

- Hg removed by the ESP was low: an average of 0.2 lb Hg/10<sup>12</sup> Btu for the two units.

# 5

## SITE S6

Site S6 was selected for inclusion in the 2002 SCR testing to provide data associated with burning a compliance low-sulfur eastern bituminous coal. The primary tests were conducted on two of the four units at Site S6. On one of the units, SCR was operated for the entire testing period; however, on the other, SCR was bypassed for the majority of the test period. In addition, at Site S6, additional testing was done at the stack of a third unit (no SCR) as part of a separate test program. For comparison purposes, the results obtained at this unit are also presented in this report.

### 5.1 Site Description and Configuration

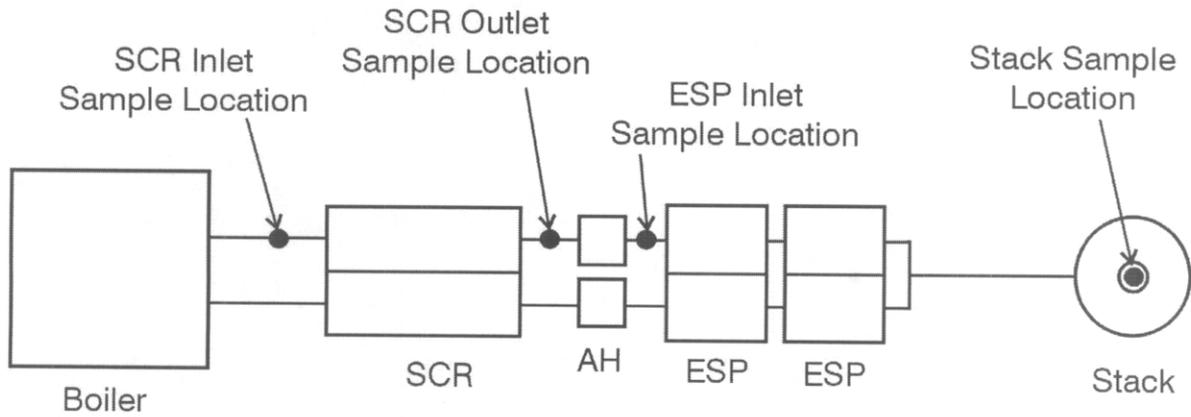
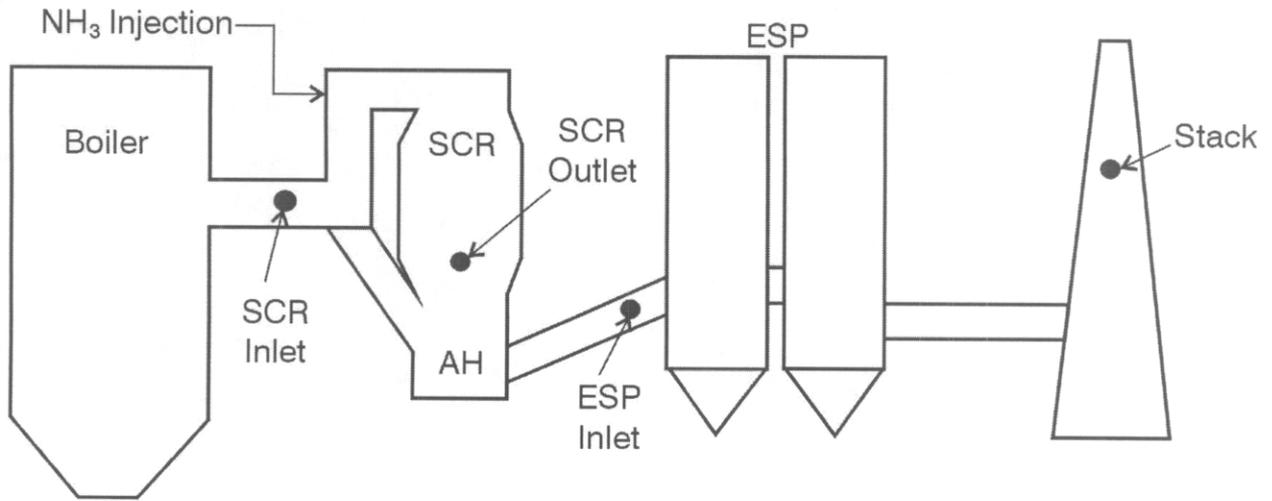
Site S6 operates four units consisting of two sets of similar configurations. Two of the four units have SCR units to reduce NO<sub>x</sub>, and all four units have ESPs for particulate control. The SCR catalysts at Site S6 are a honeycomb type and manufactured by Cormetech. The SCR unit has a space velocity 3800 hr<sup>-1</sup>. The SCR units have been operating for two ozone seasons. In between the two seasons, one layer of catalyst was changed. Specifications of the Site S6 units are presented in Table 5-1.

**Table 5-1**  
**Specifications of Site S6 Units<sup>a</sup>**

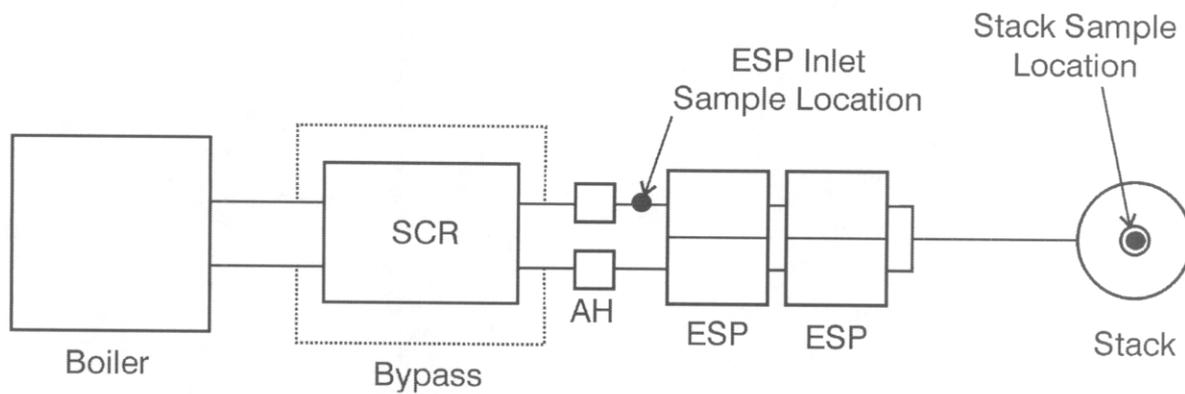
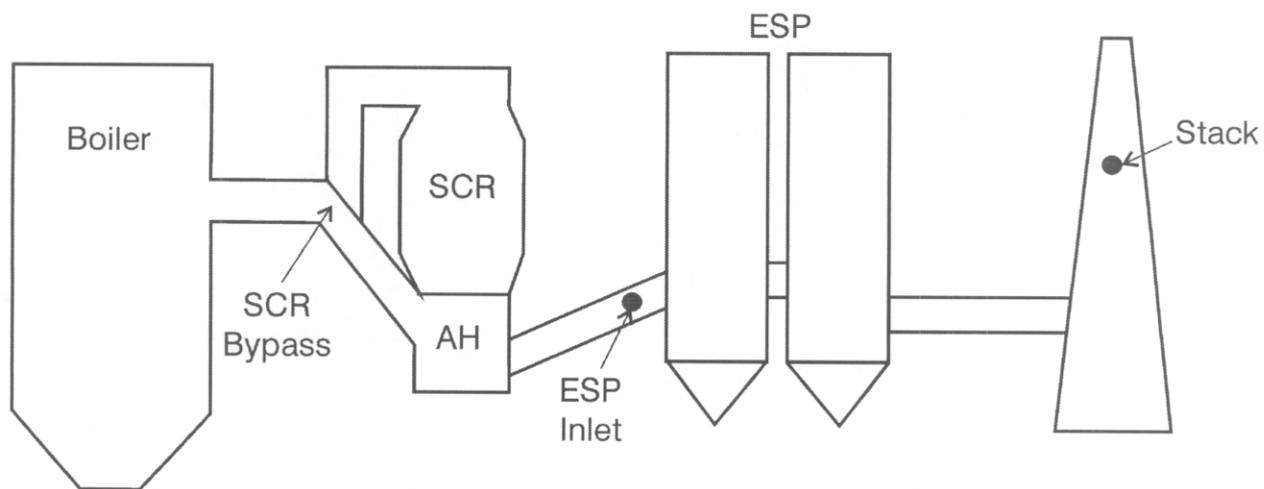
Specification	Unit 1	Unit 2	Unit 4
Fuel Type	KY and WV eastern bituminous coal	KY and WV eastern bituminous coal	KY and WV eastern bituminous coal
Boiler Capacity	700 MW	700 MW	900 MW
Boiler Type	tangentially fired	tangentially fired	tangentially fired
Low-NO <sub>x</sub> Burners	Yes	Yes	Yes
SCR	Yes	Operated in bypass mode	No
Particulate Control	ESP	ESP	ESP
SO <sub>2</sub>	Low-sulfur compliance coal	Low-sulfur compliance coal	Low-sulfur compliance coal

<sup>a</sup> Site S6 has four units. Unit 3 (no testing was done at this time) is the same as Unit 4.

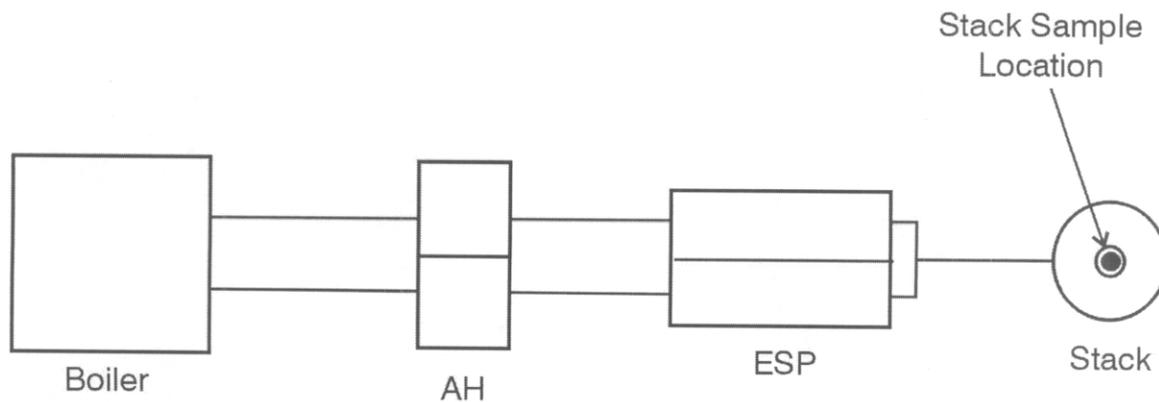
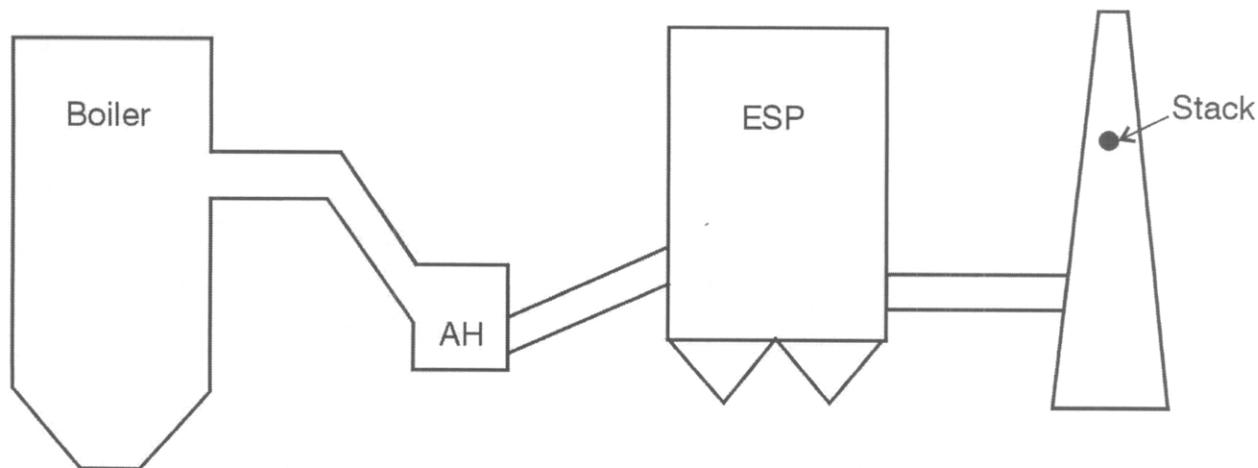
Schematics of the three test units at Site S6, including sampling locations, are shown in Figures 5-1 through 5-3.



**Figure 5-1**  
**Schematic of Site S6 Showing Sample Locations for Unit 1 with the SCR in Service from a Vertical and Horizontal Perspective**



**Figure 5-2**  
**Schematic of Site S6 Showing Sample Locations for Unit 2 with the SCR Bypassed from a Vertical and Horizontal Perspective**



**Figure 5-3**  
**Schematic of Site S6 Showing Sample Locations for Unit 4 with No SCR from a Vertical and Horizontal Perspective**

## 5.2 Sampling Approach

As stated previously, sampling at S6 was primarily conducted on two units (1 and 2) both with SCR, but the SCR unit was bypassed on Unit 2. Data collected from these similar units provided a comparison of speciated Hg emissions from SCR and no-SCR operation.

### 5.2.1 Flue Gas Sample Streams

The flue gas Hg speciation was measured using the OH method at four locations for Unit 1 (SCR) and two locations for Unit 2 (SCR bypassed). A test matrix, which identifies the location of flue gas measurements, is provided in Table 5-2. Where practical, OH measurements were conducted simultaneously across the various control devices in an effort to quantify the effect each had on Hg concentration and speciation. In addition to Hg, flue gas samples were collected to measure the total particulate loading and SO<sub>3</sub> concentrations. Additionally, NH<sub>3</sub> slip samples were collected from Unit 1 (SCR) to evaluate performance.

**Table 5-2**  
**Sampling Test Matrix for Site S6**

Date		SCR In	SCR Out	ESP In	Stack	SCR Out	SCR Out	ESP In
Begin	End	OH	OH	OH	OH	NH <sub>3</sub>	SO <sub>3</sub>	SO <sub>3</sub>
<i>Unit 1 (SCR)</i>								
09/22/02	09/26/02	4	4	4	5	2	2	2
10/08/02	10/18/02				7			
<i>Unit with SCR (Unit 2)</i>								
09/22/02	09/25/02				3			
<i>Unit 2 (SCR bypassed)</i>								
10/08/02	10/18/02			2	7		2	2
<i>Unit 4 (no SCR) – Plume Study</i>								
10/08/02	10/18/02				7			

Longer-term Hg monitoring was conducted using Hg SCEMs (PSA) located at the stack locations for each of the test units. These data provided semicontinuous Hg<sup>0</sup> and total gas-phase Hg concentrations for approximately 3 weeks.

### 5.2.2 Other Sample Streams

Samples of coal and ESP hopper ash were collected daily from the test units in an effort to obtain representative operational data related to Hg speciation. These samples were analyzed for Hg and, along with the flue gas emission data, were used to qualitatively evaluate the fate of Hg throughout the units. Daily coal samples were collected as composites from the different coal feeders. ESP hopper ash samples were collected from the first fields of the ESPs.

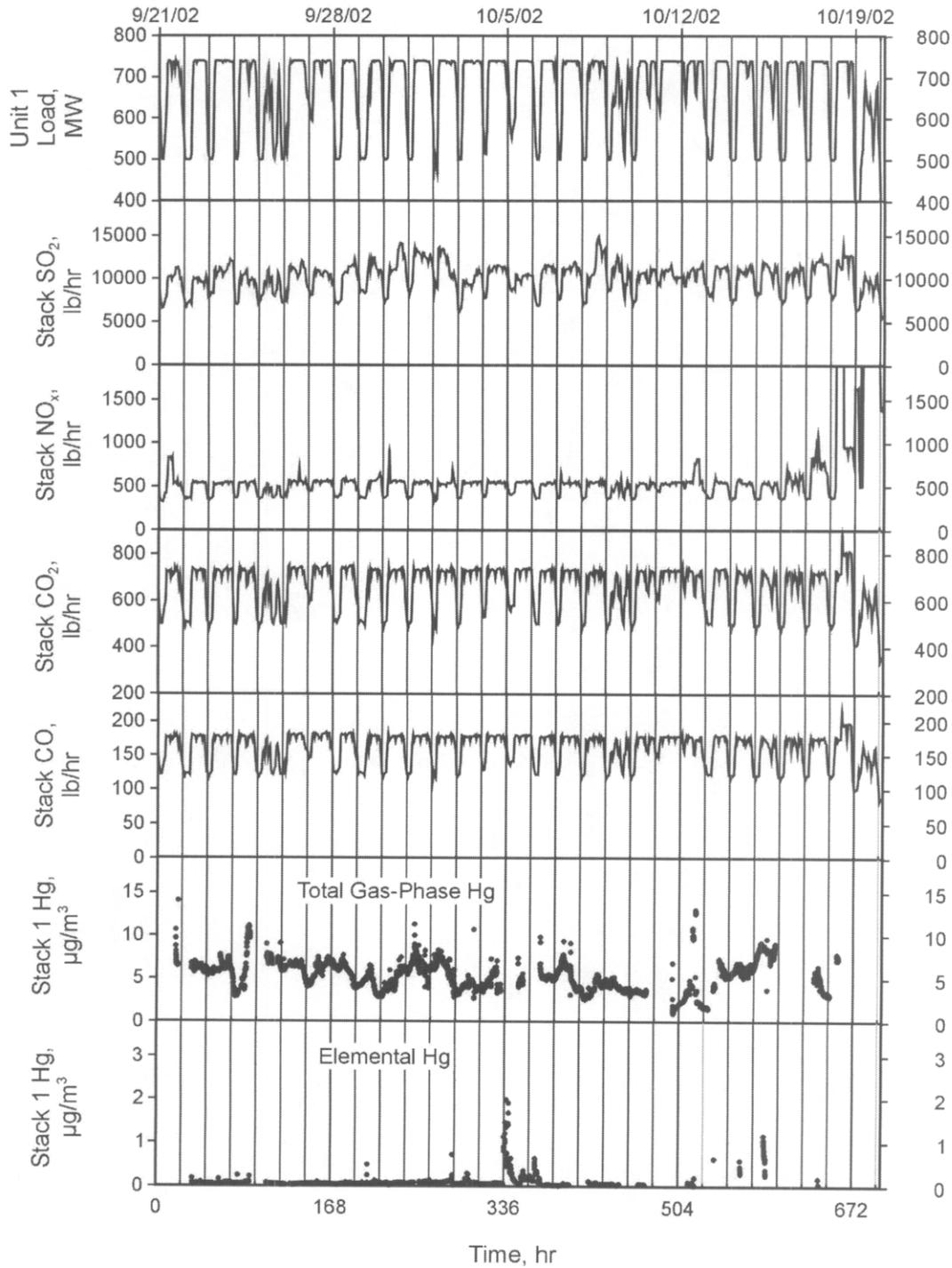
### **5.2.3 Process Operating Conditions**

Plant operational data are presented in Figures 5-4 through 5-6 for the test units. These figures summarize flue gas characteristics during the test program. Additionally, monthlong Hg SCEM data are included in these plots for comparison with plant operational data. Hg SCEM data will be discussed later in this report.

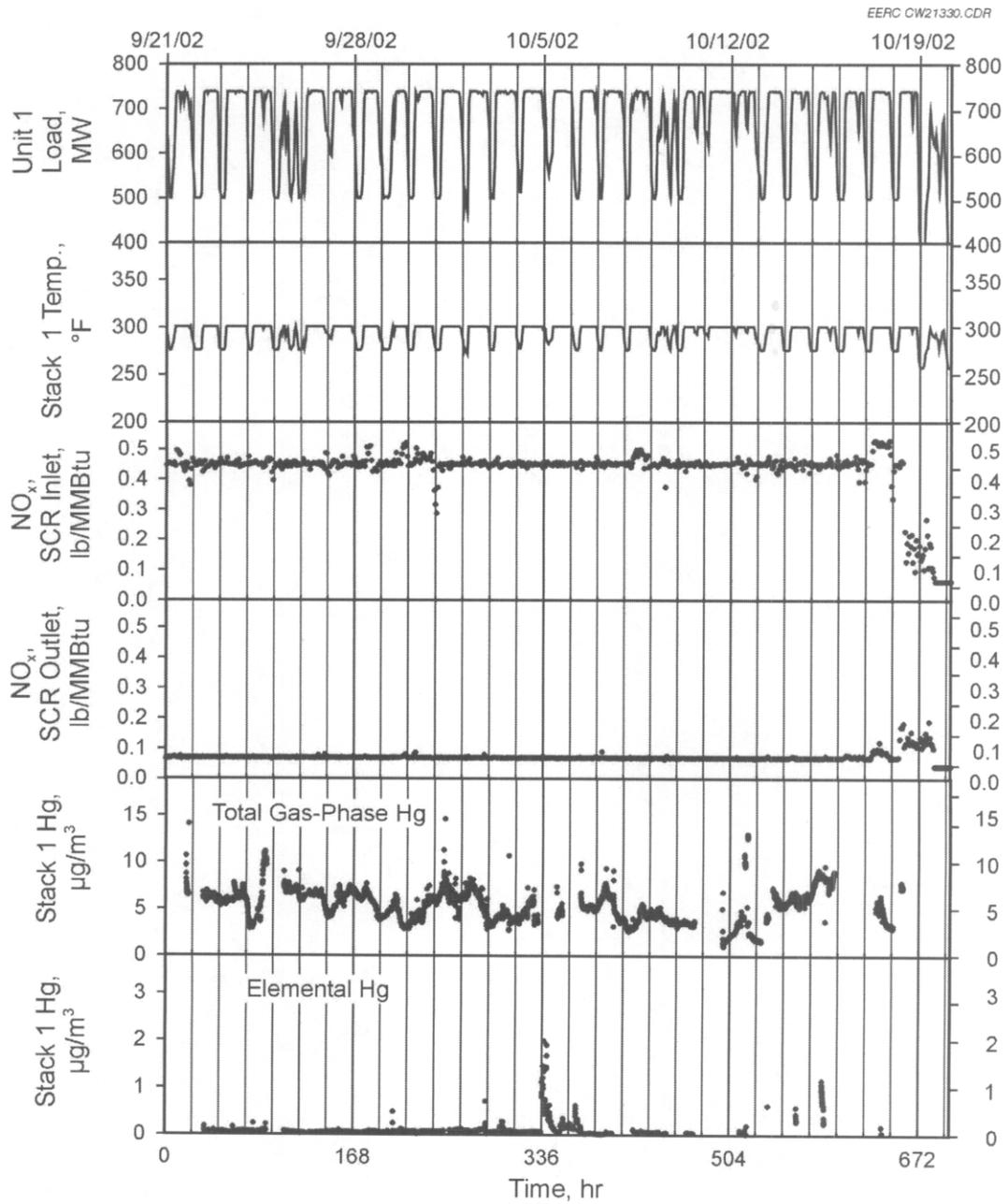
In general, during the day, the plant load at the two primary test units (Units 1 and 2) was near full load and would drop at night. However, at Unit 4 (no SCR), the plant data showed a significant load reduction at about 120 hours into the test.

A summary of auxiliary flue gas data, including percent O<sub>2</sub> and percent CO<sub>2</sub> for each sample location, is provided in Table 5-3 (the complete data set is in Table C-3 in Appendix C). In general, the percent moisture, CO<sub>2</sub>, and O<sub>2</sub> were very consistent from day to day. However, there was some air leakage across the air preheater that resulted in the O<sub>2</sub> increasing from 4.1% at the SCR inlet to 6.5% at the stack for Unit 1 (SCR). The air leakage was about the same for Unit 2 (SCR bypassed). Dust-loading measurements collected at the ESP inlet and outlet location reflect a particulate removal efficiency of >99% for both units based on an average of inlet and outlet dust loadings.

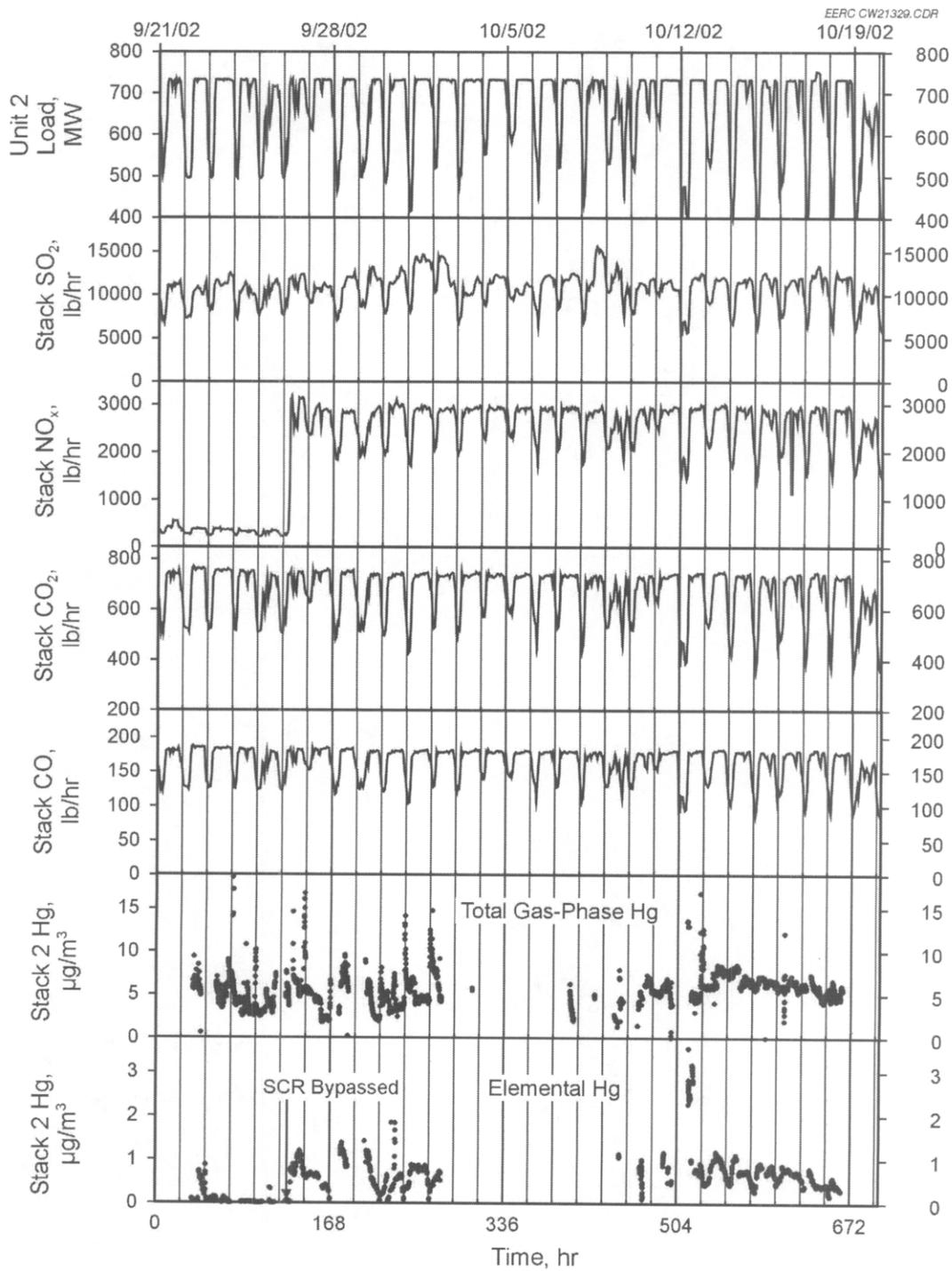
EERC CW21327.GDR



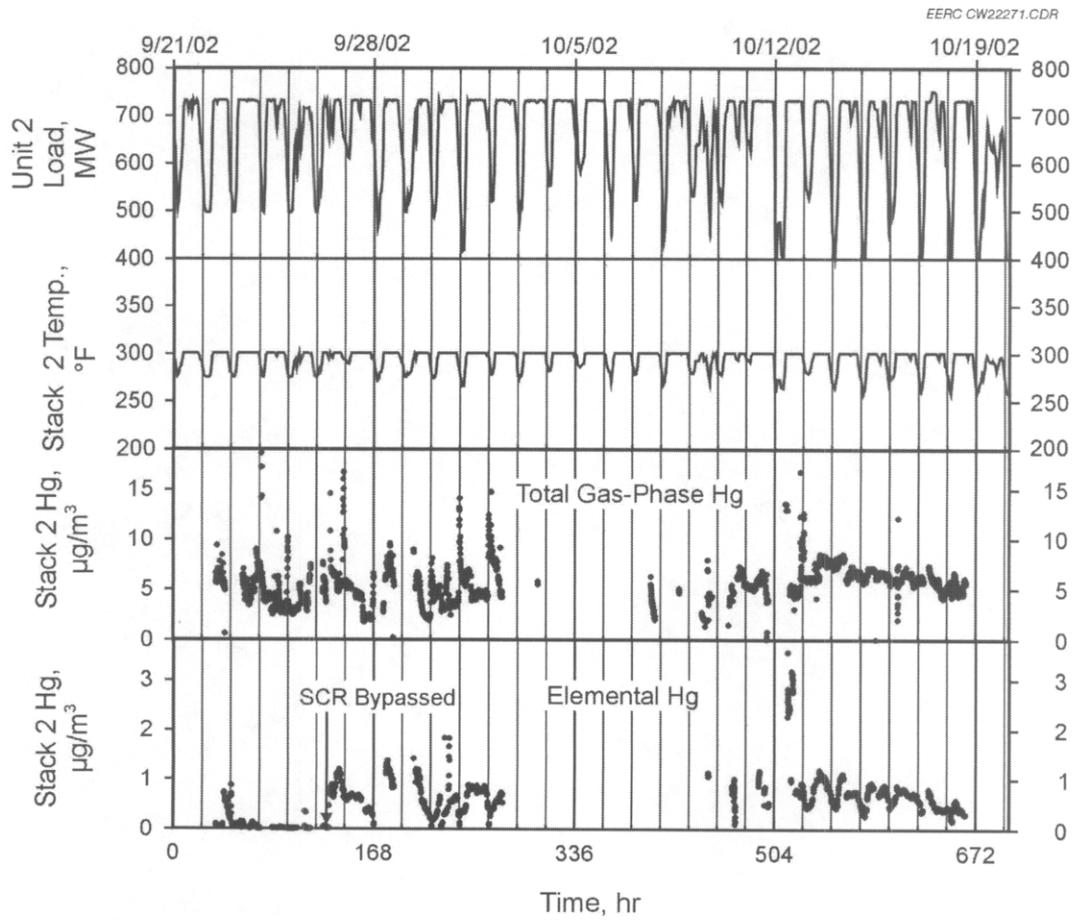
**Figure 5-4**  
**Plant Operation Data for Site S6 for Unit 1 with the SCR in Service**



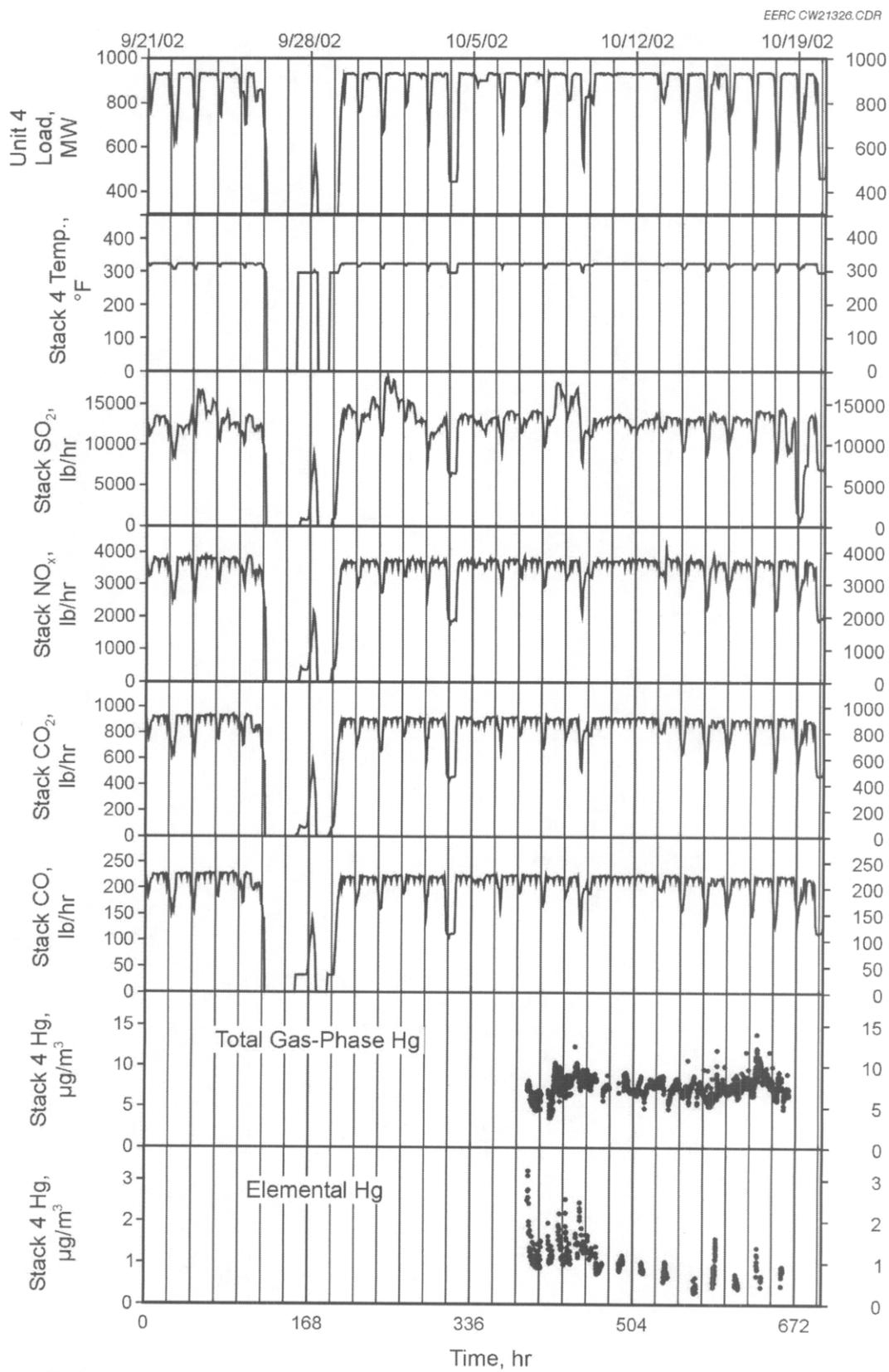
**Figure 5-4 (continued)**  
**Plant Operation Data for Site S6 for Unit 1 with the SCR in Service**



**Figure 5-5**  
**Plant Operation Data for Site S6 for Unit 2 with the SCR Bypassed**



**Figure 5-5 (continued)**  
**Plant Operation Data for Site S6 for Unit 2 with the SCR Bypassed**



**Figure 5-6**  
**Plant Operation Data for Site S5 for Unit 4 with No SCR**

**Table 5-3  
Auxiliary Flue Gas Data for Site S6**

	Moisture %	Dust, <sup>a</sup> gr/dscf	CO <sub>2</sub> , %	O <sub>2</sub> , %
<i>Unit 1 (SCR)</i>				
SCR Inlet	9.0	3.7306	14.7	4.1
SCR Outlet	8.7	4.1673	15.2	4.7
ESP Inlet	8.9	2.7321	13.8	5.0
Stack	9.3	0.0165	13.1	6.5
<i>Unit 2 (SCR bypassed)</i>				
ESP Inlet	8.3	4.2279	15.4	3.7
Stack	7.8	0.0150	13.2	6.4
<i>Unit 4 (no SCR)</i>				
Stack	7.8	0.0388	14.5	4.9

<sup>a</sup> Dust loadings were collected as part of the OH method using EPA Method 17 and, therefore, are not for compliance purposes.

## 5.3 Sampling Results

### 5.3.1 OH Flue Gas Mercury Results

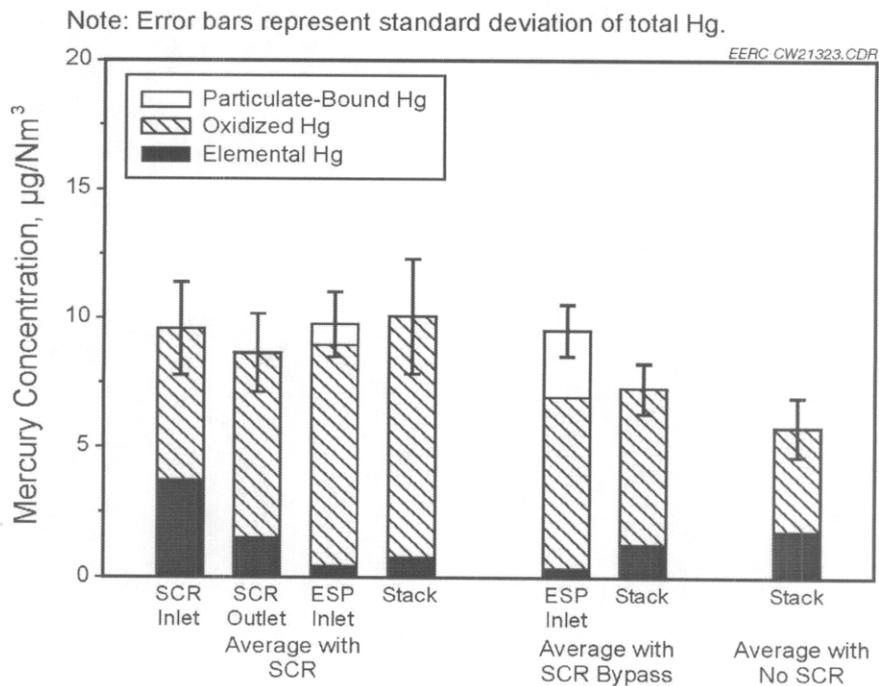
Average Hg results for flue gas sampling at Site S6 are presented in Table 5-4. The complete results are presented in Appendix B (Tables B-8 and B-9). As shown in Table 5-4, there is an increase in the concentration of Hg<sup>2+</sup> across the SCR catalyst from 60% to 82% Hg<sup>2+</sup>. There is only a slight additional increase to 87% at the ESP inlet location (this is within the variation of the data).

Comparing the ESP inlet Hg speciation results for Unit 1 (SCR) and Unit 2 (SCR bypassed) shows that the percentage of Hg<sup>2+</sup> was 69% with SCR bypassed and 87% with SCR. However, there was essentially no Hg removal across the ESP for either unit. A direct comparison including the error bars associated with the total Hg concentration for all three units is shown in Figure 5-7.

**Table 5-4**  
Average and Percentage of Total OH Mercury Results for S6<sup>a</sup>

	Average, $\mu\text{g}/\text{Nm}^3$				Percent of Total, %		
	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>	Hg <sub>Total</sub>	Hg <sub>p</sub>	Hg <sup>2+</sup>	Hg <sup>0</sup>
<i>Unit 1 (SCR)</i>							
SCR Inlet	0.04	5.8	3.8	9.6	0	60	40
SCR Outlet	0.03	7.1	1.5	8.6	0	82	18
ESP Inlet	0.80	8.5	0.5	9.8	8	87	5
Stack	0.00	9.3	0.8	10.1	0	92	8
<i>Unit 2 (SCR bypassed)</i>							
ESP Inlet	2.59	6.6	0.4	9.5	27	69	4
Stack	0.01	6.0	1.3	7.3	0	82	18
<i>Unit 4 (no SCR)</i>							
Stack	0.01	4.0	1.8	5.8	0	69	31

<sup>a</sup> All mercury results are on a dry basis corrected to 3% O<sub>2</sub>.



**Figure 5-7**  
Comparison of Mercury Speciation Results for the Three Test Units

### 5.3.2 Hg SCEM Results

Hg SCEMs were operated at the stack location of the three units tested. The Hg SCEMs were operated nearly continuously for a month. A summary of Hg SCEM data plotted over the entire test period for the three units is provided in Figures 5-8 through 5-10. The statistical average Hg SCEMs results are shown in Table 5-5. For Unit 1 (SCR), the Hg SCEM data averaged  $5.2 \mu\text{g}/\text{m}^3$  with 90% of the data falling between 2 and  $8 \mu\text{g}/\text{m}^3$ . For Unit 2 (SCR bypassed), the average Hg SCEM result was  $5.7 \mu\text{g}/\text{m}^3$ , with 90% of the data points falling within 1.3 and  $10.1 \mu\text{g}/\text{m}^3$ . For Unit 4 (no SCR), the Hg SCEM data averaged  $7.5 \mu\text{g}/\text{m}^3$  with 90% of the data points falling between 5.9 and  $9.1 \mu\text{g}/\text{m}^3$ . Although there is some difference between the OH data and the Hg SCEM averages, the results are within the statistical variability of the data.

The variability of the  $\text{Hg}^{2+}$  is shown in Figures 5-11 and 5-12. As can be seen, there appears to be a decrease in the percentage of  $\text{Hg}^{2+}$ , and there was more variability when SCR was bypassed. However, as was shown by the OH method, the percentage of  $\text{Hg}^{2+}$  at the stack was high (>90%) both with and without SCR.

At about 125 hours into the test (see Figure 5-5), there does appear to be a small increase in  $\text{Hg}^0$  concentration that corresponds with SCR being bypassed. Figure 5-13 presents the Hg SCEM data during this time period.

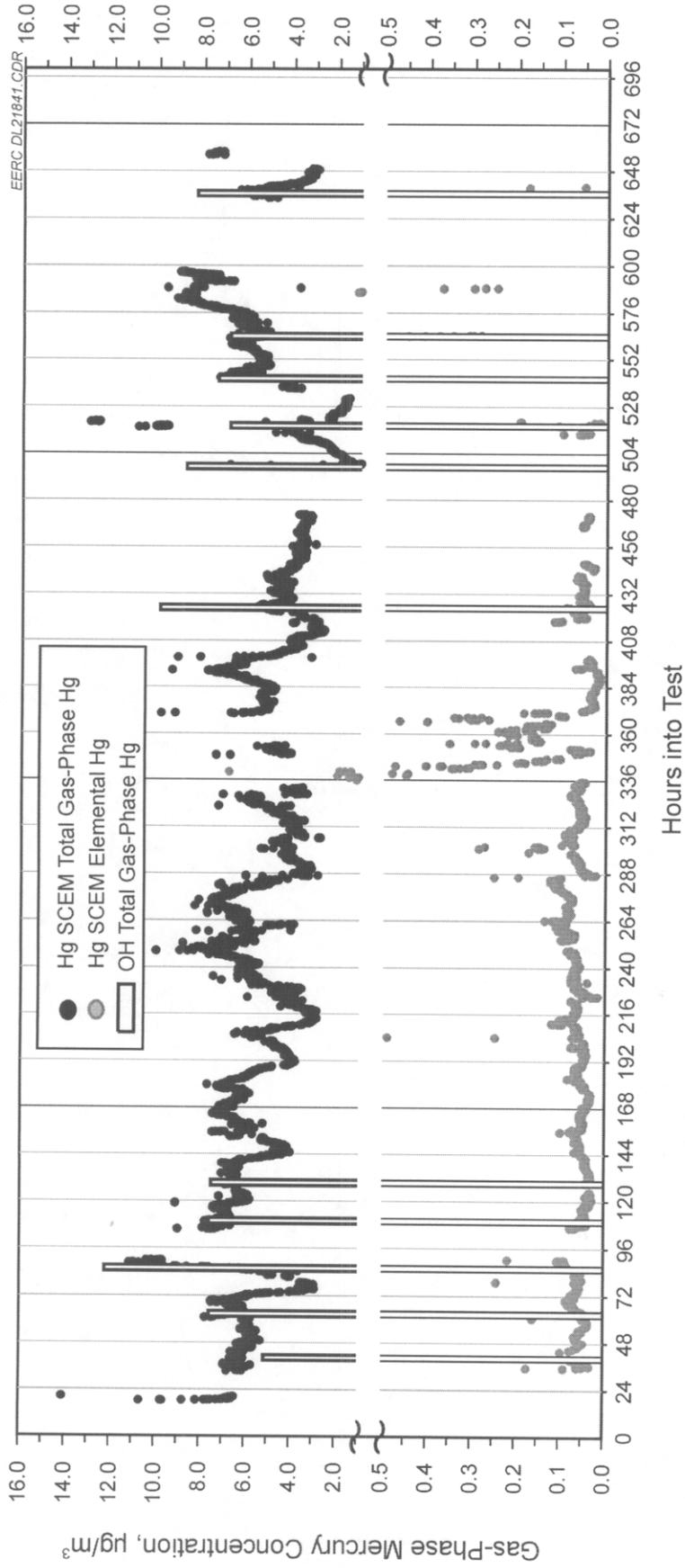


Figure 5-8  
Hg SCEM Results for Site S6 for Unit 1 with the SCR in Service

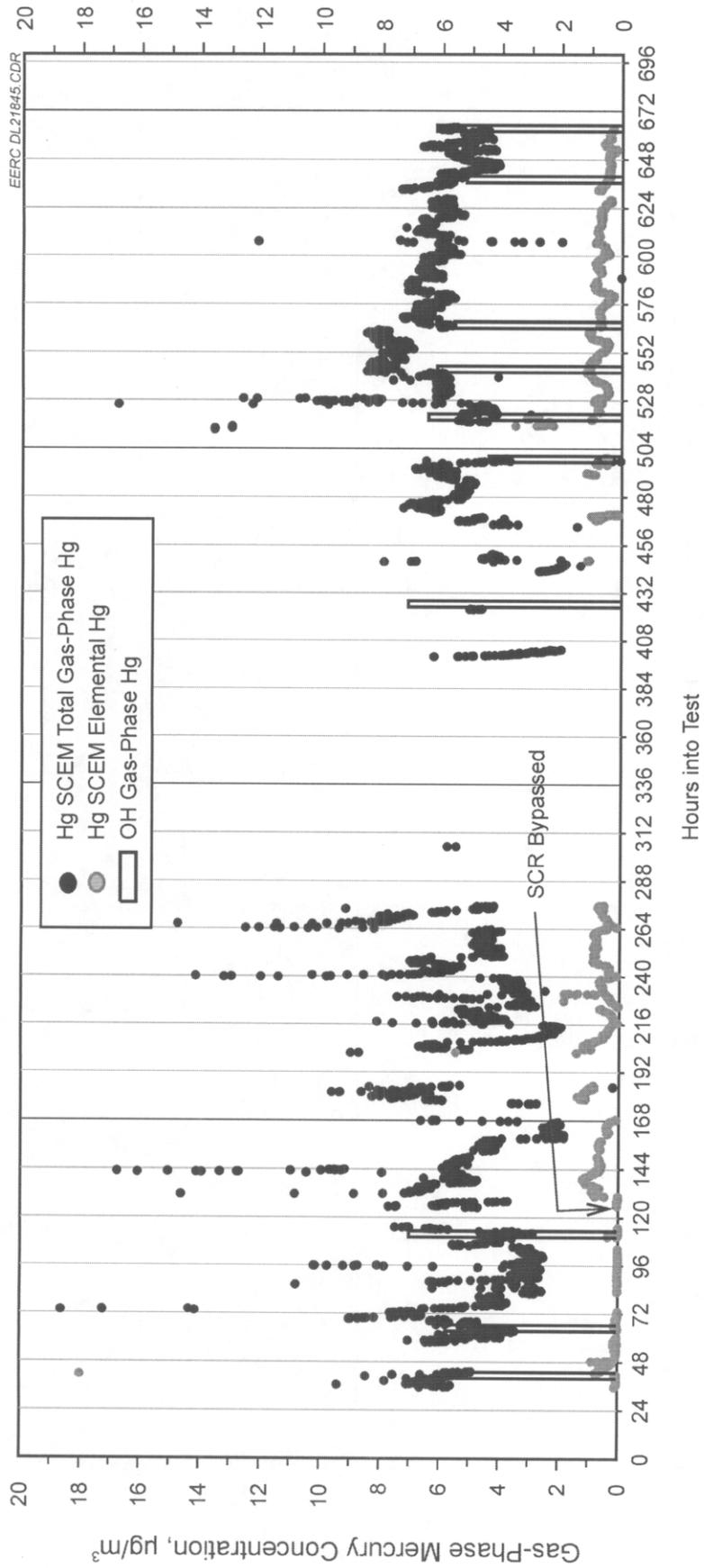


Figure 5-9  
Hg SCEM Results for Site S6 for Unit 2 with the SCR Bypassed

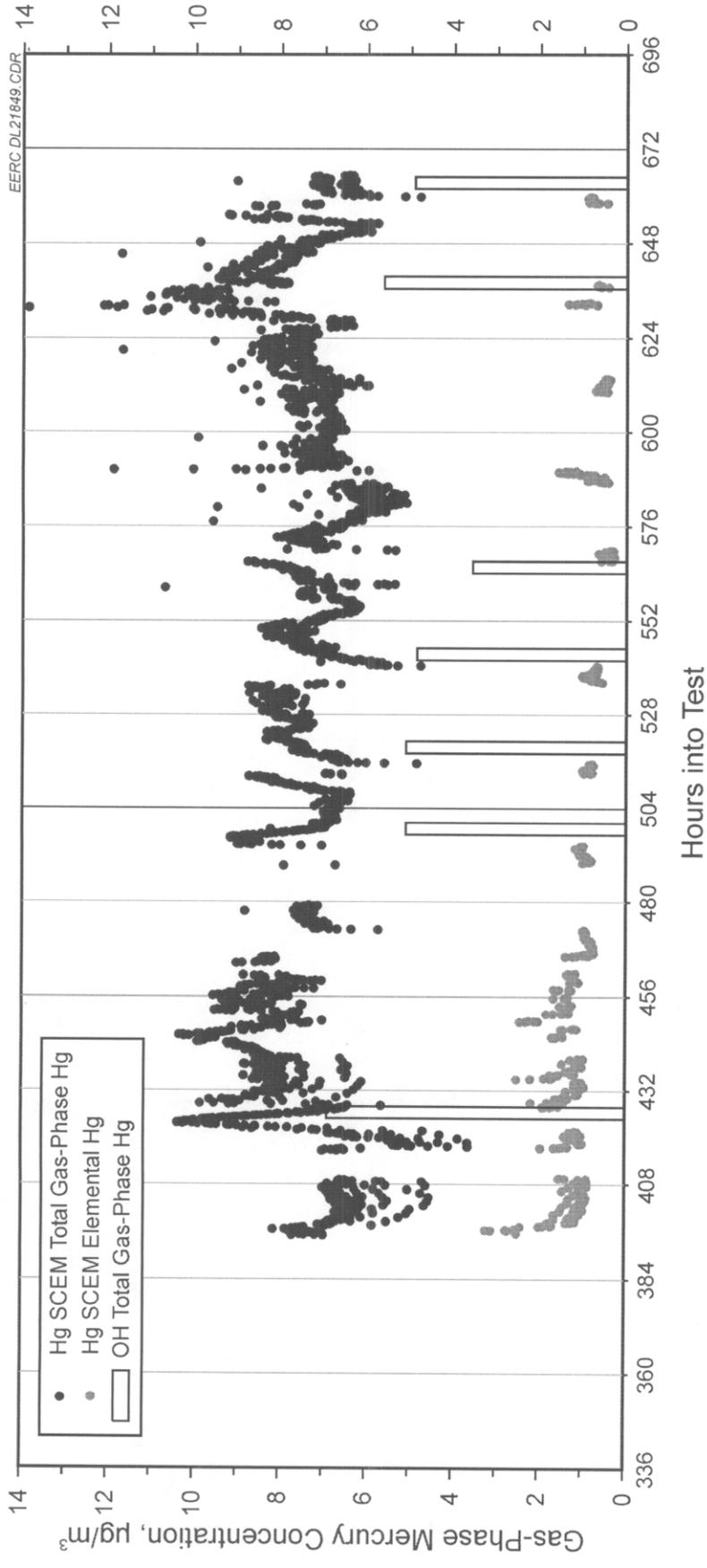
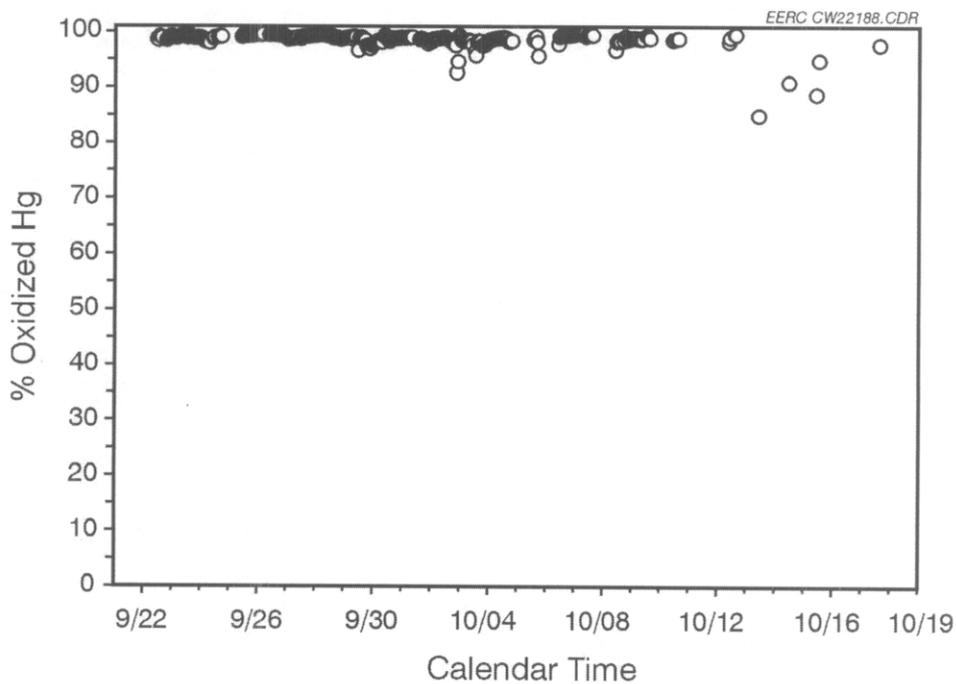


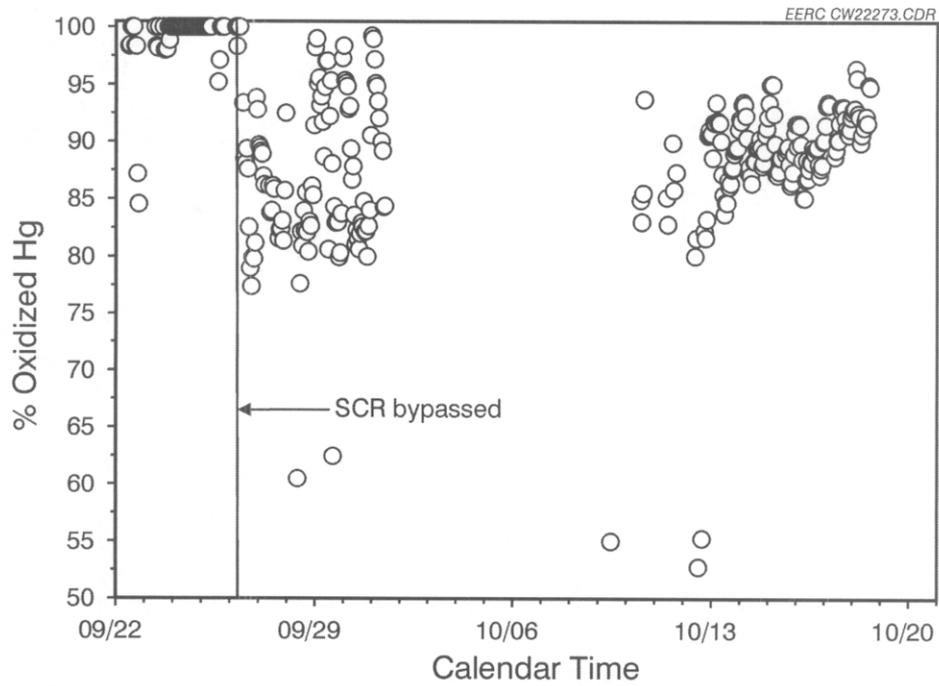
Figure 5-10  
Hg SCEM Results for Site S6 for Unit 4 with No SCR

**Table 5-5**  
**Statistical Variation of the Mercury Results Based on the Hg SCEM Data for Site S6**

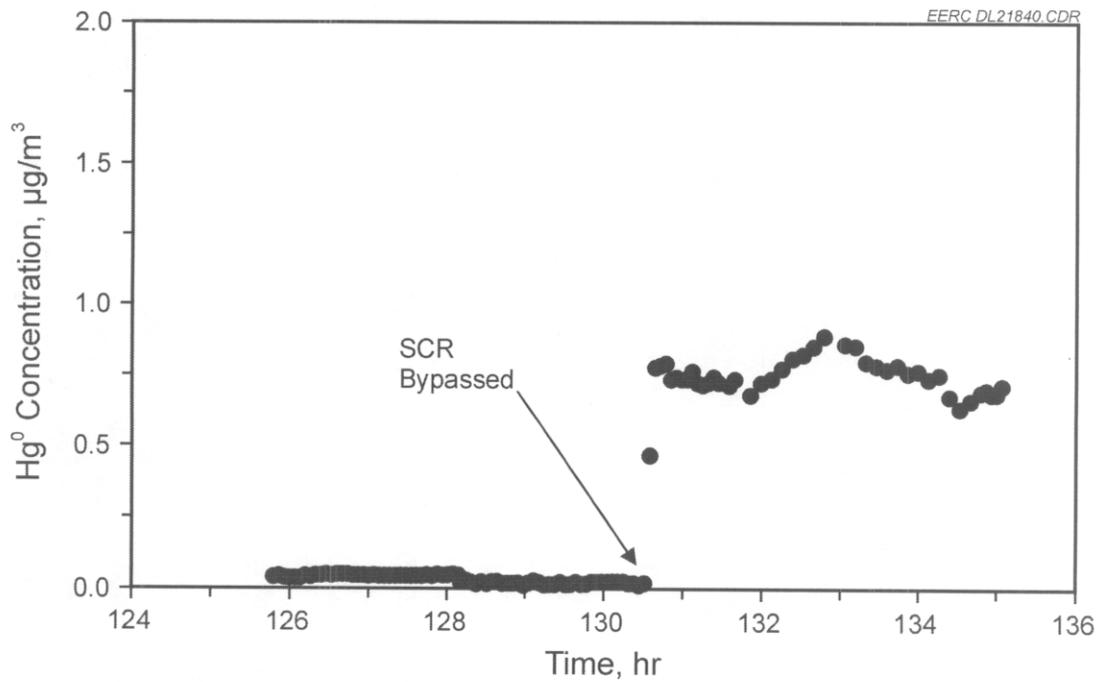
Mercury	Unit	Operation	Average, $\mu\text{g}/\text{m}^3$	Std. Dev., $\mu\text{g}/\text{m}^3$	Upper 90% CI, $\mu\text{g}/\text{m}^3$	Lower 90% CI, $\mu\text{g}/\text{m}^3$
Hg(total)	1	With SCR	5.2	1.7	8.0	2.4
Hg <sup>0</sup>	1	With SCR	0.1	0.2	0.4	0.0
Hg(total)	2	SCR bypassed	5.8	2.7	10.2	1.4
Hg <sup>0</sup>	2	SCR bypassed	0.7	0.5	1.5	0.0
Hg(total)	4	No SCR	7.5	1.0	9.2	5.9
Hg <sup>0</sup>	4	No SCR	1.0	0.4	1.7	0.3



**Figure 5-11**  
**Average Hg<sup>2+</sup> as Measured by Hg SCEMs (total Hg - Hg<sup>0</sup>) for Site S6 Unit 1 (SCR on-line)**



**Figure 5-12**  
Average  $Hg^{2+}$  as Measured by Hg SCEMs (total Hg -  $Hg^0$ ) for Site S6 Unit 2 (SCR bypassed)



**Figure 5-13**  
Hg SCEM Results for Site S6 for Unit 2 with SCR Bypassed

### 5.3.4 Coal Analysis Results

Nine of the coal samples from S6 were analyzed for Hg and chlorides (presented in Table B-10 in Appendix B). The Hg concentrations were very consistent, averaging  $0.066 \pm 0.009 \mu\text{g/g}$ . However, the chloride content of the coal was somewhat more variable, averaging  $1020 \pm 300$  ppm. These averages are based on all coal samples analyzed regardless of the unit they were collected from. Plant personnel said that the same coal was fired in all three units.

Additional analyses were conducted on selected coal samples. Results of proximate and ultimate analyses (including the Hg and chloride concentrations for that sample) are provided in Table 5-6. In general, it appears that coal composition from all three units was very consistent.

**Table 5-6**  
**Coal Analysis for Site S6<sup>a</sup>**

Date:		9/24/2002	9/24/2002	10/8/2002	10/8/2002
Unit:		Unit 1 (SCR)	Unit 2 (SCR bypassed)	Composite <sup>b</sup>	Unit 4 (no SCR)
Mercury	ppm (dry)	0.084	0.052	0.063	0.070
Chlorine	ppm (dry)	1210	1520	1170	1320
<i>Proximate Analysis</i>					
Moisture	wt%	5.6	5.9	6.2	6.5
Volatile Matter	wt%	33.1	34.5	34.8	34.7
Fixed Carbon	wt%	49.1	49.1	47.0	47.3
Ash	wt%	12.2	10.5	12.0	11.5
<i>Ultimate Analysis</i>					
Hydrogen	wt%	5.2	5.3	5.3	5.3
Carbon	wt%	70.7	71.0	67.8	68.5
Nitrogen	wt%	1.5	1.7	1.6	1.7
Sulfur	wt%	0.9	0.8	1.2	1.1
Oxygen	wt%	9.5	10.8	12.1	12.0
Heating Value	Btu/lb	11,936	12,142	12,159	11,837
F <sub>d</sub> Factor <sup>c</sup>	dscf/10 <sup>6</sup> Btu	10,357	10,181	9727	10,085

<sup>a</sup> Except where noted, all results are on an as-received basis.

<sup>b</sup> Composite of all three units.

<sup>c</sup> As defined by EPA Method 19.

### 5.3.5 ESP Ash Analysis

ESP hopper ash samples were collected daily throughout the test period from each unit. ESP configuration at Unit 1 (SCR) and Unit 2 (SCR bypassed) consisted of two ESPs in series. Ash samples were obtained from the first hoppers of each ESP (AB and CD) and analyzed for Hg and LOI. Unit 4 (no SCR) had only a single ESP. The ESP hopper ash Hg and LOI averages are presented in Table 5-7. Plant personnel had indicated that ash characteristics were substantially different between the first and second ESP, specifically high unburned carbon in the first ESP.

**Table 5-7**  
**Analysis of ESP Hopper Ash**

Unit	ESP AB				ESP CD			
	Ash Hg, $\mu\text{g/g}$	No. Samples	LOI, %	No. Samples	Ash Hg, $\mu\text{g/g}$	No. Samples	LOI, %	No. Samples
Unit 1 (SCR)	0.073 $\pm$ 0.014	22	3.4	4	0.066 $\pm$ 0.027	28	3.4	4
Unit 2 (SCR bypassed)	0.152 $\pm$ 0.068	20	4.8	5	0.118 $\pm$ 0.039	25	4.5	5
Unit 4 (no SCR)	0.058 $\pm$ 0.017	14	4.0	2	—	—	—	—

Results from our limited LOI analysis did not indicate a significant difference between the samples.

### 5.3.6 $\text{NH}_3$ Slip and $\text{SO}_3$ Flue Gas Results

$\text{NH}_3$  slip samples were collected at the SCR outlet. A summary of these results is provided in Table 5-8. The  $\text{NH}_3$  slip was less than 0.2 ppm for both samples, indicating an efficiently operating SCR unit. This is also illustrated by >90%  $\text{NO}_x$  removal efficiency calculated from plant operational data.

$\text{SO}_3$  testing was conducted at the SCR outlet and ESP inlet of Unit 1 (SCR) and at the air heater inlet and ESP inlet on Unit 2 (SCR bypassed). A summary of these results is also provided in Table 5-8. These data are consistent with what would be expected from a low-sulfur eastern bituminous coal. It also appeared that (with the exception of the data taken on October 11, 2002) there was some  $\text{SO}_3$  condensation on the fly ash and possibly deposition in the air heater. Comparing the data of Units 1 (SCR) and 2 (SCR bypassed) indicated that there is some conversion of  $\text{SO}_2$  to  $\text{SO}_3$  across the SCR catalyst.

**Table 5-8**  
**Flue Gas SO<sub>3</sub> and NH<sub>3</sub> Results for Site S6<sup>a</sup>**

Date	SO <sub>3</sub> , ppm		NH <sub>3</sub> Slip, ppm
	SCR Outlet	ESP Inlet	SCR Outlet
<i>Unit 1 (SCR)</i>			
9/23/2002	13.21	4.02	0.11
9/24/2002	14.07	4.19	0.17
<i>Unit 2 (SCR bypassed)</i>			
10/11/2002	5.76	7.68	
10/14/2002	8.17	2.51	

<sup>a</sup> Dry and 3% oxygen.

## 5.4 Mercury Mass Balance

Average Hg concentration in the coal and F<sub>d</sub> factors (Table 5-6) were used to estimate the Hg emission rate at the various sample locations. For the Hg associated with the ESP hopper ash, the F<sub>d</sub> factors were based on the dust-loading measurements as well as the F<sub>d</sub> factor. The results are shown in Table 5-9.

**Table 5-9**  
**Average Mercury Emission Factors for Site S6**

Unit Tested	lb Hg/10 <sup>12</sup> Btu				%	
	Coal	ESP Inlet	ESP Hopper Ash	Stack	Balance <sup>a</sup> Based on Coal Hg	Balance <sup>b</sup> Across ESP
1 (SCR)	5.5	6.1	0.40	7.6	111	131
2 (SCR bypassed)	5.5	7.3	0.93	5.5	87	88
3 (no SCR)	5.5	—	0.31 <sup>c</sup>	4.5	—	—

<sup>a</sup> Calculated balance is based on the coal Hg concentration and the ESP inlet  $[(\text{Hg}_{\text{coal}} - \text{Hg}_{\text{ESP inlet}})/\text{Hg}_{\text{coal}}]$ .

<sup>b</sup> Calculated balance is based on the ESP inlet Hg concentration and the stack  $[(\text{Hg}_{\text{stack}} + \text{Hg}_{\text{ESP hopper}})/\text{Hg}_{\text{ESP inlet}}]$ .

<sup>c</sup> The ESP inlet was not measured; therefore, the inlet dust loading used was that obtained from Unit 2 (SCR bypassed).

As shown in Table 5-9, it appears that the Hg concentration as measured in the coal is low compared to the flue gas measurements. The variability of the coal Hg was very low with a relative standard deviation of <15%. The variability of the flue gas data also was low. The relative standard deviations ranged from 11% to 22%.



# 8

## QUALITY ASSURANCE/QUALITY CONTROL

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The EERC is committed to delivering consistent and high-quality research that exceeds its clients' needs and expectations. To ensure that the goals of this project are realized, an organizationwide quality management system (QMS), authorized and supported by EERC managers, is in effect and governs all programs within the organization. The EERC established and formalized a QMS and QC procedures in August 1988. The Quality Manual defines the requirements and the organizational responsibilities for each major element of the QMS and references the supporting documents needed to provide a comprehensive program. Compliance with this manual and its supporting documents ensures that the EERC adequately fulfills governmental and private client requirements relating to quality and compliance with applicable regulations, codes, and protocols. This project was required to follow the Quality Manual, project-specific quality assurance (QA) procedures, and all revisions. The EERC Quality Assurance Manager implements and oversees all aspects of QA/QC for all research, development, and demonstration projects and reviewed the QA/QC components of this project. The project manager is responsible for ensuring that project-specific QA/QC protocols are followed.

To ascertain data quality obtained during the sampling program, the following procedures were used:

- Process operating data were examined to ensure that the OH sampling took place during steady, representative plant operation.
- Sampling and analytical analysis protocols were reviewed to ascertain how the data compared with other data generated using standard protocols.
- The reagent blanks, field blanks, and field spikes were reviewed to qualitatively determine the confidence that can be placed in the results.
- The QA/QC data results were then compared with data quality indicators to qualitatively determine the validity of the data in terms of variability and accuracy.

### 8.1 Process Data Evaluation

Plant operating data were examined to ensure that process operation was stable and representative during the OH sampling periods. Excessive scatter or significant trends in relevant process variables can indicate periods of unrepresentative unit operation. Data scatter is useful for identifying periods of operational difficulty; data trends indicate periods when steady-state operation has not been achieved. It was the intent for the Hg SCEMs to be operated both during steady-state conditions and during any upset conditions that occurred. Plant data, to the extent

available, were plotted for each of the test sites. In general, it appears that all of the OH sampling occurred either when the unit was at or near full-load conditions. When plant operational upsets occurred during OH sampling, sampling was suspended, and a new sample was taken after the plant was operating at more normal conditions. This occurred at Site S5 and is illustrated by the greater quantity of OH results.

## **8.2 Sampling Quality Control Evaluation**

Sampling precision can be estimated by comparing the results of various parameters of replicate samples, notably, velocity, moisture content, and gas composition in the stack. Sampling accuracy is usually inferred from the calibration and proper operation of the equipment and from historical validation of the methods. Field blanks are used to determine any biases that may be caused by contamination or operator errors. A field blank is defined as a complete impinger train, including all glassware and solutions, which is taken out to the field during sampling and exposed to ambient conditions. These sample trains are then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank shows contamination above instrument background, steps are taken to eliminate or reduce the contamination to below background levels. The results of the blanks can be seen in Appendix B (Tables B-1, B-3, B-5). In almost all cases, the field blank results were less than detection limits. For the few samples where a detectable level of Hg was measured, the concentration was low enough to be insignificant compared to the measured flue gas concentration for that Hg species.

Sampling comparability depends on whether the samples are representative and on the use of standard methods consistently applied. All methods used for the project were standard American Society for Testing and Materials or EPA sampling methods. Sampling completeness is primarily a function of providing the requisite number of samples to the analytical laboratory. In most cases, this consisted of duplicate samples.

The isokinetic sampling rate is a measure of the operational performance of sampling for particulate matter. The normal acceptance criterion for isokinetic variation is 10%. With over 90 OH samples taken during this project, five samples were outside the  $\pm 10\%$  range. Four samples were collected at the stack and, based on the very low particulate loading and Hg concentration, appeared to have no significant impact on the results. One sample, collected at the ESP outlet location, had an isokinetic measurement of greater than 100%. Again, the Hg results from this sample were not significantly affected because of the extremely low concentration of Hg and low particulate loading. A lower-than-expected isokinetic sampling rate results in an overestimation of the larger particles, resulting in an inflated dust-loading estimate. However, for these samples, the dust loading and the Hg concentrations were very similar to the other samples taken. It is believed that this deviation from the accepted isokinetic value had no significant impact on the overall conclusions.

One known concern with the OH method is a bias that occurs as a result of the close contact between the flue gas and the fly ash collected on the sampling filter. This is particularly true at high-dust sampling locations such as SCR inlet, outlet, and the inlet to the particulate control device. The degree of bias is dependent on the reactivity of the ash collected on the filter and the

flue gas temperature. This ash has the potential to adsorb or oxidize Hg. The only method of determining the extent to which the bias occurs is to compare the inlet and outlet ESP Hg<sup>0</sup> results. If there is an increase in Hg<sup>0</sup> concentration across the ESP, it indicates some oxidization occurred across the sampling filter. To determine if there was adsorption of Hg on the sample, resulting in a high particulate-bound Hg bias, the filter concentration is compared to the ESP hopper ash samples. Although representative ash samples are extremely difficult to collect from an ESP, it is possible to obtain an indication as to whether the filter is biasing the particulate-bound Hg concentration. These comparisons were made, and the results from each facility are detailed in the discussion in Sections 2–7.

### 8.3 Evaluation of Measurement Data Quality

An evaluation of the measurement data quality is based on QC data obtained during sampling and analysis. Generally, the type of QC information obtained pertains to measurement precision, accuracy, and blank effects, determined by collecting various types of replicate, spiked, and blank samples. The specific characteristics evaluated depend on the type of QC checks performed. For example, if problems with contamination occur, blank samples can be prepared at different stages in the sampling and analysis process to isolate the source of a blank effect. Similarly, replicate samples may be generated at different stages to isolate and measure the sources of variability. Table 8-1 summarizes the QA/QC measures used and the characteristic information obtained for this project.

As shown in Table 8-1, different QC checks provide different types of information, particularly pertaining to the sources of inaccuracy, imprecision, and blank effects. In general, measurement precision and accuracy are typically estimated from QC indicators that cover as much of the total sampling and analytical process as feasible. Precision and accuracy estimates are based primarily on the actual sample media documenting the precision and accuracy actually obtained, and the objectives serve as benchmarks for comparison. The effects of not meeting the objectives need to be considered in light of the intended use of the data. The results of the field and media spikes that were done as part of this project are shown in Appendix B (Tables B-2, B-4 and B-6). As can be seen in these tables, the spike recovery was excellent for field blanks completed. Although blank filters are routinely analyzed for Hg to ensure no Hg contamination on the sample, no field filter spikes were completed for the project. However, in the laboratory, known Hg calibration standards are routinely analyzed.

Other specific QC procedures that were used to measure Hg in the flue gas for this project are as follows:

- **Instrument Setup and Calibration.** The instrument used in the field for Hg determination was a Leeman Labs PS200 cold-vapor atomic absorption spectrometer. To measure Hg, the instrument was set up for absorption at 253.7 nm with a carrier gas of nitrogen and 10% w/v stannous chloride in 10% v/v HCl as the reductant. Each day, the drying tube and acetate trap were replaced and the tubing checked. The rinse container was cleaned and filled with fresh solution of 10% v/v 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 using matrix-matched standards. The detector response for the

**Table 8-1  
Elements of the QA/QC Plan**

QC Activity	Characteristic Measured
<b>Precision</b>	
Replicate Samples Collected over Time under the Same Conditions	Total variability, including process or temporal, sampling, and analytical but not bias.
Duplicate Field Samples Collected Simultaneously	Sampling plus analytical variability at the actual sample concentrations.
Duplicate Analyses of a Single Sample	Analytical variability at the actual sample concentrations.
Media-Spiked Duplicates	Sampling plus analytical variability at an established concentration.
Laboratory Control Sample Duplicates	Analytical variability in the absence of sample matrix effects.
<b>Accuracy (including precision and bias)</b>	
Media-Spiked Samples	Analyte recovery in the sample media, indicating possible interferences and other effects. In a single sample, includes both random error (imprecision) and systematic error (bias).
Laboratory Control Samples	Analyte recovery in the absence of actual sample matrix effects. Used as an indicator of analytical control.
<b>Blank Effects</b>	
Field Blank	Total sampling plus analytical blank effect, including sampling equipment and reagents, sample transport and storage, and analytical reagents and equipment.
Reagent Blank	Blank effects from reagents used.

given standard was then 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 to verify the calibration. This QC standard is 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. After the initial QC standardizations were completed, standards were run every five samples to check the slope of the calibration curve. All samples were run in duplicate, and one in every ten samples was spiked to verify analyte recovery. A QC chart is maintained at the EERC to monitor the long-term precision of the instrument. The results of these calibrations are available upon request of any EERC client.

- **Presampling Preparation.** All data sheets, volumetric flasks, and Petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks and logged, then analyzed on-site. The outlet filter samples were placed in premarked Petri dishes and taken back to the EERC, where they were

analyzed using mixed-acid digestion techniques. The labels contained identifying data, including date, time, run number, sample port location, and the name of the sampler.

- **Glassware and Plasticware Cleaning and Storage.** All glass volumetric flasks and transfer pipettes used in the preparation of analytical reagents and calibration standards were designated Class A to meet federal specifications. Prior to being used for the sampling, all glassware was washed with hot, soapy water, then rinsed with deionized water three times, soaked in 10%  $v/v$  nitric acid for a minimum of 4 hr, rinsed an additional three times with deionized water, and dried. The glassware was then stored in closed containers until it was used at the plant. All glassware cleaning solutions are periodically checked for Hg. In all cases, the measured Hg concentration was below detection limits.
- **Analytical Reagents.** All acids to be used for the analysis of Hg were trace metal-grade or 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 0.5% and were traceable to National Institute of Standards and Technology standard reference materials.

## 8.4 OH Method Error Analysis

The precision of Hg measurements is estimated to be in the order of  $\pm 10\%$ – $30\%$ , depending upon the total Hg concentration, its proximity to the method detection limit and, possibly, other flue gas constituents. In addition, flue gas sampling at internal streams such as the SCR inlet and outlet and the ESP inlet are often single-point samples, may not be uniform (stratified), and thus may not represent the true flue gas distribution of the power plant. These uncertainties in the total Hg measurements must be taken into account when data are interpreted. However, these uncertainties are not expected to have a significant effect on the overall conclusions of this study.

For example, if the “actual” Hg concentrations at the ESP inlet and the stack are 10 and 1 lb/trillion Btu, respectively, then the total Hg removal would be 90%. If the measurements at both the inlet and outlet were assumed to have a  $\pm 20\%$  error, then the inlet concentration could be measured at either 8 or 12 lb/trillion Btu and the outlet concentration at either 1.2 or 0.8 lb/trillion Btu. The estimated Hg removal could range from as low as 85% to as high as 93%.

The calculated Hg removal is much more sensitive at sites where the Hg removal efficiencies are very low. For example, if the “actual” Hg concentrations at the ESP inlet and the stack were 10 and 9 lb/trillion Btu, respectively, then the total Hg removal would be 10%. If the measurements at both the inlet and outlet were assumed to have a  $\pm 20\%$  error, then the inlet concentration could be measured at either 8 or 12 lb/trillion Btu and the outlet concentration at either 7.2 or 11.8 lb/trillion Btu. Thus the calculated Hg removal could range from as low as  $-48\%$  to as high as 40%.



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# A

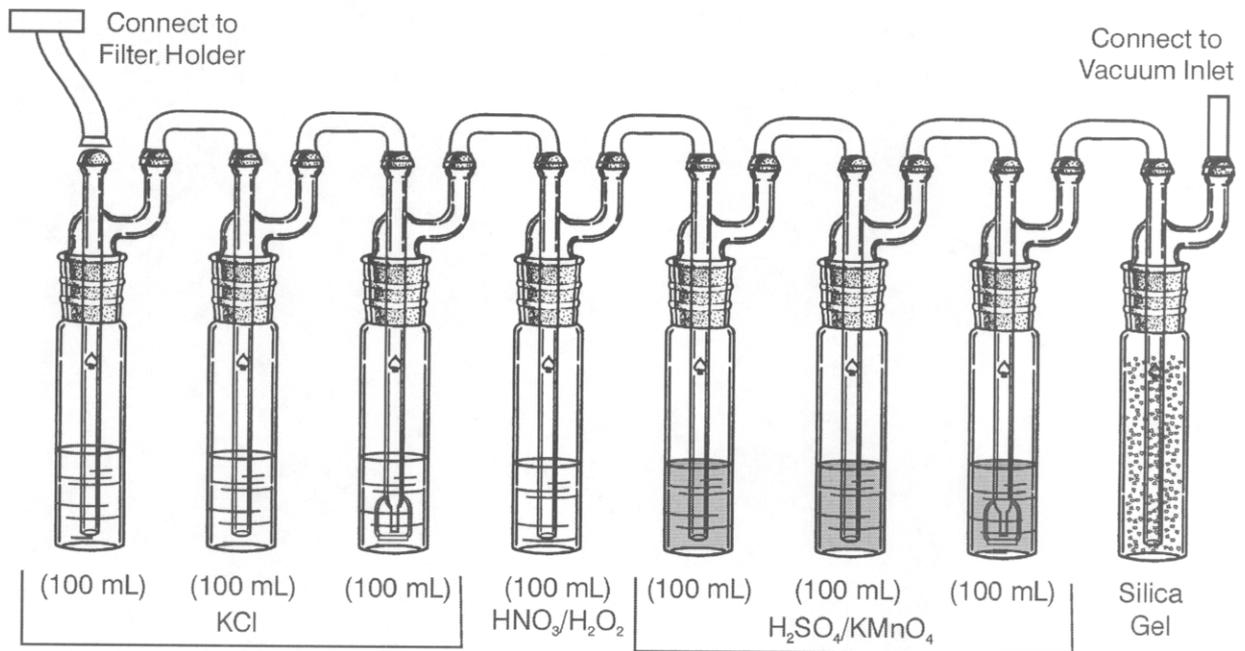
## SAMPLING METHODS AND PROCEDURES

This appendix provides the template for developing site-specific test plans and sampling protocols.

### Ontario Hydro Mercury Speciation Method (OH method)

This is a summary of the sampling and analytical procedures used to conduct the mercury (Hg) speciation method entitled “Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method).” The American Society for Testing and Materials D22 committee has accepted the method, and the exact method details are provided on the U.S. Environmental Protection Agency (EPA) Web page at <http://www.epa.gov/ttn/emc/prelim.html> under Preliminary Method 3. All other EPA methods are also found at the same emission measurement Web address.

The OH method follows standard EPA methods for isokinetic flue gas sampling (EPA Methods 1–3 and EPA Method 5/17). Figure A-1 presents a schematic of the Hg speciation sample train.



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**Figure A-1**  
**Schematic of the OH Mercury Speciation Train**

Table A-1 presents a list of sample train components for the OH configuration.

**Table A-1**  
**Sample Train Components for the OH Method**

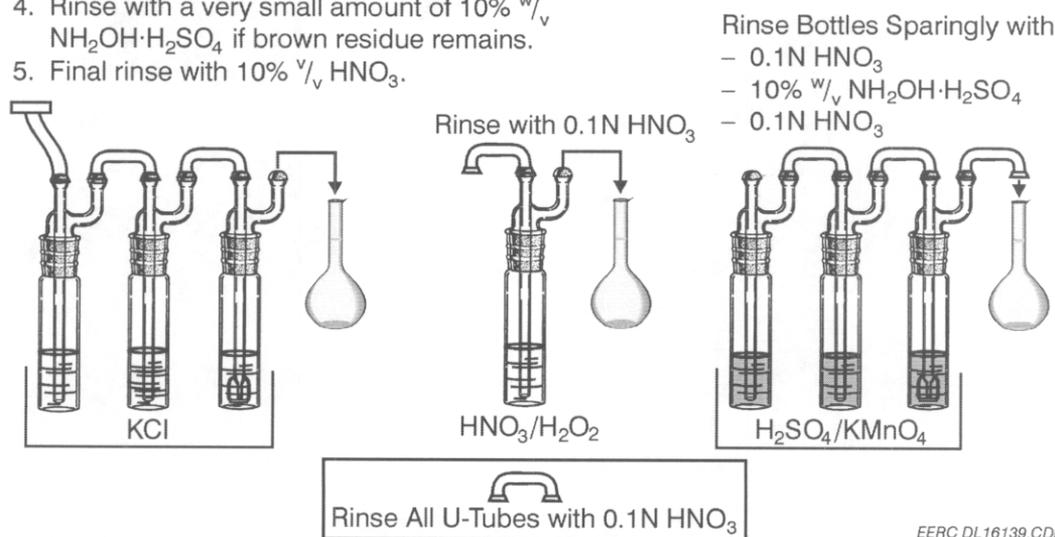
Component	Details
Nozzle	Glass, quartz, or Teflon-coated stainless steel
Filter	Quartz, in glass or Teflon-coated stainless steel holder
Probe	Glass or Teflon, heated to gas temperature
Connector Line	If needed, Teflon line used to connect from probe to impingers, heated to a minimum of 248°F (120°C).
Impingers 1 and 2	1 mol/L KCl solution; modified Smith Greenburg (SG) impinger
Impinger 3	1 mol/L KCl solution; standard SG impinger
Impinger 4	5% nitric acid/10% hydrogen peroxide; modified SG impinger
Impingers 5 and 6	4% potassium permanganate/10% sulfuric acid; modified SG impinger
Impinger 7	4% potassium permanganate/10% sulfuric acid; standard SG impinger
Impinger 8	Silica gel; modified SG impinger

A sample is withdrawn from the flue gas stream isokinetically through the filtration system, which is followed by a series of impingers in an ice bath. Particulate-bound Hg is collected on the front half and filter;  $Hg^{2+}$  is collected in impingers containing 1 N potassium chloride solution; and elemental Hg is collected in one impinger containing a 5% nitric acid and 10% peroxide solution and three impingers containing a solution of 10% sulfuric acid and 4% potassium permanganate. An impinger containing silica gel collects any remaining moisture. The filter media is quartz fiber filters. The filter holder is glass or Teflon-coated. An approximate 2-hr sampling time was used, with a target sample volume of 1–2.5 standard cubic meters.

Figure A-2 is a schematic of the sample recovery procedure for the impinger train. The samples were recovered into precleaned glass bottles with vented Teflon-lined lids. The following sample fractions were recovered (specific rinse solutions are contained in the method):

1. The sample filter
2. The front-half rinse (includes all surfaces upstream of the filter)
3. Impingers 1 through 3 (KCl impingers) and rinses
4. Impinger 4 ( $HNO_3/H_2O_2$  impinger) and rinses
5. Impingers 5–7 ( $H_2SO_4/KMnO_4$  impingers) and rinses

1. Rinse filter holder and connector with 0.1N HNO<sub>3</sub>.
2. Add 5% w/v KMnO<sub>4</sub> to each impinger bottle until purple color remains.
3. Rinse with 10% v/v HNO<sub>3</sub>.
4. Rinse with a very small amount of 10% w/v NH<sub>2</sub>OH·H<sub>2</sub>SO<sub>4</sub> if brown residue remains.
5. Final rinse with 10% v/v HNO<sub>3</sub>.



**Figure A-2**  
**Sample Recovery Scheme for the OH Mercury Speciation Train**

6. Impinger 8 (silica gel impinger [note that this sample is weighed for moisture determination and not included in the Hg analysis])

The sample fractions were prepared and analyzed as specified in the method and summarized below:

- *Ash Sample (Containers 1 and 2)* – The particulate catch was analyzed using EPA Method 7043 or equivalent (see Table 3) or using a Milestone DMA-80 Hg analyzer. However, if the particulate catch was less than 1 gram (as was the case at the outlet of the particulate control device), the entire sample of the particulate collected on the filter (including the filter) was subsequently digested using EPA Method 3051, followed by analysis using EPA 7471A.
- *KCl Impingers (Container 3)* – The impingers were prepared using H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and KMnO<sub>4</sub> solutions as specified in the method.
- *HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (Container 4)* – The impinger solutions were prepared using HCl and KMnO<sub>4</sub> solutions as specified in the method.
- *H<sub>2</sub>SO<sub>4</sub>/KMnO<sub>4</sub> Impingers (Container 5)* – The impinger solutions were prepared using hydroxylamine hydrochloride as specified in the method.

Each prepared fraction was analyzed for total Hg by cold-vapor atomic absorption (CVAA). CVAA is a method based on the absorption of radiation at 253.7 nm by Hg vapor. The Hg is reduced to the elemental state and aerated from solution in a closed system. The Hg vapor passes through a cell positioned in the light path of an atomic absorption (AA) spectrometer. Hg concentration is proportional to the indicated absorbance. A soda-lime trap and a magnesium perchlorate trap must be used to precondition the gas before it enters the absorption cell.

## Continuous Mercury Monitors

Four different Hg semicontinuous emission monitors (Hg SCEMs) were used for these tests: the Semtech Hg 2010, PS Analytical (PSA) Sir Galahad, Tekran, and OhioLumex. These instruments, when used in conjunction with the Energy & Environmental Research Center (EERC) or PSA conversion systems, with some caveats as explained in the report, were able to measure speciated Hg. The instruments are briefly described below.

### **Atomic Fluorescence-Based Hg SCEMs**

The PSA Sir Galahad and the Tekran are fluorescence-based instruments. The Sir Galahad analyzer was initially used to monitor total Hg continuously in the urban environment and natural gas. The Tekran analyzer was initially used to primarily monitor ambient Hg. As was the case for this project, both of these instruments can be used in a variety of gaseous media including combustion flue gas. These analyzers are based on the principle of atomic fluorescence (AF), which provides an inherently more sensitive signal than AA. The systems use a gold-impregnated silica support for preconcentrating the Hg and separating it from potential interferences that degrade sensitivity.

These instruments require a four-step process to obtain a flue gas Hg measurement. In the first step, conditioned flue gas is pumped through a gold trap, which is maintained at a constant temperature. Before the Hg is desorbed from the gold trap, a flushing step is initiated to remove any flue gas that may be present because it has a damping effect on the Hg fluorescence. When this is completed, the analysis step begins. The heating coil is activated, and the gold trap is heated to desorb the Hg from the trap. The Hg is carried into the fluorescence detector in an inert gas stream of argon or nitrogen, depending on the Hg concentration. The gold trap is then cooled in preparation for the next sample. The time for the entire process is about 5 min.

The systems are calibrated using  $\text{Hg}^0$  as the primary standard. The  $\text{Hg}^0$  is contained in a closed vial, which is held in a thermostatic bath. The temperature of the Hg is monitored, and the amount of Hg is measured using vapor pressure calculations. Typically, the calibration of these units has proven to be stable over a 24-hr period.

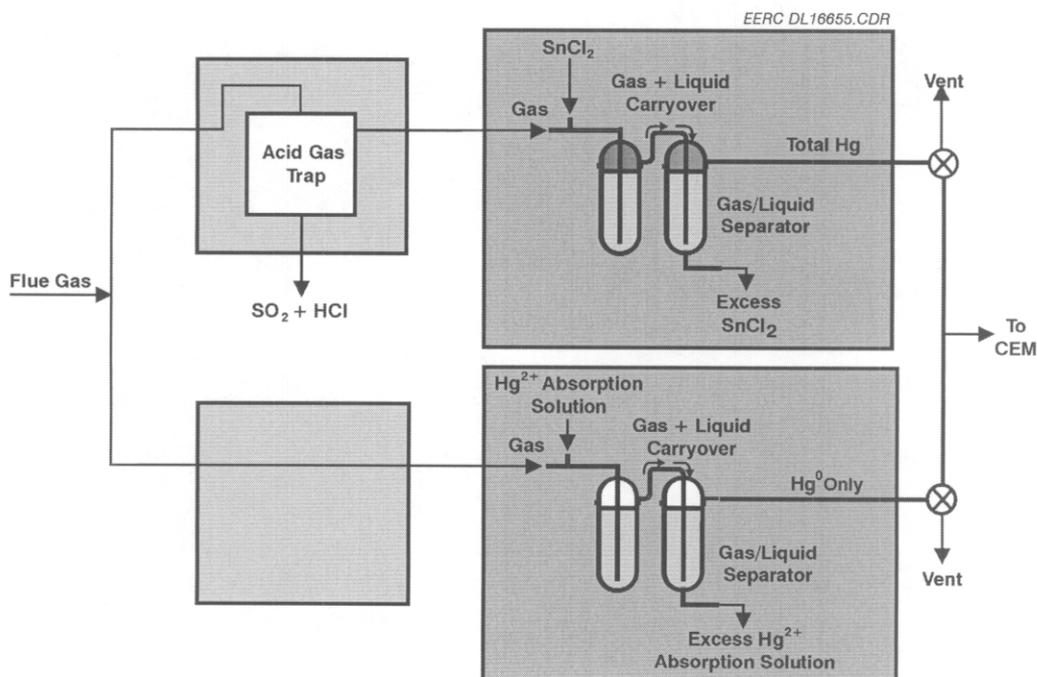
### **Atomic Absorption-Based Hg SCEMs**

Both the Semtech Hg analyzer (Semtech Metallurgy AB, Lund, Sweden) and the OhioLumex instruments are portable Zeeman-modulated CVAA spectrometers that can monitor  $\text{Hg}^0$  continuously. These analyzers use Zeeman effect background correction by applying a modulated magnetic field to a Hg lamp to minimize interferences from the presence of  $\text{SO}_2$ , moisture, hydrocarbons, and fine particulate in the flue gas sample. The primary difference between the Semtech and the OhioLumex instruments is the AA path length. The Semtech has a path length of about 0.5 m compared to 9.7 m for the OhioLumex. The result is a much lower detection limit for the OhioLumex. The operating range of the Semtech is listed as 0.3 to 160  $\text{mg}/\text{Nm}^3 \text{Hg}^0$ ; however, in practice, the lower limit of quantification is about 2  $\mu\text{g}/\text{Nm}^3$ . The OhioLumex has the potential to measure as low as 0.1  $\text{ng}/\text{Nm}^3$ . It should be noted that the

Semtech Hg 2010 has also been certified by TUEV Rheinland for determining compliance with the German legal limit of  $50 \mu\text{g}/\text{Nm}^3$  for total Hg from waste incinerators.

### Flue Gas Pretreatment/Conversion

Whether the Hg SCEM uses CVAA or AF to measure Hg, some form of gas pretreatment is necessary before accurate measurement of total Hg (or speciated Hg) is obtained. Figure A-3 illustrates the EERC pretreatment system used with Hg SCEMs. For the CVAA-type systems, only  $\text{Hg}^0$  can be directly analyzed. Therefore, all Hg forms in the flue gas must be converted to  $\text{Hg}^0$ . For this purpose,  $\text{SnCl}_2$  is used as a reductant. To use an Hg SCEM for Hg speciation measurements, first only  $\text{Hg}^0$  (bypassing the  $\text{SnCl}_2$ ) is measured, followed by a measurement of the total Hg by reducing the  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  with  $\text{SnCl}_2$  prior to analysis. The  $\text{Hg}^{2+}$  concentration was calculated by difference.



**Figure A-3**  
Schematic of the EERC Pretreatment/Conversion System for Use with Hg SCEMs

For the AF Hg SCEMs, a pretreatment/conversion system is also needed, but for different reasons. The first reason is to remove gaseous contaminants ( $\text{HCl}$ ,  $\text{SO}_3$ , etc.) from flue gas prior to the gold trap, thus preventing the trap from becoming poisoned permanently. The second reason is that both  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  collect on the trap; if the instrument is to be used to provide Hg speciation data, then the  $\text{Hg}^{2+}$  must be removed from the gas stream so that the  $\text{Hg}^0$  concentration can be measured. To do this, either a heated carbonate trap (the EERC system) or a basic  $\text{SnCl}_2$  trap (PSA system) is used. For all the tests discussed in this report, the PSA system was used.