

# MERCURY EMISSION MEASUREMENT AT A CFB PLANT

Final Report

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## **JV 131 – MERCURY EMISSION MEASUREMENT AT A CFB PLANT**

### **ABSTRACT**

In response to pending regulation to control mercury emissions in the United States and Canada, several projects have been conducted to perform accurate mass balances at pulverized coal (pc)-fired utilities. Part of the mercury mass balance always includes total gaseous mercury as well as a determination of the speciation of the mercury emissions and a concentration bound to the particulate matter. This information then becomes useful in applying mercury control strategies, since the elemental mercury has traditionally been difficult to control by most technologies. In this instance, oxidation technologies have proven most beneficial for increased capture.

Despite many years of mercury measurement and control projects at pc-fired units, far less work has been done on circulating fluidized-bed (CFB) units, which are able to combust a variety of feedstocks, including cofiring coal with biomass. Indeed, these units have proven to be more problematic because it is very difficult to obtain a reliable mercury mass balance. These units tend to have very different temperature profiles than pc-fired utility boilers. The flexibility of CFB units also tends to be an issue when a mercury balance is determined, since the mercury inputs to the system come from the bed material and a variety of fuels, which can have quite variable chemistry, especially for mercury. In addition, as an integral part of the CFB operation, the system employs a feedback loop to circulate the bed material through the combustor and the solids collection system (the primary cyclone), thereby subjecting particulate-bound metals to higher temperatures again. Despite these issues, CFB boilers generally emit very little mercury and show good native capture.

The Energy & Environmental Research Center is carrying out this project for Metso Power in order to characterize the fate of mercury across the unit at Rosebud Plant, an industrial user of CFB technology from Metso. Appropriate solids were collected, and flue gas samples were obtained using the Ontario Hydro method, mercury continuous emission monitors, and sorbent trap methods. In addition, chlorine and fluorine were determined for solids and in the flue gas stream.

Results of this project have indicated a very good mercury mass balance for Rosebud Plant, indicating  $105 \pm 19\%$ , which is well within acceptable limits. The mercury flow through the system was shown to be primarily in with the coal and out with the flue gas, which falls outside of the norm for CFB boilers.

## TABLE OF CONTENTS

LIST OF FIGURES .....	ii
LIST OF TABLES .....	ii
NOMENCLATURE .....	iii
EXECUTIVE SUMMARY .....	iv
INTRODUCTION .....	1
Background .....	1
Project Summary .....	1
Project Participants.....	2
GOALS AND OBJECTIVES.....	2
DESCRIPTION OF TEST UNIT AND SAMPLING LOCATIONS.....	3
TESTING SCHEDULE AND METHODS .....	3
Hg CEM Sampling .....	5
OH Method Sampling .....	5
ST Method Sampling .....	6
Mini-ESPs .....	7
Solids Sampling and Mercury Balance .....	7
PROJECT RESULTS .....	7
Coal and Limestone Analysis.....	7
Ash Results.....	10
Flue Gas Sampling .....	10
Unit Operations and Plant Data.....	16
Mass Balances at Rosebud .....	16
CONCLUSIONS.....	18
ASSUMPTIONS AND CALCULATIONS .....	Appendix A

## LIST OF FIGURES

1	Schematic of Rosebud Station.....	4
2	Speciated mercury results across the unit .....	14
3	Hg CEM data.....	15
4	Boiler data .....	16
5	Stack CO <sub>2</sub> , moisture, and O <sub>2</sub> .....	17
6	SO <sub>x</sub> and NO <sub>x</sub> .....	17

## LIST OF TABLES

1	Test Program Organization and Responsibilities .....	2
2	Test Schedule for Rosebud Station Unit .....	4
3	Flue Gas-Sampling Test Matrix for Rosebud Station .....	4
4	Coal Analysis Results.....	8
5	Coal Mineral Analysis Results .....	8
6	Limestone Analysis Results .....	9
7	Limestone Mineral Analysis Results.....	9
8	Ash Analysis Results.....	11
9	Ash Mineral Analysis Results .....	12
10	Speciated Flue Gas Hg Results from OH Method Samples, $\mu\text{g}/\text{dNm}^3$ at 3% O <sub>2</sub> .....	14
11	Sorbent Trap Results, $\mu\text{g}/\text{dNm}^3$ at 3% O <sub>2</sub> .....	15
12	Flue Gas Component Data .....	19
13	Mercury Mass Balances at Rosebud .....	20

## NOMENCLATURE

AH	air heater
APCD	air pollution control device
ASTM	ASTM International
BH	baghouse
CELP	Colstrip Energy Limited Partnership
CEM	continuous emission monitor
CFB	circulating fluidized-bed
CVAAS	cold-vapor atomic absorption spectroscopy
DI	deionized
DOE	Department of Energy
EERC	Energy & Environmental Research Center
EPA	Environmental Protection Agency
ESP	electrostatic precipitator
FT-IR	Fourier transform infrared
LOI	loss on ignition
NIST	National Institute of Standards and Technology
OH	Ontario Hydro
pc	pulverized coal
PRB	Powder River Basin
QA/QC	quality assurance/quality control
ROSI	Rosebud Operating Services, Inc.
ST	sorbent trap
XRFA	x-ray fluorescence analysis

## JV TASK 131 – MERCURY EMISSION MEASUREMENT AT A CFB PLANT

### EXECUTIVE SUMMARY

In response to pending regulation to control mercury emissions in the United States and Canada, several projects have been conducted to perform accurate mass balances at pulverized coal (pc)-fired utilities. Part of the mercury mass balance always includes total gaseous mercury as well as a determination of the speciation of the mercury emissions and a concentration bound to the particulate matter. This information then becomes useful in applying mercury control strategies, since the elemental mercury has traditionally been difficult to control by most technologies. In this instance, oxidation technologies have proven most beneficial for increased capture.

Despite many years of mercury measurement and control projects at pc-fired units, far less work has been done on circulating fluidized-bed (CFB) units, which are able to combust a variety of feedstocks, including cofiring coal with biomass. Indeed, these units have proven to be more problematic because it is very difficult to obtain a reliable mercury mass balance. These units tend to have very different temperature profiles than pc-fired utility boilers. The flexibility of CFB units also tends to be an issue when a mercury balance is determined, since the mercury inputs to the system come from the bed material and a variety of fuels, which can have quite variable chemistry, especially for mercury. In addition, as an integral part of the CFB operation, the system employs a feedback loop to circulate the bed material through the combustor and the solids collection system (the primary cyclone), thereby subjecting particulate-bound metals to higher temperatures again. Despite these issues, CFB boilers generally emit very little mercury and show good native capture.

The Energy & Environmental Research Center (EERC) is carrying out this project for Metso Power in order to characterize the fate of mercury across the unit at Rosebud Plant, an industrial user of CFB technology from Metso. This unit is a nominal 42-MW boiler that produces electricity from the combustion of “waste” coal from the Rosebud Mine. Solids were sampled for this project, including coal and limestone inputs and bottom ash, fly ash, and air preheater ash as outputs. In addition, to establish a mercury mass balance, flue gas samples were obtained using the Ontario Hydro (OH) method, the sorbent trap method, and mercury continuous emission monitors (Hg CEMs).

Further, Metso Power indicated an interest in determining the mass balance for chlorine and fluorine across the system. Therefore, solids were analyzed for these halogens at the EERC. Metso Power personnel conducted halogen sampling using Fourier transform infrared (FT-IR) and presented the results to the EERC for establishing the system balance.

Results of this project have indicated a very good mercury mass balance for Rosebud plant, indicating  $105 \pm 19\%$ , which is well within acceptable limits. A Hg CEM showed an average over the 1-week period of  $7.4 \mu\text{g}/\text{dNm}^3$  at 3% O<sub>2</sub> at the stack. The OH method indicated that 3.5% of the flue gas at the baghouse inlet was particulate-bound Hg, confirming the minimal mercury capture across the baghouse. The OH method also indicated 23% oxidized Hg in the

flue gas at the baghouse inlet and stack. Sorbent trap analysis confirmed the gas-phase mercury measurements of the Hg CEMs at the stack and baghouse inlet.

Mineral mass balances indicated slightly more (130% mass balance) output than input according to the feed rates and estimated output flows for the system, which could be correct given the change in fuel and the amount of bed material circulating in the system at the beginning of the test period.

# **JV TASK 131 – MERCURY EMISSION MEASUREMENT AT A CFB PLANT**

## **INTRODUCTION**

### **Background**

Metso Power is one of the world's main suppliers of circulating fluidized-bed (CFB) combustors, with industrial applications of its power technologies located throughout the world. Metso focuses on power generation using solid fuels and excels at providing boilers that can burn a wide variety of opportunistic fuels, including biomass, coal, and refuse-derived fuels. As such, these boilers are valuable in industrial settings that wish to use their available feedstocks, including their industrial waste, to provide cogeneration of power and steam and/or hot water. Boilers using the Metso CFB technology are especially suited to small commercial applications of 350 MW or less, such as the boiler in this project.

The utility industry has gained a fairly clear understanding of mercury emissions from pulverized coal (pc)-fired generators, which has, to some extent, been applied in other industrial applications. However, significant data gaps for CFB units still exist for mercury. These units are difficult to understand because of the feedback loops for the bed material, which carries the bed material through the combustor several times, making it difficult to obtain a good mass balance or to determine the true amount of particulate-bound mercury at a given time. In addition, mercury comes from not only the fuels, but from the bed material, limestone in this case. Both of these system inputs can have tremendous variability.

Because of the expertise the Energy & Environmental Research Center (EERC) has gained in conducting mercury measurement for several types of plants, including those for CFBs, the EERC was chosen to conduct testing to obtain a valid and reliable mercury balance across the Metso combustor at the Rosebud Power Plant.

### **Project Summary**

Rosebud Power Plant, which served as the host site for this project, is owned by the Colstrip Energy Limited Partnership (CELP) and operated by Rosebud Operating Services, Inc. (ROSI). Rosebud Power Plant has a CFB combustor that burns local Powder River Basin coal for the production of power. This project involved a 1-week sampling campaign in May 2008 to address the need to obtain an accurate mercury balance across Metso's CFB combustor. The goal of the project was to evaluate mercury speciation, capture, and emissions in the flue gas and to perform a mercury mass balance by collecting solid samples entering and leaving the unit while the unit operations and coal supply were maintained at steady-state conditions. In addition, Metso wanted to determine the mineral balances across the system. Chemical analysis of solids by the EERC was complemented by Fourier transform infrared (FT-IR) sampling conducted on the unit by Metso personnel.

## Project Participants

The EERC led this project for Metso Power, with cofunding provided by the U.S Department of Energy (DOE) National Energy Technology Laboratory. Table 1 outlines the project organizational structure and indicates the primary people who were responsible for the tests at Rosebud’s facilities.

**Table 1. Test Program Organization and Responsibilities**

Person and Project Role	Contact Information
Reyhaneh Shenassa, Metso Power Project Advisor	(704) 541-1453 reyhaneh.shenassa@metso.com
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## GOALS AND OBJECTIVES

The overall goal of the testing at the Rosebud Power Plant was to evaluate mercury speciation and emissions and perform a mercury balance across the unit. In addition, Metso Power later added to the original scope of work, indicating a desire to obtain a solids analysis for chlorine and fluorine. The specific objectives to support this goal include the following:

- Measure mercury flue gas concentrations using Hg continuous emission monitors (Hg CEMs) at the inlet and outlet of the baghouse (BH).
- Acquire mercury speciation data with the Ontario Hydro (OH) method at three locations in the power system: air heater (AH) inlet, BH inlet, and BH outlet (same as the stack location).
- Validate the Hg CEM data using a sorbent trap (ST) method sampling at the BH inlet and outlet.
- Measure O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, and CO concurrently with OH method sampling.

- Conduct sampling of coal, limestone, bottom ash, AH hopper ash, and BH hopper ash to establish mercury concentrations.
- Establish a mercury material balance to track and understand the fate of mercury across the boiler, AH, and BH.
- Assess mercury emissions from the test unit and quantify the reduction obtained across the unit.
- Measure F and Cl in the flue gas using FT-IR (by Metso Power personnel), and compare this to chemical analysis of system feedstocks and by-products conducted at EERC laboratories.

## **DESCRIPTION OF TEST UNIT AND SAMPLING LOCATIONS**

Rosebud Station is located 6 miles north of Colstrip, Montana. The unit has been operational since 1990. Specific unit information is outlined below:

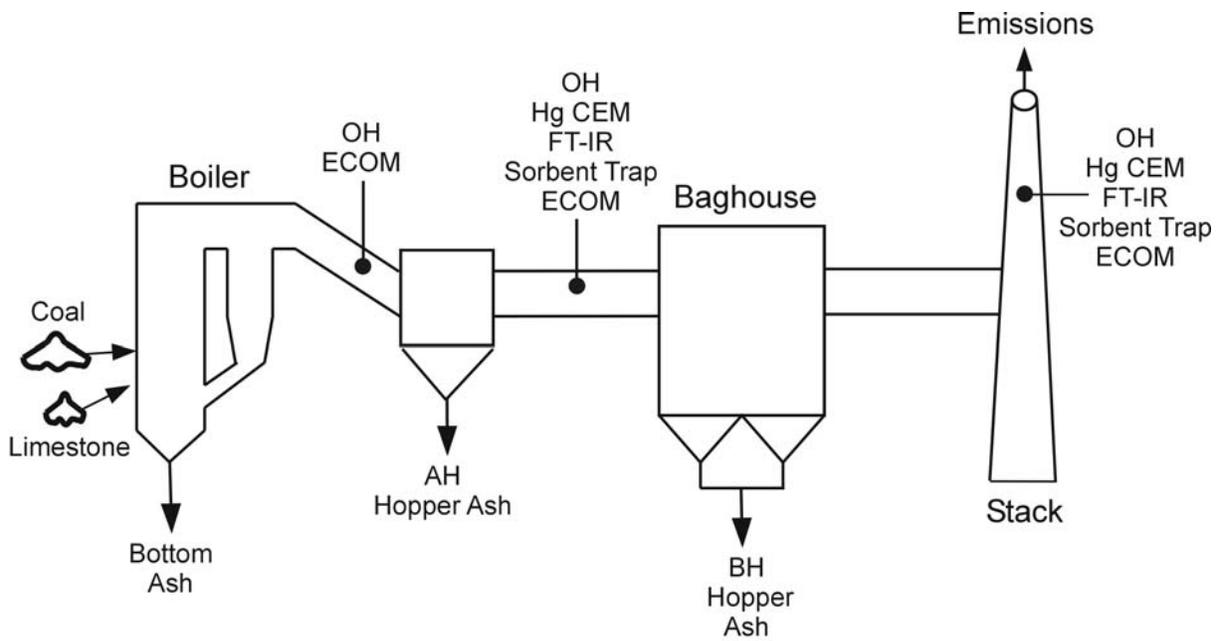
- The boiler is a CFB combustor manufactured by Metso Power that produces 42 MW of energy; four coal feeders provide fuel.
- The fuel for the system is a locally mined Powder River Basin (PRB) coal from the Rosebud Western Energy Mine.
- The system also uses limestone as bed material, also obtained locally.
- The sole air pollution control device (APCD) is a nine-compartment baghouse manufactured by Brandt Environmental Corporation.

A schematic of the unit with sampling locations is shown in Figure 1.

## **TESTING SCHEDULE AND METHODS**

This project was conducted in May 2008 by the EERC, with FT-IR sampling conducted by Metso Power personnel. A mobile laboratory system was taken on-site at Rosebud by the EERC in order to perform in-field analysis of the OH method and ST method samples. This was critical in order to establish both the total mercury concentrations at the BH inlet and outlet, as well as to determine the mercury speciation across the system.

The test schedule for this project is shown in Table 2. The flue gas sampling matrix and test methods that were used for various parameters are shown in Table 3.



EERC JT32008.CDR

Figure 1. Schematic of Rosebud Station.

**Table 2. Test Schedule for Rosebud Station Unit**

Testing Dates	Activities
5/16/08	Travel, safety orientation, preparatory systems setup
5/17/08–5/18/08	Sampling systems setup and shakedown to ensure valid results
5/19/08–5/21/08	Sampling using Hg CEMs, OH, ST, ECOM, <sup>1</sup> FT-IR, solids
5/22/08–5/23/08	Sampling: Hg CEMs, ECOM, FT-IR, solids
5/24/08–5/25/08	Teardown, travel

<sup>1</sup> ECOM America.

**Table 3. Flue Gas-Sampling Test Matrix for Rosebud Station**

Sampling Method (parameters)	AH Inlet	BH Inlet	Stack
OH (Hg)	Three samples	Three samples	Three samples
ST (Hg)		Three paired traps	Three paired traps
Hg CEM (Hg)		Continuous	Continuous
FT-IR (F, Cl)		3 days	2 days
ECOM (O <sub>2</sub> , CO <sub>2</sub> , SO <sub>2</sub> , NO, NO <sub>2</sub> , CO)	5 days	5 days	5 days

## Hg CEM Sampling

Sampling, mentioned in the table above, was performed using several methods. Hg CEMs used on this project were manufactured by Tekran. The systems are based upon atomic fluorescence spectroscopy as the base analytical method and use of a set of gold traps for preconcentration. A wet-chemistry conversion system precedes the analyzer and uses a liquid flow path to continuously reduce  $\text{Hg}^{2+}$  to elemental mercury ( $\text{Hg}^0$ ), resulting in a sample stream of total mercury. Although data are obtained every 2.5 minutes, the data are normalized to a 15-minute average. One Hg CEM was located at the inlet to the BH, and one was sited at the BH outlet/stack. The systems are calibrated daily using  $\text{Hg}^0$  as the primary standard to ensure proper quality assurance/quality control (QA/QC). In addition, a Cavkit consisting of a  $\text{Hg}^0$  source was used to verify convenience of a known concentration of mercury through the probe, conversion unit, and analyzer.

## OH Method Sampling

The OH method (ASTM D6784-02) is a U.S. Environmental Protection Agency (EPA)-approved method used to obtain both total and speciated mercury concentrations, as well as particulate-bound mercury concentrations, using wet-chemistry sampling methods. The OH method was used to periodically measure flue gas mercury concentrations and provide mercury speciation data. Sampling occurred simultaneously at the AH inlet, the BH inlet, and the BH outlet/stack.

OH method samples were withdrawn from the flue gas stream isokinetically through a probe/mini-electrostatic precipitator (ESP)/filter system, maintained at the flue gas temperature, followed by a series of impinger solutions in an ice bath. Particle-bound mercury ( $\text{Hg}_p$ ) was collected in the mini-ESP and on a quartz filter in the front half of the sampling train.  $\text{Hg}^{2+}$  was collected in impingers containing a chilled aqueous potassium chloride solution.  $\text{Hg}^0$  was collected in subsequent impingers (one impinger containing a chilled aqueous acidic solution of hydrogen peroxide and three impingers containing chilled aqueous acidic solutions of potassium permanganate).

Samples were recovered and analyzed for mercury in the EERC mobile lab set up on-site. The OH method samples were typically prepared and analyzed the same day of collection or the following day. Hg was determined by CVAAS using a Leeman Labs Hydra AA automated Hg analyzer. Results were initially reported as  $\mu\text{g/L}$  and then converted to  $\mu\text{g/dNm}^3$ .

The instrument used in the field for mercury determination was a Leeman Hydra AA. The instrument was set up for absorption at 253.7 nm, with a carrier gas of nitrogen and 10% stannous chloride in 10% HCl as the reductant. Each day the tubing was checked, and the rinse container was cleaned and filled with a fresh solution of 10% HCl. After the pump and lamp were turned on and warmed up for 45 minutes, the aperture was set to manufacturer specifications. A four-point calibration curve was then completed. The detector response for a given standard was logged and compared to specifications to ensure the instrument had been properly set up. A QC standard of a known analyte concentration was analyzed immediately after the instrument was standardized in order to verify the calibration. This QC standard was

prepared from a different stock than the calibration standards. It was required that the values obtained read within 5% of the true value before the instrument was used for sample analysis. After the initial QC standard was completed, a check standard was run every ten samples to check the slope of the calibration curve. This check fell within  $\pm 10\%$  of the current calibration curve or recalibration was required. One in every ten samples was run in triplicate and spiked to verify analyte recovery. Triplicate results fell within 10% of the average, and spiked samples were within  $\pm 15\%$  of the true value, or repeat analysis of the set of samples was required. A QC chart is also maintained at the EERC to monitor the long-term precision of the instrument.

All data sheets, volumetric flasks, and sample containers used for sample recovery were marked with preprinted labels to ensure proper cross-referencing. The liquid samples were recovered into premarked volumetric flasks, logged, and then analyzed on-site. The filter samples were placed in premarked sample containers and then taken back to the EERC, where they were analyzed. The labels contained identifying data including date, time, run number, sample port location, and project identifier.

All glass volumetric flasks and transfer pipets used in the preparation of analytical reagents and calibration standards were designated as Class "A" to meet federal specifications. Prior to being used for sampling, all glassware was washed with soapy water, rinsed with deionized (DI) water, soaked in 10%  $\text{V/V}$  nitric acid for a minimum of 4 hours, rinsed an additional three times with DI water, and dried. The glassware was stored in closed containers until it was used at the plant.

All acids used for the analysis of mercury were trace metal-grade. Other chemicals used in the preparation of analytical reagents were analytical reagent-grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within  $\pm 0.5\%$  and traceable to the National Institute of Standards and Technology (NIST) standard reference materials.

As part of QA/QC procedures, a field blank was associated with sampling at each location for the test period. A field blank is defined as a complete impinger train, including all glassware and solutions that are taken to the location during sampling and exposed to ambient conditions. These sample trains were then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. Field blanks are used to identify contamination.

Also as part of QA/QC, a field spike was associated with each OH method test day. A field spike was prepared by the field manager at a level similar to the field samples. These sample trains were taken apart and the solution recovered and analyzed in the same manner as those sample trains used for sampling activities. The target range, as per the method, for recovery of the field spike is  $\pm 20\%$ . All field spike recoveries were within the target range.

### **ST Method Sampling**

To further assist validation of the Hg CEM measurements, the EERC collected six ST method samples (three at the BH inlet and three at the stack). ST sampling has been shown appropriate and accurate for short-term mercury measurement in pc-fired combustion units and

was successfully evaluated as part of this project. The ST samples were collected following the EPA Method 30B procedure with dual two-stage traps. Samples were recovered and analyzed for mercury in the EERC mobile lab set up on-site.

### **Mini-ESPs**

Because of the dust loading at the AH and BH inlet locations and the potential bias in mercury speciation that can result as part of the sampling method, OH method sampling at the two inlet locations was carried out using miniature (sampling-sized) ESPs prior to the impinger train to minimize or eliminate the bias in mercury speciation seen as a result of pulling the flue gas through a packed bed on the sample filter. This methodology was necessary to obtain accurate particulate-bound mercury data, which are critical to the understanding of the fate of the mercury across the PCD. This is especially true for the case of a CFB, where the relatively high amount of unburned carbon typically results in a significant bias toward particulate-bound mercury when only a filter is used for OH method sampling. During testing at the Rosebud Power Plant, the ESPs were used during the first set of OH method samples to determine the lack of particulate-bound Hg in the fly ash upstream of the baghouse and also to verify the lack of bias in the sampling method because of the use of a filter element. Subsequent sampling utilized EPA Method 17 in-stack filtration to accurately measure Hg species in the flue gas.

### **Solids Sampling and Mercury Balance**

For this project, samples were taken twice a day for the system inputs, coal and limestone, and by-products, which included bottom ash, AH ash, and BH hopper ash. Solid samples were analyzed for Hg and, along with mass flow data provided by the plant data collection system (DCS), were used to calculate the mass flows of mercury in and out of the system. These data were used to determine the fate of Hg across the system, and mass balances were calculated for each set of samples.

## **PROJECT RESULTS**

### **Coal and Limestone Analysis**

Coal samples were collected from the drop chutes (four) at Rosebud prior to the belts and were combined into two composites daily (sampled twice a day) for the 5-day sampling campaign; these 1-gallon samples were taken to the EERC for analysis. A total of ten coal samples were analyzed for Hg, Cl, F, proximate-ultimate, and Btu analyses using standard ASTM International (ASTM) or EPA methods as part of the EERC project. The limestone was sampled from the taps (two) in the limestone building.

Chemical analysis results for the coal and limestone are shown in Tables 4 through 7.

Proximate and ultimate analyses were conducted on the composite coal samples using ASTM Methods D3172, D5142, and D3176. A Mitsubishi Model TOX-100 total chlorine

**Table 4. Coal Analysis Results**

	Date:	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	Time:	12:15	16:55	10:05	15:35	8:00	15:00	8:30	13:30	8:40	14:15
Hg	µg/g (dry)	0.107	0.104	0.0726	0.0555	0.0649	0.0581	0.0603	0.0527	0.0754	0.0848
Cl	µg/g (dry)	9.0	6.2	<5	5.4	14.5	7.4	<5	5.6	6.0	6.8
F	µg/g (dry)	52.9	52.2	51.8	53.9	56.1	51.7	52.0	53.2	58.0	60.4
Proximate											
Moisture	wt%	22.80	24.50	25.40	24.50	24.30	25.40	25.40	25.70	25.00	25.50
Volatile Matter	wt%	27.57	27.38	26.86	27.46	28.20	27.96	27.95	28.22	28.06	30.88
Fixed Carbon	wt%	35.71	37.69	37.51	37.93	37.79	37.73	37.85	37.53	38.10	34.50
Ash	wt%	13.92	10.43	10.23	10.11	9.71	8.91	8.79	8.55	8.83	9.12
Ultimate											
H	wt%	5.95	6.15	6.33	6.16	6.31	6.24	6.24	6.43	6.22	6.32
C	wt%	49.70	50.04	49.64	50.26	51.32	50.64	50.66	50.70	50.40	49.58
N	wt%	0.96	0.97	0.95	0.97	0.99	0.99	0.99	0.97	0.94	0.96
S	wt%	1.20	0.73	0.71	0.68	0.69	0.74	0.75	0.66	0.73	0.71
O	wt%	28.26	31.68	32.14	31.82	30.98	32.48	32.57	32.69	32.87	33.30
Heating Value	Btu/lb	8225	8539	8327	8500	8540	8468	8531	7849	8590	8339

∞

**Table 5. Coal Mineral Analysis Results**

	Date:	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	Time:	12:15	16:55	10:05	15:35	8:00	15:00	8:30	13:30	8:40	14:15
SiO <sub>2</sub>	wt%	6.85	4.45	4.40	4.32	4.02	3.67	3.60	3.65	3.79	3.95
Al <sub>2</sub> O <sub>3</sub>	wt%	2.06	1.83	1.87	1.96	1.85	1.70	1.71	1.69	1.80	1.77
Fe <sub>2</sub> O <sub>3</sub>	wt%	1.00	0.57	0.55	0.65	0.57	0.60	0.46	0.46	0.52	0.53
TiO <sub>2</sub>	wt%	0.13	0.08	0.08	0.08	0.07	0.07	0.07	0.07	0.07	0.07
P <sub>2</sub> O <sub>5</sub>	wt%	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
CaO	wt%	1.03	1.03	1.03	1.04	1.00	0.89	0.92	0.91	0.87	0.86
MgO	wt%	0.48	0.43	0.44	0.45	0.44	0.39	0.41	0.40	0.40	0.38
Na <sub>2</sub> O	wt%	0.03	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01
K <sub>2</sub> O	wt%	0.08	0.08	0.08	0.07	0.07	0.06	0.06	0.06	0.06	0.07
SO <sub>3</sub>	wt%	2.17	1.86	1.68	1.45	1.60	1.46	1.48	1.23	1.25	1.40
Closure <sup>1</sup>	%	99.6	99.5	99.5	99.5	99.6	99.6	99.6	99.5	99.5	99.4

<sup>1</sup>As calculated from the coal ash analysis.

**Table 6. Limestone Analysis Results**

	Date:	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	Time:	12:20	17:05	10:10	15:40	8:00	15:15	8:30	13:35	8:45	14:20
Hg	µg/g (dry)	0.0060	0.0060	0.0060	0.0060	0.0061	0.0080	0.0081	0.0079	0.0061	0.0040
Cl	µg/g (dry)	21	13	9	10	10	12	48	8	7	6

**Table 7. Limestone Mineral Analysis Results**

	Date:	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	Time:	12:20	17:05	10:10	15:40	8:00	15:15	8:30	13:35	8:45	14:20
SiO <sub>2</sub>	wt%	5.3	5.9	5.8	6.1	6.2	6.4	6.1	5.5	5.8	4.9
Al <sub>2</sub> O <sub>3</sub>	wt%	0.9	1.0	0.9	1.0	1.2	1.2	1.0	1.0	1.0	0.9
Fe <sub>2</sub> O <sub>3</sub>	wt%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO <sub>2</sub>	wt%	0.06	0.06	0.06	0.06	0.08	0.08	0.06	0.07	0.07	0.06
P <sub>2</sub> O <sub>5</sub>	wt%	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
CaO	wt%	53.3	52.8	52.7	53.1	52.9	52.1	52.7	53.3	53.1	54.3
MgO	wt%	0.60	0.61	0.60	0.61	0.61	0.67	0.64	0.65	0.63	0.58
Na <sub>2</sub> O	wt%	0.06	0.07	0.06	0.06	0.07	0.06	0.06	0.06	0.06	0.06
K <sub>2</sub> O	wt%	0.09	0.11	0.10	0.11	0.15	0.16	0.12	0.11	0.11	0.09
SO <sub>3</sub>	wt%	0.10	0.11	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Closure <sup>1</sup>	%	60.4	60.7	60.3	61.1	61.2	60.7	60.7	60.7	60.8	60.9

<sup>1</sup>Low values due to the presence of carbonate in the sample.

analyzer was used to perform ASTM Method D6721-01 (Standard Test Method for Determination of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry). ASTM D5987 Total Fluorine in Coal and Coke by Pyrohydrolytic Extraction and Ion Selective Electrode or Ion Chromatograph Method was used for fluorine determination. Coal Hg content was determined using CVAAS according to EPA Method 245.1 and EPA SW-846 Method 7470. Coal samples were subjected to preparation via low-temperature ashing and, along with limestone, were analyzed for mineral analysis using ASTM D4326 Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence. By convention, these results are reported as the oxides. The coal data were converted to percent oxides in the coal based on the ash content of the coal. The closure values for the coal are those from the analysis of the coal ash. These values show the completeness of the analysis; the numbers are slightly lower than 100% primarily because of the unburned carbon remaining in the sample. The closure values for the limestone are near 60% because of the presence of carbonate (the actual sample is CaCO<sub>3</sub> not CaO as reported by convention) which is not detected with the method.

### **Ash Results**

The particle-bound Hg in the ash samples was determined using EPA Method 7473 (Mercury in Solids and Solutions by Thermal Decomposition Amalgamation and Atomic Absorption Spectrophotometry). Hg concentrations were reported as µg/g on a dry basis.

Bottom ash, AH hopper ash, and BH hopper ash samples were collected and combined into their respective composite samples (two a day). The bottom ash was collected from the taps (both east and west sides) on the conveyor prior to the hoppers on the ground level. It should be noted that the test coal produced less bottom ash than normal, with no amount obtained for some of the test days. The AH hopper ash was sampled from the two hopper compartments. The BH ash samples were collected from the nine hoppers (compartments) in the BH.

Each of the ash samples was analyzed for Hg, Cl, F, and loss on ignition (LOI) using standard ASTM or EPA methods at the EERC. The ash samples were also subjected to mineral analysis (XRFA [x-ray fluorescence analysis]) to determine chemical composition. Tables 8 and 9 show the chemical analyses that were performed for the by-product samples.

### **Flue Gas Sampling**

Flue gas sampling for mercury consisted of the OH method, ST sampling, and operation of two Hg CEMs. The three locations for flue gas sampling (shown in Figure 1) provide mercury flue gas data for the economizer outlet/AH inlet (~500°F), BH inlet (prior to dust removal, ~350°F), and at the stack (~340°F). OH method sampling was conducted to obtain flue gas samples from the AH inlet duct, the BH inlet duct, and the stack. These samples were collected simultaneously to obtain the most representative data for the comparison of mercury concentrations and speciation across the unit. Figure 2 shows the OH method data with averages and an error bar representing one standard deviation. Table 10 lists the speciated mercury data for each of the OH method samples.

**Table 8. Ash Analysis Results**

Date:		5/19/08	5/19/08	5/20/08	5/21/08	5/22/08					
Time:		13:40	18:50	16:45	12:30	11:00					
Bottom Ash											
Hg	µg/g (dry)	0.0040	<0.002	0.0039	0.0020	0.0020					
Cl	µg/g (dry)	6.0	6	7	9	6					
F	µg/g (dry)	80.0	82	82	83	81					
LOI	%	1.03	0.44	1.28	4.62	2.01					
AH Hopper											
Date:		5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
Time:		13:35	17:15	10:20	18:00	12:45	18:00	11:00	18:10	11:35	15:00
Hg	µg/g (dry)	0.0049	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Cl	µg/g (dry)	19.0	20	13	15	14	15	14	15	15	20
F	µg/g (dry)	67.0	81	79	81	96	100	101	81	86	94
LOI	%	0.31	0.52	0.21	0.96	0.67	0.55	0.36	0.84	0.24	0.67
BH Composite											
Date:		5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
Time:		12:00	13:40	8:00	14:10	8:00	12:50	8:00	11:30	8:00	12:00
Hg	µg/g (dry)	0.0239	0.0100	0.0100	0.0080	0.0100	0.0080	0.0081	0.0020	0.0120	0.0120
Cl	µg/g (dry)	46.7	35.0	39.1	35.2	39.2	34.4	31.5	21.6	36.1	35.0
F	µg/g (dry)	142	176	172	173	188	194	157	123	172	162
LOI	%	3.86	1.82	2.02		3.59	2.43	2.29	3.01	4.28	4.80

**Table 9. Ash Mineral Analysis Results**

Bottom Ash	Date:	5/19/08	5/19/08	5/20/08	5/21/08	5/22/08
	Time:	13:40	18:50	16:45	12:30	11:00
SiO <sub>2</sub>	wt%	33.4	30.9	32.8	26.1	28.2
Al <sub>2</sub> O <sub>3</sub>	wt%	4.1	4	3.8	4.6	4.4
Fe <sub>2</sub> O <sub>3</sub>	wt%	6.29	6.31	6.44	8.51	7.67
TiO <sub>2</sub>	wt%	0.33	0.33	0.31	0.37	0.36
P <sub>2</sub> O <sub>5</sub>	wt%	0.08	0.08	0.08	0.09	0.08
CaO	wt%	46.8	50.4	48.2	50.4	48.8
MgO	wt%	1.37	1.38	1.35	1.52	1.42
Na <sub>2</sub> O	wt%	0.15	0.15	0.14	0.14	0.24
K <sub>2</sub> O	wt%	0.50	0.52	0.05	0.47	0.48
SO <sub>3</sub>	wt%	6.56	5.48	5.99	7.22	7.85
Closure	%	99.6	99.6	99.2	99.4	99.5

AH Ash	Date:	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	Time:	13:35	17:15	10:20	18:00	12:45	18:00	11:00	18:10	11:35	15:00
SiO <sub>2</sub>	wt%	23.4	22.9	25.8	23.5	25.7	25.5	21.5	23.6	20.7	20.3
Al <sub>2</sub> O <sub>3</sub>	wt%	6.1	6.2	6.7	6.0	6.5	6.2	6.0	6.5	6.0	5.7
Fe <sub>2</sub> O <sub>3</sub>	wt%	6.09	5.41	6.12	5.84	5.98	6.75	5.41	4.99	5.56	5.53
TiO <sub>2</sub>	wt%	0.34	0.33	0.34	0.33	0.33	0.34	0.32	0.31	0.30	0.29
P <sub>2</sub> O <sub>5</sub>	wt%	0.09	0.08	0.09	0.09	0.09	0.09	0.09	0.09	0.08	0.07
CaO	wt%	55.8	57.3	52.9	56.4	54.0	52.9	59.4	57.6	59.3	58.8
MgO	wt%	1.41	1.38	1.42	1.38	1.41	1.48	1.39	1.38	1.29	1.26
Na <sub>2</sub> O	wt%	0.16	0.16	0.17	0.17	0.16	0.16	0.14	0.16	0.16	0.15
K <sub>2</sub> O	wt%	0.69	0.68	0.71	0.67	0.66	0.63	0.60	0.65	0.52	0.49
SO <sub>3</sub>	wt%	5.24	4.88	4.99	4.94	4.63	5.44	4.64	4.22	5.47	6.75
Closure	%	99.3	99.3	99.2	99.3	99.5	99.5	99.5	99.5	99.4	99.3

Continued...

**Table 9. Ash Mineral Analysis Results (continued)**

BH Composite	Date:	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	Time:	12:00	13:40	8:00	14:10	8:00	12:50	8:00	11:30	8:00	12:00
SiO <sub>2</sub>	wt%	21.0	18.5	18.5	18.9	20.0	19.4	17.8	22.8	17.0	17.7
Al <sub>2</sub> O <sub>3</sub>	wt%	7.7	6.7	6.8	7.0	7.6	7.3	6.6	6.2	6.7	7.0
Fe <sub>2</sub> O <sub>3</sub>	wt%	2.16	1.78	1.53	1.57	1.58	1.80	1.86	3.28	1.63	2.34
TiO <sub>2</sub>	wt%	0.49	0.43	0.42	0.43	0.46	0.44	0.40	0.31	0.41	0.40
P <sub>2</sub> O <sub>5</sub>	wt%	0.10	0.10	0.11	0.11	0.11	0.11	0.10	0.09	0.10	0.09
CaO	wt%	52.4	57.0	58.4	59.1	60.4	61.5	63.1	60.5	60.7	62.9
MgO	wt%	1.76	1.64	1.65	1.67	1.77	1.71	1.63	1.33	1.60	1.58
Na <sub>2</sub> O	wt%	0.24	0.13	0.11	0.11	0.12	0.11	0.11	0.16	0.11	0.12
K <sub>2</sub> O	wt%	0.47	0.42	0.41	0.44	0.44	0.44	0.39	0.73	0.35	0.33
SO <sub>3</sub>	wt%	7.61	6.20	6.53	6.74	6.83	6.52	5.59	3.87	6.21	6.78
Closure	%	93.9	92.9	94.5	96.1	99.3	99.3	97.6	99.3	94.8	99.2

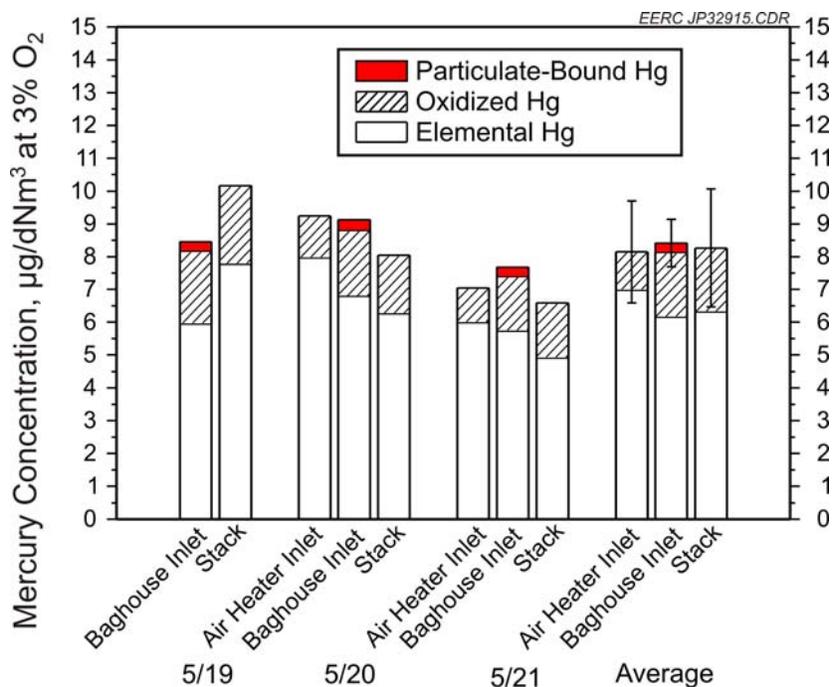


Figure 2. Speciated mercury results across the unit.

**Table 10. Speciated Flue Gas Hg Results from OH Method Samples,  $\mu\text{g}/\text{dNm}^3$  at 3%  $\text{O}_2$**

	Date:	5/19/08	5/20/08	5/21/08
Stack	Time:	11:20	10:00	9:25
Particulate		0.011	<0.00002	0.00002
Oxidized		2.39	1.79	1.68
Elemental		7.77	6.25	4.91
Total		10.17	8.04	6.59
	Date:	5/19/08	5/20/08	5/21/08
BH Inlet	Time:	11:20	10:00	9:27
Particulate		0.29	0.32	0.28
Oxidized		2.22	2.01	1.66
Elemental		5.94	6.79	5.73
Total		8.45	9.12	7.67
	Date:	5/20/08	5/21/08	
AH Inlet	Time:	10:05	9:50	
Particulate		<0.05	<0.05	
Oxidized		1.28	1.06	
Elemental		7.96	5.99	
Total		9.24	7.04	

The speciation data show that there is very little particulate-bound Hg in the flue gas, which explains the low capture of mercury across the baghouse. There is some oxidized mercury present (~20%), which would indicate the possibility of capturing some of the mercury with injection of sorbent material. To obtain significant capture of mercury for this unit would most likely require the use of a sorbent enhancement additive as well as a sorbent.

Sorbent trap samples were collected at the BH inlet and stack simultaneously. The primary purpose for collecting these samples was to get comparable data (total gas-phase mercury) to validate the CMMs. Three sets of inlet/outlet sorbent trap samples were collected. Table 11 lists the results of these samples. The ST sampling was carried out using duplicate two-section traps as outlined in Method 30B. All the sample traps showed less than 5% breakthrough (percentage in the second section) and less than 10% relative deviation between the duplicate traps as required by the method for valid samples.

Two Hg CEMs were operated: one at the stack and one at the baghouse inlet. The Hg CEM data were averaged for each 15-minute time frame and corrected to 3% O<sub>2</sub>. Figure 3 shows the data for the CEMs.

**Table 11. Sorbent Trap Results,  $\mu\text{g}/\text{dNm}^3$  at 3% O<sub>2</sub>**

Date and Time	5/19/08 16:40	5/20/08 14:05	5/21/08 13:50
Stack	7.7	7.7	7.7
BH Inlet	7.3	7.4	9.6

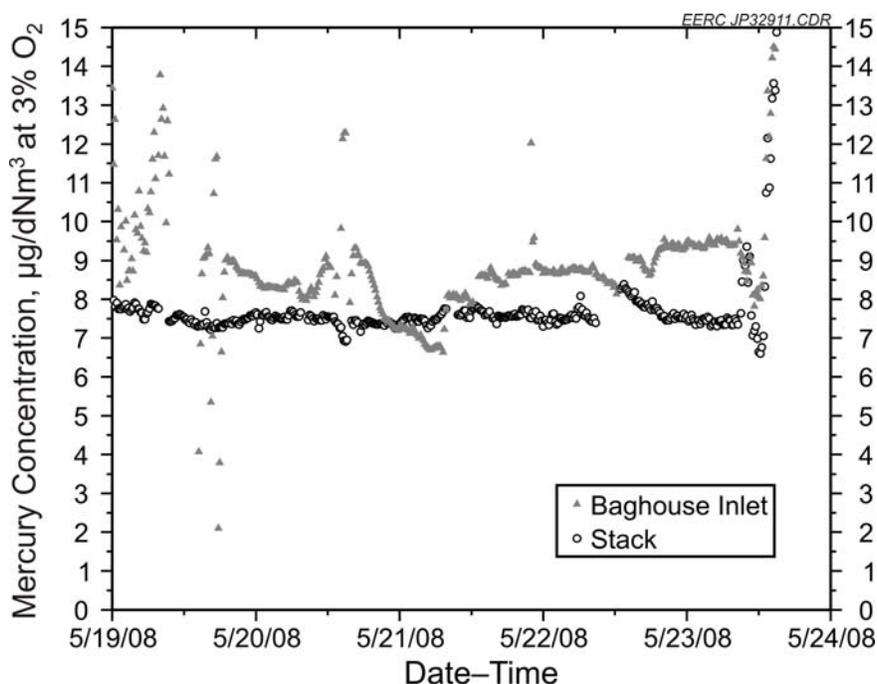


Figure 3. Hg CEM data.

The data show fairly consistent mercury emissions with the exception of Friday (5/23/08) afternoon. As part of the testing, sootblowing was completed before the testing started to avoid any effects it might have had on mercury emissions during testing. On Friday afternoon, sootblowing was carried out specifically to capture those effects. As the data show, an increase in mercury emissions was shown during sootblowing activities.

### Unit Operations and Plant Data

As part of the test sequence, the test fuel was started on the Friday prior to testing (5/16/08), and as mentioned, sootblowing activities were carried out prior to sampling activities. Plant DCS data were collected in parallel to the sampling activities to monitor gas flow, unit load, coal and limestone feed, as well as CEM data. Figures 4–6 detail the boiler information and CEM data.

In addition to the plant data, a portable flue gas analyzer was used to sample flue gas components twice a day. Table 12 shows the data collected for O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, and CO. The data show the consistency of the unit over the week of testing.

### Mass Balances at Rosebud

Mass balances for mercury were calculated from the flow data and analytical data and are shown in Table 13. The average mercury mass balance was 105% which is reasonable given the complexity of the system and the nature of trace elements such as mercury. Mass balances were

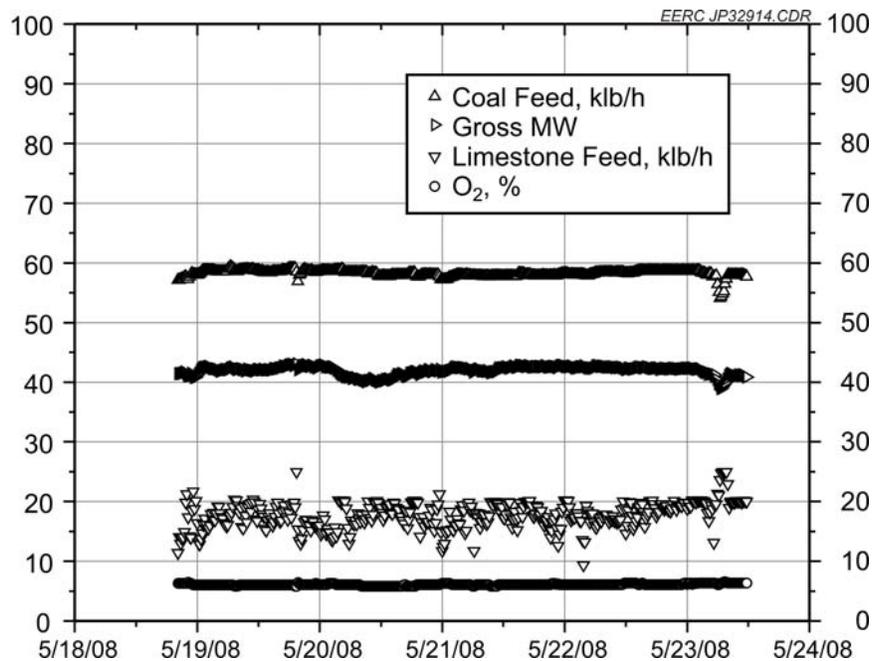


Figure 4. Boiler data.

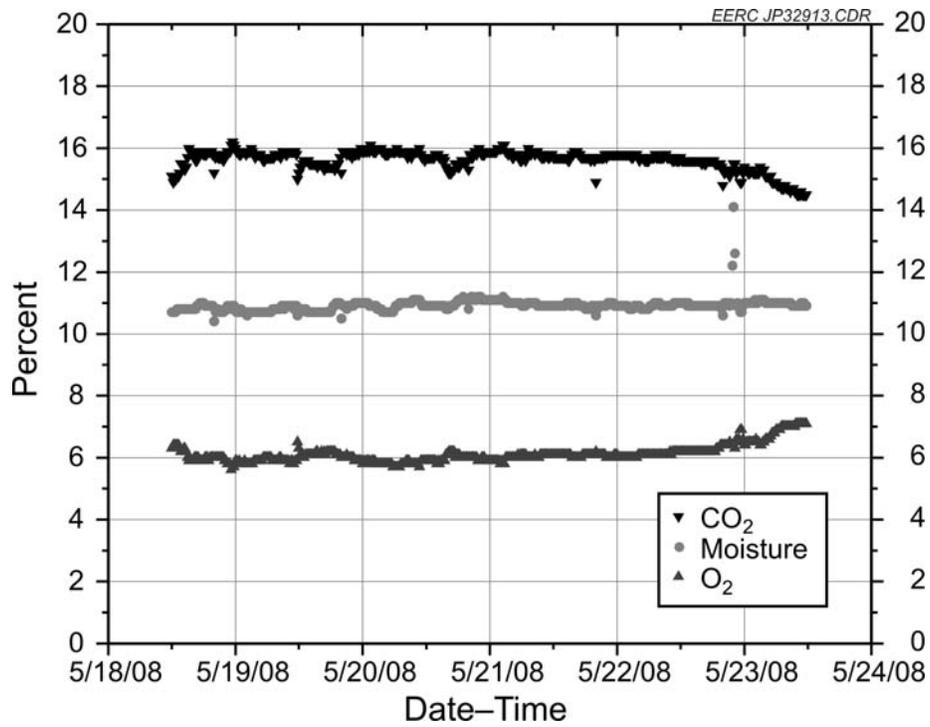


Figure 5. Stack CO<sub>2</sub>, moisture, and O<sub>2</sub>.

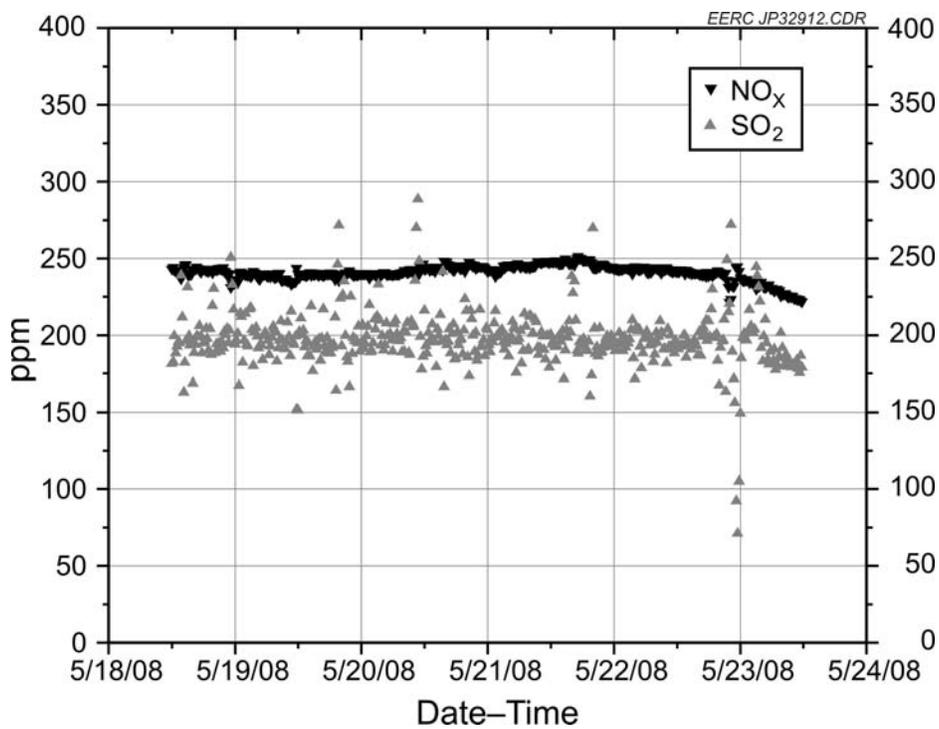


Figure 6. SO<sub>x</sub> and NO<sub>x</sub>.

calculated from the mineral analyses as well and were used to gauge the accuracy of the mass flow values for the coal, limestone, and ash obtained as part of the sampling effort. The balances for the major elements in the system (excluding Ca because of the large input from limestone) show that the outputs were calculated to be approximately 30% greater than the inputs. Although this is not out of the ordinary for a complex system such as a CFB, these results prompted further investigation. The proximate/ultimate analyses of the coal were used to complete a combustion calculation for the fuel and unit. Comparison of these calculated values with the coal flow values obtained from the DCS indicate very good agreement for the coal flow. Perturbation of the limestone mass flows for the balance calculations indicate that the DCS flow values could be higher than actual flows, but in either case the limestone flows could not account for all of the discrepancy. Another possibility is that, with the switching of fuel, the mass of the bed material changed over the sampling period. This is also supported by the fact that the bottom ash output decreased over the sampling period because of the fuel switch. Most likely, the combination of errors in mass flows and changes in bed material load due to the switch in fuel account for the mass balances being slightly over 100%. It should be noted that the mercury mass balances are not affected to any degree by these potential errors because the mercury was found primarily in the flue gas.

The fate of mercury across the unit shows that most of the mercury (97% based on these data) exits the unit with the flue gas out the stack. As previously mentioned, it is recommended that as part of any mercury control strategy, the use of sorbent enhancement additive would be beneficial to increase the percentage of oxidized mercury prior to sorbent injection. Additionally, since there are planned changes to the boiler (specifically modification of the cone in the primary cyclone), it is recommended that any major boiler modifications are completed prior to carrying out further research and development for mercury control options. By modifying the boiler and/or primary cyclone, the underlying chemistry of the flue gas and ash exiting the boiler will be affected, which could strongly influence the outcome of the mercury control (capture) technologies employed. By delaying tests until after unit modifications are made, there would be much greater assurance of the validity and representativeness of the test results for long-term application.

## CONCLUSIONS

- Flue gas mercury concentrations and speciation were obtained by the OH method, ST method, and CMMs to assess the mercury capture and emissions from the Rosebud Station.
- Coal, limestone, and ash samples were collected and analyzed to complete a mass balance for Hg and determine its fate.
- A mass balance of the mercury was completed showing a balance of 105%.
- The fate of mercury was determined to be primarily (97%) exiting with the flue gas out of the stack.

**Table 12. Flue Gas Component Data**

Stack	Date: Time:	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
O <sub>2</sub>	%	5.6	5.9	6.0	6	6.1	7.4	6.1	6.5	6.5
CO	ppm	2	1	2	2	2	1	1	2	2
NO	ppm	279	293	291	295	302	267	291	289	289
NO <sub>2</sub>	ppm	2	2	2	2	2	1	2	2	2
NO <sub>x</sub>	ppm	281	295	291	297	304	268	293	291	291
SO <sub>2</sub>	ppm	206	193	83	0	161		119	160	174
CO <sub>2</sub>	%	13.6	13.4	13.3	13.3	13.2	12.0	13.2	12.8	12.8
BH In	Date: Time:	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	
O <sub>2</sub>	%	6.8	7.2	5.7	7.4	5.9	5.8	5.8	6.1	
CO	ppm	1	1	2	0	1	0	0	2	
NO	ppm	275	266	295	70	306	319	313	306	
NO <sub>2</sub>	ppm	0	1	0	1	1	2	1	2	
NO <sub>x</sub>	ppm	277	263	295	71	307	321	314	308	
SO <sub>2</sub>	ppm	153	62	48	1	2	0	4	4	
CO <sub>2</sub>	%	12.6	12.2	13.6	13.2	13.4	13.5	13.5	13.2	
AH In	Date: Time:		5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08		
O <sub>2</sub>	%		5.4	5.2	5.4	5.5	6.6	5.6		
CO	ppm		2	17	2	4	2	2		
NO	ppm		315	303	319	307	279	309		
NO <sub>2</sub>	ppm		1	0	1	1	1	1		
NO <sub>x</sub>	ppm		316	303	320	308	280	310		
SO <sub>2</sub>	ppm		6	81	4	3		21		
CO <sub>2</sub>	%		13.8	14.0	13.8	13.7	12.8	13.6		

**Table 13. Mercury Mass Balances at Rosebud**

	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	a.m.	p.m.								
<b>Coal</b>										
lb Cw/hr	59422	57237	58695	57500	57231	57717	57291	62269	56898	58610
Hg lb/lb Cw	8.26E-08	7.85E-08	5.42E-08	4.19E-08	4.91E-08	4.33E-08	4.50E-08	3.92E-08	5.66E-08	6.32E-08
Hg oz/hr	0.078537	0.071908	0.050862	0.038550	0.044987	0.040026	0.041235	0.039011	0.051481	0.059244
<b>Limestone</b>										
lb L/hr	16476	17433	17268	17052	18046	17199	17610	17290	18613	20315
Hg lb/lb L	6.00E-09	6.00E-09	6.00E-09	6.00E-09	6.10E-09	8.00E-09	8.10E-09	7.90E-09	6.10E-09	4.00E-09
Hg oz/hr	0.001582	0.001674	0.001658	0.001637	0.001761	0.002201	0.002282	0.002186	0.001817	0.001300
% In	2	2	3	4	4	5	5	5	3	2
<b>Ash</b>										
%	13.92	10.43	10.23	10.11	9.71	8.91	8.79	8.55	8.83	9.12
lb/hr	8272	5970	6004	5813	5557	5143	5036	5324	5024	5345
Ash+Limestone lb/hr	24,748	23,403	23,272	22,865	23,603	22,342	22,645	22,614	23,637	25,661
<b>Bottom Ash</b>										
%	5	5	0	5	5	0	5	0	0	0
lb B/hr	1237	1170	0	1143	1180	0	1132	0	0	0
Hg oz/lb B	6.40E-08	0.00E+00		6.24E-08	3.20E-08		3.20E-08			
Hg oz/hr	0.000079	0.000000	0.000000	0.000071	0.000038	0.000000	0.000036	0.000000	0.000000	0.000000
% In	0	0	0	0	0	0	0	0	0	0
<b>AH Ash</b>										
%	5	5	5	5	5	5	5	5	5	5
lb A/hr	1237	1170	1164	1143	1180	1117	1132	1131	1182	1283
Hg oz/lb A	7.84E-08	0.00E+00								
Hg oz/hr	0.000097	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
% In	0	0	0	0	0	0	0	0	0	0

Continued...

**Table 13. Mercury Mass Balances at Rosebud, (continued)**

	5/19/08	5/19/08	5/20/08	5/20/08	5/21/08	5/21/08	5/22/08	5/22/08	5/23/08	5/23/08
	a.m.	p.m.								
Fly Ash										
%	90	90	95	90	90	95	90	95	95	95
lb F/hr	22273	21063	22109	20578	21243	21225	20381	21484	22455	24378
Hg oz/lb F	3.82E-07	1.60E-07	1.60E-07	1.28E-07	1.60E-07	1.28E-07	1.30E-07	3.20E-08	1.92E-07	1.92E-07
Hg oz/hr	0.008517	0.003370	0.003537	0.002634	0.003399	0.002717	0.002641	0.000687	0.004311	0.004681
% In	11	5	7	7	7	6	6	2	8	8
Flue Gas										
dNm <sup>3</sup> /hr	169,131	161,746	165,534	163,022	167,172	164,797	163,569	179,148	161,254	163,982
at 3% O <sub>2</sub>										
Hg oz/dNm <sup>3</sup>	2.71E-07	2.58E-07	2.68E-07	2.53E-07	2.77E-07	2.45E-07	2.39E-07	2.75E-07	2.67E-07	3.80E-07
Hg oz/hr	0.045816	0.041715	0.044367	0.041281	0.046312	0.040364	0.039044	0.049305	0.043058	0.062336
% In	57	57	84	103	99	96	90	120	81	103
Hg										
In oz/hr	0.080118	0.073582	0.052520	0.040187	0.046749	0.042227	0.043517	0.041197	0.053297	0.060544
Out oz/hr	0.054509	0.045085	0.047904	0.043987	0.049749	0.043080	0.041722	0.049993	0.047370	0.067017
Balance % (O/I)	68	61	91	109	106	102	96	121	89	111

**APPENDIX A**  
**CALCULATIONS AND ASSUMPTIONS**

## MERCURY CALCULATIONS AND ASSUMPTIONS

### MERCURY CONTINUOUS EMISSION MONITORS

Continuous mercury monitoring (CMM) data were corrected for flue gas oxygen to obtain values standardized to 3% O<sub>2</sub>.

$$\text{Hg}(\mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2) = \text{Hg concentration at } 3\% \text{ O}_2$$

$$\text{Hg}(\mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2) = \text{Hg}(\mu\text{g}/\text{dNm}^3) \times \frac{21 - \% \text{O}_2}{18}$$

$$\text{Hg}(\mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2) = 6.8 \times \frac{21 - 5.6}{18} = 6.5 \mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2$$

Where:

$$\text{Hg} (\mu\text{g}/\text{dNm}^3) = \text{Mercury concentration from CMM}$$

### ONTARIO HYDRO (OH) METHOD SAMPLING

#### Volume of Gas Sample

$$V_m(\text{std}) = \text{Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscf}$$

$$V_m(\text{std}) (\text{dscf}) = \frac{K_1 \times V_{mc} \times P_m}{T_m + 460}$$

$$V_m(\text{std}) = \frac{17.64 \times 36.1194 \times 29.762}{69 + 460} = 35.846 \text{ dscf}$$

Where:

$$K_1 = 17.64 \text{ R/in. Hg}$$

$$V_{mc} = V_m \times C_m = \text{Volume of gas sample as measured by dry-gas meter, corrected for meter calibration (} C_m = \text{meter calibration coefficient) (dcf)}$$

$$P_m = \text{Meter pressure (in. Hg)}$$

$$T_m = \text{Meter temperature (}^\circ\text{F)}$$

### Volume of Water Vapor

$V_w(\text{std})$  = Volume of water vapor in the gas sample, corrected to standard conditions, scf

$$\begin{aligned} V_w(\text{std}) (\text{scf}) &= K_2 \times H_2O(\text{g}) \\ V_w(\text{std}) &= 0.04715 \times 80.3 = 3.786 \text{ scf} \end{aligned}$$

Where:

$K_2$  = 0.04715 ft<sup>3</sup>/g  
 $H_2O(\text{g})$  = Mass of liquid collected in impingers and silica gel (g)

### Water Vapor in the Gas Stream

$B_{ws}$  = Water vapor in the gas stream, proportion by volume

$$B_{ws} = \frac{V_w(\text{std})}{V_m(\text{std}) + V_w(\text{std})}$$

$$B_{ws} = \frac{3.786}{35.846 + 3.786} = 0.0955$$

### Dry Molecular Weight

$M_d$  = Dry molecular weight of stack gas, lb/lb-mol

$$M_d (\text{lb/lb-mol}) = 0.440 \times (\%CO_2) + 0.320 \times (\%O_2) + 0.280 \times (\%N_2 + \%CO)$$

$$M_d = 0.440 \times 12.6 + 0.320 \times 6.8 + 0.280 \times 80.6 = 30.3 \text{ lb/lb-mol}$$

Where:

% (CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO) = Percent (CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO) by volume, dry basis

### Molecular Weight

$M_s$  = Molecular weight of stack gas, wet basis, lb/lb-mol

$$M_s (\text{lb/lb-mol}) = M_d \times (1 - B_{ws}) + 18.0 \times B_{ws}$$

$$M_s = 30.3 \times (1 - 0.0955) + 18.0 \times 0.0955 = 29.1 \text{ lb/lb-mol}$$

### Average Stack Gas Velocity

$V_s$  = Average stack gas velocity, ft/sec

$$V_s (\text{ft/sec}) = K_3 \times C_p \times (\Delta p)^{1/2} (\text{avg}) \times \left[ \frac{T_s + 460}{P_s \times M_s} \right]^{1/2}$$

$$V_s = 85.49 \times 0.84 \times 0.8831 \times \left[ \frac{338 + 460}{28.72 \times 29.1} \right]^{1/2} = 62.0 \text{ ft/sec}$$

Where:

$$K_3 = 85.49 \text{ ft/sec} \times \left[ \frac{\text{lb}}{\text{lb - mole}} \times \frac{\text{in. Hg}}{\text{R} \times \text{in. H}_2\text{O}} \right]^{1/2}$$

$C_p$  = Pitot tube coefficient, dimensionless  
 $\Delta p$  = Velocity head of stack gas (in. Hg)  
 $(\Delta p)^{1/2}(\text{avg})$  = Average of the square root of  $\Delta p$  values  
 $T_s$  = Stack gas temperature ( $^{\circ}\text{F}$ )  
 $P_s$  = Stack pressure (in. Hg)

### Isokinetic Sampling Rate

$$I = \text{Percent of isokinetic sampling, \%}$$

$$I(\%) = \frac{K_4 \times (T_s + 460) \times V_m(\text{std}) \times 144}{P_s \times V_s \times A_n \times \theta \times (1 - B_{ws})}$$

$$I = \frac{0.09450 \times (338 + 460) \times 35.846 \times 144}{28.72 \times 62.0 \times 0.0196 \times 120 \times (1 - 0.0955)} = 103\%$$

Where:

$$K_4 = \frac{0.09450\% (\text{in. Hg})(\text{min})}{\text{R} \times \text{sec}}$$

$A_n$  = Cross-sectional area of nozzle ( $\text{in.}^2$ )  
 $\theta$  = Total sampling time (min)

### Volume of Gas Sample Corrected to 3% O<sub>2</sub>

$V_m^*(\text{std})$  = Volume of gas sample measured by the dry-gas meter ( $V_m[\text{std}]$ ), \* corrected to 3% oxygen,  $\text{Nm}^3$

$$V_m^*(\text{std}) = K_5 \times V_m(\text{std}) \times \frac{21 - \%O_2}{18}$$

$$V_m^*(\text{std}) = 0.02832 \times 35.846 \times \frac{21 - 6.8}{18} = 0.801 \text{ Nm}^3$$

Where:

$$K_5 = 0.02832 \text{ m}^3/\text{ft}^3$$

## Mercury

$$\begin{aligned} \text{Hg } (\mu\text{g}/\text{Nm}^3) &= \frac{\mu\text{g}}{\text{Vm} * (\text{std})} \\ \text{Hg} &= \frac{4.76}{0.801} = 5.94 \mu\text{g}/\text{Nm}^3 \\ \text{Particulate Hg} &= \text{Sum of mercury from filter and nozzle rinse} \\ \text{Oxidized Hg} &= \text{Sum of mercury from KCl impingers} \\ &= \text{Elemental Hg} = \text{Sum of mercury from H}_2\text{O}_2 \text{ and KMnO}_4 \text{ impingers} \end{aligned}$$

## SORBENT TRAP SAMPLING METHOD

### Calculations

$$\begin{aligned} \text{Hg } (\mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2) \text{ conditions} &= \text{Mercury concentration in the flue gas corrected to standard conditions} \\ \text{Hg } (\mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2) &= (S1 + S2) \div \text{Vcorr} \times 18/(21 - \text{O}_2) \\ \text{Vcorr (dNL)} &= \text{Volume sampled corrected to standard conditions} \\ \text{Vcorr (dNL)} &= \text{Vm} \times (\text{Pb} - \text{Elev corr}/1000) \div 29.92 \times 528 \div (460 + \text{Tm}) \\ \text{Vcorr (dNL)} &= 32.374 \times (29.64 - 0/1000) \div 29.92 \times 528 \div (460 + 90) \\ &= 30.788 \text{ dNL} \\ \text{Hg } (\mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2) &= (202 + 2.9) \div 30.788 \times 18/(21 - 5.6) \\ &= 7.78 \mu\text{g}/\text{dNm}^3 \text{ at } 3\% \text{ O}_2 \end{aligned}$$

Where:

$$\begin{aligned} \text{Vm} &= \text{Volume of gas sample measured by the dry-gas meter (dL)} \\ \text{Pb} &= \text{Barometric pressure (in Hg)} \\ \text{Elev corr} &= \text{Elevation correction for Pb to sampling elevation (ft)} \\ \text{Tm} &= \text{Meter temperature } (^\circ\text{F}) \\ \text{O}_2 &= \text{Flue gas O}_2 \text{ concentration measured (\%)} \\ \text{S1} &= \text{Measured mass of Hg in Section 1 (ng)} \\ \text{S2} &= \text{Measured mass of Hg in Section 2 and plug (ng)} \end{aligned}$$

### Fate of Mercury During Baseline and Monthlong Test Conditions (Mass Balance)

Coal Inlet Hg (Hg oz/hr)

$$\text{Coal Hg (oz/hr)} = \text{lb}_{\text{Cw}}/\text{hr} \times \text{lb}_{\text{Hg}}/\text{lb}_{\text{Cw}} \times 16 \text{ oz}/\text{lb}$$

$$\begin{aligned} \text{lb}_{\text{Hg}}/\text{lb}_{\text{Cw}} &= \mu\text{g}_{\text{Hg}}/\text{g}_{\text{Cd}} \times (1 - \% \text{moisture}/100)/1000000 \\ &= 0.107 \times (1 - 22.8/100)/1000000 \\ &= 8.26 \times 10^{-8} \end{aligned}$$

$$\begin{aligned} \text{Coal Hg (oz/hr)} &= 59422 \times 8.26 \times 10^{-8} \times 16 \\ &= 0.0785 \text{ oz/hr} \end{aligned}$$

Where:

$\text{lb}_{\text{Cw}}/\text{hr}$  = Coal feed rate (wet) as determined from combustion calculation, verified with plant data collection system coal feed data

$\mu\text{g}_{\text{Hg}}/\text{g}_{\text{Cd}}$  = Concentration of Hg in coal (dry)

$\% \text{moisture}$  = Moisture in as-received coal

Limestone Inlet Hg (Hg oz/hr)

$$\text{Limestone Hg (oz/hr)} = \text{lb}_{\text{L}}/\text{hr} \times \text{lb}_{\text{Hg}}/\text{lb}_{\text{L}} \times 16 \text{ oz/lb}$$

$$\begin{aligned} \text{lb}_{\text{Hg}}/\text{lb}_{\text{L}} &= \mu\text{g}_{\text{Hg}}/\text{g}_{\text{L}}/1000000 \\ &= 0.0060/1000000 \\ &= 6 \times 10^{-9} \end{aligned}$$

$$\begin{aligned} \text{Limestone Hg (oz/hr)} &= 16476 \times 6 \times 10^{-9} \times 16 \\ &= 0.00158 \text{ oz/hr} \end{aligned}$$

Where:

$\text{lb}_{\text{L}}/\text{hr}$  = Limestone feed rate as determined from plant DCS data

$\mu\text{g}_{\text{Hg}}/\text{g}_{\text{L}}$  = Concentration of Hg in limestone

Ash + Limestone (lb/hr)

$$\begin{aligned} &= \text{lb}_{\text{Cw}}/\text{hr} \times \% \text{ash}/100 + \text{lb}_{\text{L}}/\text{hr} \\ &= 59422 \times 13.92/100 + 16476 \\ &= 24748 \text{ lb/hr} \end{aligned}$$

Where:

$\text{lb}_{\text{Cw}}/\text{hr}$  = Coal feed rate in lb/hr

$\% \text{ash}$  = Ash content of coal in %

$\text{lb}_{\text{L}}/\text{hr}$  = Limestone feed rate in lb/hr

$$\begin{aligned}
\text{Bottom Ash (or BA) (lb/hr)} &= 5\% \text{ ash} + \text{limestone input} \\
&= 5/100 \times 24748 \\
&= 1237 \text{ lb/hr}
\end{aligned}$$

Where:

5% of the total ash is estimated to be collected as bottom ash

$$\begin{aligned}
\text{Air Heater (or AH) Ash (lb/hr)} &= 5\% \text{ ash} + \text{limestone input} \\
&= 5/100 \times 24748 \\
&= 1237 \text{ lb/hr}
\end{aligned}$$

Where:

5% of the total ash is estimated to be collected as air heater ash

$$\begin{aligned}
\text{Fly Ash (or FA) (lb/hr)} &= 90\% \text{ ash} + \text{limestone input} \\
&= 90/100 \times 24748 \\
&= 22273 \text{ lb/hr}
\end{aligned}$$

Where:

90% of the total ash is estimated to be collected as fly ash

Bottom Ash Hg (oz/hr)

$$\begin{aligned}
\text{BA Hg (oz/hr)} &= \text{lb}_{\text{BA}}/\text{hr} \times \text{oz}_{\text{Hg}}/\text{lb}_{\text{BA}} \\
\text{oz}_{\text{Hg}}/\text{lb}_{\text{BA}} &= \mu\text{g}_{\text{Hg}}/\text{g}_{\text{BA}}/1000000 \times 16 \text{ oz/lb} \\
&= 0.0040 / 1000000 \times 16 \\
&= 6.4 \times 10^{-8} \\
\text{BA Hg (oz/hr)} &= 1237 \times 6.4 \times 10^{-8} \\
&= 0.000079 \text{ oz/hr}
\end{aligned}$$

Where:

$\text{lb}_{\text{BA}}/\text{hr}$  = Bottom ash collection rate as calculated above  
 $\mu\text{g}_{\text{Hg}}/\text{g}_{\text{BA}}$  = Concentration of Hg in bottom ash  
 Air Heater Ash Hg (oz/hr)

$$\begin{aligned} \text{AH Hg (oz/hr)} &= \text{lb}_{\text{AHA}}/\text{hr} \times \text{oz}_{\text{Hg}}/\text{lb}_{\text{AHA}} \\ \text{oz}_{\text{Hg}}/\text{lb}_{\text{AHA}} &= \mu\text{g}_{\text{Hg}}/\text{g}_{\text{AHA}}/1000000 \times 16 \text{ oz/lb} \\ &= 0.0049/1000000 \times 16 \\ &= 7.84 \times 10^{-8} \end{aligned}$$

$$\begin{aligned} \text{AH Hg (oz/hr)} &= 1237 \times 7.84 \times 10^{-8} \\ &= 0.000097 \text{ oz/hr} \end{aligned}$$

Where:

$$\begin{aligned} \text{lb}_{\text{AHA}}/\text{hr} &= \text{Air heater ash collection rate as calculated above} \\ \mu\text{g}_{\text{Hg}}/\text{g}_{\text{AHA}} &= \text{Concentration of Hg in air heater ash} \end{aligned}$$

Fly Ash Hg (oz/hr)

$$\begin{aligned} \text{FA Hg (oz/hr)} &= \text{lb}_{\text{FA}}/\text{hr} \times \text{oz}_{\text{Hg}}/\text{lb}_{\text{FA}} \\ \text{oz}_{\text{Hg}}/\text{lb}_{\text{FA}} &= \mu\text{g}_{\text{Hg}}/\text{g}_{\text{FA}}/1000000 \times 16 \text{ oz/lb} \\ &= 0.0239/1000000 \times 16 \\ &= 3.82 \times 10^{-7} \end{aligned}$$

$$\begin{aligned} \text{FA Hg (oz/hr)} &= 22273 \times 3.82 \times 10^{-7} \\ &= 0.0085 \text{ oz/hr} \end{aligned}$$

Where:

$$\begin{aligned} \text{lb}_{\text{FA}}/\text{hr} &= \text{Fly ash collection rate as calculated above} \\ \mu\text{g}_{\text{Hg}}/\text{g}_{\text{FA}} &= \text{Concentration of Hg in fly ash} \end{aligned}$$

$$\begin{aligned} \text{Flue Gas Hg (oz/hr)} &= \text{dNm}^3/\text{hr} \times C_{\text{Hg}} \\ C_{\text{Hg}} &= \text{Hg } (\mu\text{g}/\text{dNm}^3) \times 2.205(\text{lb}/\text{kg}) \times 16(\text{oz}/\text{lb}) \times 10^{-9}(\text{kg}/\mu\text{g}) \\ &= 7.7 \times 2.205 \times 16 \times 10^{-9} \\ &= 2.7 \times 10^{-7} \text{ (oz/dNm}^3 \text{ at 3\% O}_2\text{)} \end{aligned}$$

$$\begin{aligned} \text{Flue Gas Hg (oz/hr)} &= 169131 \times 2.7 \times 10^{-7} \\ &= 0.046 \text{ oz/hr} \end{aligned}$$

$$\begin{aligned}
 \text{Mercury Balance \%} &= \text{Out(oz/hr)/In(oz/hr)} \times 100\% \\
 \text{Out (oz/hr)} &= \text{BA Hg} + \text{AH Hg} + \text{FA Hg} + \text{Flue Gas Hg (oz/hr)} \\
 &= 0.000079 + 0.000097 + 0.0085 + 0.046 \\
 &= 0.055 \text{ oz/hr} \\
 \text{In (oz/hr)} &= \text{Coal Hg} + \text{limestone Hg (oz/hr)} \\
 &= 0.0785 + 0.00158 \\
 &= 0.080 \text{ oz/hr} \\
 \text{Mercury Balance \%} &= 0.055/0.080 \times 100 \\
 &= 68\%
 \end{aligned}$$