

JV TASK 26 – MERCURY AND LEAD SAMPLING AT MINNESOTA POWER'S BOSWELL ENERGY CENTER

Final Report
(for the period March 31 to September 1, 2000)

Prepared for:

AAD Document Control
U.S. Department of Energy
National Energy Technology Laboratory
PO Box 10940, MS 921-143
Pittsburgh, PA 15236-0940

*DOE Cooperative Agreement No. DE-FC26-98FT40321--08; UND Fund 4729
Performance Monitor: Dr. Richard Read*

Prepared by:

Dennis L. Laudal

Energy & Environmental Research Center
University of North Dakota
PO Box 9018
Grand Forks, ND 58202-9018

DOE DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

ACKNOWLEDGMENT

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40321. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE.

EERC DISCLAIMER

LEGAL NOTICE This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by DOE and Minnesota Power, Inc. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

TABLE OF CONTENTS

| | |
|---|-----|
| LIST OF FIGURES | ii |
| LIST OF TABLES | ii |
| LIST OF ACRONYMS AND UNITS | iii |
| EXECUTIVE SUMMARY | iv |
| 1.0 INTRODUCTION | 1 |
| 2.0 PLANT AND SAMPLING LOCATION DESCRIPTIONS | 1 |
| 2.1 Unit 2 | 1 |
| 2.2 Unit 3 | 2 |
| 2.3 Unit 4 | 4 |
| 3.0 TESTING REQUIREMENTS | 6 |
| 4.0 OPERATING CONDITIONS | 6 |
| 5.0 TEST METHODS | 11 |
| 5.1 Sampling Apparatus | 12 |
| 5.2 Sampling Procedure | 12 |
| 5.3 Sample Recovery | 13 |
| 6.0 TEST RESULTS | 13 |
| 7.0 SAMPLE CALCULATIONS | 14 |
| 7.1 Volume of Gas Sample | 14 |
| 7.2 Volume of Water Vapor | 16 |
| 7.3 Water Vapor in the Gas Stream | 16 |
| 7.4 Molecular Weight | 17 |
| 7.5 Average Stack Gas Velocity | 17 |
| 7.6 Isokinetic Sampling Rate | 17 |
| 7.7 Volume of Gas Sample Corrected to 3% O ₂ | 18 |
| 7.8 Lead Concentration | 18 |
| 7.9 Lead Emission Factors | 18 |
| 8.0 QUALITY ASSURANCE AND QUALITY CONTROL | 18 |

LIST OF FIGURES

1 Schematic for Unit 2 2

2 Unit 2 baghouse outlet test port locations and traverse point distances 3

3 Schematic of Unit 3. 4

4 Unit 3 cross section of the outlet sampling location 5

5 Schematic of Unit 4 6

6 Unit 4 stack test port locations and traverse point distances 7

7 Schematic of the EPA Method 12 inorganic lead sampling train 11

8 EPA Method 12 recovery procedure 13

LIST OF TABLES

ES-1 Summary of Lead Emissions at the Boswell Energy Center iv

ES-2 Summary of Lead Emission Factors at the Boswell Energy Center iv

1 Unit 2 Test Data 8

2 Unit 3 Test Data 9

3 Unit 4 Test Data 10

4 Stack Gas Test Methods 11

5 Lead Concentration in the Coal Fired at the Boswell Energy Center During Mercury ICR Testing 14

6 Coal Analysis 15

7 Summary of Lead Concentrations Exiting the Stack at the Boswell Energy Center 15

8 Summary of Lead Emission Factors at the Boswell Energy Center 16

9 Field Blank Results 19

LIST OF ACRONYMS AND UNITS

| | |
|------|--|
| AAS | atomic absorption spectroscopy |
| µg | micrograms |
| CCV | continuing calibration verification |
| EERC | Energy & Environmental Research Center |
| EPA | U.S. Environmental Protection Agency |
| ESP | electrostatic precipitator |
| GCV | greater caloric value |
| ICR | EPA Information Collection Request |
| ICV | initial calibration verification |
| ID | inside diameter |
| IDL | instrument detection limit |
| OD | outside diameter |
| Pb | lead |

**PERFORMANCE TESTING FOR LEAD EMISSIONS FROM UNITS 2, 3, AND 4
AT THE BOSWELL ENERGY CENTER**

EXECUTIVE SUMMARY

At the request of the Minnesota Power, Inc., the Energy & Environmental Research Center sampled for lead at the stack (or duct directly leading to the stack) for three units at the Boswell Energy Center.

All sampling was done in triplicate using U.S. Environmental Protection Agency (EPA) Method 12, with sampling procedures following EPA Methods 1 through 4. During the test program, lead sampling was done using EPA Method 12 in the duct at the outlet of the baghouse serving Unit 2 and the duct at the outlet of the wet particulate scrubber serving Unit 3. For Unit 4, lead sampling was done at the stack. The specific objective for the project was to determine the concentration of lead in the flue gas being emitted into the atmosphere from the Boswell Energy Center.

The results for the testing are shown in Tables ES-1 and ES-2.

TABLE ES-1

Summary of Lead Emissions at the Boswell Energy Center¹

| Unit No. | Run 1 Flue Gas Concentration, µg/m ³ | Run 2 Flue Gas Concentration, µg/m ³ | Run 3 Flue Gas Concentration, µg/m ³ | Average, µg/m ³ |
|----------|--|--|--|-------------------------------|
| 2 | 2.5 | 2.5 | 1.7 | 2.2 ± 0.38 |
| 3 | 22.8 | 22.3 | 26.0 | 23.7 ± 1.64 |
| 4 | 15.7 | 13.3 | 9.8 | 12.9 ± 2.97 |

¹ The concentrations are presented on a 3% oxygen basis.

TABLE ES-2

Summary of Lead Emission Factors at the Boswell Energy Center¹

| Unit No. | Run 1, lb/10 ¹² Btu | Run 2, lb/10 ¹² Btu | Run 3, lb/10 ¹² Btu | Average, lb/10 ¹² Btu |
|----------|-----------------------------------|-----------------------------------|-----------------------------------|-------------------------------------|
| 2 | 1.8 | 1.8 | 1.2 | 1.6 ± 0.34 |
| 3 | 16.2 | 15.8 | 18.5 | 16.8 ± 1.46 |
| 4 | 11.2 | 9.5 | 7.0 | 9.2 ± 2.11 |

¹ Calculations based on EPA Method 19.

PERFORMANCE TESTING FOR LEAD EMISSIONS FROM UNITS 2, 3, AND 4 AT THE BOSWELL ENERGY CENTER

1.0 INTRODUCTION

At the request of the Minnesota Power, Inc., the Energy & Environmental Research Center (EERC) sampled for lead at the stack (or duct directly leading to the stack) for three units at the Boswell Energy Center. All sampling was done in triplicate using U.S. Environmental Protection Agency (EPA) Method 12, with sampling procedures following EPA Methods 1 through 4. During the test program, lead sampling was done using EPA Method 12 in the duct at the outlet of the baghouse serving Unit 2 and the duct at the outlet of the wet particulate scrubber serving Unit 3. For Unit 4, lead sampling was done at the stack. The specific objective for the project was to determine the concentration of lead in the flue gas being emitted into the atmosphere from the Boswell Energy Center. The test program was performed during the period of May 8 through 11, 2000.

This report presents the test data, sample calculations, and results, and a discussion of the lead sampling performed at the Boswell Energy Center. The detailed test data and test results, raw test data, process data, laboratory reports, and equipment calibration records are provided in Appendices A, B, and C. The testing was observed by Stuart Arkley and Steve Sommer from the Minnesota Pollution Control Agency. In addition, the testing was observed by Joe Muller, Environmental Compliance Officer for the Boswell Energy Center.

2.0 PLANT AND SAMPLING LOCATION DESCRIPTIONS

The Boswell Energy Center consists of four electric generating units. All of the units at this station burn western subbituminous coal delivered to the station by rail from the Powder River Basin area of Montana and Wyoming.

2.1 Unit 2

Identical Units 1 and 2, built in the late 1950s, each have a heating input rating of 750 MMBtu/hr and a generating capacity of 74 MW gross. These units are equipped with Riley wall-fired boilers with low-NO_x burners. A baghouse is used to control the particulate emission for both Units 1 and 2. The baghouses use reverse air for cleaning and are designed for 99.7% particulate collection efficiency with an air-to-cloth ratio of 1.9:1. The flue gas temperatures range from 300° to 400°F and are ducted to a common stack for use as reheat for Unit 3 particulate scrubber flue gases. See Figure 1 for the Unit 2 schematic.

The lead sampling was performed at the outlet of the baghouse in a vertical section of the 120- × 1230-in. (internal dimensions) steel ductwork. The ports were positioned horizontally at a location 5.5 equivalent diameters (55 ft) downstream and 0.5 diameters (5 ft) upstream of the nearest gas stream flow disturbances. EPA Method 1 requires a minimum of 30 traverse points,

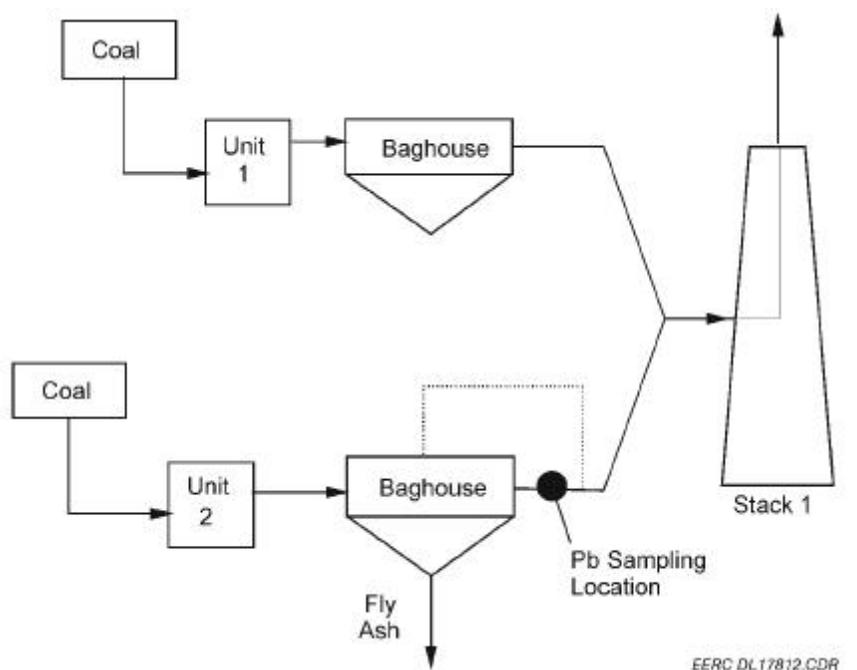


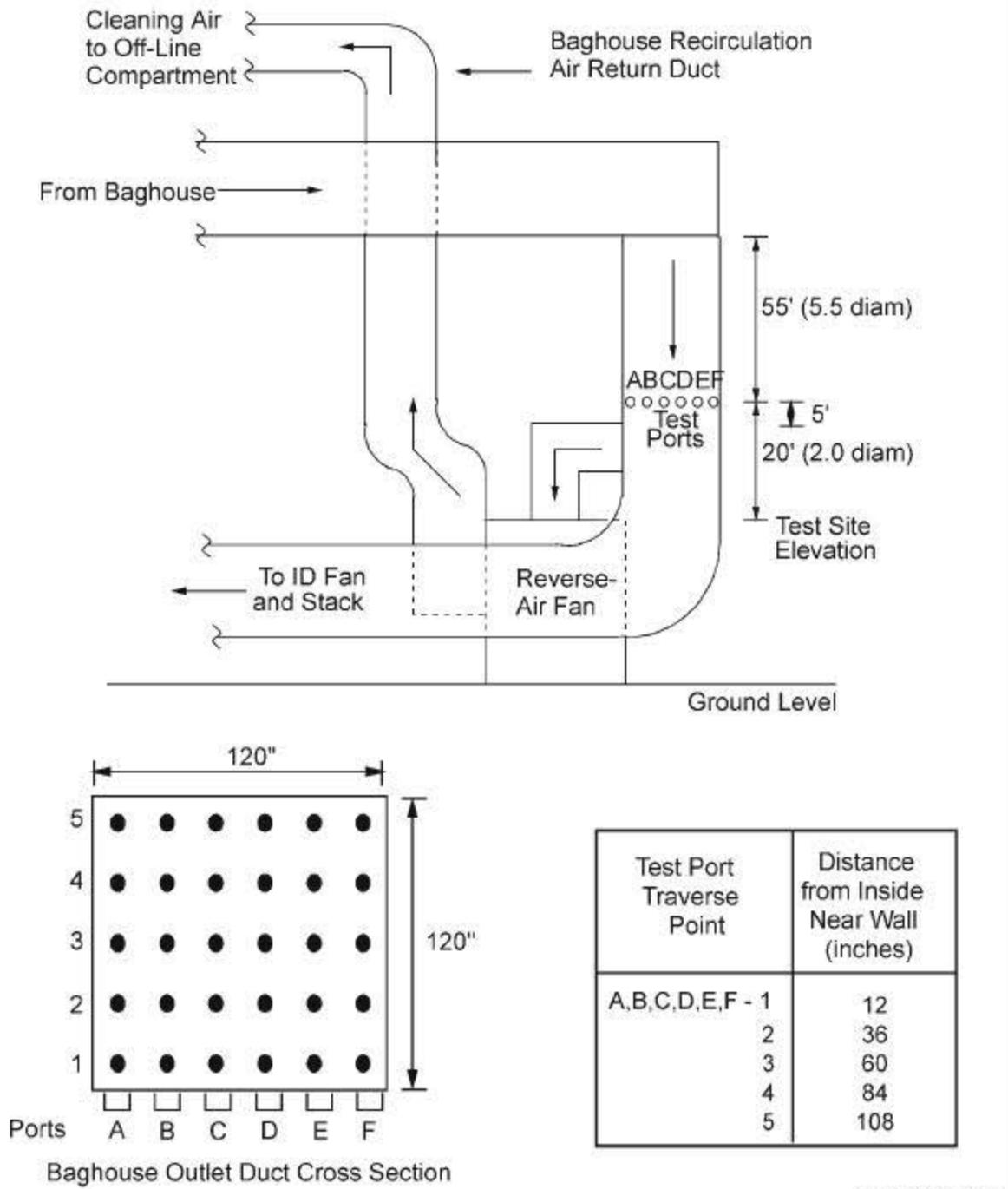
Figure 1. Schematic for Unit 2.

5 per port axis for this configuration, The baghouse outlet test port locations and traverse point distances are indicated in Figure 2.

2.2 Unit 3

Units 3 was constructed in the early 1970s and has a heat input rating of 3355 MMBtu/hr and a generating capacity of 375 MW gross. This unit has a tangentially fired Combustion Engineering boiler equipped with a Krebs Engineers Elbair wet scrubber for particulate control. This scrubber uses high-pressure water sprays and punch plates for the particulate collection system. The induced-draft fans are located in the wet gas stream exiting the scrubber. Hot flue gas is added from Units 1 and 2 to reheat Unit 3 flue gas as it exits the stack. The wet scrubber is designed for 96% particulate collection efficiency and also removes approximately 25% of the SO₂. Figure 3 is a schematic of Unit 3.

The lead sampling at Unit 3 was conducted at the existing sample ports in the exhaust duct following the wet particulate scrubber. As was true for Unit 2, samples could not be collected at the stack because the flue gases from Units 1, 2, and 3 use a common stack. The sample ports are located 4 ft upstream of where the flow turns 90° up into the stack and 10 ft downstream from a bend in the duct leading from the scrubber discharge fans. The sampling location for the exhaust duct from the Unit 3 wet particulate scrubber did not meet EPA Method 1 criteria. However, it was the only possible location. The sampling ports are located in a horizontal section of the steel ductwork that is 15 ft wide by 30 ft deep. Five sample ports (A through E) are aligned on the top of the duct. Because of the 30-ft depth of the duct, only one-half of it was traversed for sampling.



EERC DL17809.CDR

Figure 2. Unit 2 baghouse outlet test port locations and traverse point distances.

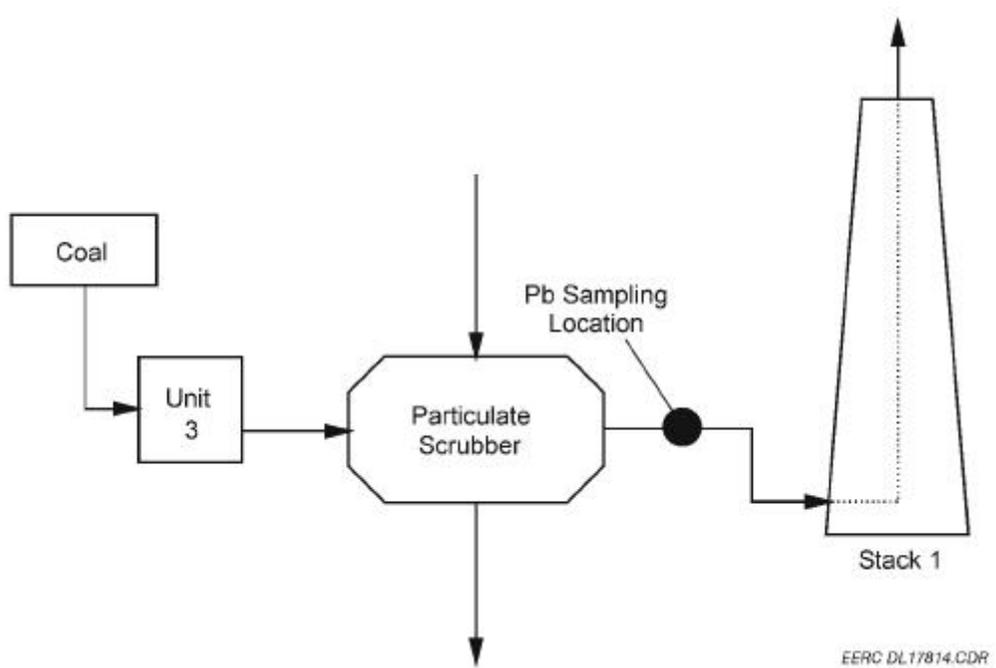


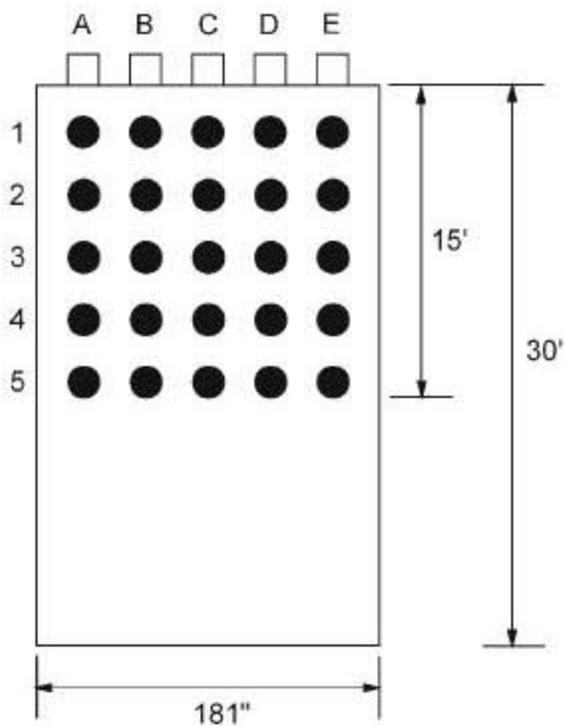
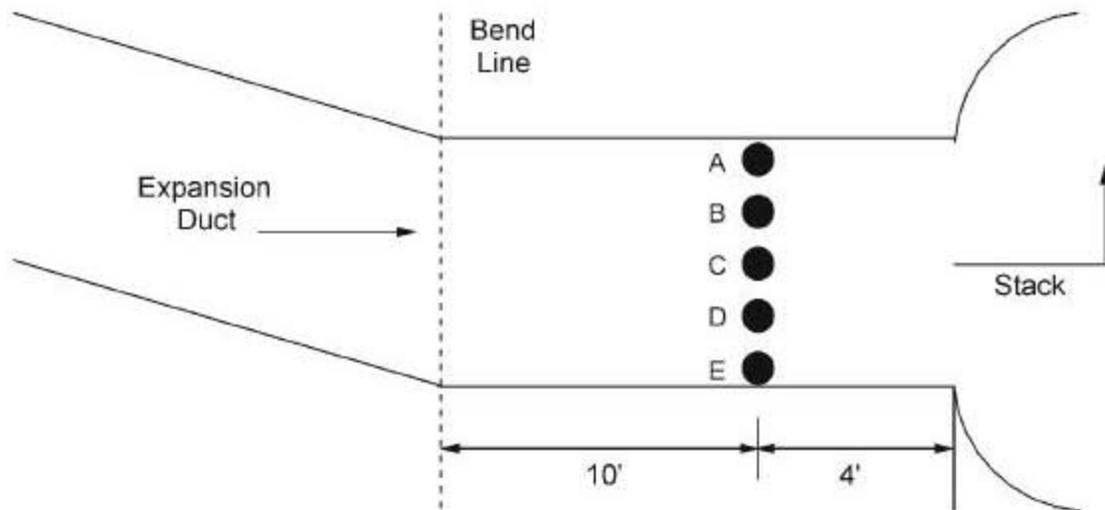
Figure 3. Schematic of Unit 3.

Sample traverse points for one-half (15 ft) of the duct depth were selected according to EPA Method 1. A schematic and cross section of the outlet sampling location are shown in Figure 4.

2.3 Unit 4

Unit 4 was constructed in early 1980 and is the largest boiler at the Boswell Energy Center, with a heating input rating of 5109 MMBtu/hr and a generating capacity of 580 MW gross. This unit has a tangentially fired Combustion Engineering boiler designed for staged combustion to reduce NO_x emissions. This unit is equipped with an air quality control system supplied by Peabody Process Systems. It consists of four separate modules, each having a venturi scrubber. The venturi scrubber is designed for 99.7% particulate collection efficiency and 84.4% SO₂ removal (with designed reheat). The reheat bypass is equipped with an electrostatic precipitator (ESP) to maintain particulate emissions within specifications. The maximum bypass flow to the ESP is 5% of the total flue gas and is nominally 2% (see Figure 5).

A total of four 6-in. test ports are in place on the 37-ft, 4-in.-ID stack that serves Unit 4. The test ports are located 324 ft (8.7 diameters) from the nearest downstream disturbance and 235 ft (6.4 diameters) from the stack discharge point. A total of three points per port (12 points total) were sampled. The Unit 4 stack is an ideal test location and satisfies all EPA Method 1 criteria for test port location. See Figure 6 for a schematic of the Unit 4 stack test locations.



| Test Port/ Traverse Point | Distance from Inside Near Wall (inches) |
|---------------------------------|---|
| A,B,C,D,E-1 | 18 |
| 2 | 54 |
| 3 | 90 |
| 4 | 126 |
| 5 | 162 |

EERC DL17810.CDR

Figure 4. Unit 3 cross section of the outlet sampling location.

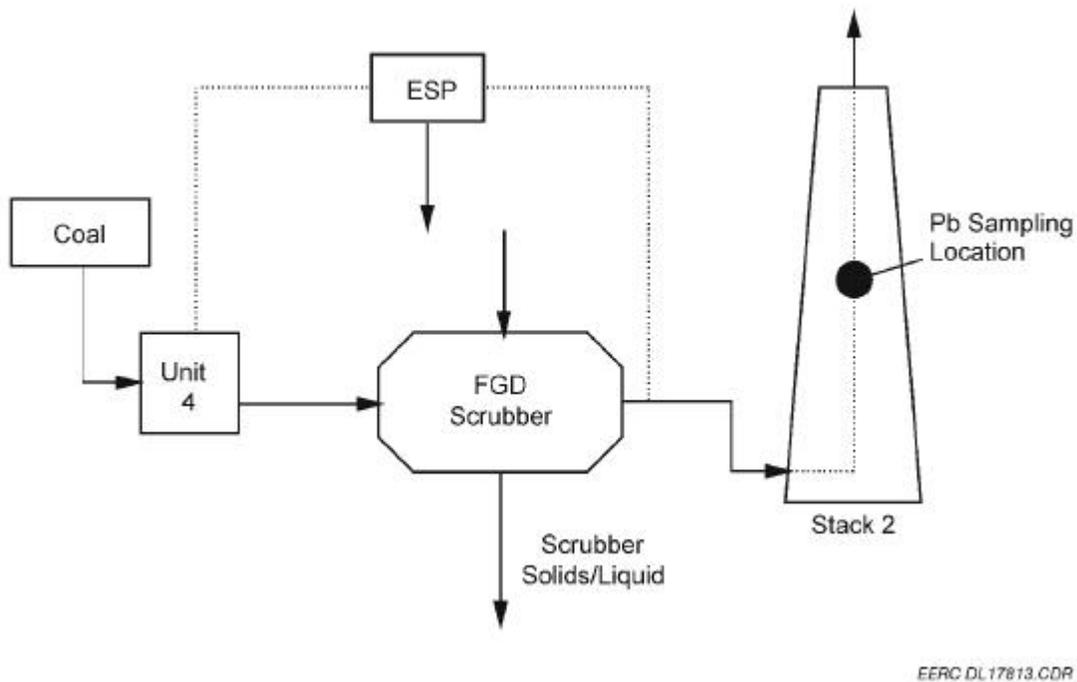


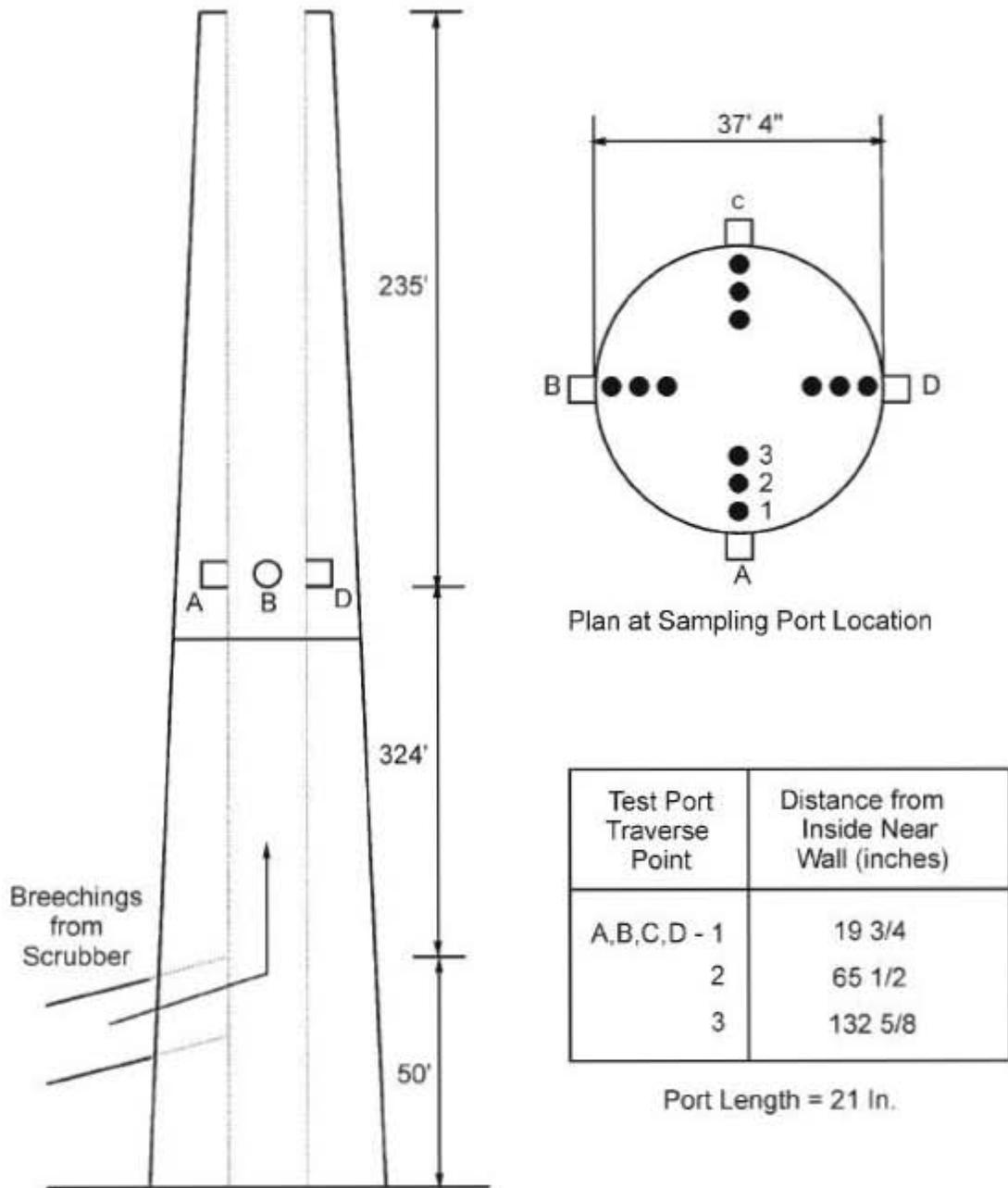
Figure 5. Schematic of Unit 4.

3.0 TESTING REQUIREMENTS

The emission units tested for lead, described in Section 3.0, are Stack Vent #003, Emission Units #002 and #003, and Stack Vent #004 and Boiler #004. There are no emission limits on these units for lead. Extensive coal sampling was done during the mercury Information Collection Request (ICR) test program, and these samples were subsequently analyzed for lead. At Unit 4, a second set of coal samples was taken during the lead testing for comparison purposes. The lead samples were taken using EPA Method 12 protocol.

4.0 OPERATING CONDITIONS

Unit operation during testing was at or near nominal full load (>80%) and at steady state. In addition, all pollution control equipment on all units were fully operational. The results presented in this report are at worst-case conditions because the units were operated at or near full load. Tables 1–3 present a summary of the sampling and plant data for each of the test periods. The detailed reports are presented in the three appendices.



EERO DL17811.GDR

Figure 6. Unit 4 stack test port locations and traverse point distances.

TABLE 1¹

Unit 2 Test Data

| | Run 1 | Run 2 | Run 3 |
|-----------------------------------|-----------------|---------|---------|
| Test Data | | | |
| Test Date | 5/8/00 | 5/8/00 | 5/8/00 |
| Time Begun | 13:16 | 14:55 | 17:40 |
| Total Sampling Time, min | 150 | 150 | 151.9 |
| Process Conditions | | | |
| Average Duct Temperature, °F | 323 | 323 | 331 |
| Average Duct Velocity, ft/sec | 44.1 | 39.8 | 42.8 |
| Flue Gas Moisture, % | 9.95 | 10.06 | 10.34 |
| Flue Gas O ₂ , % | 6.0 | 5.7 | 5.6 |
| Flue Gas CO ₂ , % | 13.5 | 13.8 | 13.9 |
| Flue Gas NO _x , ppm | 225.4 | 222.8 | 226.3 |
| Average Opacity, % | 10.4 | 10.6 | 10.0 |
| Wet Molecular Weight, lb/lb-mole | 29.2 | 29.2 | 29.2 |
| Production Data | | | |
| Coal Feed Rate, 1000 lb/hr | NA ² | NA | 59.3 |
| Gross Load, MW | 55.9 | 55.9 | 55.9 |
| Input, MMBtu/hr | 548 | 548 | 539 |
| Sample Data | | | |
| Sample Volume, dscf | 74.497 | 69.215 | 73.512 |
| Dust Loading, ³ gr/scf | 0.00255 | 0.00442 | 0.00481 |
| Isokinetic Variation, % | 96.7 | 99.2 | 98.1 |

¹ Multiple sample boxes were used and tests overlapped.² Data are not available.³ The dust loading is not a valid EPA Method 5 value, as the acetone rinse and condensables were not done. These results are provided for comparison purposes only.

TABLE 2

Unit 3 Test Data

| | Run 1 | Run 2 | Run 3 |
|-----------------------------------|---------|---------|---------|
| Test Data | | | |
| Test Date | 5/9/00 | 5/9/00 | 5/9/00 |
| Time Begun | 13:00 | 17:45 | 20:47 |
| Total Sampling Time, min | 125.1 | 126.7 | 125.0 |
| Process Conditions | | | |
| Average Duct Temperature, °F | 121 | 122 | 108 |
| Average Duct Velocity, ft/sec | 22.2 | 20.1 | 20.1 |
| Flue Gas Moisture, % | 12.98 | 13.38 | 13.23 |
| Flue Gas O ₂ , % | 5.9 | 6.0 | 6.2 |
| Flue Gas CO ₂ , % | 13.5 | 13.5 | 13.1 |
| Flue Gas NO _x , ppm | 422.1 | 423.8 | 393.8 |
| Wet Molecular Weight (lb/lb-mole) | 28.8 | 28.7 | 28.7 |
| Production Data | | | |
| Coal Feed Rate, 1000 lb/hr | 351.0 | 351.7 | 331.0 |
| Gross Load, MW | 319.3 | 320.0 | 301.5 |
| Heat Input, MMBtu/hr | 3205 | 3212 | 3026 |
| Sample Data | | | |
| Sample Volume, dscf | 37.411 | 34.265 | 33.917 |
| Dust Loading, ¹ gr/scf | 0.02629 | 0.02591 | 0.02543 |
| Isokinetic Variation, % | 95.2 | 95.7 | 93.4 |

¹ The dust loading is not a valid EPA Method 5 value, as the acetone rinse and condensables were not done. These results are provided for comparison purposes only.

TABLE 3

Unit 4 Test Data

| | Run 1 | Run 2 | Run 3 |
|-------------------------------------|---------|---------|---------|
| Test Data | | | |
| Test Date | 5/10/00 | 5/11/00 | 5/11/00 |
| Time Begun | 13:00 | 9:20 | 13:35 |
| Total Sampling Time, min | 125.1 | 120.0 | 120.0 |
| Process Conditions | | | |
| Average Duct Temperature, °F | 152 | 151 | 164 |
| Average Duct Velocity, ft/sec | 28.8 | 28.6 | 31.9 |
| Flue Gas Moisture, % | 20.04 | 16.20 | 16.65 |
| Flue Gas O ₂ , % | 4.6 | 5.0 | 5.4 |
| Flue Gas CO ₂ , % | 14.7 | 14.4 | 14.1 |
| Flue Gas NO _x , lb/MMBtu | 0.23 | 0.23 | 0.24 |
| Flue Gas SO ₂ , lb/MMBtu | 0.16 | 0.11 | 0.15 |
| Average Opacity, % | 17.9 | 18.5 | 18.4 |
| Wet Molecular Weight (lb/lb-mole) | 29.3 | 29.4 | 29.4 |
| Production Data | | | |
| Coal Feed Rate, 1000 lb/hr | 597.2 | 596.5 | 635.1 |
| Gross Load, MW | 532.5 | 542.1 | 551.4 |
| Heat Input, MMBtu/hr | 5371 | 5371 | 5723 |
| Sample Data | | | |
| Sample Volume, dscf | 23.0 | 28.6 | 31.9 |
| Dust Loading, ¹ gr/scf | 0.01626 | 0.01518 | 0.00906 |
| Isokinetic Variation, % | 92.1 | 96.3 | 93.8 |

¹ The dust loading is not a valid EPA Method 5 value, as the acetone rinse and condensables were not done. These results are provided for comparison purposes only.

5.0 TEST METHODS

EPA Method 12, Determination of Inorganic Lead Emissions from Stationary Sources, was used to determine the lead in the flue gas at the Boswell Energy Center. This method was used in conjunction with the sampling procedures as outlined in EPA Methods 1 through 5. The sampling procedures used for the testing are shown in Table 4. A schematic of the sampling train is shown in Figure 7.

TABLE 4

| Stack Gas Test Methods | |
|------------------------|---|
| Test Method | Purpose |
| EPA Method 1 | Sample and velocity traverses. |
| EPA Method 2 | Determination of stack velocity and volumetric flow rate. |
| Portable Instrument | Measurement of O ₂ and CO ₂ (Eco-America Instrument). |
| EPA Method 4 | Determination of moisture in stack gases. |
| EPA Method 12 | Determination of inorganic lead from stationary sources. |

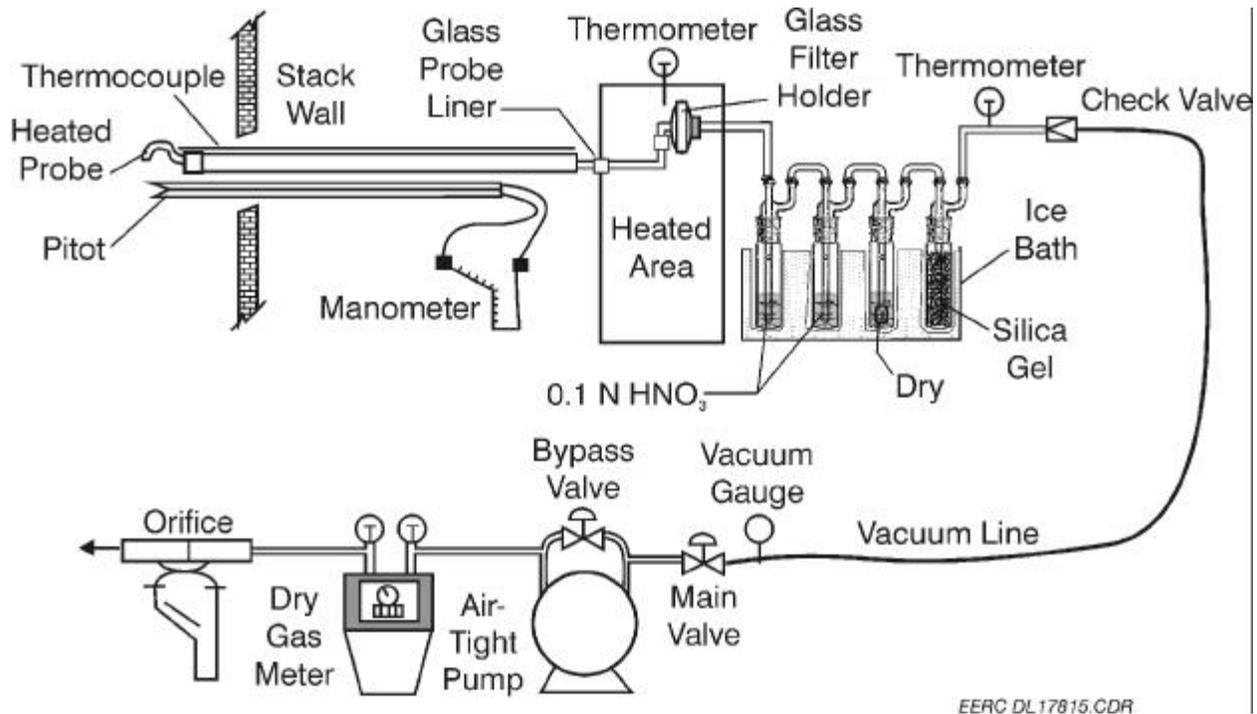


Figure 7. Schematic of the EPA Method 12 inorganic lead sampling train.

5.1 Sampling Apparatus

The sampling train consists of a “gooseneck” nozzle constructed of quartz and connected to a heated glass probe liner. The probe line was connected to a Teflon[®]-coated stainless steel filter holder containing a quartz glass filter. The filter was heated in a hot box to $120^{\circ} \pm 14^{\circ}\text{C}$. The back half of the filter holder was connected to a series of impingers with insulated Teflon tubing. A combination Type S pitot tube and Type K thermocouple was used to measure the duct velocity and temperature.

5.2 Sampling Procedure

Prior to sampling, traverse points were selected on the basis of EPA Method 1 requirements and the available ports, as discussed in Section 3.0 of this report. The sample nozzle size was determined according to the known moisture content of the flue gas from the ICR report.

The impinger boxes and filters were assembled and weighed in an on-site trailer. The impingers were set up as stated in EPA Method 12. As shown in Figure 7, four impinger bottles are used for this sampling procedure. The first, third, fourth impingers use a modified Greenberg-Smith design with a straight tube. The second impinger uses the standard Greenberg-Smith tip. The first two impingers are charged with approximately 100 mL of reagent-grade 0.1 N HNO₃ solution. The third impinger is dry, and the fourth contains silica gel to remove any residual water.

Once the impinger box and filter were weighed and assembled in an on-site trailer, they were taken to the sample site and attached to the probe, hot box, and sampling box. The filter was then brought to temperature and leak-checked according to the procedures outlined in EPA Method 5. Upon successful completion of the leak check, the probe was inserted at the first traverse point and the sampling began. The sampling box used by the EERC for this test is an automatic system developed by Grasby-Anderson. The sampling box automatically calculates and maintains isokinetic sampling and records all appropriate data. These results are provided in the appendices.

Upon completion of sampling at a port, the sampling box was turned off and the probe, filter, and impinger box moved to the next port. The previously described procedure was then repeated at each port. When the sample run was completed and the probe leak-checked, all necessary data were recorded from the sample box. The filter was then disconnected from the sample probe, and the sample probe was thoroughly rinsed using 0.1 N HNO₃ and distilled deionized water into a 250-mL flask. It should also be noted that at each sample location, a calibrated Eco-America portable gas analyzer was used to measure the flue gas O₂ and CO₂ concentration.

5.3 Sample Recovery

The recovery procedure as outlined in EPA Method 12 is shown in Figure 8. Each of the lead samples was recovered into three containers: the probe rinse, the impinger solutions, and the filter. Note: Container 3, the silica gel in Figure 8, is not analyzed for lead. The moisture content of the flue gas was determined by weighing each impinger before and after sampling. On-site, the filter was carefully removed from the filter holder and placed in a petri dish. Any residual particulate matter left on the front half of the filter holder was brushed onto the filter. The impinger solutions were combined into one flask and then, along with all connectors, rinsed with 0.1 N HNO₃ solution, which was then added to the flask. This flask was properly labeled and stored. At each sampling site, a blank solution was recovered for analysis.

6.0 TEST RESULTS

The lead concentrations in the coal were determined using coal samples collected during the EPA ICR for mercury that was conducted for Units 2, 3, and 4. It is unknown why the lead concentration in the first coal sample collected for Unit 3 was an order of magnitude higher than in the other two samples. The sample was analyzed several times, and the results were the same. One set of coal samples was taken at Unit 4 during the time when the lead sampling was being conducted. This was done because of the desire to obtain an additional mercury sample at the Unit 4 scrubber inlet. The coal lead results are shown in Table 5. As can be seen, there was little

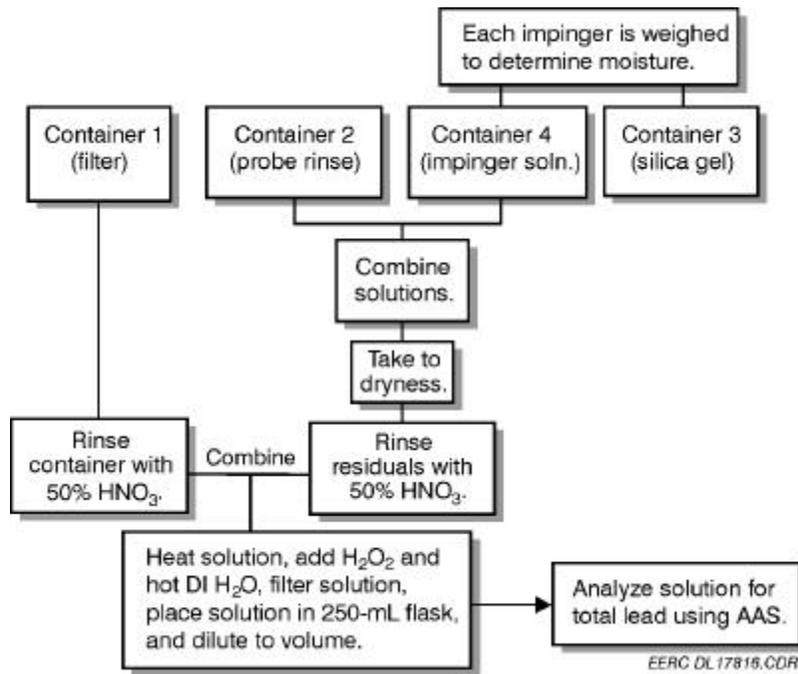


Figure 8. EPA Method 12 recovery procedure.

TABLE 5

Lead Concentration in the Coal Fired at the
Boswell Energy Center During Mercury ICR Testing¹

| Unit No. | Run 1, $\mu\text{g/g}$ | Run 2, $\mu\text{g/g}$ | Run 3, $\mu\text{g/g}$ | Run 4, ² $\mu\text{g/g}$ | Average, $\mu\text{g/g}$ |
|----------|------------------------|------------------------|------------------------|-------------------------------------|--------------------------|
| 2 | 3.2 | 4.1 | 3.6 | NA ³ | 3.6 ± 0.5 |
| 3 | 26.5 | 5.4 | 6.9 | NA | 12.9 ± 11.8 |
| 4 | 3.7 | 3.5 | 4.1 | 2.8 | 3.5 ± 0.5 |

¹ Results are reported on a dry basis.

² This sample was taken during the time when lead sampling was being completed for Unit 4.

³ Data are not available.

change in the coal lead concentration for the two sets of samples taken for Unit 4. Also from the mercury ICR report, the coal ultimate and proximate analysis is provided in Table 6. These values were used to determine the lead emission factors using EPA Method 19 protocols.

A summary of the EPA Method 12 lead emission at each of the three units tested is shown in Tables 7 and 8. The lead samples for Unit 4 had more variation than those measured for the other two units. This appears to be a result of the variation in particulate loading at the outlet of the absorber towers. As shown in Table 7, the lead concentration at the stack tracked almost exactly with the particulate loading at the stack. This would make sense, because the lead is primarily emitted in the form of particulate matter.¹

7.0 SAMPLE CALCULATIONS

Sample calculations are included for each of the calculated parameters. Data from the Unit 2 location during Run 1 were used.

7.1 Volume of Gas Sample

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

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

$V_m(\text{std})$ = $17.64 * 79.899 * 1 * 28.29 / (75 + 460) = 74.497 \text{ dscf}$

¹ Brown, T.D; Smith, D.N.; Hargis, R.A.; O'Dowd, W.J. Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate. Critical Review, *J. Air Waste Manage. Assoc.* **1999**, June, 1-97.

TABLE 6

Coal Analysis¹

| | Unit 2 | Unit 3 | Unit 4 |
|---------------------------|--------|--------|--------|
| Proximate Analysis | | | |
| Volatile Matter, % | 43.01 | 42.52 | 42.87 |
| Ash, % | 7.80 | 8.11 | 7.78 |
| Total Moisture, % | 26.5 | 27.4 | 26.0 |
| Ultimate Analysis | | | |
| Total Moisture, % | 26.5 | 27.4 | 26.0 |
| Carbon, % | 70.42 | 70.27 | 70.43 |
| Hydrogen, % | 4.61 | 4.48 | 4.49 |
| Nitrogen, % | 0.99 | 1.00 | 0.98 |
| Sulfur, % | 0.64 | 0.68 | 0.57 |
| Oxygen, % | 15.55 | 15.46 | 15.76 |
| Heating Value, Btu/lb | 12,115 | 12,032 | 12,053 |

¹ Taken from mercury ICR Report.

TABLE 7

Summary of Lead Concentrations Exiting the Stack at the Boswell Energy Center¹

| Unit No. | Run 1 Flue Gas Concentration, $\mu\text{g}/\text{m}^3$ | Run 2 Flue Gas Concentration, $\mu\text{g}/\text{m}^3$ | Run 3 Flue Gas Concentration, $\mu\text{g}/\text{m}^3$ | Average, $\mu\text{g}/\text{m}^3$ |
|----------|---|---|---|--------------------------------------|
| 2 | 2.5 | 2.5 | 1.7 | 2.2 ± 0.38 |
| 3 | 22.8 | 22.3 | 26.0 | 23.7 ± 1.64 |
| 4 | 15.7 | 13.3 | 9.8 | 12.9 ± 2.97 |

¹ The concentrations are presented on a 3% oxygen basis.

TABLE 8

Summary of Lead Emission Factors at the Boswell Energy Center¹

| Unit No. | Run 1, lb/10 ¹² Btu | Run 2, lb/10 ¹² Btu | Run 3, lb/10 ¹² Btu | Average, lb/10 ¹² Btu |
|----------|--------------------------------|--------------------------------|--------------------------------|----------------------------------|
| 2 | 1.8 | 1.8 | 1.2 | 1.6 ± 0.34 |
| 3 | 16.2 | 15.8 | 18.5 | 16.8 ± 1.46 |
| 4 | 11.2 | 9.5 | 7.0 | 9.2 ± 2.11 |

¹ Calculations based on EPA Method 19.

Where:

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

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

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

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

7.2 Volume of Water Vapor

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

$V_{w(std)} (scf) = K_2 * H_2O(g)$

$V_{w(std)} = 0.04715 * 174.6 = 8.232 \text{ scf}$

Where:

$K_2 = 0.04715 \text{ ft}^3/\text{g}$

$H_2O(g) = \text{Mass of liquid collected in impingers and silica gel, g}$

7.3 Water Vapor in the Gas Stream

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

$B_{ws} = V_{w(std)} / (V_m(std) + V_{w(std)})$

$B_{ws} = 8.232 / (74.899 + 8.232) = 0.0995 \text{ or } 9.95 \% \text{ water vapor}$

7.4 Molecular Weight

Dry Basis

$$\begin{aligned}M_d &= \text{Dry molecular weight of stack gas, lb/lb-mole} \\M_d \text{ (lb/lb-mole)} &= 0.440 * (\%CO_2) + 0.320 * (\%O_2) + 0.280 * (\%N_2 + \%CO) \\M_d &= 0.440 * 13.5 + 0.320 * 6.0 + 0.280 * 80.5 = 30.4 \text{ lb/lb-mole}\end{aligned}$$

Where:

$$\%(\text{CO}_2, \text{O}_2, \text{N}_2, \text{CO}) = \text{Percent (CO}_2, \text{O}_2, \text{N}_2, \text{CO) by volume, dry basis in the flue gas}$$

Wet Basis

$$\begin{aligned}M_s &= \text{Molecular weight of stack gas, wet basis, lb/lb-mole} \\M_s \text{ (lb/lb-mole)} &= M_d * (1 - B_{ws}) + 18.0 * B_{ws} \\M_s &= 30.4 * (1 - 0.0995) + 18.0 * 0.0995 = 29.2 \text{ lb/lb-mole}\end{aligned}$$

7.5 Average Stack Gas Velocity

$$\begin{aligned}V_s &= \text{Average stack gas velocity, ft/sec} \\V_s \text{ (ft/sec)} &= K_3 * C_p * (\Delta p)^{1/2} \text{ avg} * [(T_s + 460) / (P_s * M_s)]^{1/2} \\V_s &= 85.49 * 0.84 * 0.617 * [(323 + 460) / (27.07 * 29.2)]^{1/2} = 44.1 \text{ ft/sec}\end{aligned}$$

Where:

$$\begin{aligned}K_3 &= 85.49 \text{ ft/sec}[(\text{lb/lb-mole})(\text{in. Hg})/(\text{°R})(\text{in. H}_2\text{O})]^{1/2} \\C_p &= \text{Pitot tube coefficient, dimensionless} \\ \Delta p &= \text{Velocity head of stack gas, in. Hg} \\T_s &= \text{Stack gas temperature, °F} \\P_s &= \text{Stack pressure, in. Hg}\end{aligned}$$

7.6 Isokinetic Sampling Rate

$$\begin{aligned}I &= \text{Percent of isokinetic sampling} \\I \text{ (\%)} &= K_4 * (T_s + 460) * V_m(\text{std}) / (P_s * V_s * A_n / 144 * \theta * (1 - B_{ws})) \\I &= 0.09450 * (323 + 460) * 74.4972 / (27.07 * 44.1 * 0.0507 / 144 * 150 * (1 - 0.0995)) = 97.0\%\end{aligned}$$

Where:

$$\begin{aligned}K_4 &= 0.09450 \text{ in. Hg} * \text{min}/\text{°R} * \text{sec} \\A_n &= \text{Cross-sectional area of nozzle, in.}^2 \\ \theta &= \text{Total sampling time, min}\end{aligned}$$

7.7 Volume of Gas Sample Corrected to 3% O₂

$V_{m@(\text{std})}$ = Volume of gas sample measured by the dry gas meter ($V_{m(\text{std})}$),
@corrected to 3% oxygen, Nm^3

$V_{m@(\text{std})}$ = $V_{m(\text{std})} * (20.9 - \%O_2) / 18 * K_5$

$V_{m@(\text{std})}$ = $74.497 * (20.9 - 6.0) / 18 * 0.02832 = 1.758 \text{ Nm}^3$

Where:

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

7.8 Lead Concentration

Pb (μg) = $4.4 \mu\text{g}$ (total collected during sampling)

Pb (3% O₂) = $\mu\text{g Pb} / V_{m@(\text{std})}, \mu\text{g}/\text{Nm}^3$

Pb = $4.4 / 1.758 = 2.5 \mu\text{g}/\text{Nm}^3$

Pb (stack O₂) = $4.4 / V_{m(\text{std})} * K_5, \mu\text{g}/\text{Nm}^3$

Pb = $4.4 / 74.497 * 0.02832 = 2.1 \mu\text{g}/\text{Nm}^3$

7.9 Lead Emission Factors

These values were calculated on the basis of emission factors for subbituminous coal as outlined in EPA Method 19. The method used is based on the proximate and ultimate analysis of the coal, as shown in Table 6.

$Pb_E (\text{lb}/10^{12} \text{ Btu})$ = $F_d * C_d * 10^6 * [20.9/(20.9 - \%O_2)]$

Pb_E = $9728 * 1.3021 \times 10^{-10} * 10^6 [(20.9/(20.9 - 6))] = 1.8 \text{ lb} / 10^{12} \text{ Btu}$

Where:

$F_d (\text{dscf}/10^6 \text{ Btu})$ = $[(3.64 * (\%H) + 1.53 * (\%C) + 0.57 * (\%S) + 0.14 * (\%N) - 0.46 * (\%O)) * 10^6] / \text{GCV}$

F_d = $[(3.64 * 4.62 + 1.53 * 70.79 + 0.57 * 0.62 + 0.14 * 0.99 - 0.46 * 15.67) * 10^6] / 12158 = 9728 \text{ dscf} / 10^6 \text{ Btu}$

C_d = Pb concentration at stack O₂ in lb/dscf

C_d = $2.1 / (4.536 \times 10^8 * 0.02832) = 1.3021 \times 10^{-10} \text{ lb}/\text{dscf}$

8.0 QUALITY ASSURANCE AND QUALITY CONTROL

Field QA/QC activities associated with the collection of EPA Method 12 lead emission samples included pre- and posttest calibration of sampling equipment, adherence to the proper sampling method procedures, documentation of field data, recovery of samples without contamination, and collection of appropriate blank samples.

Copies of the field data sheets are contained in the appendices. Chain-of-custody forms included in each laboratory report provide a list of all samples collected and submitted for analysis during the test program. These laboratory reports are also provided in the appendices. Proper field sampling procedures include sampling at 100% isokinetic \pm 10% and maintaining sample train leakage rates at \leq 0.02 cfm.

For these tests, one field blank was submitted for each sampling location, with the exception of Unit 4, where a field blank was not done. A field blank is defined as a sample impinger train that is assembled exactly as those used for the sampling. This train is then taken to the sampling location but not used. When the sampling is completed, the field blank is recovered in the same manner as the sample. The results for the field blanks and a reagent blank (see Table 9) show that in all cases, the lead blanks were $< 1 \mu\text{g/L}$ (the lower limit of quantification for the atomic absorption spectroscope). This indicates that there was not sample contamination.

The QA/QC for the graphite furnace atomic absorption spectrometer involves calibration using commercially available standards of either 1000 mg/L or 10,000 mg/L. Appropriate serial dilutions are made to obtain desired concentrations. The instrument is calibrated with a blank and three standards that will bracket the concentration of analyte in the samples. Mean absorbance values are recorded in a log book for all standards each time the instrument is calibrated. Immediately after the instrument is calibrated, an initial calibration verification (ICV) standard is run. This standard is prepared from a stock solution separate from that used for the calibration standards and should read $\pm 5\%$ of the actual value. The concentration of the ICV should be between the middle and upper end of the calibration curve.

Each result reported is the mean of three replicate readings that have less than 10% relative standard deviation. This determines instrument precision and helps ensure that the auto-sampler is functioning properly and that the sample is not adhering to the capillary during the delivery. Analyte spikes of known concentrations are prepared and analyzed at a frequency of one out of every ten or one sample from each batch to confirm analyte recovery. The amount of analyte added should be approximately equal to the amount found in the sample. A range of 50%–150%

TABLE 9

| Field Blank Results | |
|----------------------|--|
| Sample | Lead Concentration in Solution, $\mu\text{g/L}$ |
| Unit 2 – Field Blank | <1.0 |
| Unit 3 – Field Blank | <1.0 |
| Unit 4 – Field Blank | NA |
| Reagent Blank | <1.0 |

of the read value is acceptable, except when no analyte is detected, then the amount added should be enough to read well within the calibration range. Recovery of the added spike is calculated as follows:

$$\% \text{ recovery} = \frac{(\text{sample} + \text{spike}) - (\text{sample})}{(\text{spike})} \times 100\%$$

Acceptable ranges for analyte recovery are 85%–115% for samples reading above the instrument reporting level ($10 \times \text{IDL}$ [instrument detection limit]) and 50%–150% for samples reading below the instrument reporting level. Spike volume relative to the sample aliquot volume should be as small as possible, but not so small that it cannot be dispensed accurately. The solution used for spiking should be from a stock separate from that used for the calibration standards.

A continuing calibration verification (CCV) standard is run every ten samples and at the end of every run to check the slope of the calibration curve. This CCV is one of the original calibration standards and should read $\pm 10\%$ of the true value or the instrument is recalibrated and the samples since the last acceptable CCV are reanalyzed.