample collection conditions	Mercury content of the fly ash, µg Hg/g
	Rate, 10^3 lb/hr	Pressure, psig	Temperature, °F			
Slag top, cyclone.	702	1,268	899	Illinois No. 6, Hvcb.	Mechanical collector hopper.	0.10±0.02
Slag top, pulverized coal.	723	1,293	799	Illinois No. 6, Hvcb.	Electrostatic precipitator hopper.	.26± .04
Dry bottom, tangential.	461	1,450	928	Kentucky No. 6, Hvbb.	Mechanical dusty collector hopper.	.22± .02

While a mercury material balance was not possible in the case of the powerplants, an estimate can be made for two of the powerplants based on available information. Ruch and coworker (9) found the average mercury content of Illinois No. 6 coal (based on 32 samples) to be 0.16±0.07 microgram mercury per gram (µg Hg/g) coal. As the average ash content of the coals is reported as 11.8 percent, the mercury accounted for in the ash would amount to 7 percent for the first powerplant and 19 percent for the second.

CONCLUSIONS

The investigations conducted to date indicate that, contrary to current assumptions, not all the mercury content of coal enters the environment as vapor when the coal is burned. In all cases observed in the present study, some of the mercury remained with the fly ash. Contact between the fly ash and flue gas after cooling was probably the reason for the retention of mercury in the fly ash. If this is true, then further contact at lower temperatures might lead to greater retention of mercury by the fly ash.

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