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Advanced Emissions Control Development Program

Phase II Final Report

Revision 1

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1.0 REPORT SUMMARY

The objective of the Advanced Emissions Control Development Program (AECDP) is to develop practical, cost-effective strategies for reducing the emissions of air toxics from coal-fired boilers. Ideally, the project aim is to effectively control air toxic emissions through the use of conventional flue gas cleanup equipment such as electrostatic precipitators (ESPs), fabric filters (baghouse), and wet flue gas desulfurization. Development work to date has concentrated on the capture of mercury, other trace metals, fine particulate and hydrogen chloride.

Following the construction and evaluation of a representative air toxics test facility in Phase I, Phase II focused on the evaluation of mercury and several other air toxics emissions. The AECDP is jointly funded by the United States Department of Energy's Federal Energy Technology Center (DOE), the Ohio Coal Development Office within the Ohio Department of Development (OCDO), and Babcock & Wilcox– a McDermott company (B&W).

The control of mercury by a wet scrubber was found to depend on several factors including the scrubber design, scrubber operation, and the type of upstream particulate control device. The effective control of mercury in bituminous coal-fired flue gas was demonstrated with a conventional wet scrubber. The wet scrubber achieved removal of oxidized mercury at efficiencies greater than 80% for three bituminous Ohio coals. When operated downstream of a baghouse, wet scrubber operating conditions that provided high SO_2 control also resulted in efficient mercury control.

Mercury species and emissions were tracked through the entire utility coal utilization process, including pre-combustion, combustion and post combustion processes for several Ohio coals. Commercial coal cleaning provided mercury emissions reductions of 45 to 56 percent on a raw coal basis. Particulate control devices can effectively remove the particulate-phase mercury. The ESP and baghouse, which provide negligible control of vapor-phase mercury, can impact the speciation of the vapor-phase mercury in the flue gas. Conventional wet scrubber operation (SO_2 removal > 90%) following a baghouse resulted in mercury emission control between 82 to 92 percent for flue gas generated from commercially cleaned Ohio bituminous coal. Conventional wet scrubber operation following an ESP resulted in mercury emission control between 23 to 80 percent for flue gas generated from commercially cleaned Ohio bituminous coal. As the majority of Eastern and Midwestern bituminous coal shipments are already cleaned to meet customer specifications, wet scrubber technology may provide the best option towards the reduction of existing mercury emissions from utility stacks.

Some general comments that can be made about the control of air toxics while burning a high-sulfur bituminous coal are as follows: 1) particulate control devices such as ESP's and baghouses do a good job of removing **non-volatile** trace metals, 2) mercury goes through particulate control devices almost entirely uncontrolled 3) wet scrubbing can effectively remove hydrogen chloride and 4) wet scrubbers show good potential for the removal of mercury when operated under certain conditions, however additional work is needed to understand the relationship between the wet scrubber's operating conditions and mercury capture. Phase III will address this need.

Phase III (Advanced Concepts and Comparison Coals) testing will be directed at the development of new air toxics emissions control strategies and devices, to further reduce the emissions of selected toxics. Testing will be conducted to extend the air toxics data library to include a broader range of coal types. Finally, the development work on advanced air toxics emissions measurement and monitoring techniques begun in Phase II will continue into Phase III.

2.0 EXECUTIVE SUMMARY

The objective of the Advanced Emissions Control Development Program (AECDP) is to develop practical, cost-effective strategies for reducing the emissions of air toxics from coal-fired boilers. Ideally, the project aim is to effectively control air toxic emissions through the use of conventional flue gas cleanup equipment such as electrostatic precipitators (ESPs), fabric filters (baghouse), and wet flue gas desulfurization (wet FGD). Development work to date has concentrated on the capture of mercury, other trace metals, fine particulate and hydrogen chloride. The AECDP is jointly funded by the United States Department of Energy's Federal Energy Technology Center (DOE), the Ohio Coal Development Office within the Ohio Department of Development (OCDO), and Babcock & Wilcox – a McDermott company (B&W).

The project is divided into three phases. Phase I was aimed at providing a reliable, representative test facility to study air toxics. A full-flow ESP and partial flow baghouse and wet scrubber were added to the existing complement of Clean Environment Development Facility (CEDF) flue gas treatment systems. A schematic of the CEDF and the project test equipment is provided in Figure 2.1. The general design philosophy was to install systems that would be representative of existing commercial systems, yet provide a high degree of flexibility in both operation and configuration. Completed tasks in Phase I also included equipment verification, air toxics benchmarking and the establishment of a database.

During the verification process, the test facility operation was compared with commercial systems in order to apply the program results to utility systems. The CEDF was numerically modeled to yield combustion zone temperatures, flow patterns, and residence times representative of commercial boilers. Careful control of the flue gas cooling rate through the boiler convection pass and air heater simulators provides a gas time-temperature profile that is similar to commercial units to generate similar levels and forms of trace substances. Measurements performed in Phase I confirmed that representative gas phase time-temperature profiles and surface metal temperatures are maintained throughout the furnace and convection pass while firing a bituminous coal.

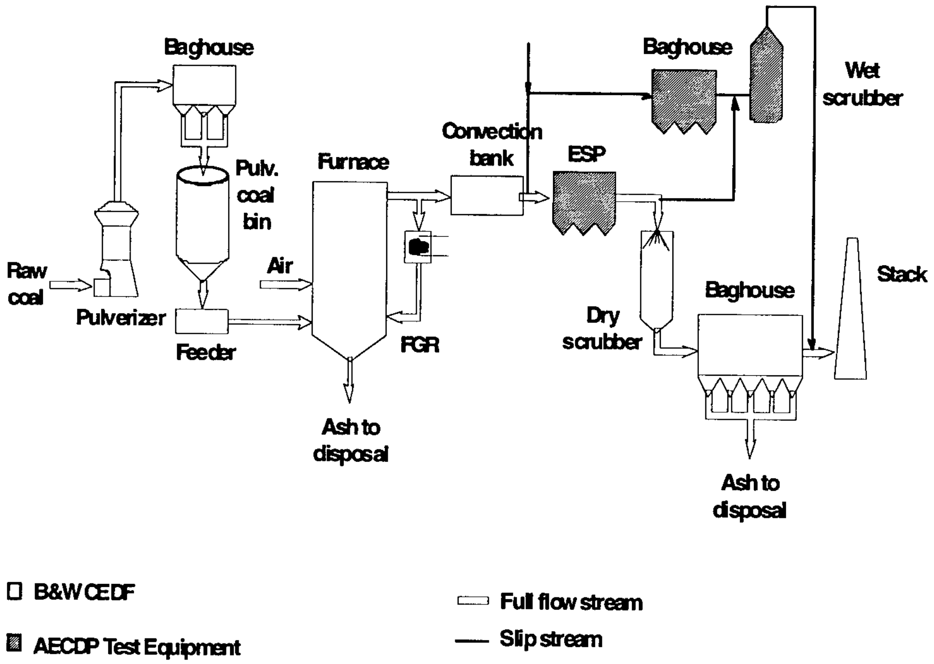

Figure 2.1 - Clean Environment Development Facility

Although the flue gas and tube metal temperature measurements conducted in the CEDF furnace and convection pass suggested that the air toxics generated by the CEDF should be representative of field emissions, air toxic benchmarking measurements were also performed to quantify the air toxics emissions from the boiler and the back-end equipment. Air toxic emission verification was achieved through comparison of the air toxics measured from the CEDF with the emissions predicted by the trace element content in the coal and the draft emission modification factors (EMF) established by the EPA. The similarity between the predicted and measured emissions indicated that the hazardous air pollutants (HAPs) emitted from the CEDF are representative of commercial units firing bituminous coal.

In Phase II (Optimization of Conventional Systems), the first two tests were directed at the development of air toxics control strategies, based on conventional particulate and SO_2 control equipment. Test Series 1 focused on mercury speciation measurements, particulate and vapor-phase trace metal emissions and fine particulate emissions. Emphasis was placed on characterization of ESP and baghouse trace element emissions control performance. The control of mercury emissions with a wet limestone scrubber was broadly characterized during Test Series 2 at conditions representative of a range of commercial scrubber operation. Test Series 3 provided data on the impacts of coal properties on mercury emissions for several Ohio steam coals. The impact of coal cleaning on mercury emissions was investigated through the testing of commercially cleaned coals and their associated parent (uncleaned) coals. Two advanced measurement systems, a mercury monitor and a Fourier Transform Infrared Spectrometry analyzer (FTIR), were also evaluated in this phase.

Sampling and Analytical Procedures

An accurate measure of the mercury species (elemental and oxidized) is essential to the development of mercury control options since the forms impact the performance of emissions control equipment. EPA Method 29 was selected as the EPA-approved grab sampling method for *total* mercury and to provide consistency with the Phase I efforts. The Ontario Hydro method, which has been evaluated by several organizations to provide an improved measure of the elemental and oxidized mercury species relative to EPA Method 29, was most frequently employed. Improvements were made in the developmental Ontario Hydro method to accurately measure mercury in coal-fired flue gas. Initially, total mercury emissions as measured by EPA Method 29 were higher than measured with the Ontario Hydro method. The lower mercury levels measured by the Ontario Hydro method were primarily related to the selection of a preservative intended to retard loss of mercury during the analytical recovery of the sample trains. Permanganate was then selected as the preservative on the basis of the visual color change and stronger oxidizing properties than the previous dichromate preservative. The use of the permanganate preservative during the second and third test series resulted in improved agreement in the measure of total mercury emissions between the two methods. Total mercury emissions from the CEDF boiler as measured by Method 29 and Ontario Hydro are compared in Figure 2.2.

Particulate Control Devices

The potential for improved control of particulate metal emissions was investigated. Of the particulate metals, arsenic, cadmium, chromium, lead, manganese and nickel have been specified in the interim final U.S. EPA report, *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units*, as potential health risks. Operating temperature, flue gas humidification, and baghouse fabric were evaluated as cost-effective means of reducing particulate and trace metal emissions.

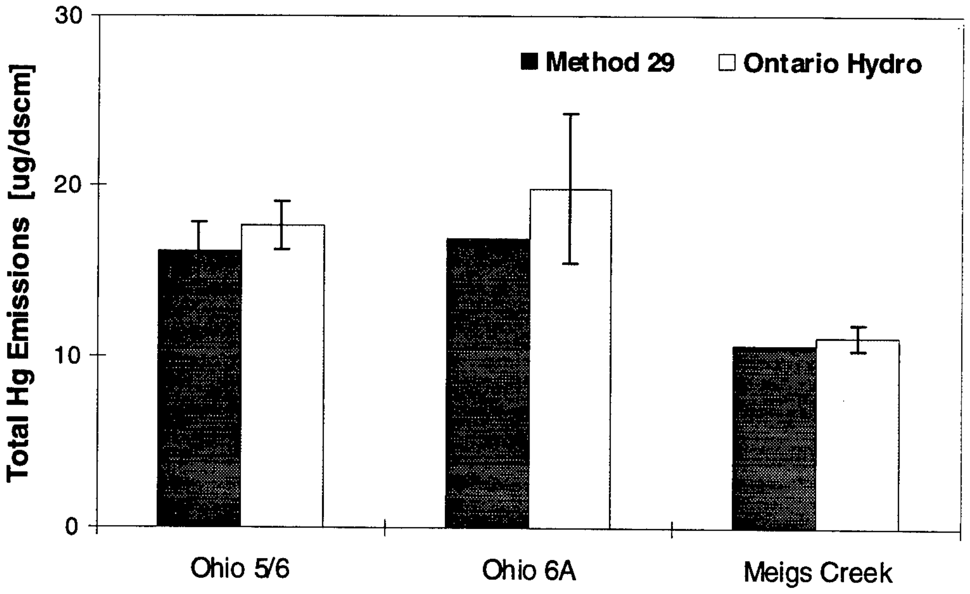

Figure 2.2 – Comparison of Total Uncontrolled Mercury Emissions According to EPA Method 29 and Ontario Hydro

The partitioning of metals between the vapor and particulate phases was measured while firing a blend of Ohio 5 and 6 coals. The comparable results from Phase I and Phase II demonstrated the reproducibility of CEDF operation with regard to trace metal emissions. Particulate partitioning greater than 99% was consistently measured for the trace metals with the exception of cadmium, selenium, and mercury. Total emissions control exceeded 97% for the pulse-jet baghouse and 95% for the ESP for many of the trace metals. The exceptions were arsenic, cadmium, selenium, and mercury. The higher level of particulate metal control achieved by the baghouse can be attributed to the lower particulate emissions from the baghouse compared to the ESP.

Arsenic, cadmium, chromium, selenium, and mercury were selected for further study on the basis of their perceived health risk, volatility, and potential for improvements in emissions control. Evaluated methods of reducing trace metal and particulate emissions from the particulate control devices included changes in operating temperature, ESP electrical conditions, and baghouse fabric. Highlights from these tests include:

> Reduction of particulate emissions by the ESP resulted directly in reduced arsenic and chromium emissions but did not measurably influence total cadmium and selenium emissions.
>
> Humidification was evaluated as a method of decreasing total ESP particulate and metals emissions. However, at the high level of particulate control (<0.01 lb/million Btu) achieved prior to humidification, flue gas humidification was not observed to have a significant effect on particulate or particulate-bound metals emissions. ESP humidification provided a modest reduction in the gas-phase chromium emissions.
>
> Particulate-phase emissions of arsenic, cadmium, and selenium downstream of the GORE-TEX® fabric were significantly lower than for the more conventional Ryton fabric. The average arsenic, cadmium, and selenium emissions were between 56 to 69% lower downstream of the GORE-TEX® fabric relative to the Ryton fabric. The improvement in metals control by the GORE-TEX® fabric directly correlated to an average 58% reduction in particulate emissions also obtained while using GORE-TEX®.

> Further reductions of the particulate and particulate-phase metals were achieved with the wet scrubber. Particulate emissions were reduced by approximately 30% across the scrubber leading to reductions in particulate-phase arsenic, chromium and cadmium emissions.

In anticipation of fine particulate (PM 2.5) regulations, particle size distribution measurements were conducted to characterize particulate and unburned carbon emissions from a low-NO_x burner. Field studies performed on commercial boilers have shown that low-NO_x burners tend to produce fly ashes that are finer and which have a lower bulk density than fly ashes produced from turbulent burners. Analysis of the material collected on the individual stages of a cyclone impactor suggest that the majority of the fine particulate (< 2.5 microns) emitted by the CEDF low-NO_x burner was less than 0.5 micron and that nearly half the unburned carbon was substantially sub-micron. This submicron material (or soot) may not be well controlled by an electrostatic precipitator due to the size and conductivity of the material.

Total baghouse mercury control varied from 0 to 16% for three different Ohio bituminous coals (Ohio 5/6, Ohio 6A, Meigs Creek). The majority of the mercury removal can be attributed to the mercury adsorbed onto the particulate entering the baghouse. The role of unburned carbon on the amount of mercury on the particulate and, therefore, also on the mercury removal achieved by the particulate control device is uncertain. The impact of baghouse temperature on mercury emissions was examined over the baghouse temperature range of 280 - 350 °F for the baseline Ohio 5/6 coal. Temperature reduction did not alter total mercury emissions although reduced baghouse temperature did favor the transformation of elemental mercury across the baghouse.

The primary contribution of a conventionally operated baghouse toward the removal of vapor-phase mercury emissions from a scrubbed utility power plant appears to be the conversion of elemental mercury by the fly ash filter cake. The proportion of the mercury species from the boiler was fairly consistent for the four Ohio bituminous coals characterized. On average, 18% of the uncontrolled vapor-phase mercury was in the elemental form as illustrated in Figure 2.3. However, once the flue gas passed through the baghouse, the proportion of elemental mercury was reduced. Two different baghouse fabrics, Ryton and GORE-TEX®, were evaluated for their impact on elemental mercury emissions. The elemental mercury emissions measured at the baghouse outlet were comparable between fabrics,

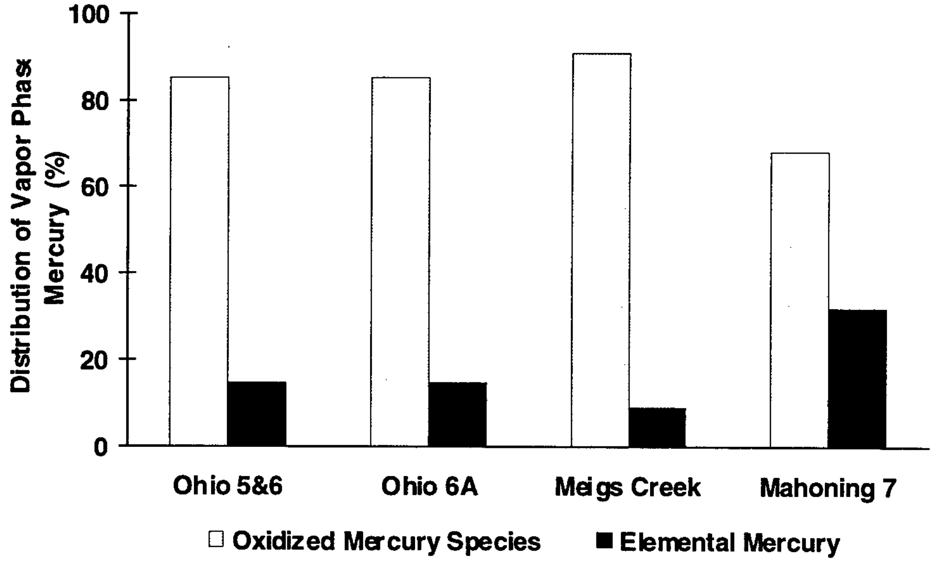

Figure 2.3 – Characterization of Uncontrolled Mercury Emissions for Ohio Bituminous Coals

suggesting that the transformation was primarily due to the bituminous coal fly ash. Increased levels of oxidized mercury corresponding to the oxidation of elemental mercury were periodically measured during Ohio 5/6 tests and consistently measured during subsequent Ohio 6A and Meigs Creek tests. The extent of oxidation of elemental mercury was consistent for each of the Ohio bituminous coal fly ashes. The average baghouse outlet elemental mercury concentration was 46% lower than the inlet for the Ohio 6A coal, 72% lower for the Meigs Creek coal and 65 - 70% lower for the Ohio 5/6 coal at a baghouse temperature of 310 °F. As a result, a baghouse/wet scrubber system may have potential for total mercury emissions reduction due to the conversion of elemental mercury to a more soluble form. This was seen during Ohio 6A and Meigs Creek tests when higher mercury control was obtained by the wet scrubber preceded by a baghouse when directly compared to an ESP/wet scrubber configuration. It should be noted that the improvement in mercury control measured for the baghouse/wet scrubber combination was too large to be attributed solely to the conversion of elemental mercury across the baghouse. Differences in mercury control across the wet scrubber when preceded by an ESP versus a baghouse are discussed in subsequent sections of this report and will be evaluated in more detail in Phase III.

However, ESPs are the dominant particulate emissions control systems installed at U.S. commercial coal-fired generating plants. The AECDP test data suggests that ESPs can remove a significant portion of the particulate-phase mercury but have a limited effect on vapor-phase mercury. In contrast to the baghouse, the ESP had no measurable impact on the elemental mercury concentration for the three Ohio coals tested. Modifications to the flue gas temperature over the range of 250 - 300 °F had no impact on elemental mercury emissions from the ESP for the baseline Ohio 5/6 coal.

Flue Gas Desulfurization Devices

Wet scrubber mercury emissions control data reported in the literature and cited by EPA as the basis for evaluating emissions from existing systems represents a relatively narrow range of scrubber design and operating conditions. The draft U.S. EPA report, *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units - Interim Final Report* [1], notably estimated a median mercury emissions control efficiency of 17% for wet scrubbers with a range of 0 to 59% on the basis of sampling at five commercial plants. Underestimating mercury removal in the existing population of FGD systems and the potential for additional mercury emissions reductions in new FGD installations may result in an over-estimation of U.S. utility mercury stack emissions. Mercury emissions control was characterized for a wet limestone scrubber over a range of conditions representative of commercial scrubber design and operation. Key wet scrubber design and operating parameters included tray configuration, oxidation mode, liquid-to-gas ratio (L/G) and slurry pH. Evaluation of the four selected variables was intended to expand the characterization of mercury control of limestone scrubbers operating on bituminous coal-fired generating units in the U.S.

Total mercury control achieved by the wet scrubber was variable over a wide range of scrubber operating conditions, tower configurations and coal type. Control of oxidized mercury was generally greater than 80%, despite the changes in operating condition, tower configuration, and coal type. Elemental mercury, which may account for up to 35% of the mercury generated by bituminous coal combustion, was not well controlled by the wet scrubber.

Total mercury emissions control across the scrubber for the same coal was influenced by whether the ESP or baghouse was used for upstream particulate emissions control. This effect is shown in Figure 2.4 for a single wet scrubber operating condition. Consistently high mercury control was achieved by the baghouse/wet scrubber system when the scrubber was configured for high SO_2 removal. An apparent contribution towards the difference in mercury control is the higher fraction of oxidized mercury in the flue gas from the baghouse compared to the ESP. A second contribution to the difference in total mercury control was the measurable increase in elemental mercury emissions across the scrubber when operated after the ESP.

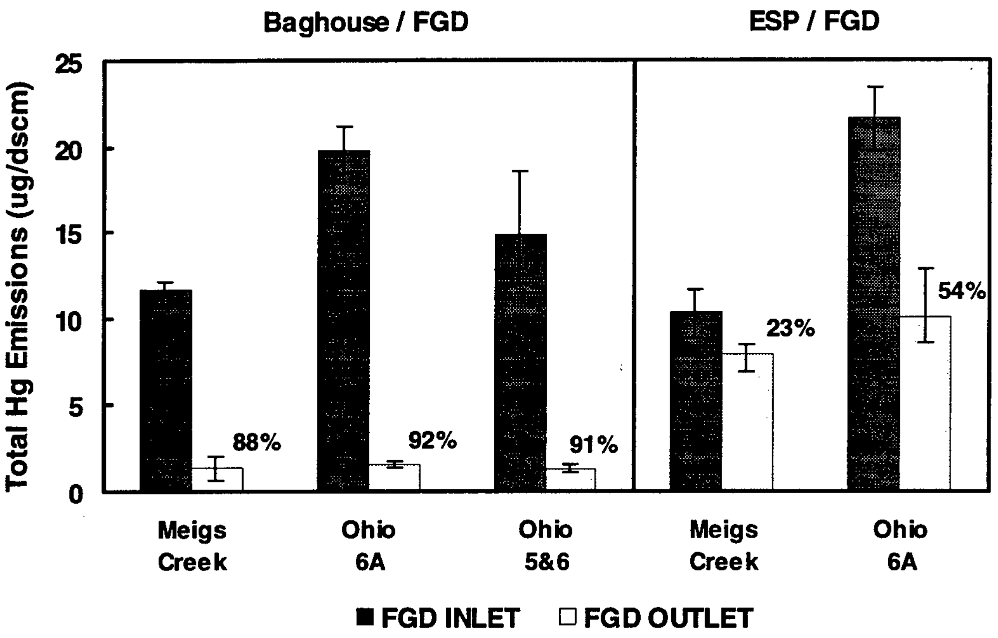

Figure 2.4 – Summary of Wet Scrubber Total Mercury Control

Extensive parametric testing was performed with the baghouse/wet scrubber system with the baseline Ohio 5/6 coal. Mercury control improved with increased L/G for both an open and tray tower configuration over a range of slurry pH. Emissions of oxidized mercury were reduced as the L/G was increased. The slurry pH did not have a significant impact on oxidized mercury emissions. Elemental mercury emissions from the wet scrubber were fairly constant over the wide L/G range investigated. A gas flow distribution tray in the wet scrubber enhanced both SO_2 and total mercury emissions control over a wide range of L/G and pH. The enhancement of SO_2 and total mercury control by the tray was pronounced at low L/G operating conditions. The major contribution towards the lower mercury emissions was the improved removal of soluble oxidized mercury emissions when the tray was installed. Elemental mercury emissions were generally unaffected by the tray configuration. In addition, SO_2 and mercury emissions from the tray tower were less variable than from the open tower at similar operating conditions. The better consistency in SO_2 and mercury emissions with the tray tower configuration relative to the open tower may be due to the reduction of flue gas channeling.

Total mercury control was not measurably affected by a switch from forced to natural oxidation for limited tests performed at high L/G test conditions. However, during the tests in which the wet scrubber was configured in the "natural oxidation" mode, elemental mercury emissions were consistently lower than when the scrubber was operated in the "forced oxidation" mode.

The relationship between wet scrubber SO_2 removal efficiency and mercury emissions control was examined. Parametric tests with a single coal evaluated the impact of wet scrubber operating conditions on both mercury and SO_2 control. Wet scrubber operating conditions that provided for low SO_2 control efficiency tended to also result in low mercury control for the bituminous coal-fired flue gas. Changes in wet scrubber operation to enhance SO_2 control such as the installation of a tray or an increase in L/G improved mercury control.

During the wet scrubber parametric tests, the scrubber by-products were analyzed to determine the fate of the controlled mercury emissions. The majority of the mercury captured in the wet scrubber typically ended up in the solid phase of the scrubber discharge during scrubber operation that provided for high SO_2 emission control. Extremely low quantities of mercury were generally measured in the FGD filtrate (liquid). Scrubber conditions that resulted in higher mercury levels in the scrubber filtrate by-product included operation at low pH and low L/G and borderline slurry oxidation stoichiometries. The elevated levels of mercury detected in the absorber filtrate stemming from scrubber operation at low L/G, low pH and low oxidation stoichiometries should be verified.

A second FGD system was evaluated for mercury control. Total mercury control across a dry scrubber/baghouse system was characterized for two Ohio coals. In spite of the varying levels of mercury and sulfur in the coals, comparable total mercury control between 60 - 65 percent was achieved.

Coal Cleaning

The contribution of coal cleaning toward the reduction of mercury emissions from coal-fired electric utility boilers was evaluated. About 75 to 80% of the bituminous coal consumed by the power generation industry is cleaned to some extent. The effect of coal washing on mercury and chlorine in both the coal and on boiler emissions was examined for three Ohio bituminous coals. The cleaned coals were slightly enriched in chlorine by the cleaning process, indicating that chlorine may be more concentrated in the bulk raw coal than in the ash fractions. Coal cleaning produced a significant decrease in mercury concentration for all three coals, with mercury reductions ranging from 36 to 47 %. As expected, sulfur also decreased as a result of cleaning for all three of the coals.

For the three Ohio coals evaluated, the reduction in mercury concentration in the coal from washing correlated to the percent reduction of ash. Based on these results, pre-combustion cleaning for mercury reduction in Ohio coals appears to be related to the efficiency of the ash removal in the cleaning process. The complexity of the commercial cleaning process or the extent of washing was not observed to have an effect on the mercury removal beyond the efficiency of the ash removal. The average reduction in mercury emissions from the boiler attributable to the commercial coal cleaning process was 49%, and ranged between 45 to 56 %. Mercury emission reductions resulting from coal cleaning were higher than the mass removal in the coal as the increased coal heating value translates to a lower coal feed rate.

Mercury species and emissions were tracked through the entire utility coal utilization process, including pre-combustion, combustion and post-combustion processes for several Ohio coals. As indicated in Figure 2.5, the major reduction in mercury emissions resulted from coal cleaning and wet scrubber operation. The contribution of coal cleaning towards the abatement of mercury emissions relative to the raw coal source averaged 49%. The conventionally operated baghouse and ESP effectively reduced the particulate-phase mercury emissions but controlled a negligible amount of the vapor-phase mercury. When the wet scrubber was operated downstream of the baghouse, between 82 to 92% of the remaining vapor-phase mercury emissions were controlled for the three Ohio bituminous coals. Mercury control averaged 23 – 80% for two Ohio coals when the wet scrubber was operated downstream of the ESP. As the majority of Eastern and Midwestern bituminous coal shipments are already cleaned to meet customer specifications, wet scrubber technology may provide the best option toward the reduction of existing mercury emissions from utility stacks.

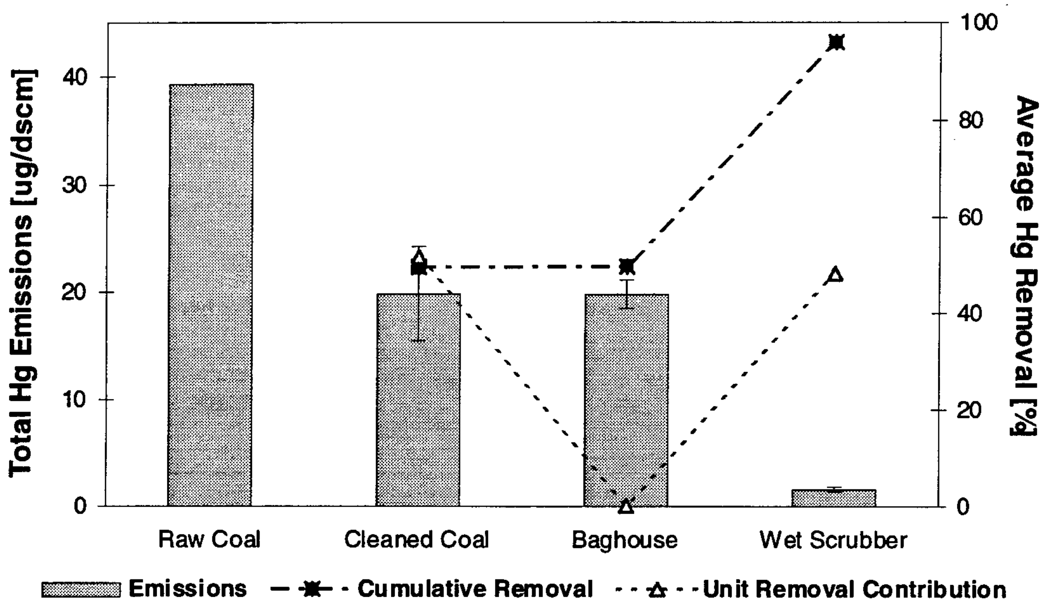

Figure 2.5 – Mercury Emissions Reduction in a Utility Equipped with a Baghouse - Ohio 6A Coal

Advanced Measurements

Two different advanced measurement techniques were evaluated for on-line or near on-line measurement of selected air toxics. Due to the current interest in mercury emissions and control from coal-fired boilers, continuous mercury analyzers were targeted. The performance capabilities of the Seefelder Messtechnik (SMT) mercury monitor system (supplied by EcoChem, West Hill, CA) were evaluated. Prior to evaluation under this program, operating experience for the total and elemental mercury analyzers was limited to facilities firing fuels other than coal. The AECDP evaluation of the SMT system presented operating and analytical difficulties due to the higher SO_2 and lower mercury concentrations present in coal-fired flue gas. An on-line Fourier Transform Infrared (FTIR) Spectrometry analyzer was also evaluated for the ability to simultaneously monitor several flue gas components, especially hydrogen chloride.

The evaluation revealed that the mercury monitor was fairly robust. However, due to the extensive interference of SO_2 even at the reduced levels downstream of the wet scrubber, the monitor system would not be applicable for the compliance to mercury standards for coal-fired power plants in its current configuration.

Although the FTIR has great capability for simultaneous concentration measurements of multiple gases, measurement is made more difficult by the presence of water vapor. The infrared spectra of water vapor overlaps, to some degree, the spectra of many of the flue gas components. One exception is HCl. At the outlet of a wet scrubber, the water vapor concentrations are very high, so that measurements of some gases are not possible at that location. Most of the constituents of the flue gas that can be measured with the FTIR have very low solubilities in water, so that removing the water from the flue gas before the measurement is a solution. However, HCl is highly soluble in water and would be effectively removed. Therefore, it is difficult to monitor many flue gas components *and* HCl simultaneously with a FTIR.

Summary

In summary, the effective control of mercury in bituminous coal-fired flue gas was demonstrated with a conventional wet scrubber. The wet scrubber provided removal of oxidized mercury at efficiencies greater than 80% for three bituminous Ohio coals over a range of operating conditions. Wet scrubber operating conditions that provided high SO_2 control also resulted in high mercury control. Mercury species and emissions were tracked through the entire utility coal utilization process, including pre-combustion, combustion and post-combustion processes for several Ohio coals. The major reduction in mercury emissions resulted from coal cleaning followed by wet scrubber operation. However, as the majority of eastern and Midwestern bituminous coal shipments are already cleaned to meet customer specifications, wet scrubber technology may provide the best option towards the reduction of existing mercury emissions from utility stacks.

Some general comments that can be made about the control of air toxics while burning a high-sulfur bituminous coal are as follows: 1) particulate control devices such as ESP's and baghouses do a good job of removing **non-volatile** trace metals, 2) mercury goes through particulate control devices almost entirely uncontrolled 3) wet scrubbing can effectively remove hydrogen chloride and 4) wet scrubbers show good potential for the removal of mercury when operated under certain conditions, however additional work is needed to understand the relationship between the wet scrubber's operating conditions and mercury capture. Phase III will address this need.

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Project Budget

The Advanced Emission Control Development Program is a five-year, three phase, $11.25 million program. The sponsors listed in the section above are contributing as follows:

- U. S. DOE – $5 million (44.45% of total cost)
- OCDO – $4.5 million (40% of total cost)
- B&W - $1.75 million (15.55% of total cost).

The cost for each of the phases is:

- Phase I – $6.7 million
- Phase II - $2.5 million
- Phase III – $2.05 million

At the completion of Phases I and II the project remains on budget and schedule.

[1] "Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units Pursuant to Section 112(n)(1)(A) of the Clean Air Act, Interim Final", EPA-453/R-96-013a, October 1996.

3.0 BACKGROUND

Promulgation of air toxics emissions regulations for electric utility plants could dramatically impact utilities burning coal, their industrial and residential customers and the coal industry. Work during the project will supply the information needed by utilities to respond to potential air toxics regulations in a timely, cost-effective, environmentally-sound manner which supports the continued use of the Nation's abundant reserves of coal, such as those in the State of Ohio.

3.1 The Clean Air Act Amendment of 1990

Title III of the CAAA's established a list of 189 hazardous air pollutants and charged the EPA with the responsibility for regulating emissions of these substances into the atmosphere as required to protect public health and the environment. The first phase of compliance is to be based on available technology, and will require many industrial plants to install the "maximum achievable control technology" (MACT). Electric utility plants are exempt from this requirement, however, pending the outcome of several risk assessment and emissions characterization studies. The EPA is scheduled to propose its plan for regulating electric utilities under Title III in the near future.

The EPA has been working with the U. S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), the Utility Air Regulatory Group (UARG), and Babcock & Wilcox to characterize air toxics emissions from existing power plants. Both DOE and EPRI have conducted major field testing programs toward this end. The results of these emissions characterization studies have been reviewed by the EPA in conjunction with the results of several on-going EPA risk assessment studies to determine the need for air toxics emissions regulations aimed at electric utilities. These field-testing programs provide considerable insight into the quantities of air toxics being emitted by power plants. However, McDermott Technology, Inc. (MTI) believes that they are only a first step toward developing an understanding of the formation, partitioning, and capture of air toxics species, and how to effectively control their emissions. While the EPA's ultimate approach is uncertain, at least some air toxics species issuing from utility stacks may be regulated. These include some of the high-risk compounds such as arsenic, cadmium, chromium, and mercury, and compounds known to be emitted in relatively large quantities such as hydrogen chloride and hydrogen fluoride. Mercury, in particular, is the subject of intensive research due to its presence in the atmosphere, subsequent deposition in lakes, and potential human health and environmental impacts. A proactive approach to the development of the technical and economic information utilities will need to assess air toxics control options is required to keep pace with regulatory actions.

3.2 Overview of the Project

The objective of this project is to develop practical strategies and systems for the simultaneous control of SO_2, NO_x, particulate matter, and air toxics emissions from coal-fired boilers in such a way as to keep coal economically and environmentally competitive as a utility boiler fuel. Of particular interest is the control of air toxics emissions through the cost-effective use of conventional flue gas clean-up equipment such as electrostatic precipitators (ESP's), fabric filters (baghouses), and SO_2 removal systems such as wet scrubbers and various "clean-coal technologies". This objective will be achieved through extensive development testing in the state-of-the-art, 10 MW_e equivalent, Clean Environment Development Facility (CEDF). The project has extended the capabilities of the CEDF to facilitate air toxics emissions control development work on "backend" flue gas cleanup equipment. Specifically, an ESP, a baghouse, and a wet scrubber for SO_2 (and air toxics) control were added -- all designed to yield air toxics emissions data under controlled conditions, and with proven predictability to commercial systems. A schematic of the CEDF and the project test equipment is shown in Figure 3.1.

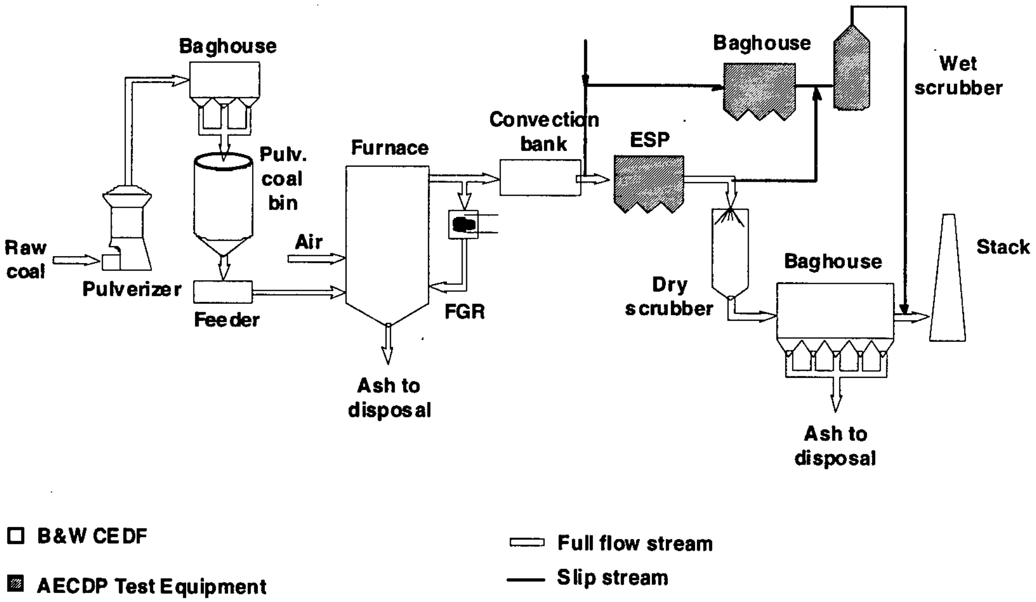


Figure 3.1 Clean Environment Development Facility

The specific objectives of the project are to:

Measure and understand production and partitioning of air toxics species in coal-fired power plant systems.

Optimize the air toxics removal performance of conventional flue gas cleanup systems.

Quantify the impacts of coal cleaning on air toxics emissions.

Identify and/or develop advanced air toxics emissions control concepts.

Develop and validate air toxics emissions measurement and monitoring techniques.

Establish an air toxics data library to facilitate studies of the impacts of coal selection, coal cleaning, and emissions control strategies on the emissions of coal-fired power plants.

3.3 Description of Project Phases

The project is divided into three phases. Phase I (Facility Modification and Benchmarking) consisted of installation, shakedown, validation, and benchmarking of the test equipment (ESP, fabric filter, and wet SO_2 scrubber) added to the CEDF. Baseline air toxics emissions and capture efficiency was established for each of the major flue gas cleanup devices: ESP, baghouse, and wet SO_2 scrubber. All tests were conducted with a high-sulfur Ohio steam coal. The work in this phase culminated in the development of a data library, or database, for use by project participants.

Phase II (Optimization of Conventional Systems) testing involved the development of air toxics control strategies based on conventional particulate and SO_2 control equipment. Development testing, engineering and evaluation was done to optimize the performance of these devices for the capture of air toxic species. Phase II testing also provided data on the impact of coal properties and combustion conditions on air toxics emissions for several steam coals. The impacts of coal cleaning on air toxics emissions were investigated through the testing of cleaned coals and their associated parent (uncleaned) coals. The development of new air toxics measurement techniques and monitoring instrumentation was also investigated in this phase.

Phase III (Advanced Concepts and Comparison Coals) testing will be directed at the development of new air toxics emissions control strategies and devices, to further reduce the emissions of selected toxics. Testing will be conducted to extend the air toxics data library to include a broader range of coal types. Finally, the development work on advanced air toxics emissions measurement and monitoring techniques begun in Phase II will continue into Phase III.

3.4 Summary of Phase I Results

Phase I -- Facility Modifications and Benchmarking -- began on November 1, 1993, and ended on February 29, 1996. Phase I activities were primarily directed at providing a reliable, representative test facility for conducting air toxic emissions control development work later in the project. The AECDP equipment installed on the CEDF consisted of an ESP, pulse-jet baghouse, and wet scrubber. All verification and air toxic tests were conducted with an Ohio high-sulfur, bituminous coal.

3.4.1 *Facility Design*

- *Fabric Filter*

The fabric filter system (Figure 3.2) consists of a pulse-jet baghouse and fly ash disposal system. The fabric filter is designed for a partial flow flue gas slipstream from the CEDF of approximately 0.6 MW_e equivalent.

Pulse-Jet Baghouse - Particulate from the flue gas stream is collected on the outside surface of porous filter bags in the baghouse. The pulse-jet baghouse is named for the manner in which the bags are cleaned. The filter cake is removed from the outer surface of the bag by a pulsed jet of compressed air supplied to its interior, which causes a sudden bag expansion. The dust is effectively removed by inertial forces as the bag reaches maximum expansion. The baghouse was initially configured with commercial size, conventional fabric filter bags to simulate air toxics capture in commercial baghouses. The baghouse design permits operation over a wide range of air-to-cloth ratio (a measure of the amount gas passing through each square foot of fabric in the baghouse), particulate loading, cleaning cycle frequency and cleaning pressure. The baghouse temperature can be varied to evaluate the effect of operating temperature on air toxics and particulate collection. The type of fuel combusted, the resulting particulate characteristics, and the particle size distribution can also affect particulate collection efficiency.

The baghouse is designed to process 6,000 lb/hr of flue gas with a particulate loading of 94 lb/hr. The baghouse was designed to reduce particulate emissions to less than the New Source Performance Standard of 0.03 lb/10^6 Btu. The primary design characteristics for the baghouse are summarized below:

AECDP Baghouse Design Summary

Compartments	two; 33 ft high x 4 ft square
Bags/Compartment	16
Bag Dimensions	6¼" diameter x 20 ft long
Air-to-Cloth ratio	3.2 to 5.2 ft/sec
Cleaning Method	Pulse-jet; on-line or off-line

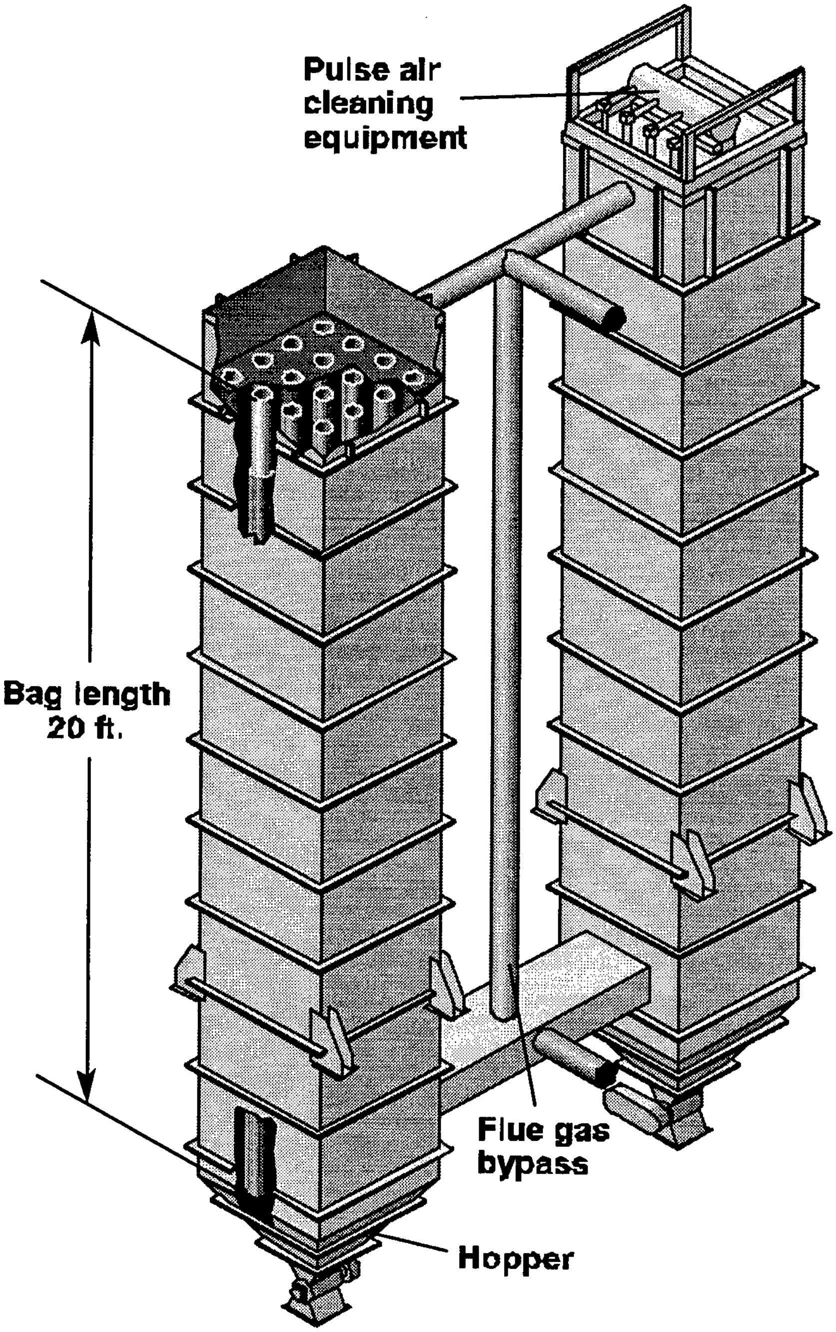


Figure 3.2 Pulse-Jet Baghouse

Fly Ash Disposal System - The fly ash collected on the fabric filter bags falls into the baghouse hoppers. From there it passes through a rotary valve into a vacuum ash handling system for transport to a disposal bin. The baghouse fly ash is typically mixed with wet scrubber by-product for landfill disposal.

Wet Scrubber

The 0.6 MW_e equivalent wet scrubber subsystems include the absorber tower, reagent feed system, mist eliminator system, and slurry dewatering and disposal system. The absorber tower (Figure 3.3) is designed to simulate a vertical section down through a commercial reactor to accurately reproduce SO_2 and air toxics removal mechanisms. Emphasis is placed on the duplication of gas/liquid interaction, minimization of wall impingement, and the proper simulation of operating parameters that affect particulate control in a wet scrubber. The wet scrubber is designed to treat the flue gas from the partial flow, pulse-jet baghouse or a flue gas slipstream from the full-flow electrostatic precipitator, and includes the equipment required to handle the associated reagent and waste streams.

Absorber - The absorber consists of the absorber tower and slurry recirculation tank. The particulate loading in the flue gas entering the absorber tower depends upon the operating efficiency of either the upstream ESP or pulse-jet baghouse, and is typically around 0.03 lb/10^6 Btu. The type of fuel influences the absorber tower operating conditions. The design is based on B&W's commercial scrubbers and incorporates a perforated-plate tray to reduce flue gas flow maldistribution. The absorber tower consists of several interchangeable modules to vary the number of perforated trays and the tray height. The modular tower design permits testing with different spray and tray configurations to best simulate the operation of conventional wet scrubbers.

The wet scrubber is designed to process 5,062 lb/hr of flue gas with a SO_2 concentration of up to 6,000 ppm. The primary design characteristics for the wet scrubber system are summarized in the following table:

AECDP Wet Scrubber Design Summary

Design limestone stoichiometry	1.1 mole Ca/mole SO_2 absorbed
Nominal SO_2 removal	90%
Design L/G ratio	267 gpm/1000 acfm
Normal L/G ratio	120 gpm/1000 acfm
Tower velocity range	5.0 to 20 ft/sec

Absorber Recirculation Tank - The absorber recirculation tank is located below the absorber tower to facilitate the gravimetric flow of reaction products into the tank. The design of the recirculation tank facilitates the evaluation of the degree of forced oxidation on SO_2 removal and air toxics collection in the wet scrubber. The air sparger system provides clean, humidified air to obtain a wide range of oxidation levels. The absorber recirculation tank is equipped with an agitator to keep the solids from settling. The pH of the slurry stream from the recirculation tank to the spray nozzles is monitored with an in-line pH sensor. The continuous pH measurement is used to control the slurry feed rate from the fresh slurry storage tank to the recirculation tank.

Reagent Feed System - This system includes a slurry storage/preparation tank, agitator, and pump and operates in a batch mode. The reagent (typically limestone) preparation system does not include a ball mill for grinding the limestone on site. Pulverized limestone is delivered to the facility. The reagent feed system is designed to handle a wide range of slurry feed rates and reagents to achieve specific levels of SO_2 control for the variety of coals.

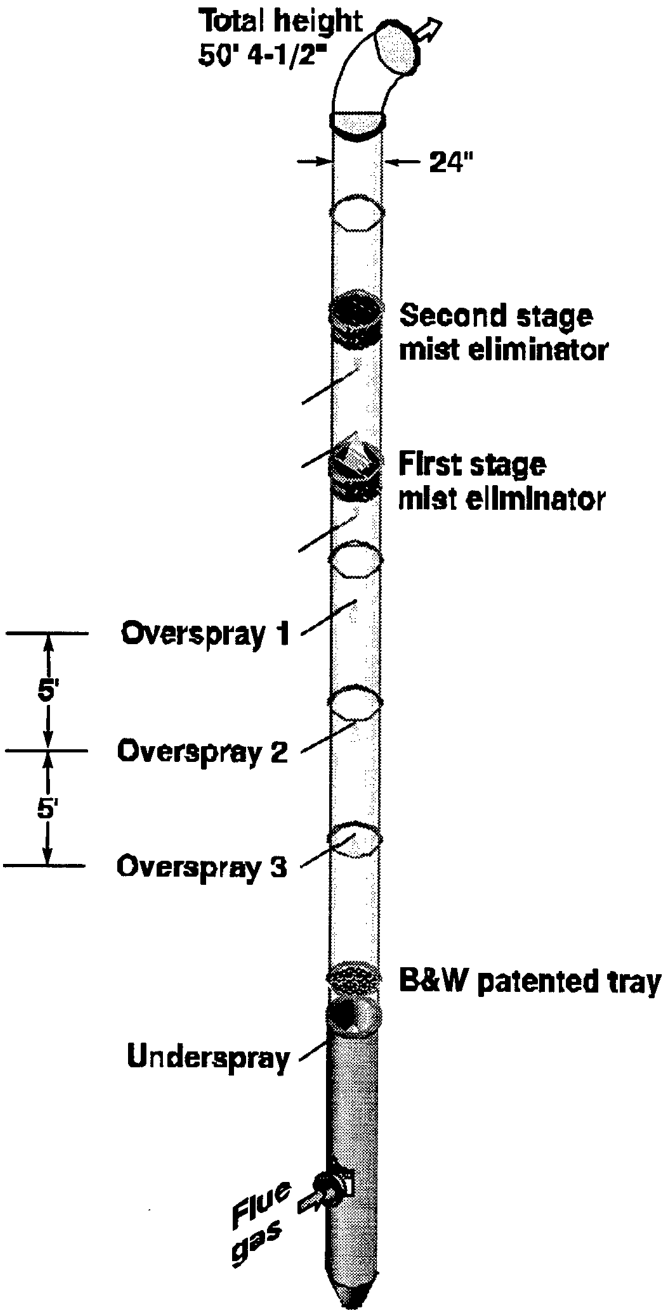


Figure 3.3 Wet Scrubber

Mist Eliminator System - Mist eliminators minimize carryover of slurry and liquid droplets generated in the absorber tower. To prevent buildup and plugging, the mist eliminators are periodically washed by way of water spray nozzles. The wet scrubber is designed to operate with vertical flow and/or horizontal flow mist eliminators. The system also includes a mist eliminator wash/recycle tank. To evaluate the impacts of mist eliminator efficiency on particulate collection efficiency and air toxics capture, sampling ports are located at the inlet and outlet of the mist eliminator sections. The modular tower design permits simple removal of the mist eliminator sections for testing purposes.

Slurry Dewatering and Disposal System - Slurry from the absorber recirculation tank is sent to the dewatering system for solids disposal and return of the clarified water. The waste slurry dewatering system consists of a hydroclone, several slurry settling tanks, clarified recycle water storage tank, an agitator and a pump. The system is designed to be run on a batch basis. The reaction products from the slurry recirculation tank are sent to the hydroclone for primary dewatering. A density transmitter in the recirculation line is used to activate the pump to the hydroclone. The hydroclone overflow is returned to the slurry recirculation tank to duplicate the slurry chemistry in a commercial scrubber. Secondary dewatering occurs in settling bins prior to mixing with fly ash or dry sorbent for landfill disposal. The clarified recycle water storage tank is equipped with a blow-down line to control the concentration of chlorides in the scrubber liquor. The blow-down on the clarified recycle water storage tank is adjustable to determine the effect of chloride level on SO_2 removal performance and the possible influence on air toxics capture.

Electrostatic Precipitator - The ESP (Figure 3.4) operates on the full flue gas flow (100 million Btu/hr, 10 MW_e equivalent) from the CEDF. The ESP was supplied by B&W's commercial Utility and Environmental Products Division. Design of the ESP follows conventional practice used commercially in power boiler emissions control. The ESP consists of discharge electrodes which impart an electric charge to ash particles in the flue gas as it passes through the ESP. The charged particles are attracted to charged collector plates and are removed from the gas stream. The plates are rapped periodically to remove the collected particles. The ash falls into hoppers below the plates and is removed from the ESP through rotary air locks.

The ESP design is sufficiently flexible to treat flue gas from a range of coals with variable ash and sulfur contents. The ESP is designed to process 102,893 lb/hr of flue gas with a particulate loading of 1883 lb/hr. The ESP is designed to reduce particulate emissions to less than the New Source Performance Standard of 0.03 lb/10^6 Btu. The ESP includes wire discharge frames and rigid discharge electrodes. Both discharge systems are used in commercial ESPs. The primary design characteristics for the ESP are summarized in the following table:

AECDP ESP Design Summary

Electric fields	four; 6m high x 4m deep
Specific collection area (SCA)	330-370 ft^2/1000 ACFM
Flue gas velocity	3.6 to 4.0 ft/sec
Migration velocity	7.5 to 9.8 cm/sec
Residence time	13 to 14 sec
Transformer rectifier sets	four; 75 kV, 125 mA

3.4.2 *Verification Tests*

To successfully apply the results of the program to utility systems, the relationship between the performance of the CEDF/AECDP test equipment and commercial units had to be established. The first step in the verification process was to verify that the flue gas treatment devices — boiler/convection pass simulator, ESP, baghouse, and wet SO_2 scrubber — operate in a manner representative of commercial units.

The 10 MW_e CEDF was carefully designed to yield combustion zone temperatures, flow patterns, and residence times representative of commercial boilers. Verification measurements confirmed that representative gas-phase time-temperature profiles *and surface metal temperatures* are maintained throughout the CEDF convection pass. Baghouse and ESP performance was confirmed through a series of particulate and opacity measurements to determine the particulate removal efficiency. Two test series were then conducted to evaluate and compare the operation of the wet scrubber with commercial units. The AECDP wet scrubber exhibited similar operating trends to a commercial unit: increased SO_2 removal with increased L/G ratio, improved SO_2 removal with increased tower velocity, and increased removal with increased spray zone height. Wet scrubber SO_2 removal performance was, as expected for a pilot unit, slightly lower than achieved by commercial systems (typically due to wall impingement).

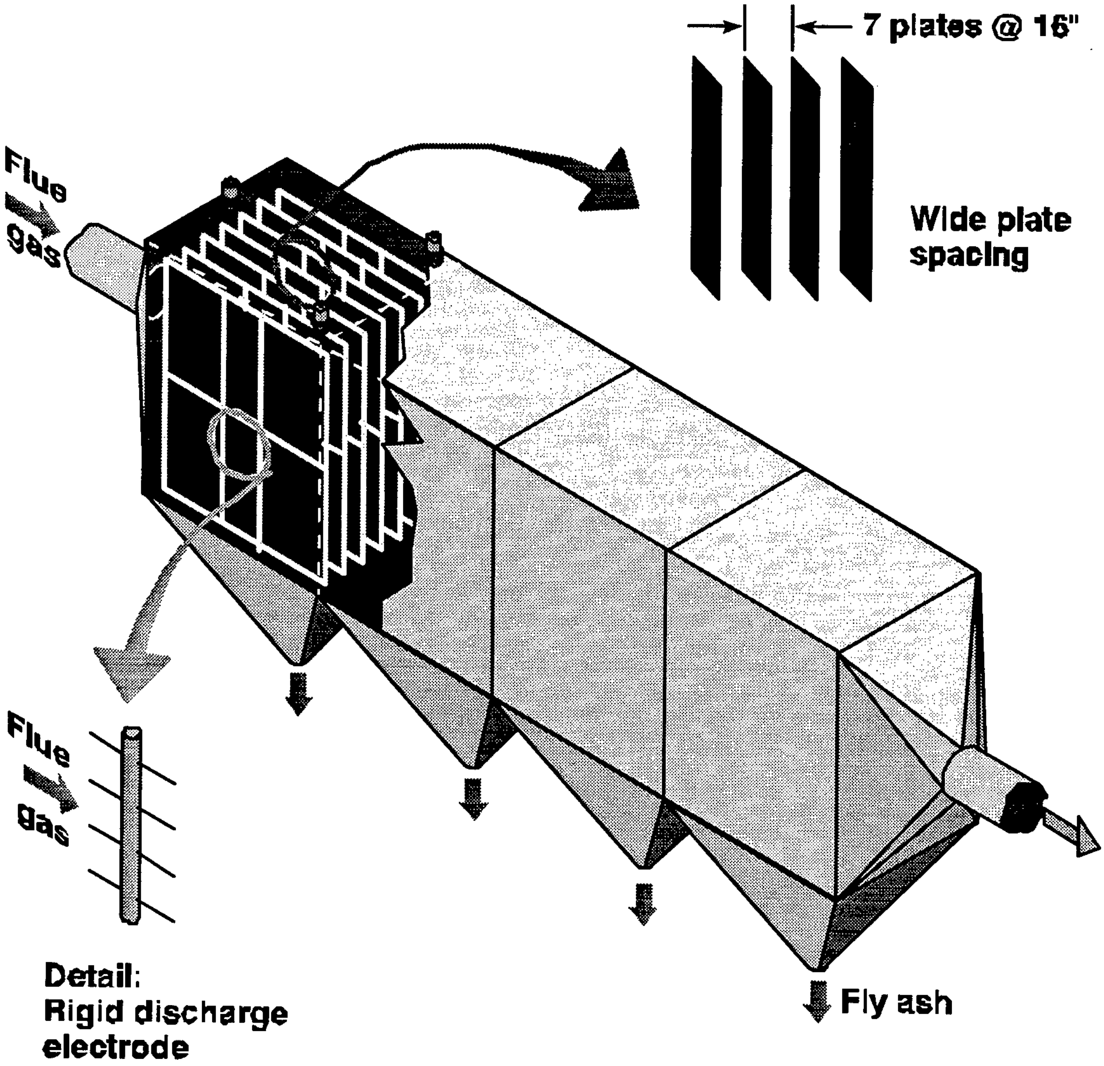


Figure 3.4 Electrostatic Precipitator

3.4.3 *Air Toxics Benchmarking*

Air toxic benchmarking tests were then performed to quantify the air toxics removal performance of the back-end equipment, and to verify that the results are comparable to those available for commercial systems. Testing focused on those substances with the highest potential for regulation, currently assumed to be mercury, fine particulate, and the acid gases hydrogen chloride and hydrogen fluoride. Mercury speciation was also targeted because of the different mercury species present in utility stacks (elemental and oxidized mercury) and their widely differing environmental fate and toxicity. The testing methods selected to sample and quantify the air toxic emissions were similar to those used in the EPRI Field Chemical Emissions Monitoring Program (FCEM) and DOE field testing programs which facilitated subsequent comparison to the available field data.

The CEDF was maintained at steady, full-load conditions throughout the benchmarking tests. Key CEDF operating parameters (coal feed rate and boiler load) had standard deviations of approximately 1% over the testing period. The high-sulfur Ohio test coal met the selection criteria: 1) it is mined in quantity, 2) it is fired by Ohio utilities, and it exhibits uniform trace element content. The test coal trace element content is within the OGS/USGS published ranges for Ohio coal, and therefore can be considered a "typical" Ohio bituminous coal from a trace element standpoint.

Measured air toxics emissions from the CEDF were compared to emissions predicted by the draft EPA emissions modification factors (EMFs) and the EPRI particulate phase metal correlations. Both correlations were developed from field emissions data taken after 1990. The measured uncontrolled CEDF emissions are in good agreement with values predicted by the use of draft EPA EMFs. The draft EMFs generally predict slightly higher boiler emissions than measured. However, the similarity between the predicted and measured emissions indicate that the HAPs generated by the CEDF are representative of commercial front-fired boilers firing bituminous coals.

The majority of the trace "particulate" metals exhibited field-documented behavior where the metals are removed at about the same level of efficiency as the particulate ash. In general, the particulate-phase metals (antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, and nickel) were primarily associated with the inlet particulate and this was reflected in the high metals removal efficiencies across the ESP and baghouse. The baghouse outlet particulate-phase metal emissions were on the same order of magnitude as the emissions predicted by both the EPA EMFs and EPRI particulate correlations with the exception of cadmium. ESP outlet particulate-phase metal emissions were generally less than the emissions predicted by the EPA EMFs and the EPRI correlations with the exception of cadmium. Wet scrubber trace element emissions were on the same order of magnitude as the predicted emissions with the exception of cadmium and chromium. The ESP and baghouse performance were comparable to the utility trace element emissions data from the DOE 8 Plant Study where particulate control limited trace element penetration to 5% or less with the exception of Cd, Hg, and Se.

As expected, the selenium, mercury, hydrogen chloride, and hydrogen fluoride emissions from the CEDF boiler were partially, if not completely, in the vapor phase. The uncontrolled hydrogen chloride and hydrogen fluoride emissions from the CEDF were consistent with the chlorine and fluorine content in the coal. However, the hydrogen chloride and hydrogen fluoride test removal efficiencies measured across the ESP and baghouse were inconsistent and inconclusive.

In all of the work to date on air toxics, the quantification of mercury species has received more attention than the other trace elements. The technical reasons for this include the variability of the fate and toxicity of the species, and their high volatility, which makes them difficult to collect in control devices. EPA Method 29 has recently been approved by the EPA for the measurement of total mercury emissions from stationary sources. Originally devised for the measurement of total mercury emissions, many researchers have reported speciated results based on Method 29.

Total uncontrolled CEDF mercury emissions averaged 10.7 ± 2.7 lb/trillion Btu and correlated quite well to the predicted emissions of 12.6 ± 2.7 lb/trillion Btu based on the coal mercury content and the mercury EPA EMF for front-fired boilers. The percentage of total mercury measured on the particulate averaged 5%, confirming the expectation that mercury would be present mainly in the vapor state. The fraction of non-elemental or oxidized mercury averaged 71% of the total uncontrolled mercury emissions and 25% was detected as elemental mercury. The speciated mercury results as measured by EPA Method 29 are comparable to those reported in the literature for bituminous coal. Total mercury removal across the baghouse was negligible, whereas total mercury removal across the ESP was unexpectedly high.

4.0 PHASE II, TEST SERIES 1: CONVENTIONAL PERFORMANCE

The activity for Test Series 1 in Phase II represents work under Task 2 - Capture of Air Toxics in Conventional Systems - as outlined in the Phase II Management/Milestone Plan. The testing primarily addressed activity under Subtask 2.1 - Electrostatic Precipitator and Subtask 2.2 - Partial-Flow Fabric Filter. The Phase II schedule is provided in Figure 4.1.

4.1 Objectives

Test Series 1 in Phase II focused on mercury speciation measurements, particulate and vapor phase trace metal emissions and fine particulate emissions. Emphasis was placed on characterization of ESP and baghouse trace element emissions control performance. These devices represent a majority of the emissions control equipment currently installed on utility boilers and, therefore, provide a basis of installed equipment for enhancing mercury and fine particulate control. In addition, an ESP for particulate emissions control precedes most wet FGD installations. The upstream equipment sets the inlet conditions for the scrubber and potentially may be used to control the distribution and form of trace elements entering the scrubber. Evaluation of the wet scrubber was the focus of the subsequent test series.

The specific objectives in approximate order of priority follow. Each of these objectives is discussed in more detail following the initial listing.

Verify ESP and baghouse trace element and mercury species emissions control observed in Phase I operation.

The high mercury removal across the ESP observed in the Phase I tests, approximately 96%, was not consistent with the majority of field emissions data in the literature. Addressing this potential inconsistency related to mercury was the highest priority for this initial Phase II test sequence.

Evaluate impact of flue gas temperature control by heat exchanger operation and humidification on mercury speciation and trace element emissions from particulate control equipment.

Humidification is a common commercially applied technique for controlling the flue gas temperature upstream of an ESP. The impact of temperature and humidification on the distribution of mercury to the particulate and vapor phases and the species of mercury present in the vapor phase was evaluated. The information generated provided a baseline for subsequent Phase II and Phase III test activity involving the evaluation of mercury emissions control alternatives for systems without SO_2 scrubbers and characterize possible approaches to controlling mercury speciation ahead of an SO_2 scrubber. The ESP was operated over an approximate temperature range of 250 to 350 °F representing the practical operating range of cold-side ESPs in industry. This testing required the installation of an atomizer ahead of the ESP for cooling the inlet gas stream using humidification

Quantify the impact of the ESP particulate emissions control efficiency on particulate-phase trace element emissions.

The ESP particulate collection efficiency data is intended to quantify the impact of high efficiency particulate control on trace metal emissions as well as provide information on the impact of additional reductions of fine particulate (PM 2.5) on trace element emissions. Three levels of control were

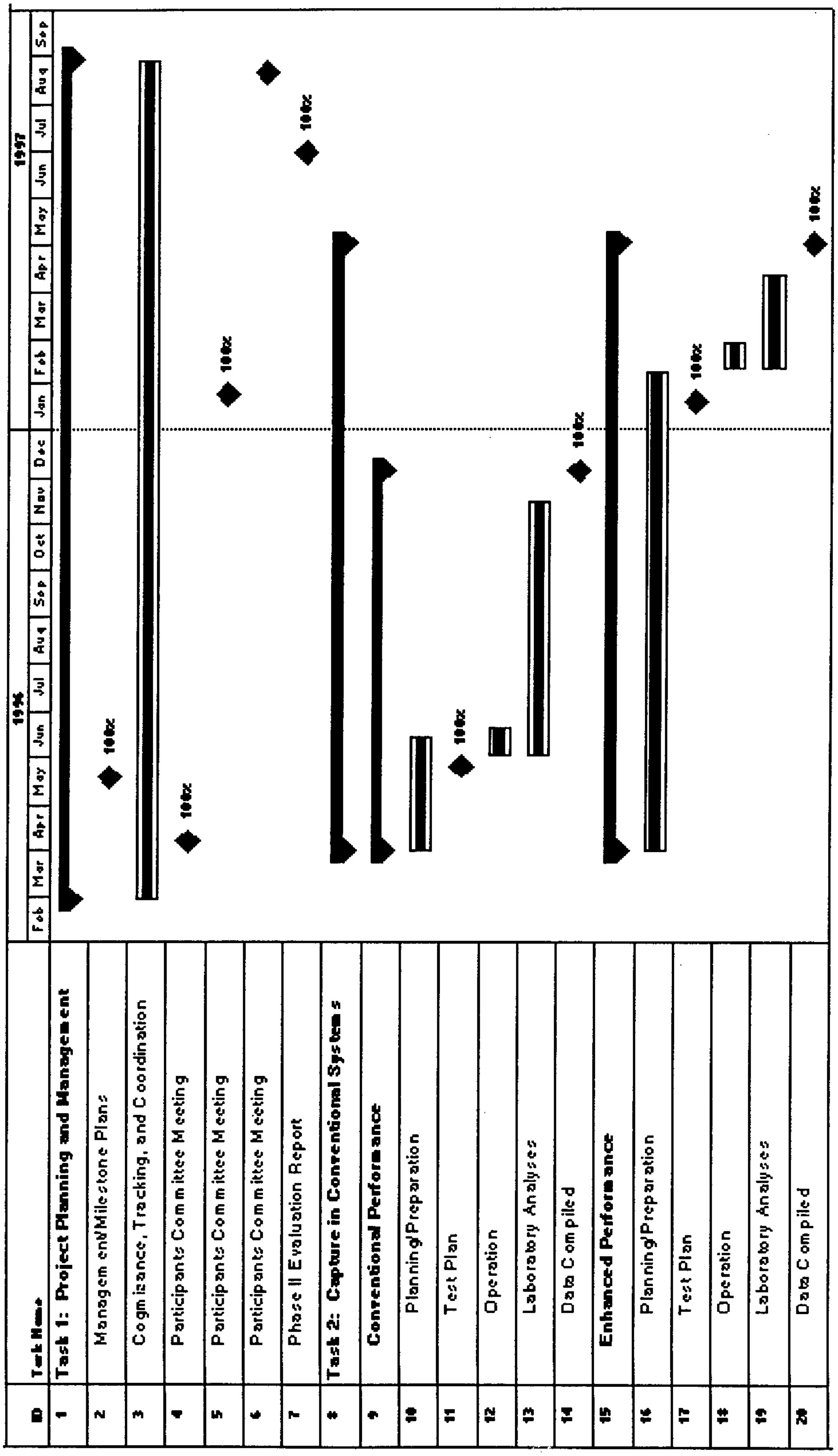


Figure 4.1 Phase II Management Plan

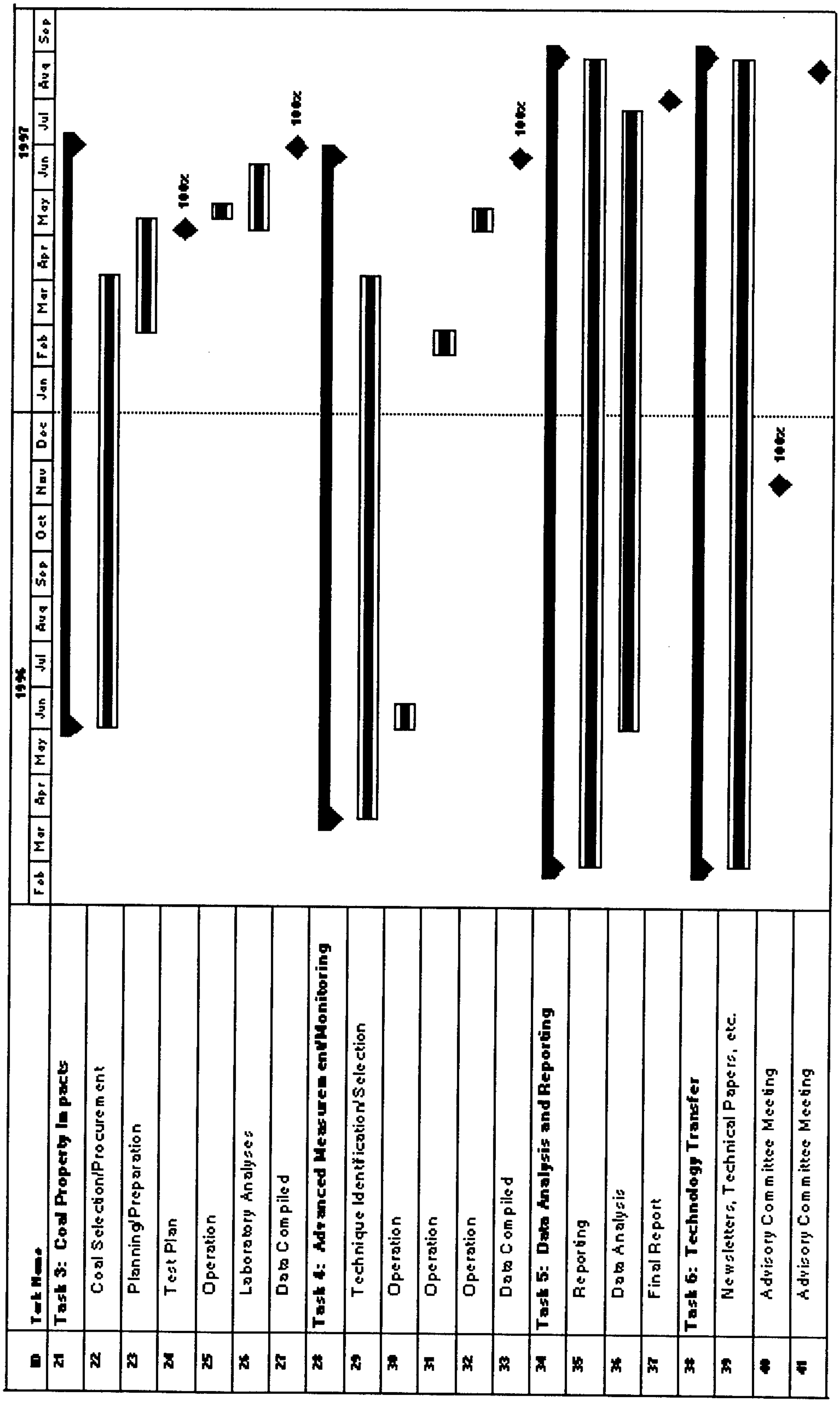


Figure 4.1 Phase II Management Plan, cont'd

anticipated - ESP outlet emissions of approximately 0.07, 0.03 and 0.01 lb/10^6 Btu - to provide information over a range representative of utility plant emissions. The general premise is that the level of emissions control is a more important consideration for the purpose of these tests than the specific operating conditions (for example, specific collection area and current density) used to vary the performance of the ESP. The project Advisory Committee had suggested that evaluation of emissions from the ESP over a range of control efficiencies would be useful to quantify the impact of enhanced performance on overall trace element emissions.

Characterize dry scrubber/baghouse mercury emissions control with a high-sulfur coal.

This test series provides characterization of dry scrubber mercury removal for a high-sulfur coal application, and extends the information in the literature, which generally focuses on lower sulfur coals. Total mercury and mercury species emissions were measured at the CEDF stack following the dry scrubber/baghouse combination.

Quantify particulate-phase trace element composition by particle size at the inlet and outlet of the ESP and baghouse and compare the two control devices.

Characterization of the particulate-phase trace element composition for various sizes at the inlet and outlet of the particulate emissions control equipment was planned. The particle size distribution (PSD) measurements with cyclone impactors were generally limited to the high-particulate stream from the boiler. The low particulate concentrations from the baghouse and ESP made the cyclone impactor measurements cost prohibitive. The resulting boiler PSD material was instead used to characterize the forms of unburned carbon emitted from low-NO_x burners in anticipation of potential fine particulate (PM 2.5) regulations.

Compare the impact of two filter bag fabrics on mercury speciation and fine particulate emissions control.

Research by other organizations has indicated that the filter bag fabric can impact the distribution of mercury species in the flue gas. Phase I measurements based on Method 29 suggested a transformation of elemental to oxidized mercury across the baghouse. Radian has also reported elemental mercury conversion across Ryton fabric[1] Conversely, EERC has reported on the basis of Method 29 measurements that Ryton fabric has no observed impact on elemental mercury vapor and mercuric chloride undergoes a chemical change in the presence of Ryton fabric[2] Mercury species behavior was compared for two different fabrics (Ryton and GORE-TEX®) using Ontario Hydro measurements. The Ontario Hydro method is believed to provide a better measure of the mercury species distribution in the flue gas than Method 29[3]

4.2 Facility Operation

During the test period, the CEDF was operated at constant, full load conditions (100 million Btu/hr, 10 MW_e equivalent). Key CEDF operating parameters (coal feed rate, load) had standard deviations of approximately 1.5%. A blend of Ohio 5 and 6 (Lower and Middle Kittanning) seams, similar to that used in Phase I, was fired. The average SO_2, NOx, O_2, HCl and particulate concentrations in the CEDF boiler flue gas are presented in Table 4.1.

One recommendation resulting from Phase I was the improvement in coal recovery for several trace metals in coal standards. The trace metal concentrations measured in the Ohio 5/6 coal blend and corresponding recoveries for the coal standards during Phase I and Phase II are compared in Table 4.2. Since a NIST coal certifiable for all the target metals is not currently available, the accuracy of the Phase II coal analysis procedure was determined by analysis of European coal standards. Table 4.2 documents the improvement in analytical coal recoveries achieved in Phase II for cadmium, cobalt and arsenic.

Table 4.1 CEDF Flue Gas Composition

Flue Gas Component	**Average Concentration**
NO_x, ppm	< 200
SO_2, ppm	2,370
CO_2, %	15.4
O_2, %	3.28
HCl, lb/10^9 Btu	84,500
Particulate, lb/10^6 Btu	3.82

Table 4.2 Coal Trace Element Analysis, ppm

Analyte	**Phase I**	**% Standard Recovery**	**Phase II**	**% Standard Recovery**
Arsenic	1.25 ± 0.42	15	7.76 ± 0.78	89
Cadmium	0.21 ± 0.11	200	0.28 ± 0.19	108
Chromium	13.97 ± 0.56	66	18.13 ± 2.17	*
Cobalt	0.94 ± 0.14	56	4.91 ± 0.19	94
Lead	3.75 ± 0.53	95	6.10 ±1.27	90
Manganese	19.00 ± 3.53	98	15.68 ± 1.74	105
Mercury	0.24 ± 0.05	92	0.25 ± 0.02	102
Nickel	9.59 ± 2.38	125	15.31 ± 5.3	*
Selenium	1.84 ± 0.24	87	2.51 ± 0.24	93
Chlorine	1,154 ± 30	*	1,018 ± 288	89

* - trace metal concentration not certified in coal standards

As in Phase I testing, each pulverized, as-fired coal sample that made up the composite samples was individually analyzed for mercury to better evaluate the coal mercury variability. The as-fired average coal mercury content based on the twenty (20) individual samples was 0.22 ± 0.04 ppm (18%). The as-fired average coal mercury content based on the eight (8) composite coal samples was 0.25 ± 0.025 ppm (10%).

4.3 Sampling and Analytical Procedures

Sampling was conducted according to EPA Method 29 and Ontario Hydro procedures. EPA Method 29 was selected as the current EPA-approved grab sampling method for *total* mercury to provide consistency with the Phase I efforts. In Method 29, oxidized mercury is collected in the initial impingers (nitric acid/peroxide) and the remaining elemental mercury is collected in the final impingers (potassium permanganate solution). It is suspected that the nitric acid/peroxide may oxidize flue gas elemental mercury resulting in an over-reporting of the oxidized mercury fraction. A schematic of the Method 29 sampling train is provided in Figure 4.2. The Ontario Hydro method, which has been evaluated by several organizations to provide an improved measure of the elemental and oxidized mercury species relative to EPA Method 29, was most frequently employed. In the Ontario Hydro method, the initial impinger solutions of Method 29 are modified. Potassium chloride (KCl) is substituted for the nitric acid/peroxide solutions to capture the oxidized component. This modification is believed to minimize the potential for oxidation of elemental mercury in the peroxide impinger solutions and provide a better measure of the mercury species distribution in the flue gas.

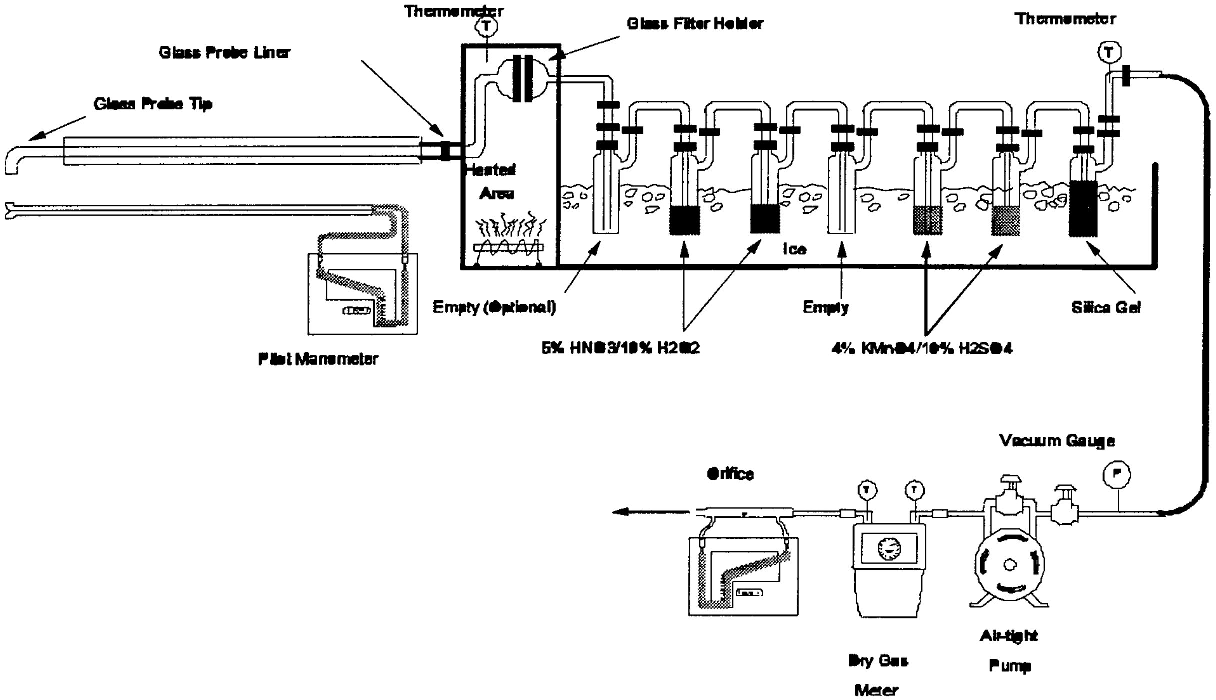


Figure 4.2 Method 29 Sampling Train

To leverage operating time, an independent sampling contractor (ATS, Inc.) performed nearby simultaneous measurements alongside MTI personnel. ATS Inc., was specifically selected on the basis of their experience in Ontario Hydro sampling and mercury analysis. Each sampling organization was also responsible for the analysis of samples collected by its personnel. Ninety-eight percent (98%) of the planned flue gas samples were obtained within one hour of the original schedule. The CEDF and backend equipment performed well over the entire 5-day test period with one significant interruption due to a blackout at the electric utility's substation.

Mercury and particulate emissions were the primary targets of the test series. In addition, other trace metals (antimony, arsenic, barium, cadmium, chromium, cobalt, lead, manganese, nickel and selenium) were selectively analyzed to provide performance data on the impact of flue gas cooling and bag fabric. The target detection limits were determined for the trace elements. Based on these limits, a four-hour Method 29/Ontario Hydro sampling period was used for most of the locations and test conditions.

4.4 Particulate Metals Behavior

The potential for improved control of particulate metals emissions was investigated in Test Series 1 of Phase II. The particulate metals arsenic, cadmium, chromium, lead, manganese, and nickel had been specified in the interim final U.S. EPA report, *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units*, as potential health risks. Table 4.3 classifies the health risk associated with the particulate metals. Operating temperature, flue gas humidification, and fabric selection were evaluated as cost-effective means of reducing particulate and trace metals emissions. The behavior of the more volatile HAPs (mercury and HCl) is addressed separately in Sections 4.6 and 4.7.

Table 4.3 Trace Metal Health Impacts

SECTION 112(b) HAZARDOUS AIR POLLUTANTS – ORIGINAL TARGETS	SECTION 112(b) HAZARDOUS AIR POLLUTANTS - POTENTIAL HEALTH RISKS
Antimony	Arsenic
Arsenic	Cadmium
Beryllium	Chromium
Cadmium	Lead
Chromium	Manganese
Cobalt	Mercury
Lead	Nickel
Manganese	Hydrogen chloride (gas only)
Mercury	Hydrofluoric acid
Nickel	
Selenium	
Hydrogen chloride (gas only)	
Hydrofluoric acid	

The specific objectives with regard to the behavior of the particulate metals in approximate order of priority follow:

Verification of ESP and baghouse trace element and mercury species emissions control observed in Phase I operation.

Evaluation of the impact of flue gas temperature variation by heat exchanger operation and humidification on mercury speciation and trace element emissions from particulate control equipment.

Quantification of the impact of the ESP particulate removal efficiency on particulate-phase trace element emissions.

Characterization of the particulate-phase trace element composition by particle size at the inlet and outlet of both the ESP and baghouse and compare results from the two control devices.

Comparison of the impact of two filter bag fabrics on mercury speciation and control of fine particulate.

One objective that was not achieved as originally envisioned was the measurement of particulate-phase trace element emissions from the particulate control devices as a function of particle size. The low particulate concentrations from the baghouse and ESP made the cyclone impactor measurements cost prohibitive. Instead, the ash collected from each ESP hopper was analyzed for trace metals content. This approach should provide similar information as it was demonstrated in Phase I that the hopper ash particle size decreased as the flue gas passed through consecutive ESP fields. Elimination of time consuming particulate size measurements permitted limited trace element measurements downstream of both the wet scrubber and full-scale combined dry scrubber/baghouse configuration.

4.4.1 Phase I Comparison

To evaluate the reproducibility of CEDF operation, the partitioning of metals to the vapor and particulate phases measured in Phase I and Phase II under similar operating conditions was compared. The partitioning of the trace metals to the boiler fly ash characterized in Phase I and Phase II is presented in Figure 4.3. Comparable levels of partitioning were measured under similar operating conditions while firing the Ohio 5/6 coal blend. Particulate partitioning of less than 99% was consistently measured for cadmium and selenium. The inconsistency of arsenic partitioning throughout the test phases may be attributed to the arsenic-specific analytical difficulties encountered in Phase I. Further comparisons of the average removal efficiencies measured across the baghouse and ESP during Phase I and Phase II are provided in Table 4.4. As discussed in a later section, the trace metal exhibiting particulate enrichment ratios of 20 and above were generally removed across the particulate control devices at efficiencies lower than those for the particulate.

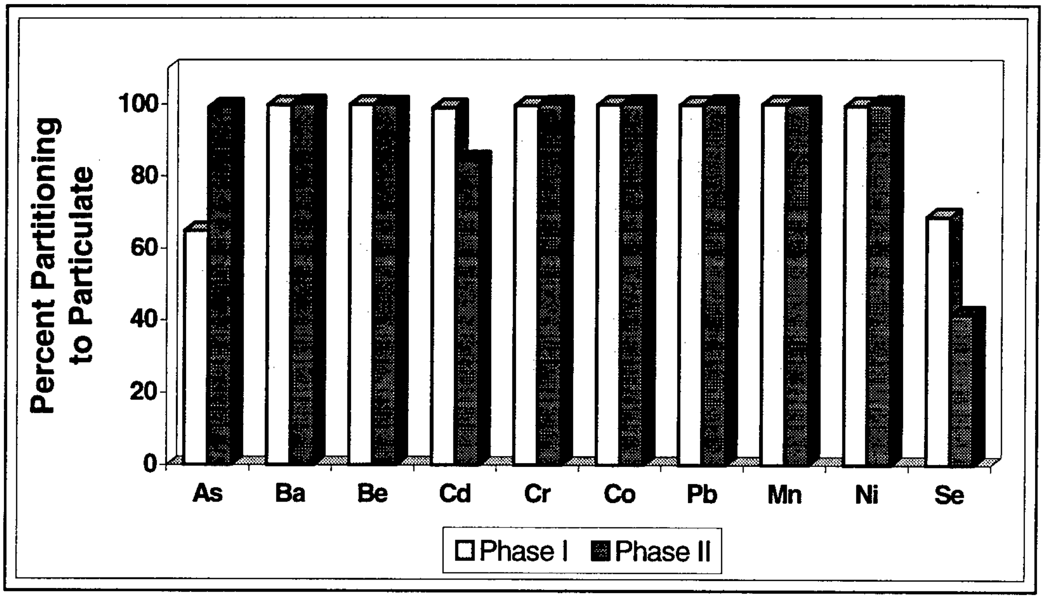


Figure 4.3 Trace Metal Partitioning to Boiler Fly Ash

Table 4.4 Comparison of Particulate Device Trace Element Control

	Baghouse Removal Efficiency [%]		ESP Removal Efficiency [%]	
Trace Element	**Phase I**	**Phase II**	**Phase I**	**Phase II**
Arsenic	60.2	**91.8**	97.8	**81.0**
Barium	97.9	97.1	98.6	96.9
Beryllium	99.9	97.4	99.9	93.7
Cadmium	86.2	**96.8**	94.8	**94.1**
Chromium	99.2	97.4	99.9	96.4
Cobalt	99.7	99.5	99.9	99.0
Lead	99.8	99.5	99.9	98.5
Manganese	99.5	98.4	99.8	98.3
Nickel	99.2	97.5	99.5	97.5
Selenium	80.7	**74.5**	95.2	**50.9**

Similar levels of trace element control across the particulate devices were observed during Phase I and Phase II with the exception of the more volatile elements: arsenic, cadmium and selenium. The higher level of particulate metal control achieved by the baghouse (in Phase II) can generally be attributed to the overall lower particulate emissions from the baghouse compared to the ESP. Baghouse particulate emissions averaged 0.003 lb/10^6 Btu corresponding to an average particulate removal efficiency of 99.93%. ESP particulate emissions averaged 0.011 lb/10^6 Btu corresponding to an average particulate removal efficiency of 99.72% during operation with typical electrical conditions. The variability in the control of the trace metals across the particulate devices (over a range of operating conditions) is illustrated in Figure 4.4. The metals exhibiting the highest variability in removal efficiency were arsenic and selenium, which also are amongst the most volatile metals, and were found to be the most likely concentrated or "enriched" on the particulate emitted from the particulate control devices.

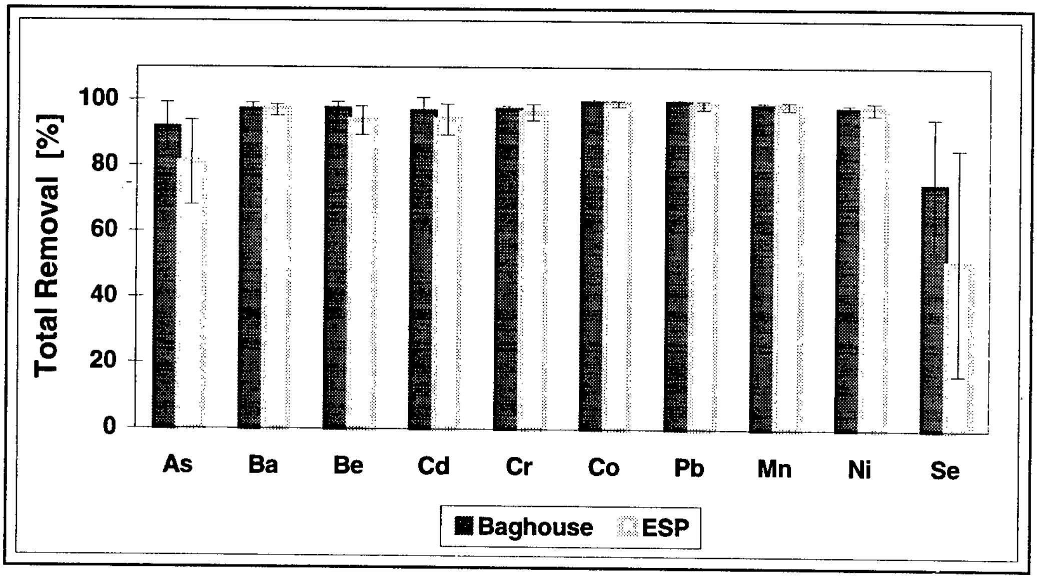


Figure 4.4 ESP and Baghouse Trace Metal Removal Efficiency

4.4.2 *Particulate Enrichment*

The sorption phenomena of trace metals onto particulate through the combustion and flue gas cooling processes in a coal-fired plant may be viewed as either a significant reduction of gaseous emission of potentially toxic trace metals or an emissions mechanism of highly contaminated particulate. The study of this mechanism provides confidence that the low volatile air toxics are consistently captured with the particulate independent of coal and particulate control device. In addition, increased understanding of the mechanisms will allow capture of the low and medium volatile species to be maximized. The ratios of trace metal concentration on the total particulate emitted from the baghouse and ESP to the trace metal concentration on the CEDF boiler fly ash, referred to as enrichment, are illustrated in Figure 4.5. Overall, the trace metal enrichment across the particulate control devices follows a similar trend, where arsenic exhibited the highest level of enrichment and lead was enriched the least. Beryllium, nickel and barium enrichment across the ESP did not follow the same pattern as enrichment across the baghouse. The lower level of enrichment on the particulate emitted from the ESP may be a function of residence time or temperature. The ESP was generally operated about 35 °F higher than the baghouse.

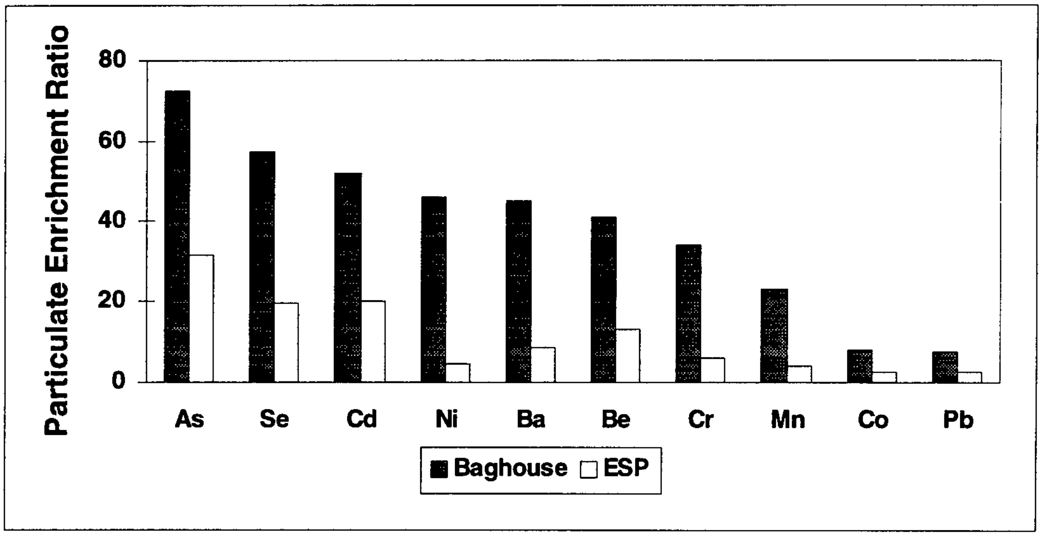


Figure 4.5 Trace Metal Enrichment Across Particulate Control Devices

The relatively finer particulate size distribution of particulate emitted from the ESP compared to the particulate loading is shown in Figure 4. 6. Approximately 15% of the outlet particulate was less than 2.5 microns. The amount of particulate collected in the stages of the cyclone was insufficient to perform trace metals analysis for measurements performed downstream of the ESP. Instead, ash samples were obtained from each ESP hopper to quantify particulate-phase trace element composition by particle size. This should provide similar information as it was demonstrated in Phase I that the hopper ash particle size decreased as the flue gas passed through consecutive fields. The metals specified by the EPA to pose a potential health risk all exhibit a general trend of increased concentration in consecutive ESP hoppers (Figure 4.7). The metals (including mercury) were further enriched on the fine particulate emitted from the ESP.

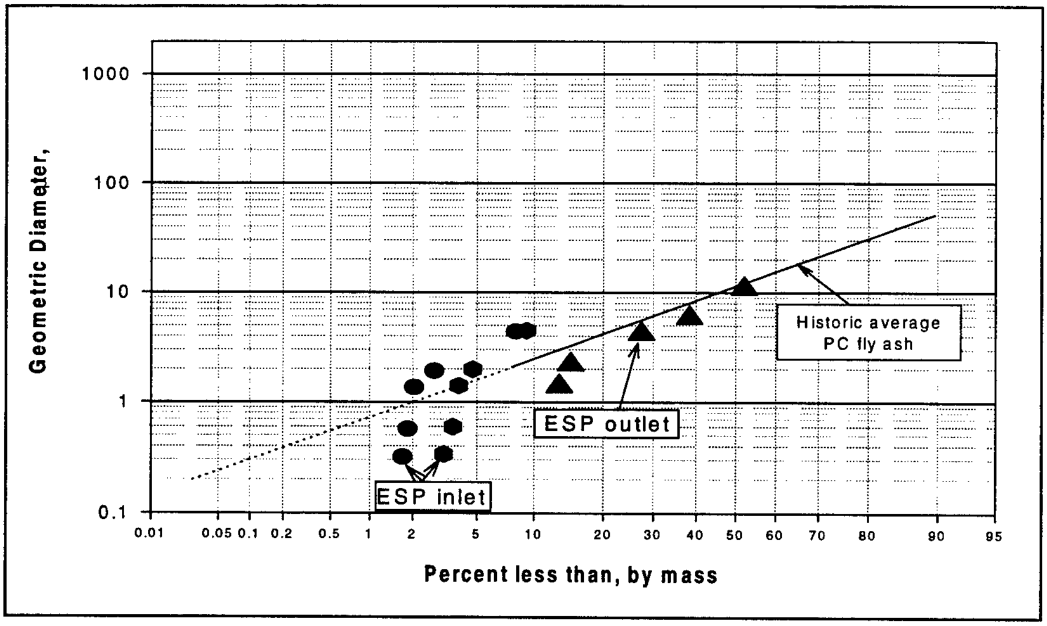


Figure 4.6 Comparison of the Particle Size Distributions at ESP Inlet and Outlet

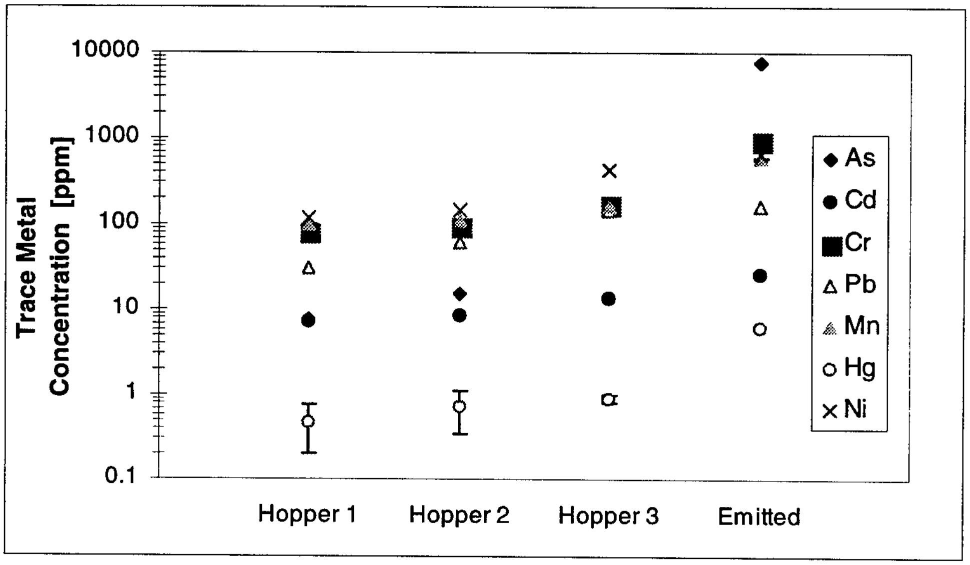


Figure 4.7 Trace Metal Concentration in Consecutive ESP Hopper Particulate

4.4.3 *Particulate Control Impacts*

Particulate emissions from the ESP in Phase I were extremely low. The ESP electrical conditions were varied during the first test series of Phase II to obtain ESP particulate emissions more representative of current commercial practice. The ESP voltage was gradually reduced to increase particulate emissions to 0.06 lb/million Btu as indicated in Figure 4.8. The intentional increase in particulate emissions provided the opportunity to correlate trace metal and particulate emissions from the ESP.

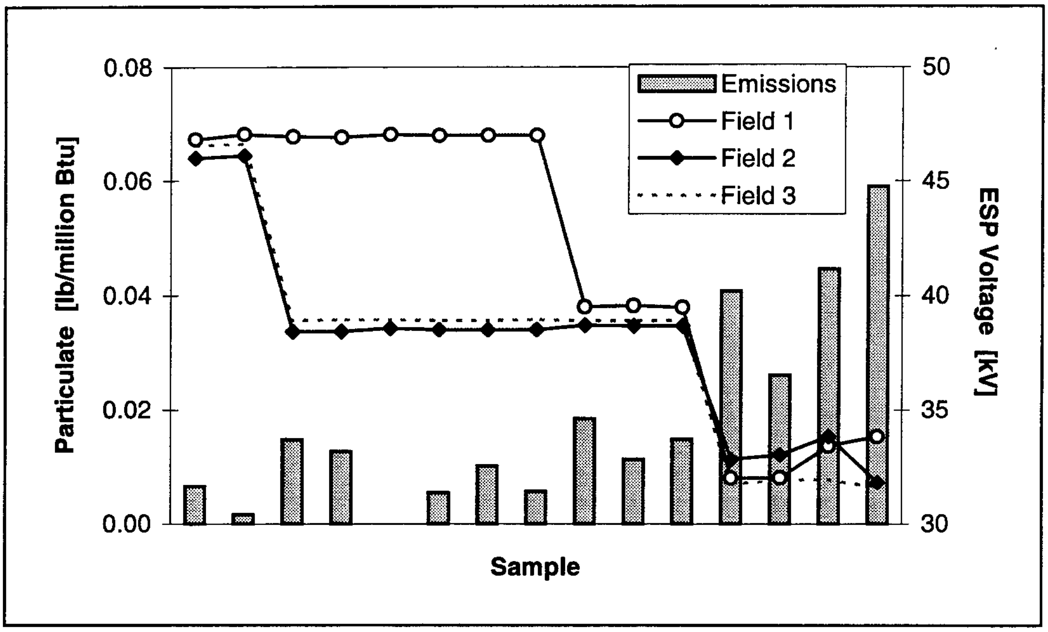
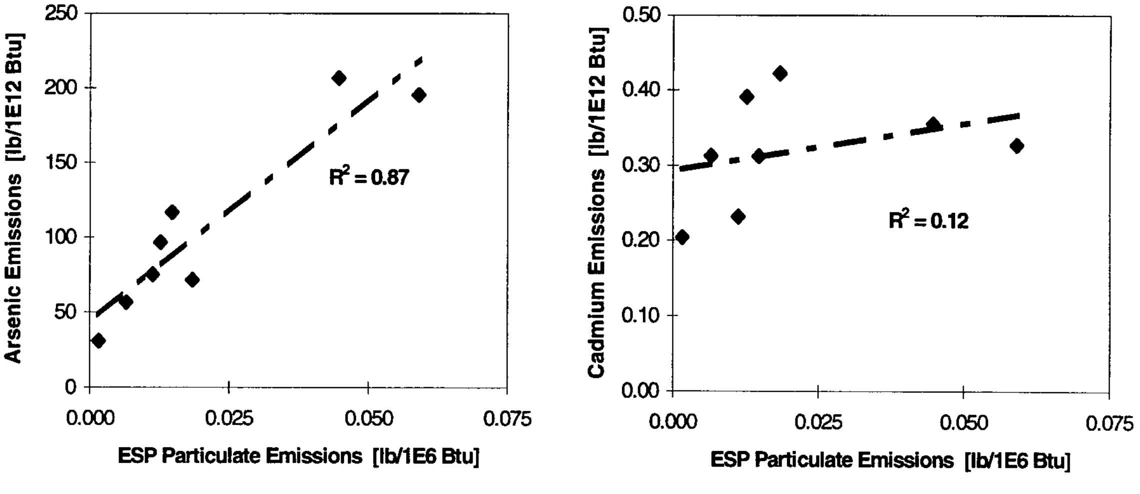
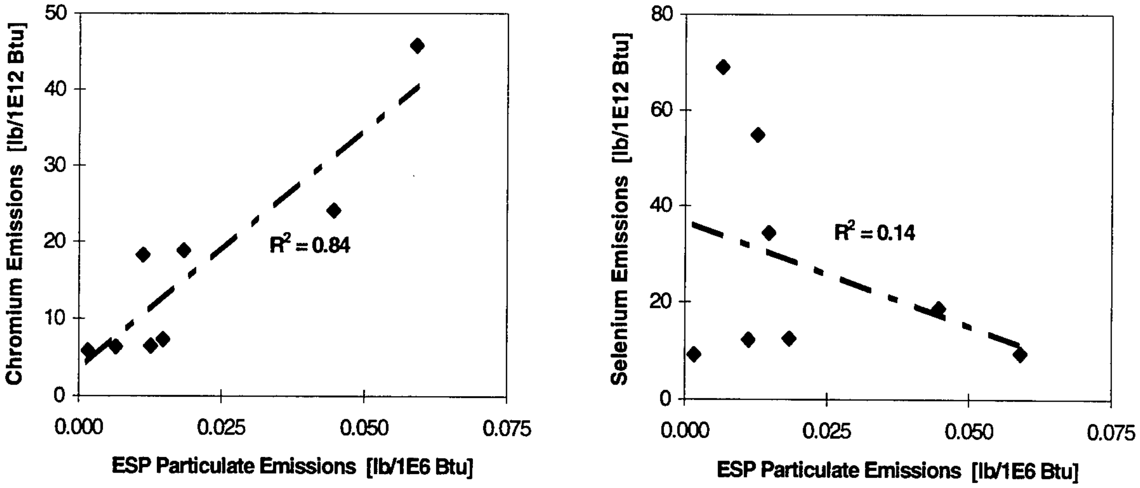


Figure 4.8 Impact of ESP Electrical Condition on Particulate

Arsenic, cadmium, chromium, and selenium were selected for the investigations of the impacts of particulate device operation on the basis of health risk, volatility, and potential for improvements in emissions control. The remaining trace metals are well-controlled by the particulate devices. Particulate and total trace metal emissions are correlated in Figures 4.9 through 4.12 for arsenic, cadmium, chromium, and selenium. The correlation is strong for arsenic and chromium, whereas, reduction in ESP particulate emissions did not influence total cadmium and selenium emissions.



Figures 4.9 and 4.10 Trace Metal and Particulate Emissions Correlation for Arsenic and Cadmium



Figures 4.11 and 4.12 Trace Metal and Particulate Emissions Correlation for Chromium and Selenium

4.4.4 Operating Condition Impact

The impacts of the operating conditions (flue gas humidification and fabric selection) on trace metals emissions across the backend control equipment are presented in Figures 4.13 through 4.16. Humidification was evaluated as a method of reducing total ESP particulate and metals emissions. However, at the high level of particulate control (<0.01 lb/million Btu) achieved prior to humidification, humidification was not observed to have a significant effect on particulate emissions. The humidification results are inconsistent for the particulate metals. Small increases in arsenic vapor and particulate emissions were observed when the flue gas was humidified. Cadmium particulate emissions remained essentially the same with humidification, whereas the vapor-phase cadmium emissions increased. Chromium particulate emissions remained essentially the same with humidification, whereas the vapor-phase chromium emissions decreased. Given the variation in the measurement of the selenium particulate ESP emissions, particulate-bound selenium emissions were not impacted by humidification. Vapor-phase selenium emissions increased with humidification. The increase in the vapor-phase emissions of arsenic, cadmium and selenium suggest that the humidification (plant) water may contribute to the emissions. However, nickel and barium were the only trace metals detected in the plant water at levels above detection.

Fabric Impact

Particulate emissions lower than the current New Source Performance Standard (NSPS) of 0.03 lb/million Btu were readily achieved with both the Ryton and GORE-TEX® fabrics. The Ryton fabric reduced particulate emissions to less than 0.01 lb/million Btu over a range of air-to-cloth (3 - 4.3 ft/min) and baghouse operating temperature (240 - 300 °F). The GORE-TEX® fabric provided discernible improvement in particulate control. Particulate penetration through the GORE-TEX® fabric was less than 0.005 lb/million Btu over a similar range of air-to-cloth ratio and baghouse operating temperature. Particulate-phase emissions of arsenic, cadmium, and selenium downstream of the GORE-TEX® fabric were significantly lower than for the Ryton fabric. The average arsenic, cadmium, and selenium emissions were between 56 to 69% lower downstream of the GORE-TEX® fabric relative to the Ryton fabric. The improvement in metals control by the GORE-TEX® fabric directly correlated to an average improvement in particulate removal efficiency of 58%. Vapor-phase cadmium and chromium emissions were not influenced by fabric type. Vapor-phase arsenic and selenium emissions appeared to vary with fabric type.

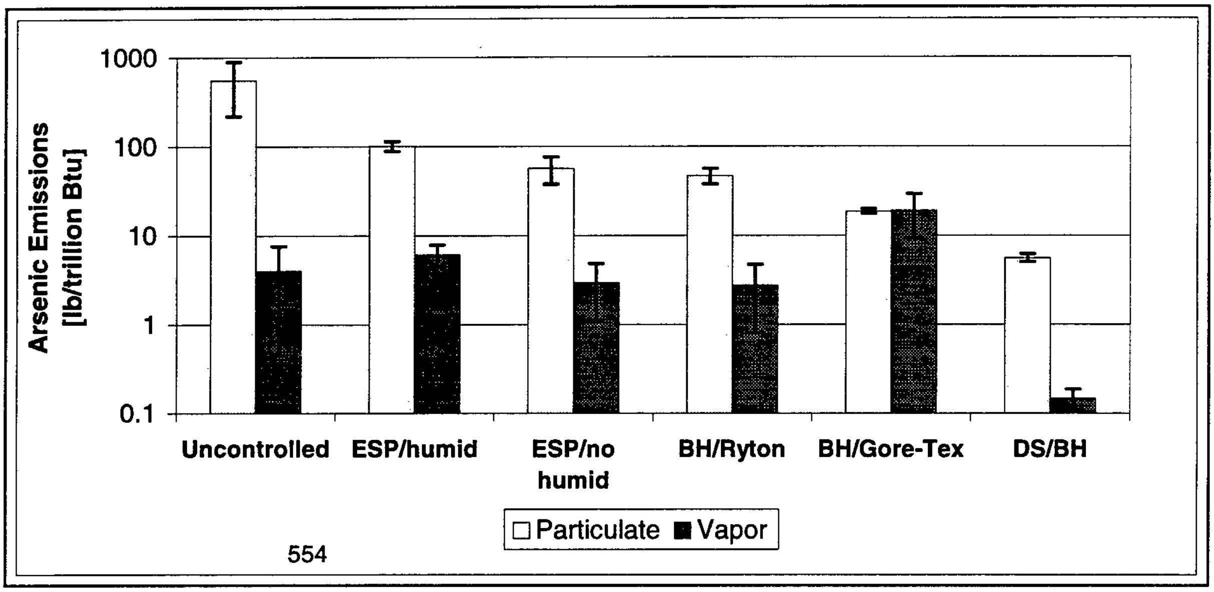


Figure 4.13 Arsenic Behavior Across Control Devices

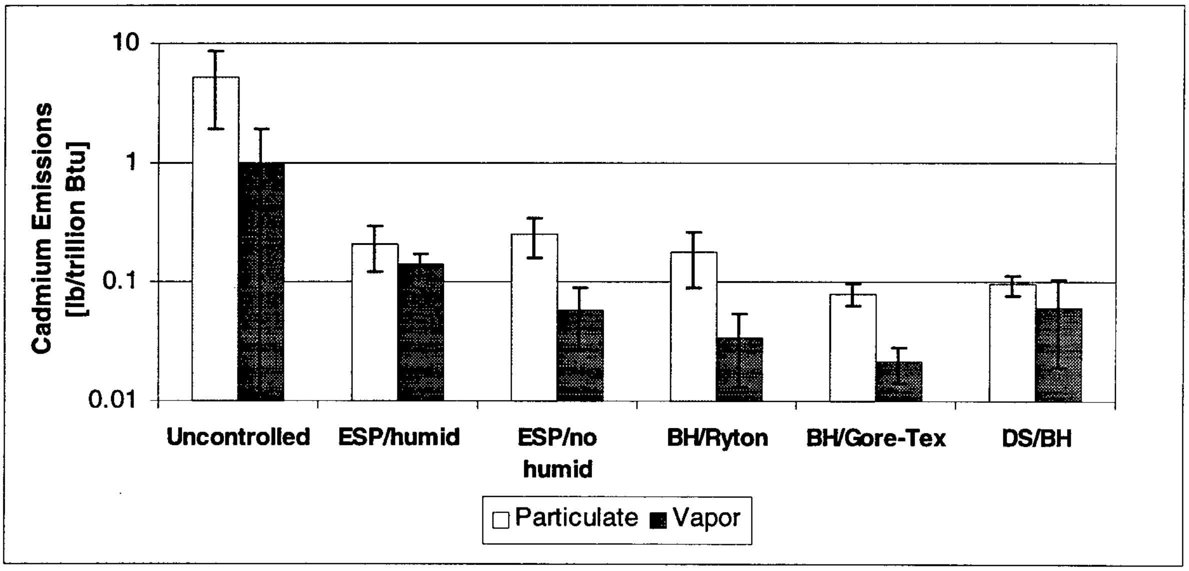


Figure 4.14 Cadmium Behavior Across Control Devices

Dry Scrubber/Baghouse

During the first test series, the dry scrubber was operated downstream of the ESP. Therefore, the operation of the dry scrubber was not entirely representative of commercial operation as the particulate emissions to the dry scrubber were quite low. The dry scrubber was maintained at 165 °F, approximately 45 degree approach to saturation. Comparison of the dry scrubber and ESP emissions in Figures 4.13 through 4.16 indicate a reduction of the vapor-phase arsenic and selenium across the dry scrubber followed by a baghouse containing Ryton bags.

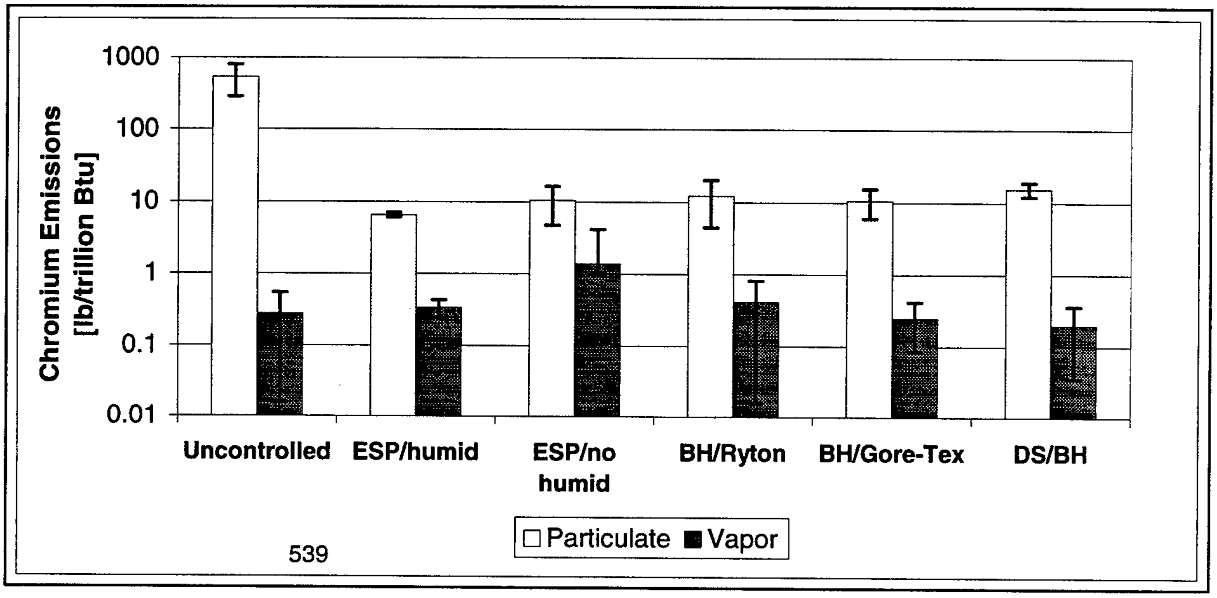


Figure 4.15 Chromium Behavior Across Control Devices

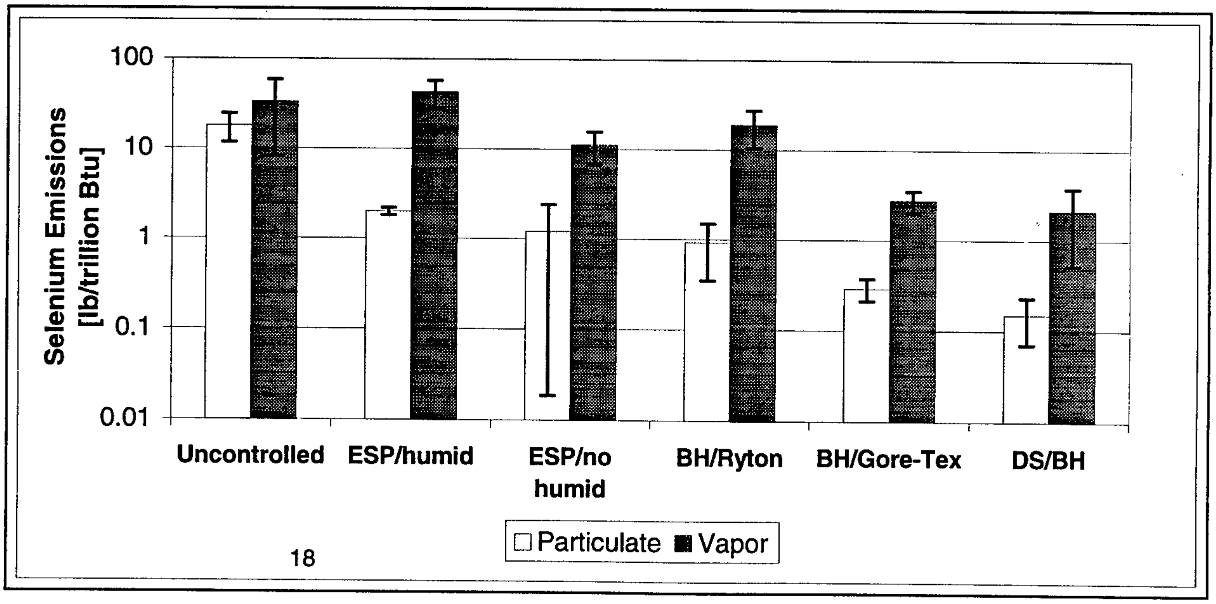


Figure 4.16 Selenium Behavior Across Control Devices

Wet Scrubber

During the Phase I operation, the particulate and trace metals emissions from the wet scrubber were typically higher than measured at the ESP outlet. A direct comparison between Phase I and Phase II test results cannot be made as the wet scrubber was operated downstream of the baghouse during the initial test series of Phase II. However, on the basis of a greater number of measurements performed in Phase II than in Phase I, both the particulate and a majority of the particulate metal emissions, were reduced across the wet scrubber. Particulate emissions from the scrubber averaged 0.003 lb/million Btu, which was approximately 70% of the average particulate loading to the scrubber. High levels of particulate-phase arsenic, chromium and cadmium removal were measured. Selenium emissions from the wet scrubber were typically higher than measured at the baghouse outlet.

4.5 Particle Size Distribution (PSD) Study

During the test period, particle size distribution measurements were performed with cyclone impactors at the boiler outlet and ESP outlet. The five-stage cyclone impactor fractionates and collects particulate material according to its aerodynamic characteristics. The resulting boiler PSD data was used to characterize particulate and unburned carbon emissions from low-NO_x burners. For the purpose of this report we define soot as submicron to micron size particles that consist largely of condensed volatiles from coal combustion. Char particles are flyash particles, larger than one micron, consisting of both ash and combustible constituents such as carbon, sulfur, and hydrogen. Unburned carbon is the measurement of total unburned carbon in both soot and char. Loss on ignition (LOI) is a measure of all oxidized constituents remaining in the flyash particle such as carbon, hydrogen, sulfur and carbonate. LOI is always higher than unburned carbon and therefore gives a conservative estimate of unburned carbon in the flyash.

Results of the cyclone impactor measurements are depicted in Figure 4.17. These data are plotted on a lognormal probability scale along with a curve that represents a historical average of PC fly ash data from the literature [4]. The shape of the particle size distribution curve for each test is self-consistent. The data for the three coarsest cyclones is comparable with the historical data. However, very little mass was present in the final two cyclones, which collected particulate between 2.5 and 0.5 micron. To address this apparent anomaly, the cyclone results were compared to some other data sources including recent field data from commercial PC-fired boilers and PSD analysis of ash hopper samples from the CEDF's ESP collected in June 1995.

Field studies performed over the past year on commercial boilers have shown that low-NO_x burners tend to produce fly ashes that are finer and which have a lower bulk density than fly ashes produced from turbulent burners. This study [5] involved the collection of fly ash from five different power plants each of which had sister units, one equipped with turbulent burners and the other equipped with low-NO_x burners. In each case, the samples were collected by extractive techniques from the flue gas upstream of the primary dust collector under non-isokinetic sampling conditions. In each case the unit with low-NO_x burners produced a finer fly ash.

Figures 4.18 and 4.19 compare the AECDP cyclone impactor data (TC4a, TC4b) with results from commercial turbulent and low-NO_x burners. The method of analysis of the fly ash samples from the commercial units was a combination of sieving the coarsest fraction of the distribution and using a Microtrac™ Particle Size Analyzer to determine the rest of the distribution. This technique measures the physical dimension of the particle whereas, the cyclones measure the aerodynamic or inertial diameter. Given the difference in the measurement technique, the coarse portion of the CEDF PSD is similar to the commercial low-NO_x burner PSD. These plots suggest that the ash distribution for the first three cyclone stages is generally representative of the commercial low-NO_x burners.

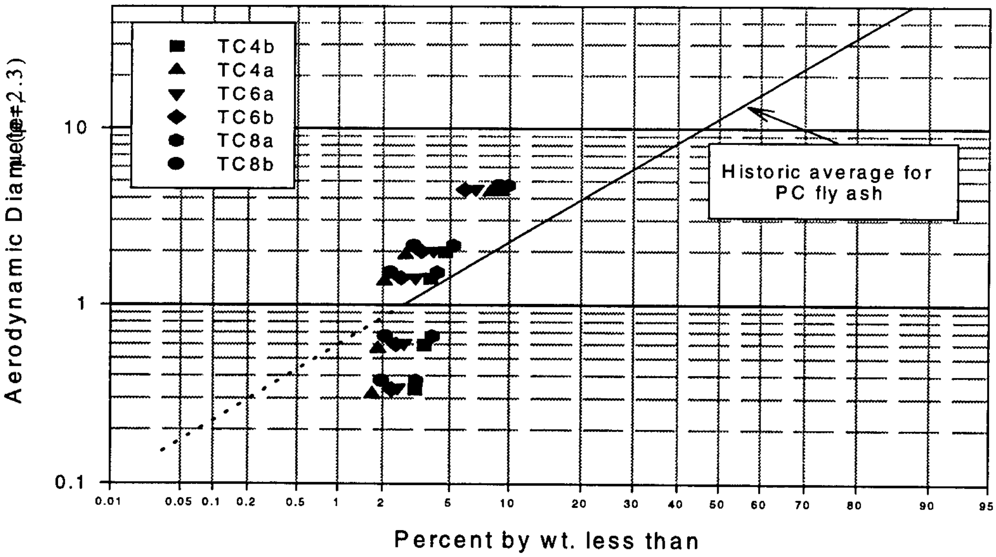


Figure 4.17 CEDF Boiler Ash Particle Size Distribution - Cyclone Impactors

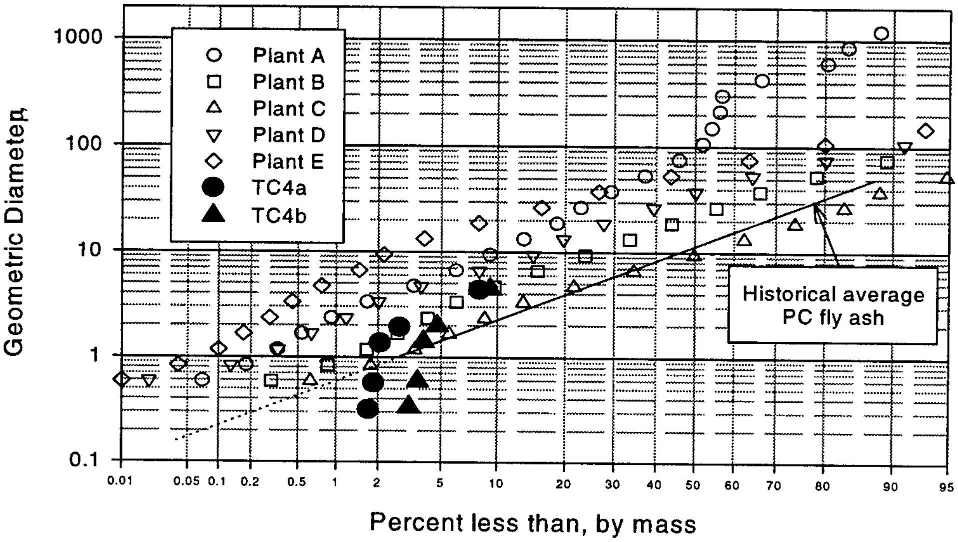


Figure 4.18 Comparison of CEDF Cyclone Data to Ash Samples From Commercial Turbulent Burners

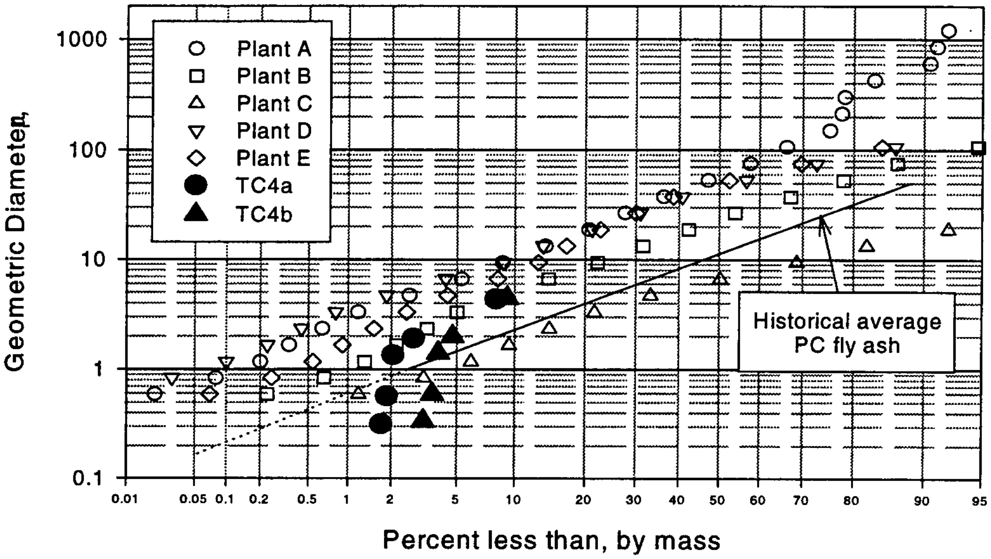


Figure 4.19 Comparison of CEDF Cyclone Data to Ash Samples From Commercial Low-NOx Burners

The cyclone data suggests that the CEDF fly ash particle size distribution is nearly void of material between about 2 microns and a point below about 0.3 microns. The mass contribution of the material less than 0.3 microns collected on the final filter was between 2 to 3.5%. By contrast, the Microtrac Analyzer suggests that there is little material less than 0.3 microns. To examine the discrepancy between the cyclone and Microtrac data and validate the operation of the cyclones, scanning electron microscope (SEM) was used to determine the size of the material collected on the first cyclone stage and final filter . Representative SEMs are presented in Figures 4.20 and 4.21. The final filter surfaces examined revealed the absence of particles larger than 0.4 micron. These scanning electron micrographs confirmed that the cyclone impactors were functioning properly. Most of the distinguishable particles on the filter appeared to be less than 0.2 micron. By contrast, both fly ash particles and char particles were readily apparent in the first stage cut.

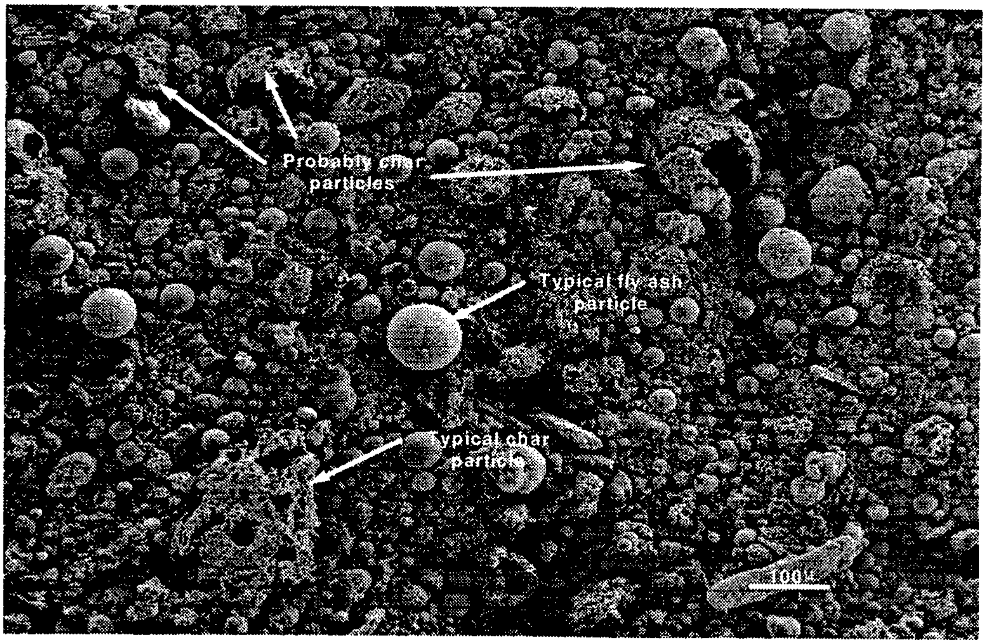


Figure 4.20 SEM of Cyclone Impactor First Stage. The Magnification is 100X.

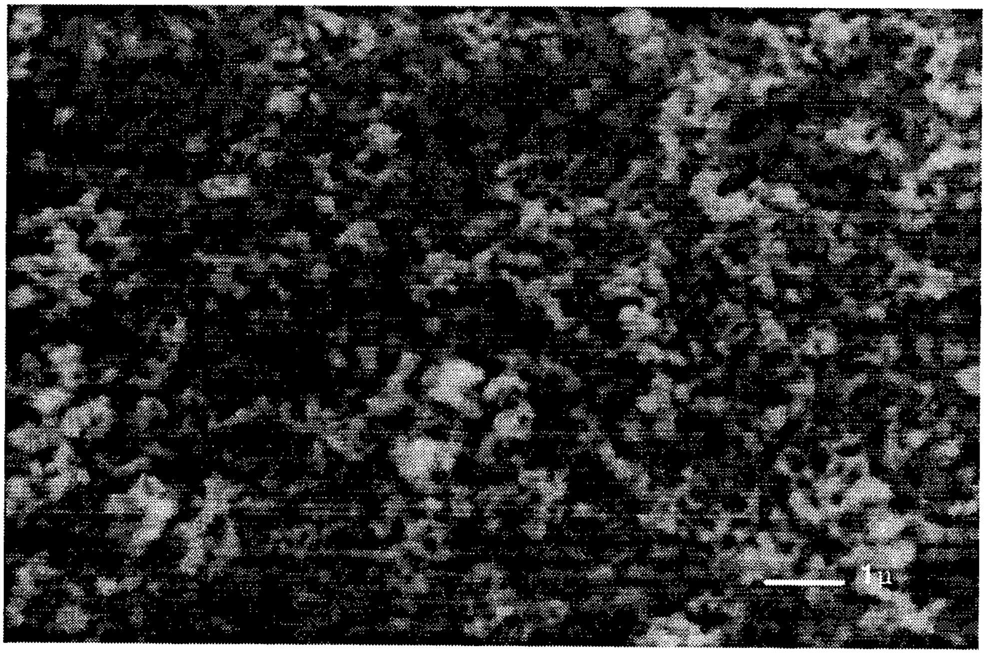


Figure 4.21 SEM of Cyclone Impactor Final Filter. The Magnification is 10,000X.

The color of the ash was observed to progressively darken across the cyclone particle size distribution, where the finest fraction was nearly black. The CEDF boiler PSD ash samples were analyzed to determine the contribution of soot (as opposed to char) to emissions from low-NO_x burners. The dark material on the back-up filter and the relatively light material on the initial stage (> 7.5 micron) were analyzed for carbon content. The carbon content on the first stage was in the range of 1.5 to 3% compared to 28 to 47% on the final filter. This study suggests that the majority of the fine particulate (< 2.5 microns) emitted by the CEDF low-NO_x burner was less than 0.5 micron and that nearly half the unburned carbon was substantially sub-micron. This submicron material (or soot) may not be well controlled by an electrostatic precipitator due to the size and conductivity of the material.

4.6 Mercury Emissions And Control

4.6.1 Potential for Mercury Emissions Regulations

At the completion of Phase II, the U.S. EPA report on HAP emissions from utility boilers required by the 1990 Clean Air Act Amendments had been released in interim form. Final release of the report was not expected until early 1998. The mandated U.S. EPA report to Congress on mercury emissions has also been delayed to allow more time for review of health risk studies. This report is not expected to be issued before 1999.

There is some evidence that some state environmental agencies are adopting a pro-active position regarding the potential control of mercury emissions rather than waiting for federal government action. The Wisconsin Department of Natural Resources (DNR) has requested that approval of a proposed merger of regulated utilities be subject to provisions requiring some efforts to reduce mercury emissions from coal-fired plants.[6] The Wisconsin DNR suggested that "retroactive credit" for mercury reductions that exceed current requirements could be applied to compliance with future emission regulations. In Massachusetts, a permit issued for a new coal-fired unit specifically required that mercury emissions be limited to 15.9 lb/10^{12} Btu.[7]

The extent of mercury emissions reduction that may be required by future regulations for coal-fired boilers remains under evaluation by U.S. EPA. For boilers firing municipal solid waste (MSW), existing regulations call for an 85% reduction of uncontrolled emissions or maximum emissions of 80 µg/Nm^3. In Germany, mercury emissions from MSW boilers are limited to 50 µg/Nm^3. Uncontrolled mercury emissions from MSW plants are significantly higher than emissions from coal-fired boilers, but there are significantly fewer MSW plants in operation. Based on analysis of the mercury contents of U.S. coals and field testing at commercial plants, uncontrolled mercury emissions from coal combustion are generally in the range of 5 to 30 µg/Nm^3, already well below the regulated level of emissions from MSW boilers.

4.6.2 *Uncontrolled Emissions*

Total uncontrolled mercury emissions from the CEDF boiler as measured by EPA Method 29 and the Ontario Hydro methods are compared in Table 4.5. Mercury emissions are reported in µg/dscm (68°F, 20°C) corrected to 3% O_2.

Table 4.5 Comparison Between Ontario Hydro and Method 29 (Dichromate Preservative)

Mercury Emissions [µg/dscm]			
Method	**Vapor Phase**	**Particulate**	**Total**
Method 29	15.9 ± 2.8	3.6 ± 1.5	19.6 ± 4.3
Ontario Hydro	8.3 ± 2.6	5.8 ± 3.1	14.1 ± 2.4

The total mercury emissions measured by Method 29 were generally higher than measured by the Ontario Hydro procedure. The lower total mercury emissions measured by the Ontario Hydro method were primarily due to the consistently lower oxidized mercury concentrations (compared to Method 29) suggesting a loss of mercury from the Ontario Hydro KCl impingers. In the absence of an oxidizing species such as peroxide, oxidized mercury could be reduced to more volatile elemental mercury. A number of preservatives (permanganate, dichromate, or peroxide) have been recommended for use in the Ontario Hydro KCl solutions to retard mercury loss during recovery [3] Dichromate was used in the first test series. The results of several in-house test programs suggested a correlation of the time between the completion of sampling and the addition of preservative to the amount of mercury loss from the Ontario Hydro impinger solutions which have been since confirmed by other researchers including the Energy & Environmental Research Center (EERC), CONSOL and Carnot[1].

The uncontrolled boiler mercury emissions measured by Method 29 and the Ontario Hydro method are broken down into the speciated fractions in Figure 4.22. The percentage of the total emissions attributed to elemental mercury measured with Method 29 by both sampling teams was consistently lower than measured with Ontario Hydro train. Higher levels of particulate mercury measured during Ontario Hydro sampling (ATS) is believed to be due to lower filter temperatures. Due to the possible loss of oxidized mercury in the Ontario Hydro KCl impinger solutions and inability of Method 29 to accurately reflect the mercury species, the discussions of mercury behavior across the control devices for the first test series are generally limited to elemental mercury as measured by the Ontario Hydro method and total mercury as measured by Method 29. As discussed in Section 5.4, modifications to reduce the loss of oxidized mercury from the Ontario Hydro sample train were successfully demonstrated during the second test series.

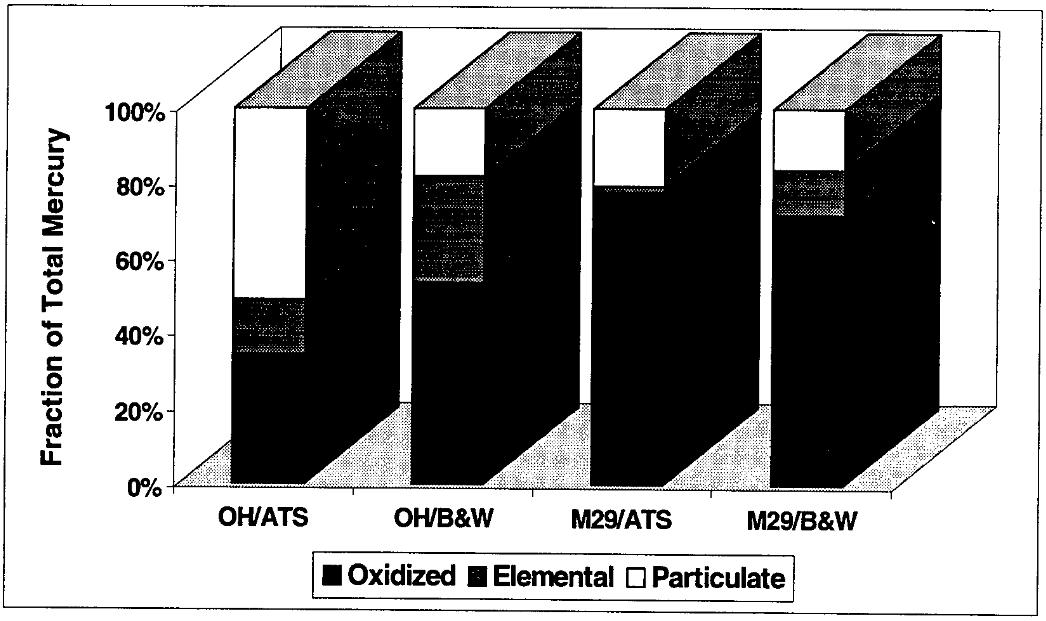


Figure 4.22 Uncontrolled Mercury Speciation Data: Ontario Hydro and Method 29

4.6.3 *Pulse-Jet Baghouse Performance*

The elemental mercury emissions entering the baghouse averaged 2.8 ± 1.0 µg/dscm (68°F, 20°C) as measured by both sampling teams in the flue gas temperature range of 300 - 350 °F. Table 4.6 compares the average elemental mercury emissions exiting the baghouse based on the Ontario Hydro method for both fabric types. The number within the parentheses signifies the number of replicate measurements. The results from both sampling teams do not suggest an impact of fabric type on elemental mercury emissions. Elemental mercury levels downstream of both fabrics were consistently lower than measured at the baghouse inlet, suggesting a transformation or removal of elemental mercury. Radian has also reported elemental mercury conversion across Ryton fabric.[1] Since the elemental mercury emissions were comparable between fabrics (for each sampling team) the transformation or removal is likely due to the high-sulfur bituminous coal fly ash. Although suspect due to loss of oxidized mercury from the Ontario Hydro KCl solutions, higher oxidized mercury were generally measured at the baghouse exit than at the inlet, supporting the possible oxidation of elemental mercury across the baghouse coal fly ash filter cake. Similar results based on Method 29 were observed in Phase I testing which suggested a transformation of elemental to oxidized mercury across the baghouse. Baghouse vapor-phase mercury removal as measured by both sampling teams with Method 29 was negligible at a baghouse temperature of 300 °F. The major mercury emissions from the baghouse were in the oxidized form.

Table 4.6 Baghouse Mercury Emissions - Ontario Hydro

Elemental Mercury Emissions [μg/dscm]		
Fabric	**ATS Measurements [μg/dscm]**	**MTI Measurements [μg/dscm]**
Ryton	0.27 ± 0.19 (6)	1.61 ± 0.51 (5)
GORE-TEX®	0.36 ± 0.18 (4)	1.26 ± 0.57 (3)

4.6.4 Electrostatic Precipitator Performance

The apparent high mercury removal across the ESP observed in the Phase I tests, approximately 96%, was not consistent with the majority of field emissions data in the literature. Elemental mercury emissions entering the ESP (and baghouse) were measured at 2.8 ± 1.0 μg/dscm throughout the test period as previously discussed. The average elemental mercury emissions (based on Ontario Hydro sampling) from the ESP as a function of ESP outlet temperature are presented in Table 4.7. As measured by both sampling teams, elemental mercury passed unaffected through the ESP over operating temperatures of 250 - 300 °F. The ESP temperature was controlled with a flue gas cooler or by flue gas humidification. The variation in total mercury emissions from the ESP (similar to the baghouse) was primarily due to variation in the oxidized fraction supporting the loss of mercury from the Ontario Hydro impinger solutions. Even with the presumed loss of oxidized mercury, the majority of the mercury emissions exiting the ESP were measured as the oxidized form. Total ESP vapor-phase mercury removal as measured by both sampling teams with Method 29 was negligible at an ESP temperature of 330 °F. This confirms that the high mercury removal across the ESP observed in Phase I, was an anomaly likely due to sampling inexperience.

Table 4.7 ESP Mercury Emissions - Ontario Hydro

Elemental Mercury Emissions [μg/dscm]			
Location	**ESP Inlet**	**ESP Outlet @ 250 °F**	**ESP Outlet @ 300 °F**
[μg/dscm]	2.8 ± 1.0 (4)	3.4 ± 1.2 (4)	3.2 ± 1.1 (3)

4.6.5 Wet Scrubber Performance

Mercury emissions control by the flue gas desulfurization (FGD) systems was not a primary focus of the Phase II test series. However, a few measurements were made to provide some characterization of the potential for mercury emissions control and to scope out parameters for future testing. Mercury emissions from the wet scrubber were measured by ATS, Inc., using the Ontario Hydro method. The limestone forced oxidation (LSFO) scrubber was operated downstream of the baghouse at two different liquid-to-gas ratios (L/G) of 81 and 22 gpm/kacfm. An average pH of 5.2 was maintained at both test conditions. The L/G range of 22 to 81 was selected to cover the range of values for the commercial FGD systems cited in the draft and interim final EPA reports on HAP emissions from fossil fuel-fired electric utility steam generating plants.[8] Current LSFO system design practice for high SO_2 removal efficiency incorporates L/G in the range of 90 to 100 gpm/kacfm.

A total of six emission measurements were obtained at the wet scrubber outlet. Two suspect measurements indicated a higher level of elemental mercury present at the scrubber outlet than the total level of mercury present at the scrubber inlet. The oxidized mercury and particulate mercury emissions measured in these two tests were consistent with the other four measurements. The wet scrubber mercury speciation measurements, excluding the two suspect test results are summarized in Table 4.8. The scrubber inlet data in Table 4.8 represents the average of 18 measurements at the baghouse outlet. Oxidized mercury results are provided as an indication of the reduction of oxidized mercury across the wet scrubber.

Table 4.8 Wet Scrubber Mercury Emissions - Ontario Hydro

Speciated Mercury Emissions [µg/dscm]			
Location	**Elemental [µg/dscm]**	**Oxidized [µg/dscm]**	**Total [µg/dscm]**
Scrubber Inlet	0.8 ± 0.7	9.0 ± 3.9	10.0 ± 4.3
Scrubber Outlet L/G 81 gpm/kacfm	1.7 ± 0.1	0.3 ± 0.3	2.0 ± 0.4
Scrubber Outlet L/G 22 gpm/kacfm	5.6 ± 1.9	0.5 ± 0.2	6.1 ± 1.8

High efficiency removal of oxidized mercury was observed at both test conditions with an average of 95%. More elemental mercury was measured at the scrubber outlet than at the inlet for the non-conventional, low L/G test condition with the Ontario Hydro method. Increased elemental mercury emissions across wet scrubbers based on Method 29 measurements have often been attributed to a sampling artifact.[9,10,11,12,] The apparent increase in the concentration of elemental mercury across the scrubber suggests that oxidized mercury absorbed by the scrubbing reagent may be reduced and off-gassed as elemental mercury. This explanation for the observed phenomenon assumes that the Ontario Hydro method measurements at the scrubber inlet and outlet adequately reflect the actual speciation at these two locations. Method development work continues to evaluate the impact of the flue gas constituents on mercury speciation measurements. [3]

4.6.6 *Dry Scrubber / Baghouse*

Ohio 5/6 Coal Blend

Mercury emissions from the CEDF full-flow lime dry scrubber/baghouse SO_2 emissions control system were measured using the Ontario Hydro method. Low particulate flue gas from the ESP was routed to the dry scrubber. The dry scrubber was conservatively operated at a 45-degree approach to saturation temperature (165°F scrubber outlet temperature) to maintain SO_2 emissions below 1.0 lb SO_2/million Btu. The coal sulfur content averaged 3.1%. SO_2 removal averaged approximately 82% over the time period when the mercury emissions were measured.

Mercury measurements around the dry scrubber/baghouse are summarized in Table 4.9. The values represent the averages of three measurements. The dry scrubber inlet mercury measurements (at the ESP outlet) were conducted simultaneously with measurements downstream of the CEDF baghouse. In a commercial dry scrubber, the particulate would not normally have been removed from the flue gas upstream of the dry scrubber. Particulate-phase mercury was low (typically less than 0.3 µg/dscm) at both the inlet and outlet of the dry scrubber system. Total mercury removal across the dry scrubber/baghouse system was approximately 64% based on Ontario Hydro sampling. Based on the Ontario Hydro measurements, the dry scrubber effectively removed approximately 97% of the oxidized and particulate phase mercury. The elemental mercury emissions measured at the inlet and outlet of the dry scrubber/baghouse system were not statistically different. Unlike the wet scrubber performance, there did not appear to be a trend toward increased levels of elemental mercury across the dry scrubber configuration. Although not substantiated, this disparity may be due to the different phase environments in the wet scrubber (aqueous) and the dry scrubber (gaseous).

Table 4.9 Dry Scrubber/Baghouse Mercury Emissions - Ontario Hydro

Speciated Mercury Emissions [μg/dscm]				
Location	**Elemental [μg/dscm]**	**Oxidized [μg/dscm]**	**Particulate [μg/dscm]**	**Total [μg/dscm]**
Dry scrubber Inlet	2.5 ± 1.6	6.8 ± 1.2	0.2 ± 0.1	9.3 ± 0.4
Stack	3.2 ± 0.5	0.2 ± 0.1	0.1 ± 0	3.4 ± 0.5

Mahoning #7 Coal

Mercury emissions were measured with the Ontario Hydro Method when a second Ohio coal, Mahoning #7, was fired in the CEDF. The Mahoning #7 coal had a significantly lower sulfur content (1.78% on a dry basis) than the Ohio 5/6 blend but a comparable mercury content (0.25 ppm). The dry scrubber was operated at a relatively high approach to saturation temperature which ranged from approximately 70 to 100 degrees. This level of operation was all that was required to maintain the SO_2 emissions below the CEDF operating permit limit of 1.2 lb $SO_2/10^6$ Btu. Uncontrolled SO_2 emissions were predicted to be approximately 2.60 lb $SO_2/10^6$ Btu based on the coal analysis. The scrubber was operating at about 68% SO_2 removal efficiency during each of the mercury sampling periods. Unlike the operation with the Ohio 5/6 coal blend, the ESP was not in service for the Mahoning 7 tests so all of the fly ash passed to the dry scrubber and baghouse.

The mercury measurements at the dry scrubber inlet and baghouse outlet are summarized in Table 4.10. Insufficient mass of particulate was obtained at the baghouse outlet for mercury analysis. Since vapor phase mercury was the primary concern, a shorter sampling time of two hours was used in these tests compared to the four hour sampling time for the Ohio 5/6 blend tests. Total mercury removal averaged 65% for the lower approach temperature and 60% for the higher approach temperature.

In contrast to the Ohio 5/6 coal tests, an apparent significant removal of elemental mercury was observed in three of the four tests. In the fourth test, the elemental mercury concentration was approximately the same at the system inlet and outlet. The observed apparent removal of elemental mercury may be tied to the higher level of unburned carbon in the fly ash for the Mahoning coal tests relative to the earlier tests. The average loss-on-ignition (LOI) of five fly ash samples taken at the convection pass outlet during the mercury emissions sampling period was 4.92%. In the previous Ohio 5/6 blend tests, the LOI averaged 2.50% based on two ESP hopper samples. In the Mahoning coal tests, the higher LOI fly ash was collected in the baghouse following the scrubber and available for reaction with mercury remaining in the flue gas following the scrubber. In the Ohio 5/6 coal blend tests, the fly ash was removed from the flue gas by the ESP upstream of the dry scrubber.

Table 4.10 Dry Scrubber Mercury Speciation Measurements - Mahoning #7 Coal

Location (# of samples)	Vapor Phase Elemental Hg (µg/dscm)	Vapor Phase Oxidized Hg (µg/dscm)	Particulate Hg (µg/dscm)	Total Hg (µg/dscm)
Dry Scrubber Inlet (4)	**5.3 ± 2.7**	**11.3 ± 3.6**	**5.7 ± 5.6**	**22.3 ± 5.3**
Stack @ 70 to 80 Degree Approach (3)	**1.6 ± 1.0**	**6.3 ± 2.7**	**NA**	**7.9 ± 3.5**
Stack @ 100 Degree Approach (1)	**1.3**	**7.6**	**NA**	**8.9**

4.6.7 Total Mercury Control Summary

In summary, the total mercury emissions measured from the various particulate and SO_2 control devices are illustrated in Figure 4.23. Negligible vapor-phase mercury removal was observed across the particulate control devices as measured by Method 29. Mercury emissions from the particulate devices were primarily in the oxidized form. On the basis of Ontario Hydro sampling, total mercury removals greater than 60% were obtained across the wet and dry scrubber systems during operation achieving conservative SO_2 control of 85% or less. Mercury emissions from the flue gas desulfurization systems were mainly in the elemental form due to the consistently high levels of oxidized mercury removal (greater than 90%).

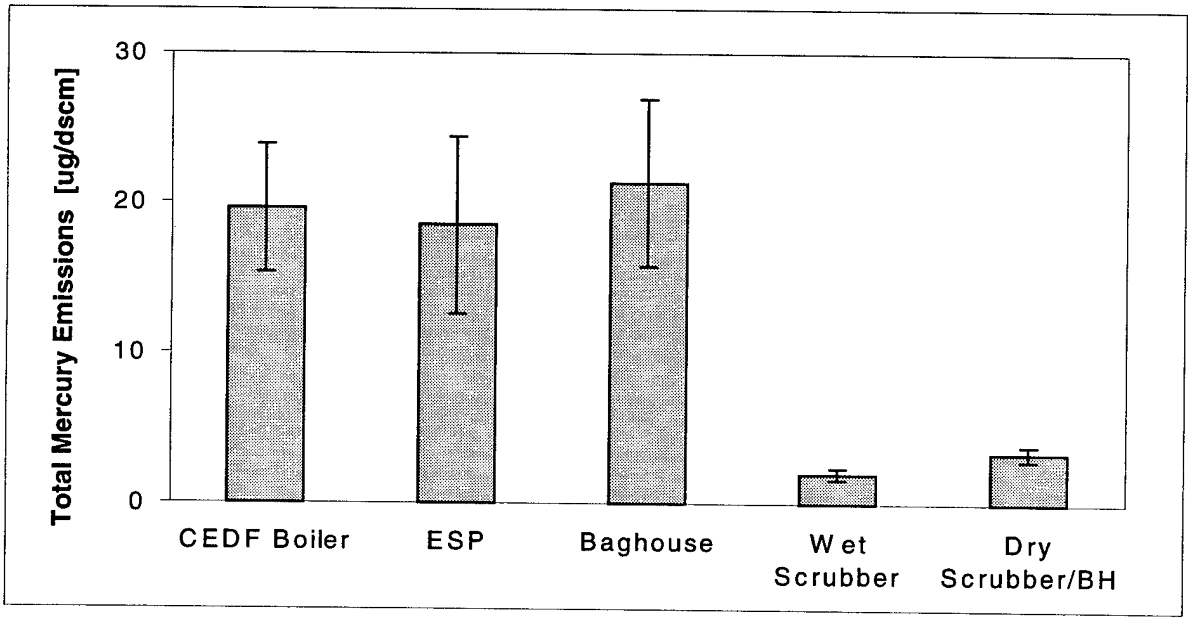


Figure 4.23 Pollution Control Device Mercury Emissions Summary

4.7 Hydrogen Chloride Emissions (Uncontrolled)

The relative quantity of HCl emissions from a coal-fired boiler may trigger the need for emissions reduction under the 1990 Clean Air Act Amendments (CAAA). Of the two methods promulgated by the EPA, Method 26A has been consistently used throughout AECDP testing as it accounts for the halides present in water droplets such as after a wet scrubber. The first set of Method 26A impingers contain a dilute 0.1 H_2SO_4 solution and the back set of impingers contain a dilute 0.1 N NaOH solution. The separation of the halides from the halogens is believed to be accomplished physically in the impingers. Halogens (Cl_2 and Br_2) have a low solubility in an acidified solution and hence tend to not be captured in three first sets of impingers containing 0.1 N sulfuric acid, whereas they are effectively captured in the 0.1 N NaOH solution. Meanwhile, the halides (HCl, HF, and HBr) are effectively captured in the 0.1 N H_2SO_4 and are therefore removed from the gas stream prior to the NaOH solution.

Method 26A measurements were limited to the boiler outlet sampling location during Test Series 1 of Phase II. Uncontrolled measured emissions of 84,520 lb/10^{12} Btu (116 ppm) were comparable to the predicted emissions (76,870 lb/10^{12} Btu) based on the coal heating value and chlorine content. The uncontrolled emissions were primarily detected in the vapor-phase (99.7%). On average, 97.4% of the total vapor phase emissions were collected in the sulfuric acid impingers and the remaining 2.6% was collected in the NaOH impinger solutions. Under the assumption that Method 26A accurately speciates, chlorine gas emissions from firing the Ohio 5/6 blend averaged 2,190 lb/10^{12} Btu or 1.7 ppm.

4.8 Sampling Methods Discussion

During Test Series 1 of Phase II, total mercury emissions as measured by Method 29 were higher than measured with the Ontario Hydro method. The lower mercury levels measured by the Ontario Hydro method compared to Method 29 coincide with observations made by other researchers when a permanganate preservative is not used to stabilize the KCl impinger solutions. Other sampling method investigations included the influence of SO_2, filter temperature and the impinger solutions digestion processes.

4.8.1 *Influence of Sulfur Dioxide*

The percentage of the total emissions attributed to elemental mercury measured with Method 29 by both sampling teams was consistently lower than measured with the Ontario Hydro train. Extensive bench-scale experiments have been conducted by EERC to examine whether flue gas constituents influence the ability of Method 29 to provide accurate speciated mercury results. Specifically these tests investigated the oxidation of elemental mercury by SO_2. EERC found that the addition of 1,500 ppm SO_2 to simulated flue gas resulted in the collection of about 10 - 12 % of the injected elemental mercury in the acidified peroxide impingers, and therefore reported as oxidized mercury.[13] During sampling with actual flue gas containing 1,500 ppm SO_2, Method 29 has been shown by EERC and Radian to overestimate the oxidized form of mercury up to 35%[13]. The elemental mercury CEDF boiler emissions averaged 1.21 µg/dcsm according to Method 29 and averaged 3.15 µg/dscm on the basis of four Ontario Hydro measurements conducted in flue gas containing 2,400 ppm SO_2. On the basis of these averages, approximately 62% of the elemental mercury was not collected in the Method 29 $KMnO_4$ impingers. This suggests that the oxidation of elemental mercury increases in the Method 29 sample train as the flue gas SO_2 concentration is increased.

However, SO_2 can also behave as a reducing agent[14,15,16]. During sampling in high SO_2 flue gas streams, a pink precipitate has been observed in the connecting glassware and neck of the first Ontario Hydro KCl impinger. Sulfur dioxide has been reported to reduce selenious acid to elemental selenium which is a reddish-pink solid[17]. Precipitated selenium in the elemental form has been quantified in wet scrubber limestone absorber filtrates. Identification of the selenium was confirmed by X-ray fluorescence. In addition to the reduction of oxidized forms of selenium, it is feasible that SO_2 may reduce oxidized mercury in wet scrubbers according to the following reduction and disproportionation reactions:

$$HgCl_2 + SO_2 + 2\,H_2O \Rightarrow Hg^0 + H_2SO_4 + 2\,HCl \quad (1)$$
$$Hg_2Cl_2 \rightleftharpoons Hg^0 + HgCl_2 \quad (2)$$

as reported in the literature. Muster, et al., postulate that oxidized mercury forms may be reduced by dissolved SO_2 and therefore re-emitted as elemental mercury, both in acid and alkaline solutions[18].

4.8.2 Filter Temperature Impacts

During Test Series 1 of Phase II, the filter temperature of the Method 29 and Ontario Hydro sample trains was maintained at 250°F for all sampling locations. The impact of the filter temperature on the particulate-phase mercury results when the flue gas temperature was maintained at approximately 300°F under constant full load conditions is shown in Figure 4.24. Even though the filter temperatures were maintained within the protocols of EPA Method 29 (248 ± 14°F), the fraction of mercury measured on the particulate increased with incremental reductions in filter temperature for the Ohio 5/6 coal fly ash. To overcome impacts of filter temperature on mercury speciation results, the filter should be maintained at the flue gas temperature. Other investigators including EERC and Radian have reported similar observations for other coal fly ashes. In the case of measurements downstream of a wet scrubber, the filter temperature should probably be maintained at 250°F as prescribed by EPA Method 29.

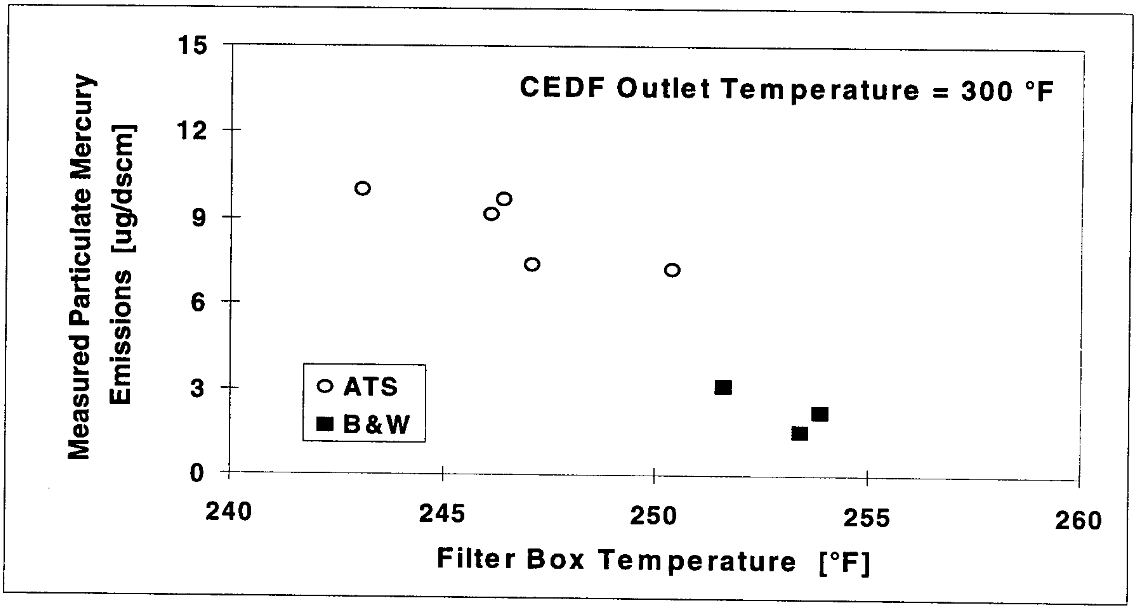


Figure 4.24 Impact of Filter Box Temperature on Mercury Particulate Emissions

4.8.3 Digestion of Ontario Hydro Solutions

Digestion of Method 29 nitric acid/peroxide impingers solutions is required to destroy the peroxide present before reduction of oxidized mercury and subsequent measurement as elemental mercury by cold vapor atomic absorption spectroscopy (CVAAS). The Ontario Hydro method followed during the initial test series did not specify the digestion of the KCl impinger solutions. Organic compounds are a positive interference at the 253.7 nm line for elemental mercury absorption measurements. At ppb levels of mercury in the impinger solutions, absorption of organic compounds could be an interference. Therefore, samples were analyzed directly (after dichromate preservation) and again after the standard method of Method 29 digestion was performed. An average 12% reduction in mercury measured in the digested KCl solutions relative to the undigested KCl solutions suggests a high bias of oxidized mercury emissions by the Ontario Hydro method possibly due to the presence of organics that may have not been sufficiently destroyed by the dichromate. By comparison, the use of permanganate as the preservative in a later test series resulted in a smaller bias in the mercury content of the digested and undigested KCl impinger solutions. The reduction in the mercury bias for undigested KCl solutions may be attributed to the stronger oxidizing properties of permanganate. Further study completed in the Phase II Test Series 2 revealed that digestion is required of the Ontario Hydro KCl impinger solutions preserved with permanganate. This is further discussed in the Test Series 2 section.

4.9 Test Series 1 Conclusions and Recommendations

Negligible removal of vapor-phase mercury across the ESP was measured according to Method 29 in Test Series 1 of Phase II. This confirms that the high mercury removal across the ESP observed in Phase I was an anomaly. Reduction of ESP temperature did not influence removal of mercury in the ESP. As measured by the Ontario Hydro method, the elemental mercury passed through the ESP unaffected over the temperature range of 250 to 300°F.

Humidification did not further improve the particulate removal performance of a well controlled ESP. The ESP controlled particulate emissions to less than 0.01 lb/million Btu prior to the use of humidification. Humidification does not appear to be a viable method of reducing particulate emissions from existing levels of 0.01 lb/million Btu.

Trace metal control across the particulate devices exceeded 94% with the exception of the more volatile elements: arsenic, mercury and selenium. The higher level of particulate metal control achieved by the baghouse can generally be attributed to the overall lower particulate emissions from the baghouse compared to the ESP. Particulate-phase metal emissions as a function of particulate emissions showed significant increases in arsenic and chromium with increased particulate emissions, while cadmium and selenium emissions were unaffected.

Evaluation of the trace element concentration on the particulate as a function of particle size showed significantly higher concentrations in the fine particulate. This was evident by the trace element enrichment of the finer particulate exiting the ESP. In addition, trace element concentrations were seen to increase in the ESP particulate captured in subsequent hoppers through the outlet. In Phase I, the fly ash particle size was shown to decrease as the flue gas passed through the ESP consecutive fields.

Lower total mercury emissions were measured by the Ontario Hydro method as compared to Method 29. This was primarily due to the consistently lower oxidized mercury concentrations suggesting a loss of mercury from the Ontario Hydro KCl impingers. In the absence of an oxidizing species such as peroxide, oxidized mercury could be reduced to more volatile elemental mercury. For continued use of the Ontario Hydro sampling train in subsequent tests, improvements in sampling methodology are required to retard mercury loss from the KCl impinger solutions. Further study completed in the Phase II Test Series 2 revealed that digestion is required of the Ontario Hydro KCl impinger solutions preserved with permanganate. This is further discussed in the Test Series 2 section.

The impact of two filter bag fabrics on mercury speciation was investigated. Elemental mercury levels downstream of the baghouse were consistently lower than measured at the baghouse inlet, substantiating the elemental mercury transformation observed in Phase I. Ontario Hydro measurements did not indicate a consistent impact of fabric type (Ryton and GORE-TEX®) on elemental mercury emissions from the baghouse. Since the elemental mercury emissions were comparable between the two fabrics, the transformation or oxidation of elemental mercury is likely due to the high-sulfur bituminous coal fly ash.

Increased levels of elemental mercury were measured across the wet scrubber with the Ontario Hydro method during non-conventional (low L/G, low pH) operating conditions. Further investigation during the second test series are recommended to determine whether the observed elemental mercury behavior was a result of a sampling artifact of the Ontario Hydro procedure or wet scrubber operation.

Total mercury control across the dry scrubber/baghouse was characterized for two Ohio coals. In spite of the varying levels of mercury and sulfur in the coals, similar total mercury control between 60 - 65 percent was achieved at approach temperatures between 45 and 100°F.

5.0 PHASE II, TEST SERIES 2: ENHANCED PERFORMANCE

5.1 Objectives

Test Series 2 of Phase II represented work under Task 2 - Capture of Air Toxics in Conventional Systems and Task 4 - Advanced Air Toxics Measurement Concepts as outlined in the Phase II Management/Milestone Plan. The testing met the specifications of Subtask 2.3 - Partial-Flow Wet SO_2 Scrubber and Subtask 4.2 - Feasibility Testing.

The primary objectives of Test Series 2 of Phase II were:

> Characterization of mercury emissions control with wet limestone scrubber operation at several conditions representative of a range of commercial scrubber designs and operation.
>
> Evaluation of a continuous mercury emissions monitor to assess use of the analyzer for characterizing mercury emissions under a variety of coal flue gas conditions.

The impacts of several key wet scrubber design and operating parameters on mercury emissions control were evaluated. These parameters included:

- Tray Configuration
- Oxidation Mode
- Liquid-to-gas Ratio
- Slurry pH

These key parameters were selected as the variables that were most likely to impact mercury removal in the wet FGD systems. The number of parameters under evaluation was limited to allow for sufficient repetition of the mercury measurements to provide confidence in any observed trends.

The relationship between SO_2 removal efficiency and mercury emissions control was examined. Wet scrubber mercury emissions control data reported in the literature and cited by EPA as the basis for evaluating emissions from existing systems represents a relatively narrow range of scrubber design and operating conditions. Evaluation of the four selected variables expands the characterization of mercury control of limestone scrubbers operating on bituminous coal-fired generating units in the U.S.

5.2 Facility Operation

A blend of Ohio 5 and 6 (Lower and Middle Kittanning) coal seams similar to that used in Phase I and the initial Phase II test series was fired. The Small Boiler Simulator (SBS) was used to generate flue gas for operation of the baghouse and wet scrubber. A developmental B&W low-NO_x burner was employed. The SBS is an integrated small-scale combustion facility that simulates the characteristic geometry, residence time and flue gas quench rate of a commercial wall-fired, vertical furnace. The convection pass design produces a flue gas time/temperature history representative of commercial boilers. The SBS has been operated extensively and the burner performance and furnace exit gas temperature (FEGT) measurements correlate well with larger scale boilers. Mercury emissions from the SBS have been shown to be comparable to those from the CEDF when the same coal is fired.

5.2.1 Small Boiler Simulator

The general operating conditions for the SBS are summarized in Table 5.1. The SBS was operated at a load sufficient to provide the desired flue gas flow rate to the AECDP baghouse. One sootblowing cycle was scheduled per eight-hour shift for cleaning the boiler tubes. Sootblowing was coordinated with the emissions sampling to avoid contamination of the sample with uncharacteristic particulate. Operation of a flue gas heat exchanger downstream of the convection pass was monitored to maintain the desired flue gas temperature at the AECDP baghouse.

Table 5.1 General SBS Operating Conditions

Operating Parameter	
Nominal Coal Flow Rate	450 - 470 lb/hour
Boiler Load	5.5 - 5.8 million Btu/hr
Pulverized Coal Size	76% through 200 mesh
Total Air Flow	5340- 5490 lb/hr
Convection Pass O_2	3.9 - 4.3%
NO_x at Boiler Outlet	240 - 400 ppm
Fly Ash LOI	2 - 6%

The flue gas generated by the SBS passed through the AECDP baghouse and then to the wet scrubber. The average SO_2, NO_x, O_2, HCl and particulate concentrations in the flue gas are presented in Table 5.2.

Table 5.2 Flue Gas Composition

Flue Gas Component	**Average Concentration**
NO_x, ppm	< 400
SO_2, ppm	2151
CO_2, %	14.27
O_2, %	4.1
HCl, lb/10^{12} Btu	144,552
Particulate, lb/10^6 Btu	1.52

5.2.2 Pulse-Jet Baghouse

The two compartment, pulse-jet baghouse contained Ryton bags in one compartment and GORE-TEX® Superflex bags in the other. The compartment containing the GORE-TEX® bags was on-line during all of Test Series 2. With one compartment in service, processing a flue gas flow of approximately 1,300 scfm, an air-to-cloth ratio of 4.2 was maintained. The baghouse inlet flue gas temperature ranged between 305 - 360 °F. The pressure drop across the baghouse averaged approximately 5.2 inches of water. The baghouse was cleaned following periods of sootblowing to remove any uncharacteristic particles from the baghouse prior to mercury sampling.

5.2.3 Wet Scrubber

The wet scrubber system includes the absorber tower, a slurry recirculation tank, a reagent feed system, and a mist eliminator wash system. The 50 foot high absorber tower is constructed of Plexiglas to permit visual observation of the slurry sprays. Pre-pulverized limestone is mixed with make-up water in the reagent feed tank. The solid content of the recirculating slurry is maintained at 12 to 15%. To achieve the desired L/G, any combination of four levels of single spray nozzles may be used. The wet scrubber is equipped with a removable gas flow distribution plate to simulate both tray tower and open spray tower scrubber designs. An air sparger ring in the bottom of the recirculation tank is used for forced oxidation operation. Spent slurry from the scrubber is dewatered using a hydroclone circuit. The hydroclone underflow is discharged to settling tanks where the solids settle out and water is decanted to the clarified recycle water tank for re-use in the scrubber. A variable speed ID fan located downstream of the scrubber is used to control the gas flow rate through the scrubber. The scrubber was run at a higher oxidation air stoichiometry than a commercial unit to maintain the desired level of near complete oxidation because of the limited available height in the absorber recirculation tank.

The ranges of key scrubber operating parameters are summarized in Table 5.3. The L/G ratio and the slurry pH were the two primary operating variables evaluated. All three levels of over-spray nozzles were used to achieve the desired high liquid-to-gas (L/G) operating conditions. Operation at the lower L/G condition required only two of the three spray levels.

Table 5.3 AECDP Wet Scrubber Operating Parameters

Nominal Slurry pH	5.4
PH Extremes	5.0 - 5.9
Nominal L/G Ratios	67 and 98 gal/1000 acf
L/G Ratio Extremes	39 and 121 gal/1000 acf
Upper-Spray Header Flow (3)	45 - 65 gpm each
Under-Tray Spray Header Flow	20 gpm
Oxidation Air Stoichiometry	3.9 - 9.4 mol/mol
Slurry Sulfite Concentration	0 - 8 mmol/L
SO_2 Removal Efficiency	32 - 98 %

The impact of operation with air sparged into the recirculation tank (forced oxidation) and without air sparging (natural oxidation) on mercury removal efficiency was also investigated. The extent of oxidation of calcium sulfite to calcium sulfate in the recirculating slurry, which impacts the composition of dissolved species in the slurry, was evaluated in terms of mercury removal efficiency. Commercial FGD systems are operating with natural oxidation and inhibited oxidation. However, the dominant industry trend for limestone systems has been toward the use of forced oxidation. The primary mode of operation was with forced oxidation.

The impact of tower configuration on mercury emissions was evaluated by operation with and without the stainless steel distribution tray in place. Both open-spray towers and tray towers are used commercially for SO_2 emissions control.

5.2.4 Coal Properties

The properties of the high-sulfur, Ohio coal were consistent during Test Series 2 of Phase II. Pulverized coal was isokinetically sampled according to ASTM D197-87. The average ultimate analysis for the composite coal samples is provided in Table 5.4.

Table 5.4 Ultimate Coal Analysis

	Average
Heating Value, Btu/lb	13,235 ± 153
Moisture, %	2.7 ± 0.3
Carbon, %	73.1 ± 0.9
Hydrogen, %	5.2 ± 0.07
Nitrogen, %	1.4 ± 0.03
Sulfur, %	3.0 ± 0.07
Oxygen, %	8.9 ± 0.2
Ash, %	5.7 ± 0.5

The average as-fired coal mercury content based on five (5) composite coal samples was 0.17 ± 0.04 ppm. As shown in Figure 5.1, the average mercury content in the Ohio 5/6 coal blend was slightly lower than measured during previous tests. Coal sample preparation by the direct coal combustion procedure and mercury analysis by cold-vapor atomic absorption spectroscopy (CVAAS) was conducted by CONSOL, Inc. On the basis of a CONSOL-sponsored round-robin study to determine the interlaboratory and intralaboratory variability in the measurement of mercury in coal, CONSOL selected the direct coal combustion preparation procedure for in-house use. The direct coal combustion procedure may minimize mercury loss sometimes encountered by the ASTM D3684-78 oxygen bomb combustion procedure followed in previous tests.

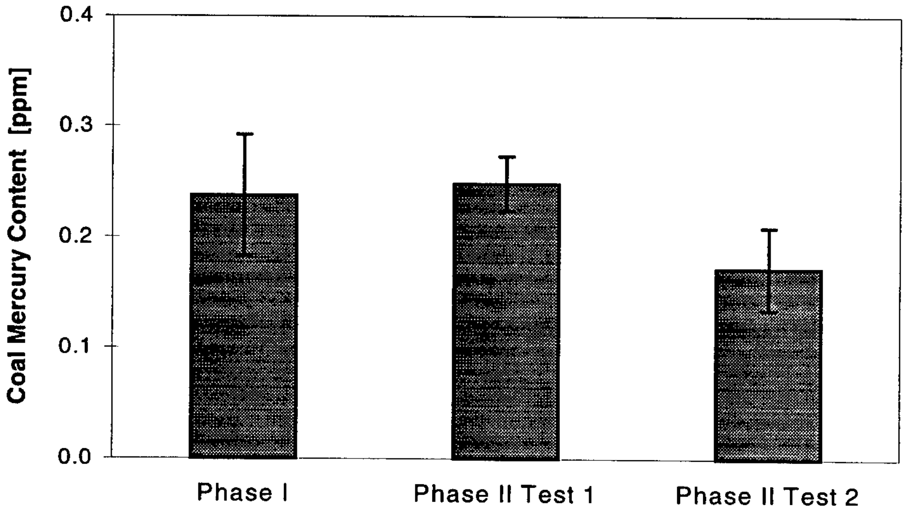


Figure 5.1 Average Mercury Content in Ohio 5/6 Test Coal

5.3 Sampling and Analytical Procedures

Experience gained in the previous test series and discussions with others working on mercury measurement techniques led to several modifications in the flue gas sampling technique. The major modifications to the approach previously used included:

- Potassium permanganate ($KMnO_4$) was added to the KCl impingers of the Ontario Hydro Method sampling train immediately after sampling to prevent loss of oxidized mercury during recovery of the sample. The $KMnO_4$ was added dropwise until the desired pink endpoint was achieved.
- The sampling time was shortened from four hours to approximately two hours. The mercury collected in the impingers remained well above the analytical detection limits and the impact of high SO_2 concentrations on the sampling train was reduced.
- The particulate filter was maintained at the flue gas temperature or a minimum of 250°F.
- The sample nozzle size was changed to reduce the rate of sampling to reduce the bubbling action and solution carry-over in the impingers. A target rate of 0.5 dscfm was used in contrast to the 0.7 to 1.0 dscfm used in the previous test series.
- Triplicate samples were obtained at the scrubber outlet at key test conditions to better characterize the variability of emissions.
- The same sampling probe assembly was used at a given location for each test to minimize variation between runs that may result from the shuffling of sampling equipment.

The flue gas was sampled at three locations - baghouse inlet, wet scrubber inlet, and wet scrubber outlet, to evaluate the total vapor-phase mercury content and the distribution of mercury species at various points in the flue gas clean-up process. Since the impact of scrubber operating conditions was of primary interest in this test series, mercury emissions were measured at the scrubber outlet for each set of scrubber operating conditions. Sufficient mercury emissions sampling at the baghouse inlet and baghouse outlet was performed to characterize total mercury and mercury speciation at these locations upstream of the scrubber. The boiler operating conditions were held steady throughout the test series.

EPA Method 29 was used as a validated method for measuring total mercury. The Ontario Hydro method was used to measure the distribution of mercury species at the scrubber inlet and outlet. The EPA Method 29 measurements were distributed throughout the test program. The Ontario Hydro method was the primary sampling technique used to characterize scrubber performance. The most recent enhancements to the method including the addition of an oxidant as a stabilizing agent were incorporated.

5.4 Mercury Methods Comparison

Total mercury emissions from the boiler and at the baghouse outlet as measured by EPA Method 29 and the Ontario Hydro method during Test Series 1 of Phase II are compared in Figure 5.2. Mercury emissions are reported in $\mu g/dscm$ normalized to 3% O_2. The lower mercury levels measured by the Ontario Hydro method compared to Method 29 coincide with observations made by other researchers when dichromate is used as a preservative.

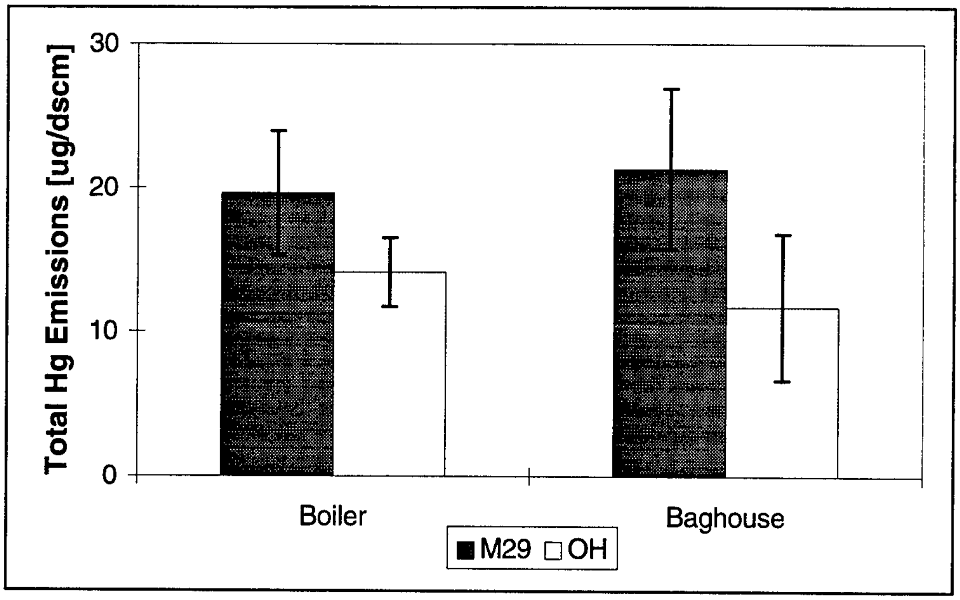


Figure 5.2 Comparison of Total Mercury According to EPA Method 29 and Ontario Hydro - Dichromate Preservation, First Test Series

The lower mercury emissions measured by the Ontario Hydro method were primarily due to the consistently lower oxidized mercury concentrations (compared to Method 29) suggesting a loss of mercury from the Ontario Hydro KCl impingers. In the absence of an oxidizing species such as peroxide, oxidized mercury could be reduced to more volatile elemental mercury. A number of preservatives (permanganate, dichromate, or peroxide) have been recommended for use in the Ontario Hydro KCl solutions to retard mercury loss during recovery[19] For the first test series, dichromate was used as a preservative. The results of the previous test series suggested a correlation of the time between the completion of sampling and the addition of preservative to the amount of mercury loss from the Ontario Hydro impinger solutions which have been since confirmed by other researchers including the Energy & Environmental Research Center (EERC), CONSOL and Carnot.[20] Immediate preservation after leak checking and rapid analytical recovery was anticipated to reduce mercury loss. In Test Series 2 of Phase II, permanganate was selected as the preservative on the basis of the resulting visual color change and stronger oxidizing properties than dichromate. As illustrated in Figure 5.3, the use of permanganate preservative during the second test series resulted in improved agreement between the two methods.

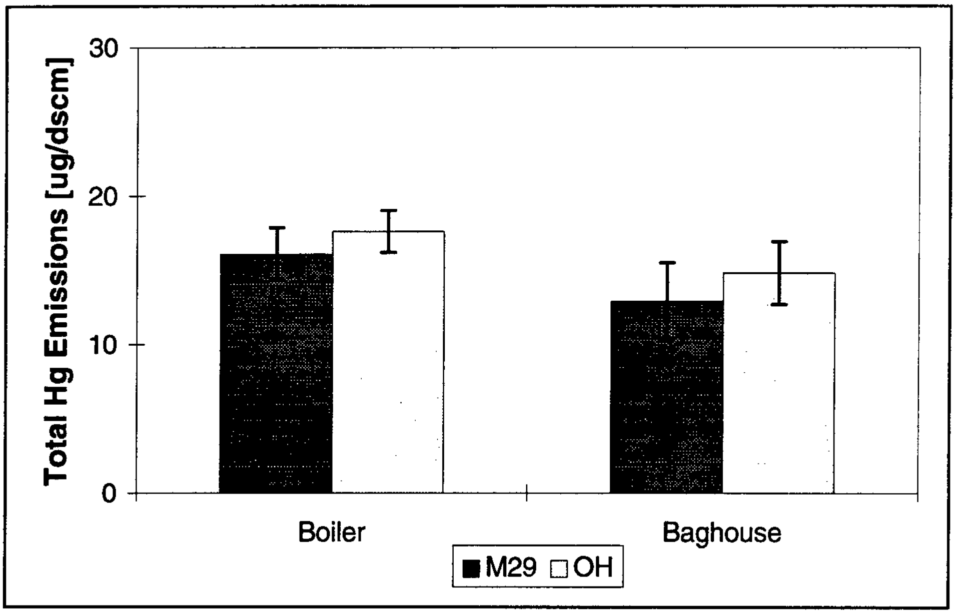


Figure 5.3 Comparison of Total Mercury According to EPA Method 29 and Ontario Hydro - Permanganate Preservation, Second Test Series

Filter Temperature Impacts

Even though the filter temperatures were maintained during the first test series within the protocols of EPA Method 29 (248 ± 14°F), the mercury concentration in the particulate accumulated on the sample filter increased with incremental reductions in filter temperature for the Ohio 5/6 coal fly ash. To minimize impacts of filter temperature on mercury speciation results, the filter in the Method 29 and Ontario Hydro sampling trains were maintained at the flue gas temperature for testing conducted under Test Series 2 of Phase II. In the case of measurements conducted downstream of a wet scrubber, the filter temperature was held constant at 250°F as prescribed by EPA Method 29.

To determine whether maintaining the filter at the flue gas temperature reduced potential sampling bias, the mercury concentrations on the filter particulate and the particulate accumulating in the baghouse hopper during the sampling period are compared in Figure 5.4. Sampling bias, if occurring, would likely increase the concentration of mercury on the filter particulate as the flue gas passes through the filter. High-particulate flue gas streams, such as those leading to the particulate control devices, required the use of a glass cyclone upstream of the particulate filter to minimize filter pressure drop. As a result of the glass cyclone, the particle size distribution of the particulate on the filter is believed to be finer than in the baghouse hopper. The fineness of the filter particulate would also contribute to the possibility of mercury adsorption onto the particulate on the filter. However, the generally comparable levels of mercury in the filter and hopper particulate indicate the absence of sampling artifacts. For the two cases where the mercury concentration in the hopper and filter particulate differ, the mercury in the hopper ash was elevated. The correlation of mercury particulate concentration and fly ash carbon carryover is not conclusive over the limited LOI range (Figure 5.5).

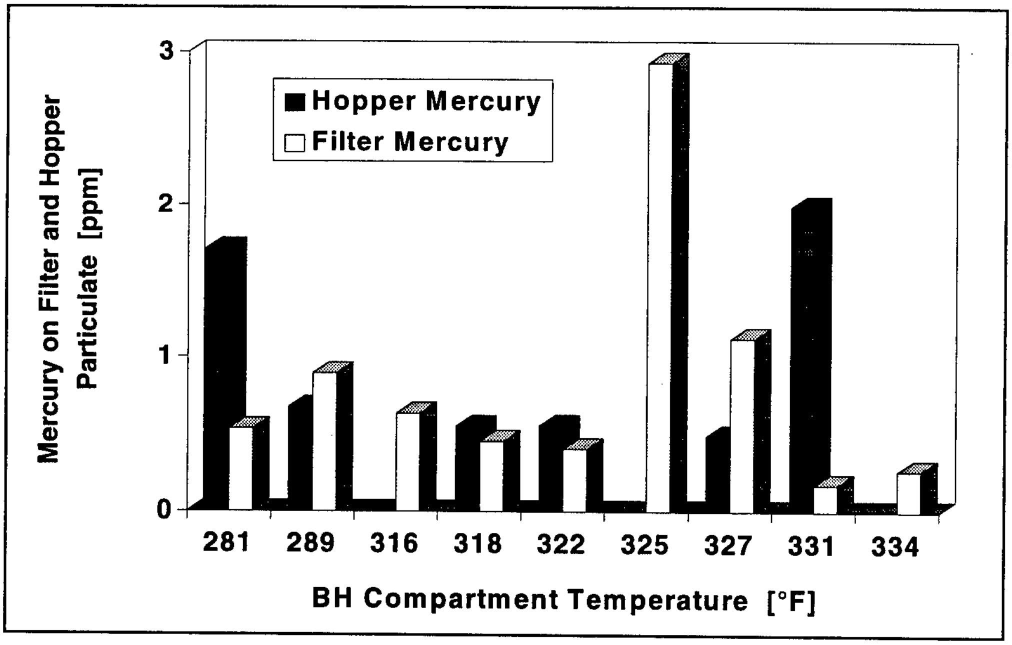


Figure 5.4 Comparison of Mercury Concentration on the Filter and Hopper Particulate

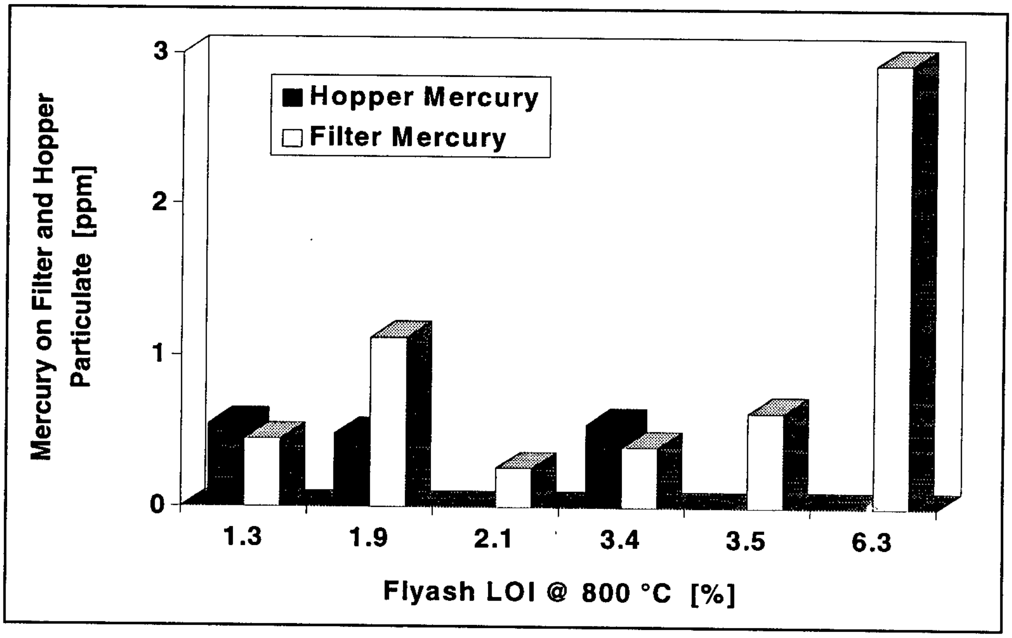


Figure 5.5 Impact of Fly Ash LOI on Mercury Adsorbed on Particulate

5.5 Baghouse Mercury Control

Baghouse mercury control can be influenced by 1) the amount of mercury absorbed on the particulate and 2) the presence and properties of the fly ash. On the basis of replicate preserved Ontario Hydro sample trains, total mercury removal across the pulse-jet baghouse averaged 16%. The majority of the net mercury removal can be attributed to the 11% of the total mercury adsorbed onto the baghouse filtercake. Extremely efficient particulate control was achieved by the GORE-TEX® fabric. Particulate emissions lower than the current New Source Performance Standard of 0.03 lb/million Btu were readily achieved with the GORE-TEX® fabrics. The GORE-TEX® fabric reduced particulate emissions to less than 0.005 lb/million Btu at an of air-to-cloth ratio of 4.2 ft/min and over a range of baghouse operating temperatures.

The baghouse compartment temperature did not affect total baghouse mercury control (Figure 5.6). Over the evaluated temperature range of 280 - 345°F, compartment temperature reduction did not result in mercury enrichment on the particulate. Other factors which were held constant, such as combustion conditions, boiler type, or unburned carbon carryover, may influence the adsorption of mercury on the particulate.

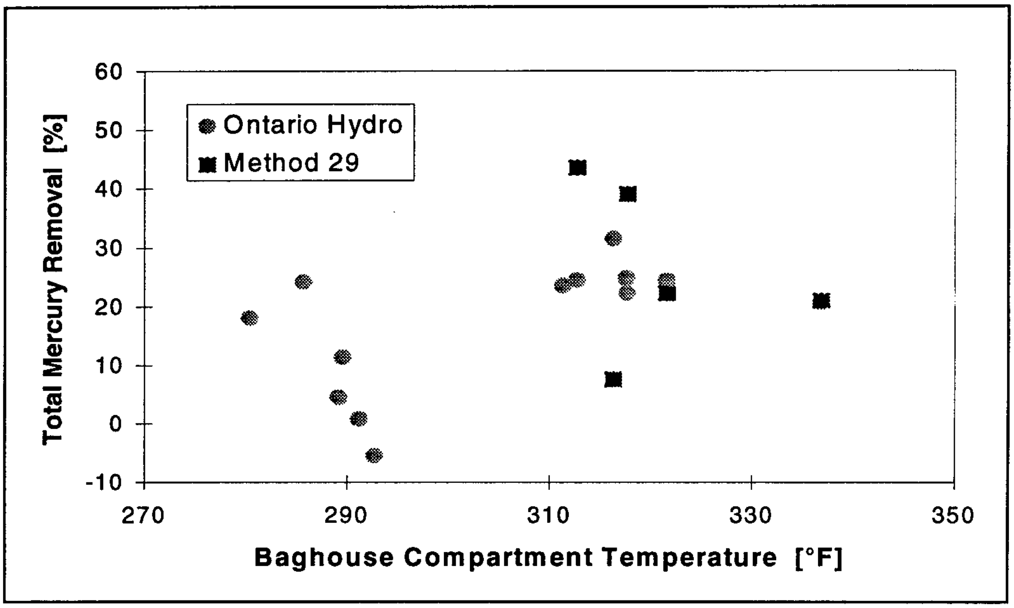


Figure 5.6 Impact of Baghouse Temperature on Total Mercury Control

During the Test Series 1 in Phase II, the low concentration of elemental mercury measured at the baghouse outlet/wet scrubber inlet was the suspected result of the conversion of elemental mercury to an oxidized state as the flue gas passed through the fly ash filter cake. Evidence of the oxidation of elemental mercury would include reduced elemental mercury and increased oxidized mercury levels measured at the baghouse outlet relative to the inlet. Unfortunately, during Test Series 1, an earlier version of the Ontario Hydro Method that did not specify the *immediate* preservation of the initial impingers, was used. A consequence of that version of the sampling technique was the loss of oxidized mercury during recovery of the sample train resulting in a high bias of the reported elemental mercury fraction. As a result of the sampling recovery procedure, corresponding increases in the oxidized mercury could not be quantified. Therefore, similar operating conditions were maintained during Test Series 2 to further investigate the elemental mercury "transformation" across the pulse-jet baghouse. Radian has also reported elemental mercury conversion across different baghouse fabrics and fly ashes[21].

Elemental mercury levels downstream of the baghouse were consistently lower than measured at the baghouse inlet, supporting the initial observations of a transformation and/or removal of elemental mercury. Figure 5.7 compares the average elemental mercury measured at the baghouse inlet and outlet during the first and second test series based on Ontario Hydro sampling. Since the elemental mercury emissions were comparable between fabrics (during the first test), the transformation appears to be primarily due to the bituminous coal fly ash. Repeat measurements during Test Series 2 confirm the conversion of elemental mercury across the Ohio 5/6 coal fly ash.

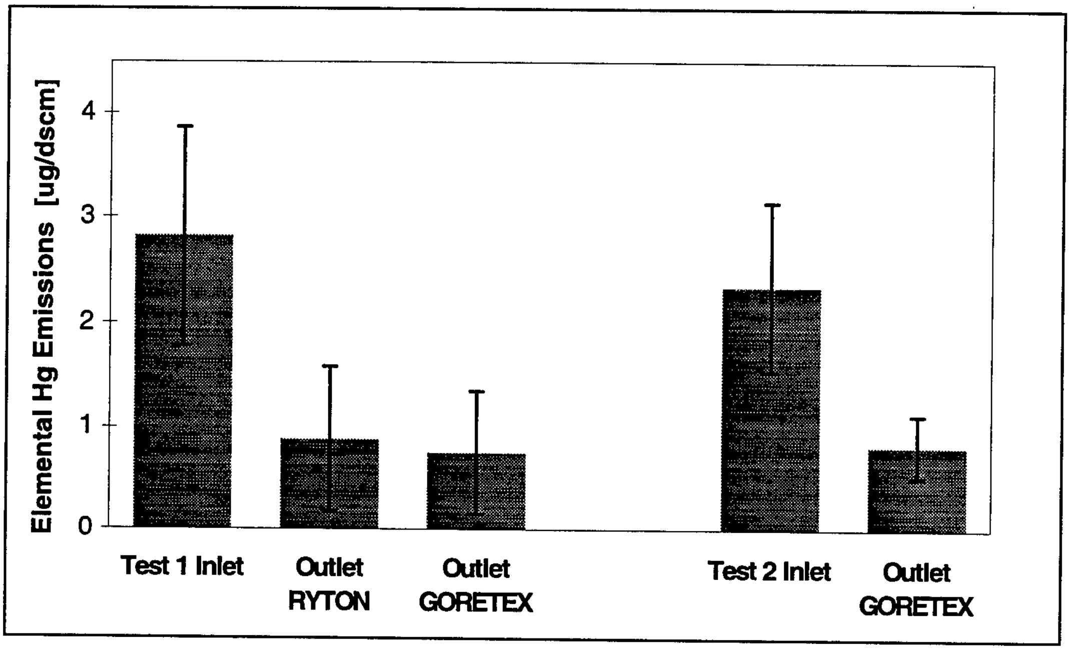


Figure 5.7 Elemental Mercury Behavior Across Baghouse - Ohio 5/6 Coal

The correlation of the elemental Hg conversion across the pulse-jet baghouse to the baghouse compartment temperature based on Ontario Hydro measurements is presented in Figure 5.8. In the lower temperature range (< 300°F) which yielded the highest elemental mercury conversions, a corresponding increase of oxidized mercury emissions was measured. However, at temperatures greater than 300°F, a positive net removal of oxidized mercury was measured across the baghouse according to the Ontario Hydro method. The increase in oxidized mercury emissions suggests that the elemental mercury emissions are transformed by oxidation across the baghouse at temperature less than 300°F. The consequence of certain particulate matter catalyzing the oxidation of elemental mercury may be increased mercury removal in a downstream wet scrubber.

The primary role of a conventionally operated baghouse toward the reduction of mercury emissions from a scrubbed utility power plant appears to be the conversion of elemental mercury by the fly ash filtercake. The combination of a baghouse and wet scrubber has a high potential for total mercury emissions reduction due to the conversion of elemental mercury to a more soluble form. Other benefits would include compliance with phase II SO_2 requirements and potential fine particulate regulations.

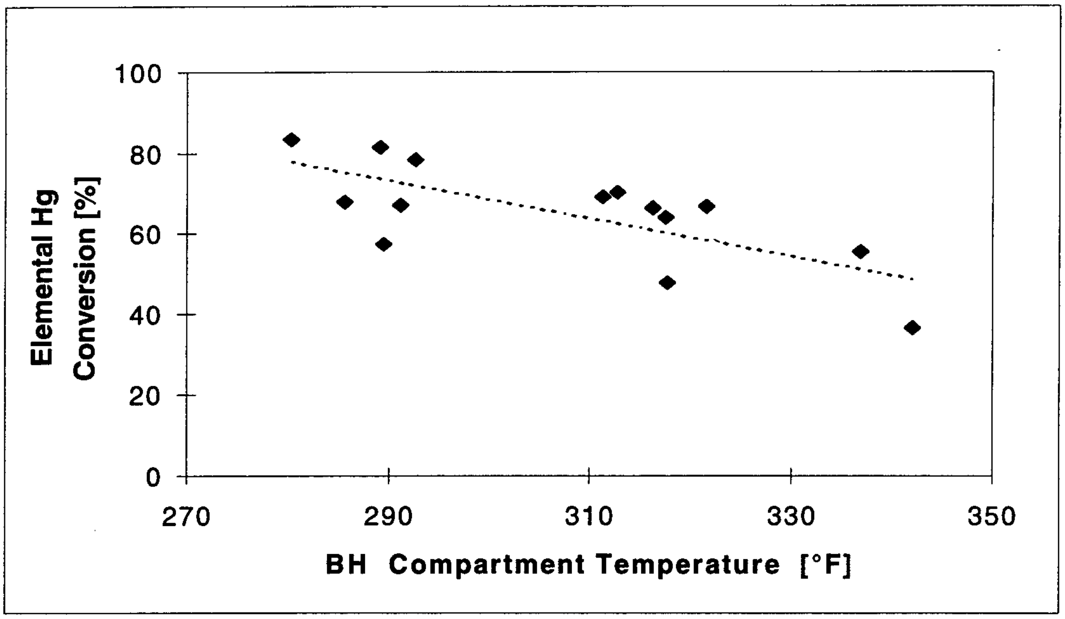


Figure 5.8 Impact of Baghouse Temperature on Elemental Mercury Conversion

5.6 Wet Scrubber Mercury Control

Flue gas desulfurization is currently the most widely used technology to control SO_2 emissions. Wet scrubbers comprise over 80% of the total capacity of existing FGD installations. Wet scrubbing processes are often categorized by reagent. Table 5.5 lists several scrubber processes and, of these, the limestone process has been most widely applied. Over half of the worldwide installations of FGD, produce a gypsum byproduct. The wet scrubber producing gypsum (referred to as Limestone Forced Oxidation, LSFO) overtook all other FGD systems in the late-1980's[22]. Of the 13,400 MW of wet scrubber installations under Phase I of the Acid Rain/Title IV Acid Depositions legislation of the Clean Air Act Amendments of 1990, 71% consisted of the LSFO process[23]. For these reasons, LSFO was the system chosen for evaluation in AECDP testing.

Table 5.5 Wet Scrubber Processes[24]

- Limestone -
  - with no oxidation inhibition (natural oxidation)
  - with inhibited oxidation
  - with in situ forced oxidation
  - with ex situ forced oxidation
  - with soluble organic or inorganic buffers
- Lime -
  - with inorganic buffers (such as magnesium oxide)
  - without buffers
- Dual Alkali -
  - sodium carbonate/calcium hydroxide
  - sodium carbonate/calcium carbonate
- Soda Ash -
  - with regeneration by steam stripping
  - without regeneration
- Magnesium oxide with thermal regeneration

Test Series 2 of Phase II focused on total and speciated mercury emissions control using a limestone wet FGD system. Pilot and commercial scale tests have indicated that wet FGD systems have potential for high mercury emissions control efficiency. The wide range of mercury emissions control performance reported in the literature for wet scrubbers is summarized in Table 5.6. (Note: the mercury removal range reported for the AECDP wet scrubber is due to many conditions tested not necessarily a high level of uncertainty.) The draft U.S. EPA report, *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units - Interim Final Report,* notably estimated a median mercury emissions control efficiency of only 17% for wet scrubbers with a range of 0 to 59% on the basis of sampling at five commercial plants. The wet scrubber sample population used as the basis for this report does not appear to reflect mercury emissions control performance by existing commercial FGD units in the eastern U.S. Bituminous coal is fired at only two of these plants. Four of these scrubbers have an open spray tower design and the fifth is a one-of-a-kind U.S. installation of the Chiyoda jet bubbling reactor (JBR) system. Three of the five units are designed for 60% SO_2 removal or less and include bypassing a portion of the flue gas around the scrubber for reheating the gas upstream of the stack. All of the units were designed to operate at an L/G ratio of less than 70 with one unit designed for an L/G of 22. In current commercial practice, a L/G ratio of 90 to 100 is typical for a limestone forced oxidation FGD system designed for 90 to 95% SO_2 removal efficiency.

Table 5.6 Flue Gas Desulfurization Mercury Control Summary

FGD System (Coal Type)	Data Source	Reported Total Mercury Emissions Reduction (%) Range	Average
Wet FGD (Bituminous)	AECDP	20 - 97	
	EPRI Pilot [25,26]	85 - 96	
	Radian [25]		50
	SRI [27]		45
	KEMA [28]	8 - 72	52
	U.S. EPA [29]	0 - 59	17
	U.S. DOE [26]		44
	CONSOL [30]	50 - 77	62
	EPRI [26]		84
Wet FGD (Sub-bituminous)	EPRI [26]	10 - 69	
Dry FGD (Bituminous)	AECDP	60 - 65	

Underestimating mercury removal in the existing population of FGD systems and the potential for additional mercury emissions reductions in new FGD installations may result in an over-estimation of U.S. utility boiler mercury emissions. Wet FGD systems are currently installed on about 25% of the coal-fired utility generating capacity in the U.S., representing about 15% of the number of coal-fired units. FGD systems provide a cost-effective, near-term mercury emissions control option with a proven history of commercial operation. For boilers already equipped with FGD systems, the incremental cost of *any* gas-phase mercury removal achieved is zero. The extent of the publicly available information base concerning the impact of basic wet scrubber design and operating conditions on mercury emissions control for bituminous coal applications needs to be expanded to provide a representative sampling of commercial FGD systems. The results of Test Series 2 of Phase II of the AECDP test program are intended to contribute to this database.

A number of factors may contribute to the wide range of wet scrubber mercury emissions control performance reported in the literature for bituminous coal applications. Significant differences in the mercury content of U.S. coals result in a wide range of mercury concentrations in the flue gas from the boiler. The form or species of mercury (elemental mercury or an oxidized compound such as $HgCl_2$) in the flue gas is thought to affect flue-gas-desulfurization (FGD) system mercury removal efficiency. Mercury speciation in the flue gas is believed to be influenced by the type of coal fired with sub-bituminous coals generating a higher relative proportion of elemental mercury than bituminous coals. EPRI pilot-scale data indicates that at a flue gas temperature of 300°F, 68% of the total vapor-phase mercury was present as elemental mercury for the sub-bituminous coal compared to 6% as elemental mercury for the bituminous coal evaluated.[31] The coal chlorine content and ash characteristics are thought to affect partitioning between the solid and vapor phases and the ratio of mercury species in the vapor phase.[31] Felsvang, DeVito, Bloom, and Meij have all observed high concentrations of oxidized mercury in utility flue gas when the coal had a high chlorine content.[32,33,34,35] Finally, the scrubber spray tower configuration, liquid-to-gas ratio (L/G), and slurry chemistry may impact the reported mercury emissions control. Scrubber configuration and operating condition were selected for initial investigation to both define the causes for the observed performance variations and maximize mercury emissions control performance of FGD systems.

The wet scrubber was operated in several modes to simulate existing commercial scrubber installations. The scrubber configurations and number of operating conditions evaluated were limited to four primary target design and operating conditions. These conditions were selected to represent the design and operating characteristics of a majority of the existing U.S. population of commercial scrubber installations. In addition, the tests covered the range of operating conditions reported in the field measurements summary used by EPA as a basis for the draft *Mercury Study Report to Congress.*

5.6.1 Impact of Tower Configuration

The bulk of existing commercial wet scrubbers in the U.S. are either open spray towers or have a perforated tray installed to distribute the gas flow over the cross section of the scrubber. Packed towers and venturi scrubbers represent smaller segments of the market. The tray also provides a region of relatively lower slurry pH, which may impact the absorption of mercury from the flue gas or the retention of absorbed mercury in the slurry. Over 20% of commercial wet scrubbers in the U.S. contain a tray.

The AECDP scrubber was operated as both a tray tower and an open spray tower over a wide range of slurry spray flux rates with a common tower velocity representative of conventional commercial scrubber operation. Installation of the gas flow distribution tray enhanced both SO_2 and total mercury emissions control over a wide L/G range as illustrated in Figures 5.9 and 5.10. The error bars shown represent the range of the triplicate measurements for each set of operating conditions. For all of the tests presented in Figures 5.9 and 5.10, the oxidation air stoichiometry was greater than 5 mol O_2/mol of SO_2 absorbed to maintain near complete oxidation and the absorber slurry pH was maintained between 5.4 to 5.5. Additional tests comparing the tray tower and open spray tower configurations at nominal scrubber operating pHs of 5.0 and 5.9 showed a similar trend.

The major contribution toward the improvement in total mercury removal was the reduction of soluble oxidized mercury emissions (Figure 5.11) when the tray was installed. Elemental mercury emissions were generally unaffected by the tray configuration. The tray tower configuration provided more consistent SO_2 and mercury emissions control than the open tower as suggested by the larger standard deviations associated with the open tower testing. Improvements in mercury control due to the tray were most pronounced at the lower L/G operating conditions.

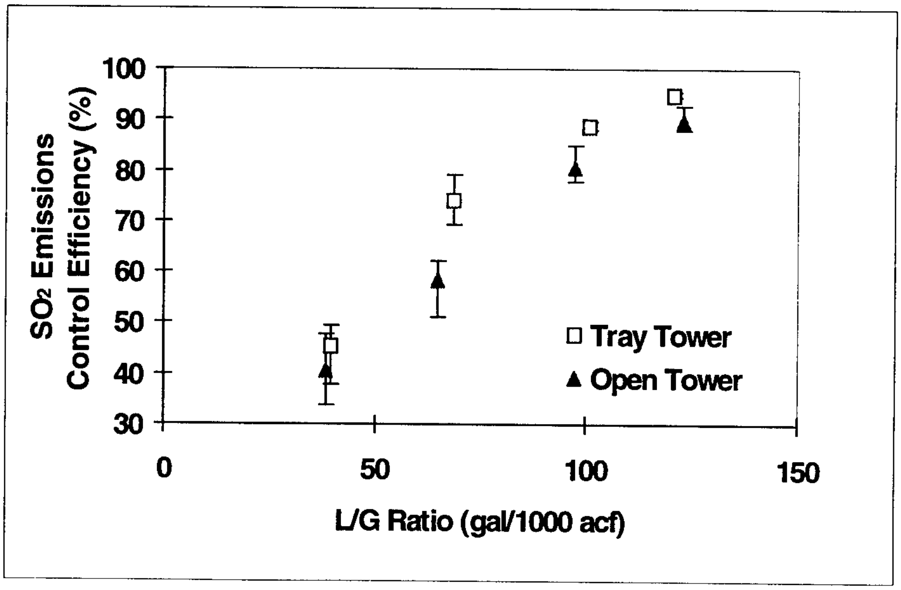


Figure 5.9 Impact of Wet Scrubber Tray on SO_2 Emissions

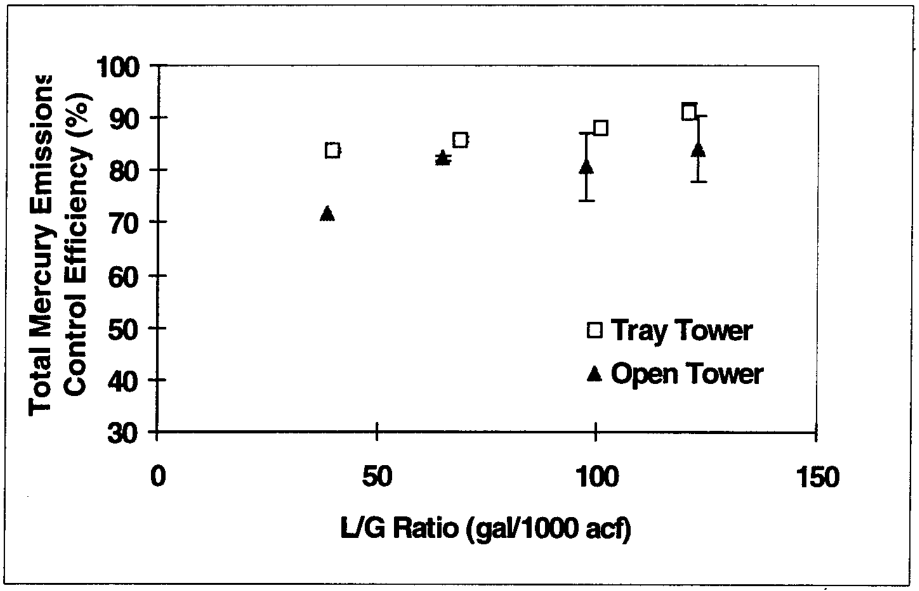


Figure 5.10 Impact of Wet Scrubber Tray on Total Mercury Emissions

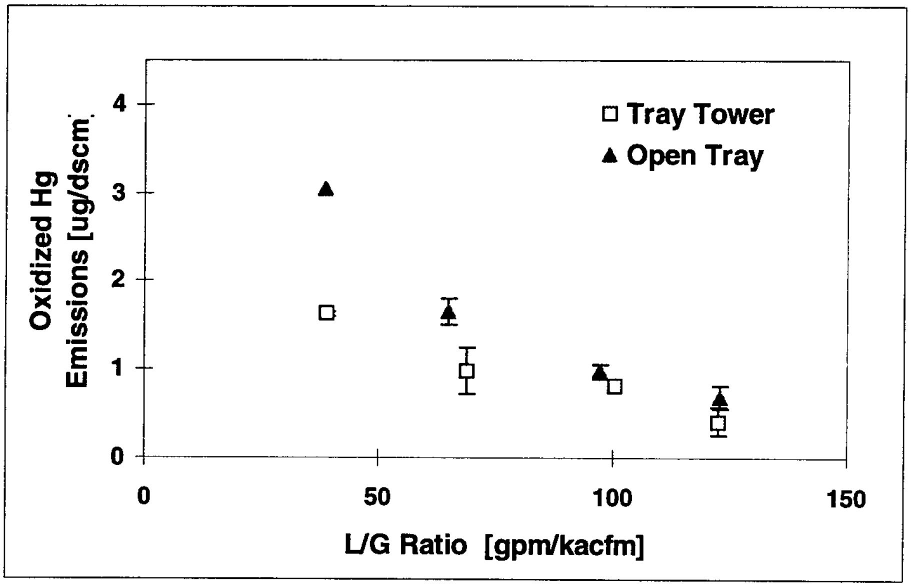


Figure 5.11 Impact of Wet Scrubber Tray on Oxidized Mercury Emissions

5.6.2 *Impact of Scrubber Operation*

The dominant design variable for all wet FGD scrubbers is the ratio of the slurry flow to gas flow in the tower, known as the L/G ratio. In the previous test series, the observed emissions of elemental mercury from the scrubber increased at low L/G operation. The current tests were planned to evaluate whether the apparent increase in elemental mercury emissions was an artifact of the sampling process or an actual phenomenon occurring in the scrubber.

The recirculating slurry pH can potentially impact mercury removal efficiency by changing the liquid phase slurry chemistry. Three levels of slurry pH were evaluated. A nominal mid-range value of approximately 5.5 was used when the impact of scrubber L/G was evaluated. The impact of operating at higher pH (5.9-6.0) and lower pH (5.0 to 5.1) extremes on mercury emissions was measured. This pH range covers the majority of commercial limestone FGD system installations.

The influence of slurry pH and L/G on mercury emissions control was evaluated for both the tray tower and open spray tower configurations. Figure 5.12 presents the impact of LSFO scrubber operation on total (vapor phase and particulate phase) mercury emissions for the tray tower. The superficial flue gas velocity was maintained at a steady value and the slurry spray flux was varied to obtain a range of L/G operating conditions. Total mercury concentration downstream of the baghouse at the scrubber inlet averaged 14.8 µg/dscm for the Ohio 5/6 coal blend. The distribution of mercury species at the scrubber inlet was 94% oxidized species and 6% elemental mercury as measured using the Ontario Hydro Method.

Vapor-phase oxidized and elemental mercury emissions for each test condition are presented in Figures 5.13 and 5.14 for the tray tower configuration. Emissions of oxidized mercury were reduced as the L/G was increased. The slurry pH did not appear to have a significant impact on oxidized mercury emissions. Wet scrubber elemental mercury emissions remained fairly consistent over the range of operating conditions and were approximately the same as the inlet elemental mercury concentration shown as the dashed line in Figure 5.14. The exception was operation at lower L/G and pH during which increased elemental mercury emissions based on Ontario Hydro sampling were measured. The relatively higher elemental mercury emissions at the low pH, low L/G condition were also observed in Test Series 1. Figure 5.15 compares the elemental mercury behavior measured during the Phase II, Test Series 1 and 2.

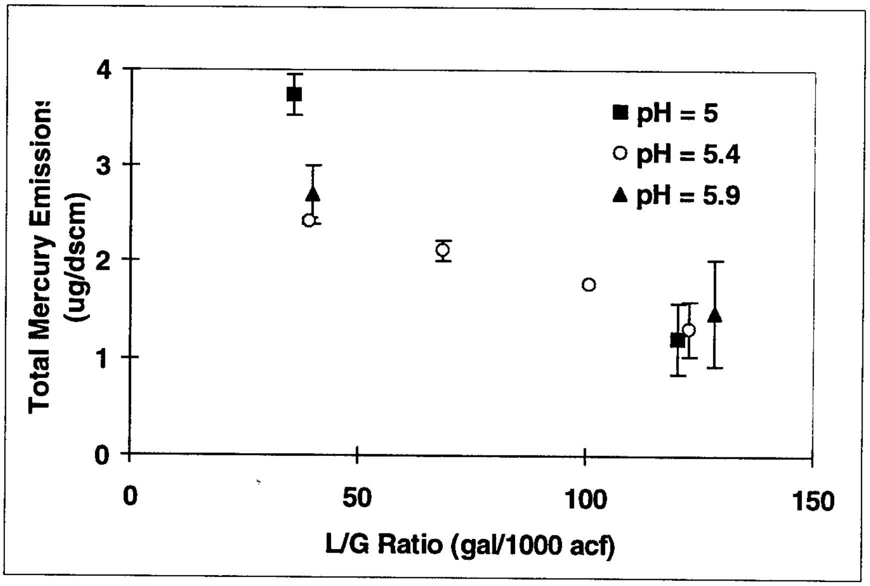


Figure 5.12 Impact of Scrubber Operating Conditions on Mercury Emissions - Tray Tower

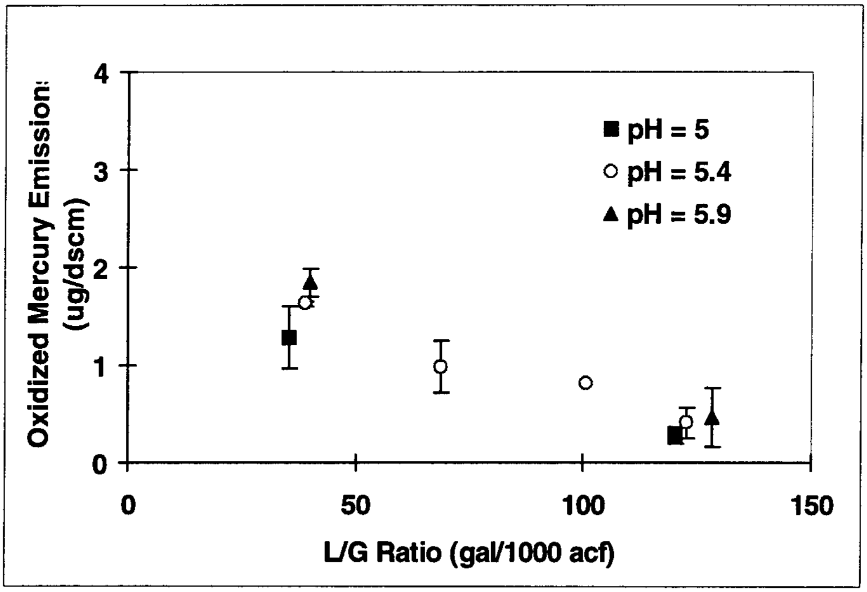


Figure 5.13 Impact of Scrubber Operating Conditions on Oxidized Mercury Emissions, Tray Tower

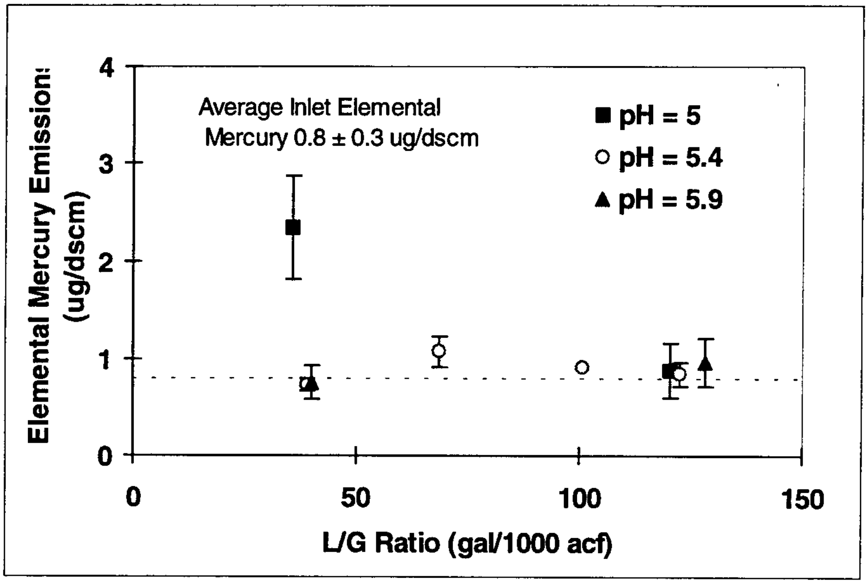


Figure 5.14 Impact of Scrubber Operating Conditions on Elemental Mercury Emissions, Tray Tower

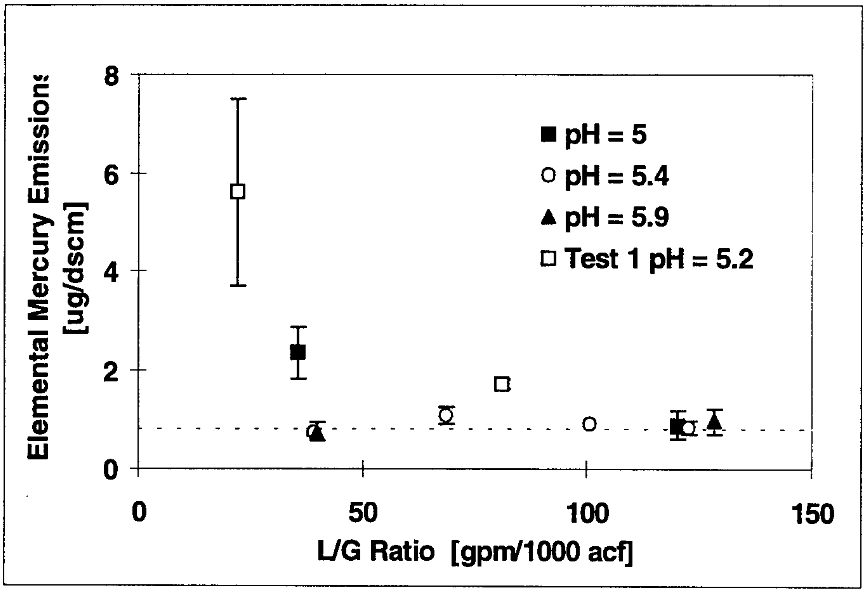


Figure 5.15 Comparison of Elemental Mercury Emissions from Phase II Test Series 1 and 2 - Tray Tower

The generation of elemental mercury across a wet scrubber has been previously reported[27,36]. The earlier data was primarily based on the Method 29 sample train which has been shown to over report oxidized mercury emissions in the presence of high SO_2.[19] The elevated elemental mercury was attributed to the high bias in the oxidized mercury measured in the high SO_2-laden flue gas at the scrubber inlet with Method 29. However, AECDP test results are largely based on the Ontario Hydro sample train, which was specifically designed to eliminate sampling bias due to the SO_2 in the flue gas. The elimination of bias in the Ontario Hydro sampling method points to the reduction of oxidized mercury (chemical reaction of Hg(II) to Hg^0) in the aqueous phase of the scrubber. CONSOL, Inc. has recently reported increases in levels of elemental mercury between the inlet and outlet for two commercial wet scrubbers characterized by Ontario Hydro sampling[30,37].

With the open tower configuration, higher total mercury emissions were detected at each combination of L/G and pH relative to the tray tower configuration. Both higher oxidized and elemental mercury emissions contributed to the higher total mercury emissions. Total, oxidized and elemental mercury emissions from the scrubber during open tower operation are presented in Figures 5.16, 5.17, and 5.18. The better consistency in SO_2 and mercury emissions with the tray tower configuration relative to the open tower may be due to the reduction of flue gas channeling resulting from the tray.

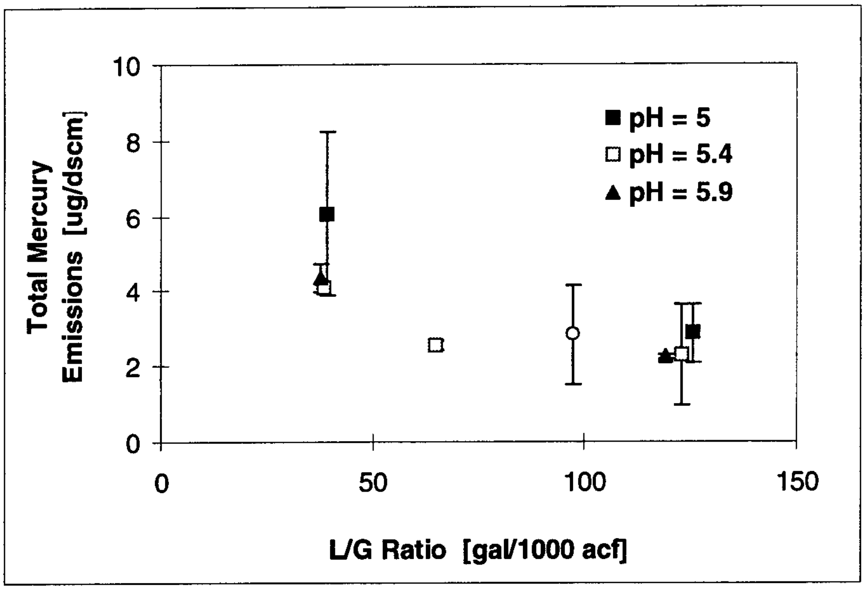


Figure 5.16 Impact of Scrubber Operating Conditions on Mercury Emissions - Open Tower

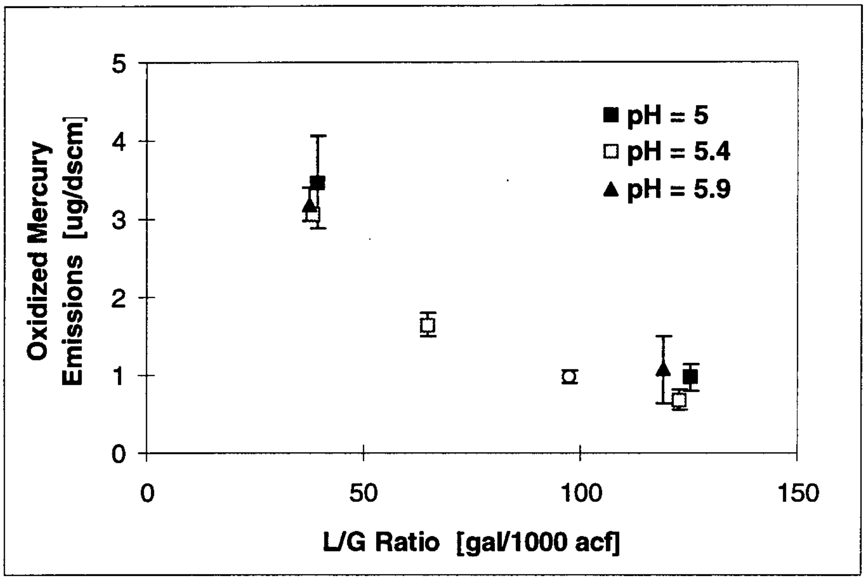


Figure 5.17 Impact of Scrubber Operating Conditions on Oxidized Emissions - Open Tower

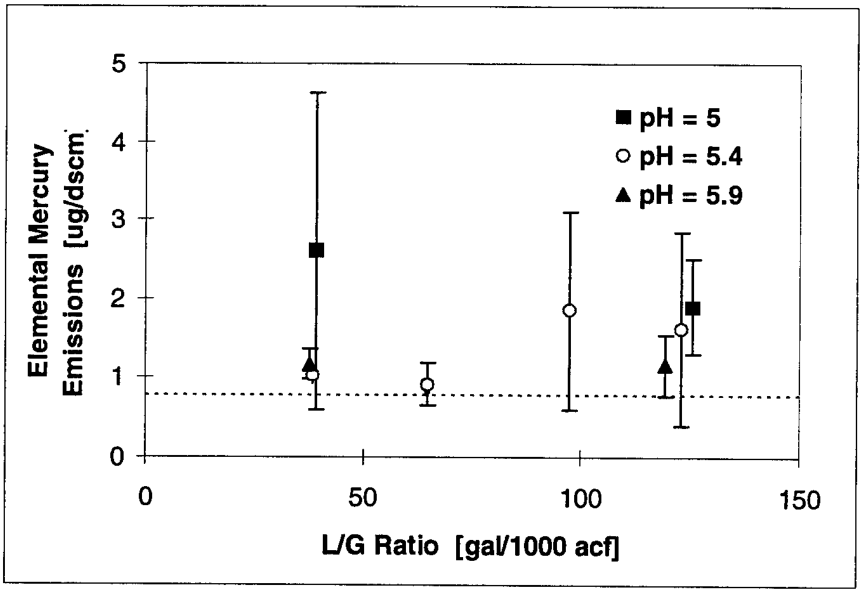


Figure 5.18 Impact of Scrubber Operating Conditions on Elemental Emissions - Open Tower

Over the practical operating pH range evaluated, slurry pH did not have a significant impact on mercury emissions at the higher L/G operating condition for either tower configuration. The increase in elemental mercury during tray operation at low pH suggests that elemental mercury emissions may be more sensitive to pH at low L/G operating conditions. The trend of increased elemental mercury at low pH, low L/G test conditions was less pronounced for the open tower. This effect may have been confounded by the higher variability in mercury emissions measured during open tower operation. For L/G ratios of 40 and less, wet scrubber elemental and therefore total mercury emissions tended to increase as the slurry pH was reduced to less than 5.3. This operating regime correlates to SO_2 removal efficiencies less than 40% for the baseline Ohio 5/6 coal blend.

5.6.3 *Impact of Oxidation Mode*

The removal of SO_2 from flue gas in limestone wet scrubbers, results in the formation of solid calcium-sulfur salts, either calcium sulfite ($CaSO_3$) or calcium sulfate (gypsum). The relative amounts of these two compounds depends on the sulfite oxidation of the system. There are three common oxidation regimes: forced oxidation, natural oxidation, and inhibited oxidation. Limestone wet scrubbers generally operate with either forced oxidation of calcium sulfite to calcium sulfate, or with inhibited oxidation of the calcium sulfite. In forced oxidation, air is sparged through the slurry to produce a marketable gypsum product or to generate a more readily disposable solid by-product. In the absence of air sparging, some natural oxidation of sulfite to sulfate inevitably occurs in the scrubber gas-liquid contact zone with the oxygen present in the flue gas according to:

$$HSO_3^- + 1/2O_2 \rightarrow SO_4^{-2} + H^+$$

Up to 30% of the sulfite may be oxidized during natural oxidation. If the conversion of sulfite to sulfate is more than 15% but less than 95%, scaling problems in the FGD system may occur. Scaling can be controlled by either fully oxidizing the recirculating slurry to greater than 95% or inhibiting the oxidation level to below 15%. In inhibited oxidation, additives (primarily elemental sulfur) are added to suppress sulfate scaling by lowering the solution sulfate ion concentration to well below saturation.

Mercury emissions measurements were planned for all three types of oxidation control. The extent of oxidation determines the amount of dissolved sulfite present in the recirculating slurry, which could impact the absorption of mercury. The majority of the planned test conditions were completed with the exception of the wet scrubber inhibited oxidation tests. However, sufficient data was gathered for the comparison of natural versus forced oxidation on mercury emissions control. Typical natural oxidation scrubber operating conditions in the tray tower are summarized in Table 5.7.

Table 5.7 Wet Scrubber Natural Oxidation Operating Parameters

Operating Parameter	Nominal Conditions
Inlet Flue Gas Flow (acfm)	2050
Nominal Slurry pH	5.8
Nominal L/G (gal/1000 acf)	120
Slurry Spray Flux (gpm/ft^2)	67
Oxidation Air Stoichiometry	

Total mercury control was not measurably affected by the switch from forced to natural oxidation for a constant L/G ratio of 120 gpm/kacfm. Based on the limited data provided in Figure 5.19, mercury control with natural oxidation may be more sensitive to changes in pH (as is the case of SO_2 control at elevated L/G ratios). Oxidized mercury emissions were reduced from approximately 14.2 µg/dscm to less than 1.5 µg/dscm for both oxidation modes at the high L/G ratio. However, natural oxidation of the slurry provided elemental mercury emissions consistently lower than forced oxidation (Figure 5.20). Elemental mercury emissions averaged 0.4 and 0.9 µg/dscm for natural and forced oxidation modes, respectively. Elemental mercury at the scrubber inlet averaged 0.8 µg/dscm as indicated by the dashed line.

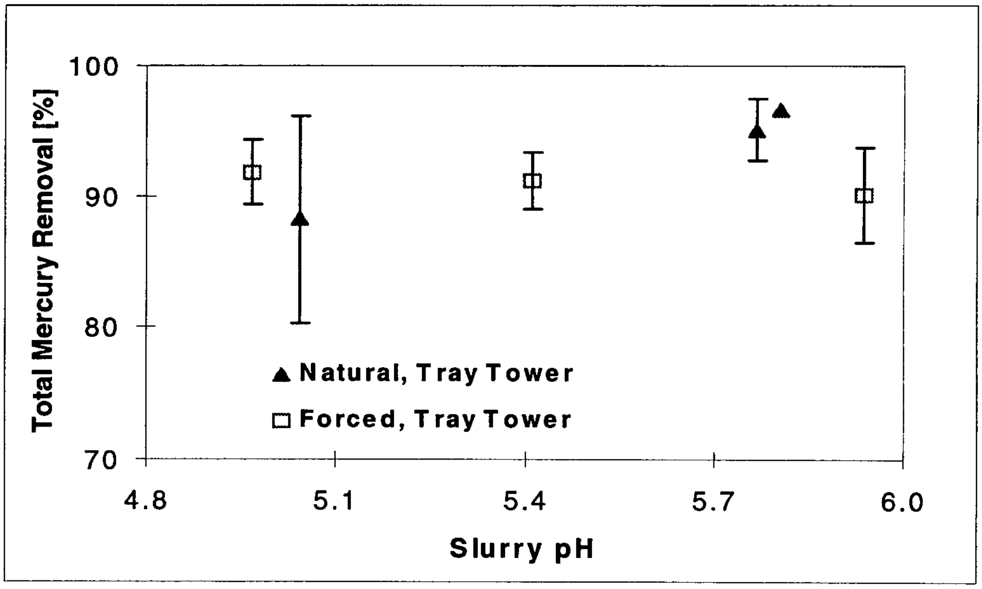


Figure 5.19 Impact of Oxidation Mode on Total Mercury Removal

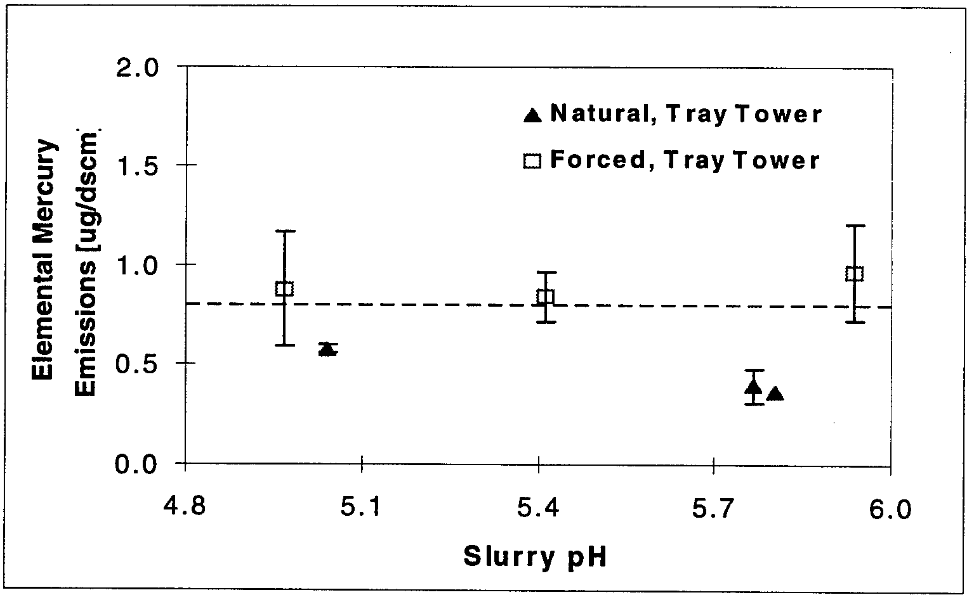


Figure 5.20 Impact of Oxidation Mode on Elemental Mercury Emissions - Tray Tower (dotted line represents Inlet Hg^0)

5.6.4 By-product Stream Evaluation

As gas-phase mercury removal is improved, the eventual fate of the mercury in the resulting wet FGD liquid or solid phase is especially important. Analyses of the reagent feed stream to the scrubber, make-up water, clarified recycle water and solid by-product were performed to quantify the amount of mercury in these primary scrubber inlet and outlet process streams. The test program provided sufficient time for the gas phase concentrations of SO_2 and mercury in the flue gas to reach steady values at the scrubber inlet and outlet. However, the individual tests were probably not long enough to assure steady-state concentrations of all dissolved species in the absorber slurry.

Samples were obtained approximately two hours after the start of each test. The limestone feed slurry was sampled from the feed slurry pump discharge on a daily basis. The absorber recirculation slurry was sampled at the point of discharge from the slurry recirculation line into the recirculation tank. A second sample of the slurry was obtained and filtered immediately to allow for measurement of the sulfite and chloride contents of the liquid phase. These absorber filtrate solutions, also analyzed for mercury in the liquid phase, were preserved with a dilute acidic solution to prevent mercury loss. Solids from the on-site filtered samples were analyzed to determine the concentration of mercury in the solid phase. Solids from the first slurry sample, later separated in the laboratory, were also analyzed for mercury to check for the movement of mercury between the liquid and solid phases.

Table 5.8 summarizes the average mercury concentration detected in the limestone feed, recirculating absorber slurry solids, the absorber filtrate and the on-site filtered solids during conventional wet scrubber operation. By-product analyses from high L/G Phase I tests are provided for comparison. As was the case in Phase I, the mercury contribution from the limestone feed was insignificant compared to the flue gas (coal). Extremely low quantities of mercury were measured in the FGD filtrate. Similar to FGD tests at the EPRI Environmental Control Test Center (ECTC), those conducted at commercial plants by CONSOL, Inc., and elsewhere, the mercury left the system with the slurry solids[27,30,35,38,39]. The output stream with the highest mercury concentration was the absorber solids which contained more mercury than the absorber filtrate. Comparison of the mercury content in the solids immediately separated on-site and later in the lab suggests there was no movement of mercury between the FGD liquid and solid phases over time.

Table 5.8 FGD Process Stream Mercury Concentration - Conventional Operation

	Limestone Feed [ppm]	Absorber Slurry [ppm]	Absorber Filtrate [ppb]	Filtered Solids [ppm]
Phase I - LSFO/Tray	< 0.05	0.8	< 10.0	N/A
Phase II - LSFO/Tray	0.011	2.7	0.7	2.3
Phase II - LSFO/Open	0.011	2.3	3.1	2.2

However, during the low L/G, low pH tests where elevated levels of gas-phase elemental mercury were measured at the scrubber outlet, relatively higher concentrations of mercury were measured in the absorber filtrate. The average mercury concentration detected in wet scrubber process streams during non-conventional forced oxidation and natural oxidation operation are presented in Table 5.9. Conversely, mercury in the filtrate was less than the limits of detection during the natural oxidation of the slurry. During the natural oxidation tests, recall that the gas-phase elemental mercury emissions were consistently lower than measured entering the scrubber. The changes in the mercury concentration in the scrubber process streams stemming from different oxidation regimes suggests that the slurry chemistry may influence the eventual fate of mercury removed by FGD processes.

Table 5.9 FGD Process Stream Mercury Concentration - Non-Conventional Operation

	Limestone Feed [ppm]	Absorber Slurry [ppm]	Absorber Filtrate [ppb]	Filtered Solids [ppm]
LSFO – Tray	N/A	0.3	37.2	N/A
LSFO – Open	N/A	1.8	16.6	2.4
Natural Oxidation	0.013	N/A	< 0.5	1.0

5.6.5 *Mercury Control Summary*

The total mercury emissions and corresponding mercury control measured for the baghouse and wet scrubber devices during the second test series are provided in Figure 5.21. The low level of total mercury removal measured across the baghouse (less than 15%) was associated with the low level of mercury present on the particulate. The high percentage of oxidized mercury emissions from the baghouse resulted in mercury emission control across the wet scrubber greater than 80%. Data from Test Series 2 of Phase II indicate that wet scrubber configuration (tray and oxidation mode) and operation (L/G ratio) impact mercury emissions. The slurry pH does not have a significant impact on the control of oxidized mercury emissions. Wet scrubber operating conditions that provided for low SO_2 control efficiency tended to also result in reduced mercury control for the bituminous coal-fired flue gas. The correlation of mercury and SO_2 control featured in Figure 5.22 may be attributed to the high ratio of oxidized-to-elemental mercury entering the scrubber. Operation with the tray tower resulted in lower SO_2 and mercury emissions at all conditions relative to the open spray tower.

Overall, total mercury control was significantly higher than the median 17% total mercury removal as reported for wet scrubbers in the EPA interim final report on hazardous air pollutant emissions from fossil-fired electric utility steam generating units. The results of Test Series 2 of Phase II suggest that the EPA interim final report understates the potential for mercury emissions control for commercial wet scrubbers treating flue gas generated from high-sulfur bituminous coal.

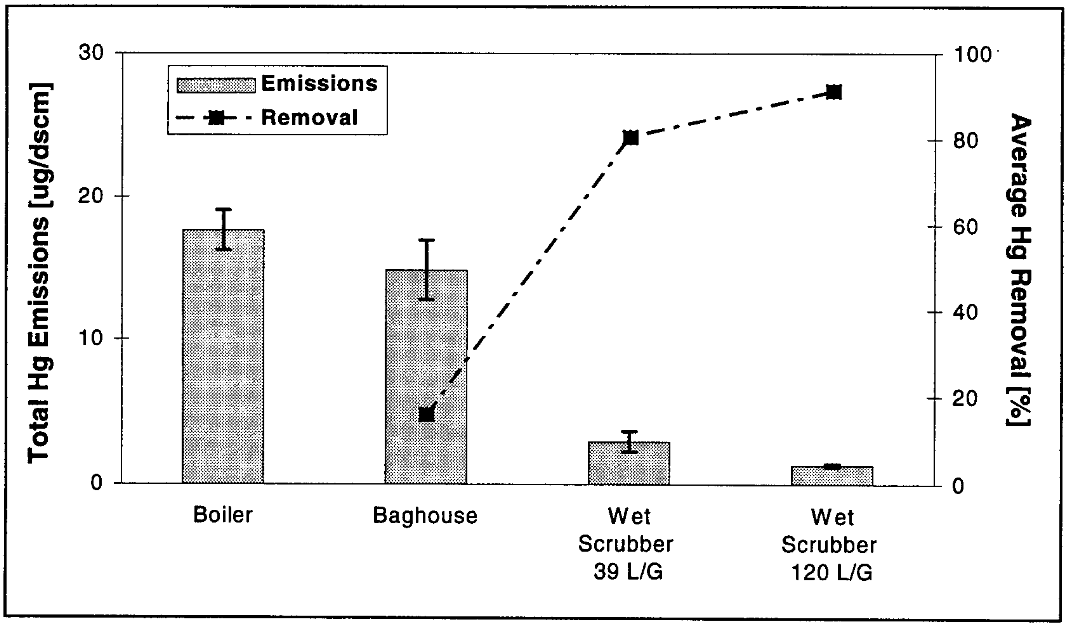


Figure 5.21 Mercury Control Summary - Test II

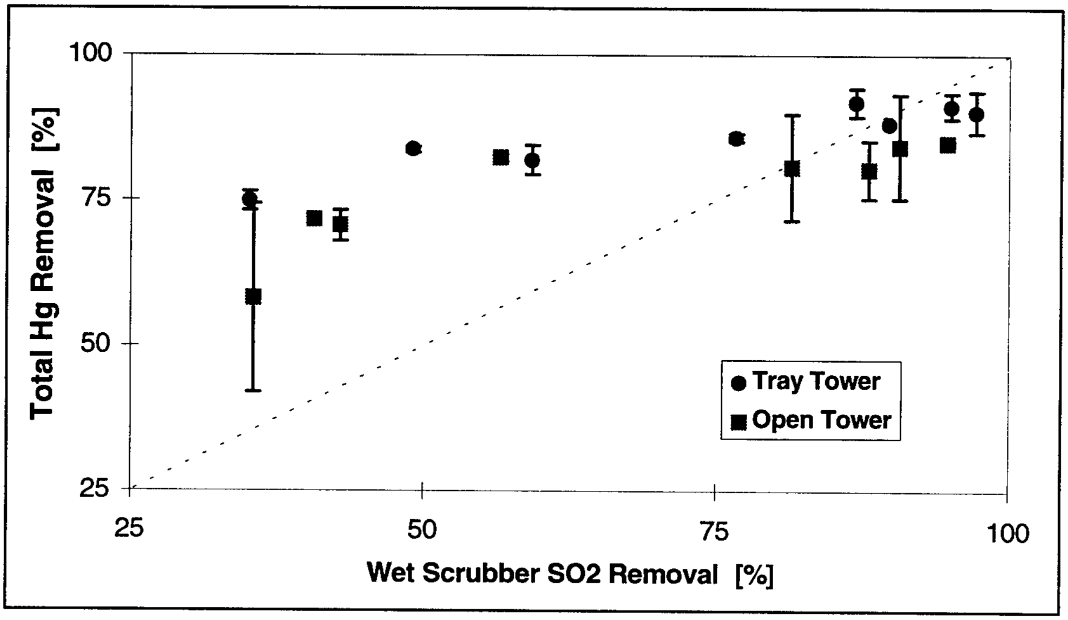


Figure 5.22 Correlation of Wet Scrubber Mercury and SO_2 Control - Ohio 5/6 Coal Blend

5.7 Hydrogen Chloride Emissions

The relative quantity of HCl emissions from a coal-fired boiler may trigger the need for emissions reduction under the 1990 Clean Air Act Amendments (CAAA). Although the second test series focused on mercury emissions control using a limestone wet FGD system, HCl emissions were also monitored. Uncontrolled measured emissions of 144,511 ± 17,550 lb/trillion Btu were approximately 30% higher than the predicted uncontrolled emissions (100,340 ± 2320 lb/trillion Btu) based on the coal heating value and chlorine content.

The total HCl emissions and corresponding total HCl removal measured for the baghouse and wet scrubber devices during the second test series are provided in Figure 5.23. Hydrogen chloride removal averaged 7% across the pulse-jet baghouse, whereas greater than 99% removal was achieved by the wet scrubber. Similar to the mercury and SO_2 emissions, HCl emissions were less variable with the tray tower configuration relative to the open tower. This was earlier attributed to the reduction of flue gas channeling by the tray. Average hydrogen chloride emissions from the tray tower (513 lb/trillion Btu) were approximately half of those emitted from the open tower (1,063 lb/trillion Btu). In summary, wet scrubbers can effectively remove both mercury and hydrogen chloride, which are currently under review for potential regulation by the U.S. EPA.

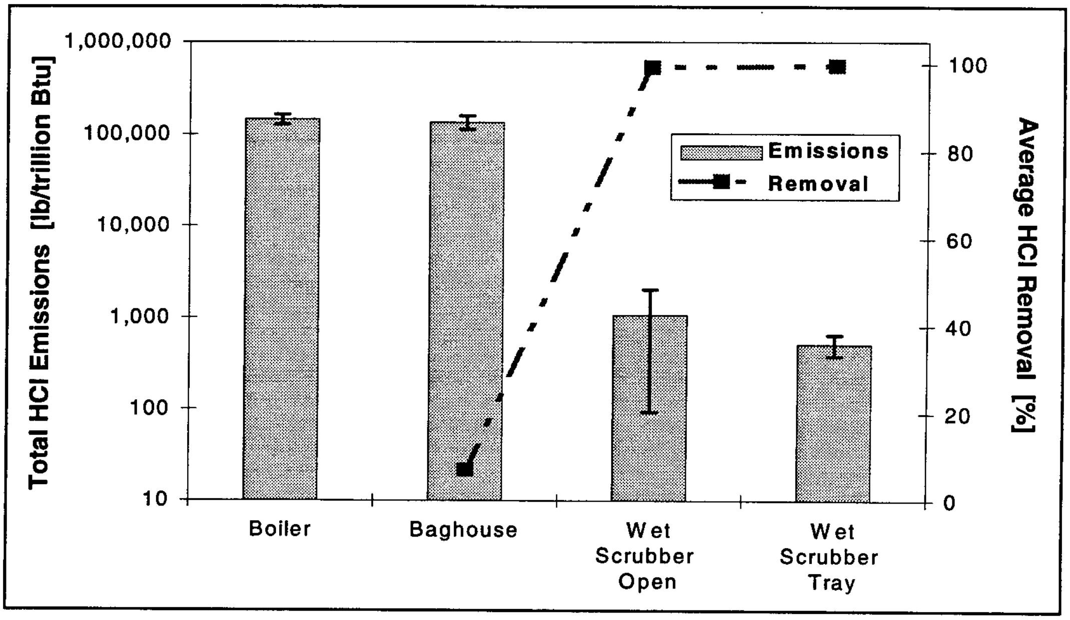


Figure 5.23 Hydrogen Chloride Control Summary - Test II

5.8 Evaluation of Air Toxic Measurement Systems

To date, this project has relied on EPA Method 29 and Ontario Hydro sample trains, sometimes refered to as grab sampling, to quantify the amounts of trace metals and mercury in flue gas. The problem with sample trains is that they do not produce "real time" measurements and that the subsequent chemical analyses is costly and time consuming. An on-line analyzer for mercury and other air toxic emissions would be extremely beneficial in the charcterization of equipment performance.

The purpose of this task, Task 4 -- Advanced Air Toxics Measurement Concepts, was to identify and/or develop advanced concepts for on-line, or near on-line, measurement of selected air toxics. Two different advanced measurement techniques were evaluated. An analyzer employing a fixed wavelength atomic absorption spectrometer detecting UV absorption was evaluated for its ability to measure total mercury, elemental mercury and particulate mercury, and a Fourier Transform Infrared Spectrometry (FTIR) was evaluated for the ability to simultaneously monitor several flue gas components and, especially, hydrogen chloride. The results of these evaluations are given in Sections 5.8.1 and 5.8.2 respectively.

5.8.1 On-Line Mercury Monitor System

The objective of this test was to evaluate the system under "real life", coal-fired, utility conditions. The analyzer was operated over a wide range conditions using gas from a wet scrubber inlet and outlet and from a dry scrubber inlet. Prior to this evaluation, tests were limited to facilities firing fuels other than coal. The AECDP evaluation presented a greater challenge because of the higher levels of SO_2 and lower levels of mercury in a coal-fired application.

Analyzer Description and Principle of Operation

The analyzer is designed to provide continuous emission monitoring of total mercury in flue gas from combustion and pyrolysis systems. The analyzer employs a fixed wavelength atomic absorption spectrometer and a sample conditioning system. Sample gas is carried through a 0.16 inch (4 mm) ID Teflon heated sample line maintained at 390°F (200°C). Nominal sample flow rate is 2.1 scfh (60 l/h). Solenoid valves automatically direct sample gas, zero gas, and calibration gas to the conditioning system and detector. In the conditioning system, sample gas is mixed with ascorbic acid/preservative in two reactors, cooled, and condensate is separated. The reaction converts all mercury, including particle-bound mercury, to elemental mercury. From the conditioner, the gas flows through a quartz glass optical cell where it is subjected to UV radiation (253.7 nm Hg line). A detector measures the amount of UV absorption and a microprocessor calculates and displays mercury concentration in (mg/Nm^3). The stated accuracy of the analyzer is 1 $\mu g/Nm^3$.

The second analyzer in the system operates on the same technical principle as the previous, except that the reactor is omitted. Oxidized and particulate mercury compounds are not converted to elemental mercury and are, therefore, not detected. Sample conditioning consists of a Teflon dust filter, cooler, and demister. Oxidized mercury is calculated from the difference between the total and elemental values.

Sulfur Dioxide Interference

Sulfur dioxide absorbs light at the same wavelength as mercury. To correct for this interference, correction curves were supplied relating various SO_2 concentrations. These correction curves were used to calculate an actual Hg concentration according to the following formula:

$$Hg_{corr} = Hg_{raw} - [m * C_{SO_2}]$$

where:

Hg_{corr} = Hg concentration corrected for SO_2 interference, $\mu g\ Hg/Nm^3$

Hg_{raw} = as measured Hg concentration, $\mu g\ Hg/Nm^3$

m = slope of interference curve

C_{SO_2} = measured SO_2 concentration, ppm

During the course of the evaluation, questions arose concerning the validity of the correction curves supplied by the vendor. Therefore, a test was conducted in which the analyzers were operated over a range of SO_2/N_2 concentrations. The data was used to generate new, and separate, correction curves. All data in this evaluation was corrected using the new correlations.

Effect of SO_2 Interference on Hg Concentration

Sulfur dioxide creates strong interference in the analyzer (about 9 µg/dscm Hg per 100 ppm SO_2). It is difficult to correct for this interference, especially if the SO_2 concentration is orders of magnitude greater than the mercury concentration, as is the case for flue gas generated from coal combustion. Fluctuations and uncertainties in the SO_2 reading can cause significant errors in the measured mercury value.

Another limitation is that the correction procedure is very sensitive to errors in determining the correction curve constants. As shown above, new correlations for SO_2 interference were developed for both the total and elemental mercury analyzers. The r^2 values, a measure of the accuracy of the curve fit, for these correlations were 0.9971 and 0.9995, respectively, indicating an excellent fit to the data. However, these correlations could not consistantly correct for the interference as demonstrated below.

In Figure 5.24, the total mercury and SO_2 concentrations are shown for a CEDF burner test. In this example, the total Hg trace trends opposite to the SO_2 for most of the data, suggesting an overcompensation for SO_2 interference. However, the data also suggests that errors in compensation can vary with time, since the last few data points show the SO_2 and total mercury trending together.

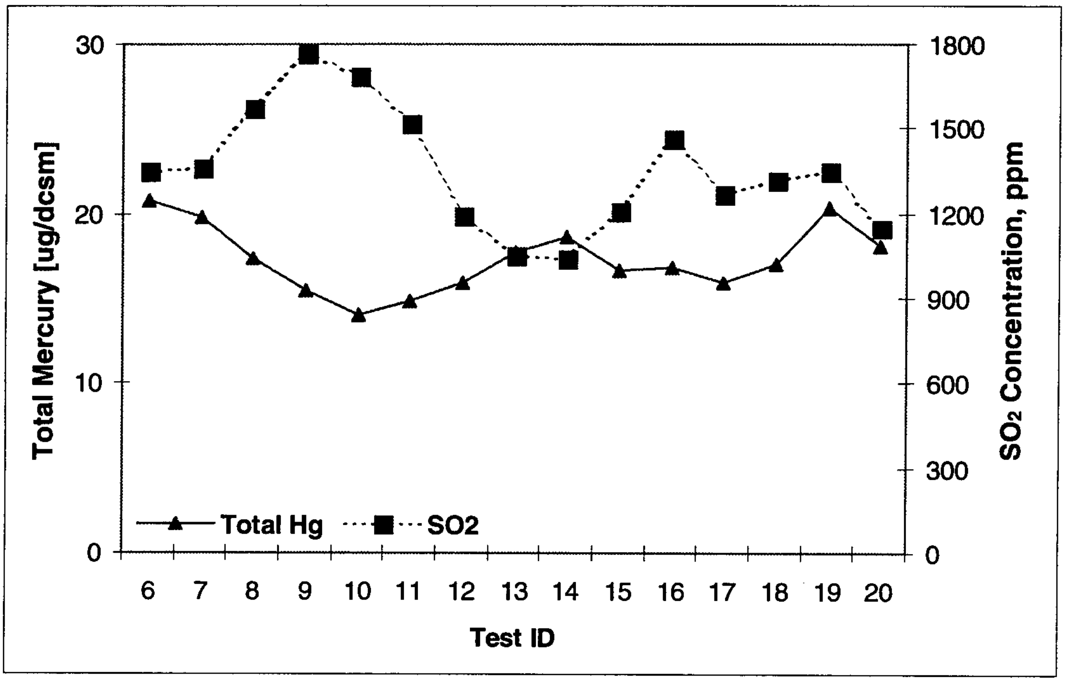


Figure 5.24 Comparison of SO_2 and Total Hg Concentrations - Burner 1

Another example of poor compensation is shown in Figure 5.25, that plots elemental mercury and SO_2 concentrations for the same test as Figure 5.24. In this instance, the calculated elemental mercury concentration trends very well with the SO_2 concentration, suggesting undercompensation for SO_2 interference.

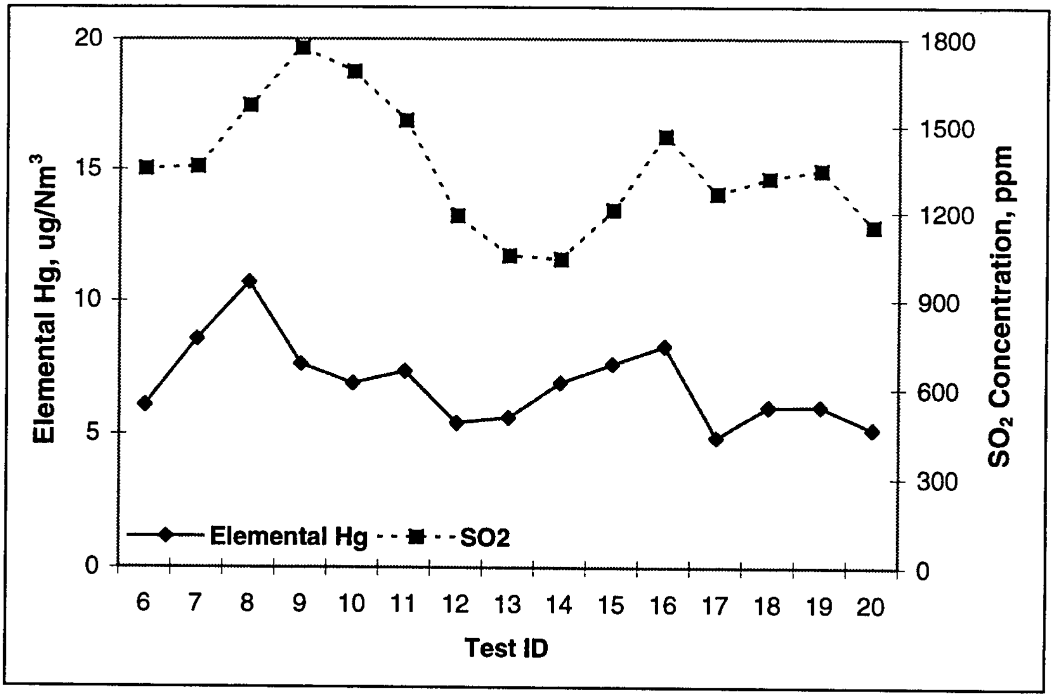


Figure 5.25 Comparison of SO_2 and Elemental Hg Concentrations

The data presented in Figures 5.24 and 5.25 illustrate that, because of the high sensitivity to SO_2 interference, even small errors in the correction proceedure can adversely affect the calculated mercury concentration. Overcompensation causes the mercury values to trends opposite to SO_2, and undercompensation causes the mercury values to be dominated by the SO_2 interference. This problem further aggravated because:

1. The SO_2 compensation appears to vary with time.
2. The analyzers experienced under- and over-compensation.
3. There is no direct method to determine the correction constants since actual mercury levels cannot be measured in real time.

Test Results and Discussion

The analyzer system was evaluated during the AECDP Phase II Test Series 2 (February 1997) and during a burner configuration tests performed in the CEDF (March 1997). During the AECDP tests, the analyzer sampled gas from upstream and downstream of the wet scrubber. During the CEDF burner tests, the analyzer sampled gas from upstream of the dry scrubber. For both programs, the total mercury analyzer was operated continuously. The elemental analyzer was used when operational problems, described below, allowed. An Anarad SO_2 analyzer was used downstream of the mercury analyzer to measure SO_2 concentration for interference correction. All data in this report was corrected to 3% O_2.

AECDP Testing

The first test of the mercury analyzer was performed during Test Series 2. The total mercury analyzer was operated continuously during the last three days, but additional problems limited the use of the elemental analyzer. The most severe of these was liquid carryover resulting from the use of sodium hydroxide and gold traps. Liquid carryover from the total mercury reactor to the elemental analyzer contaminated the sample and invalidated the measurement.

Analyzer performance was gauged by comparison to EPA Method 29 and Ontario Hydro sample train data. Figure 5.26 shows how sample train data compared to on-line data for total mercury at the wet scrubber outlet. Data from the on-line analyzer tended to be either slightly higher or significantly higher, and did not show the same trend as the sample train measurements.

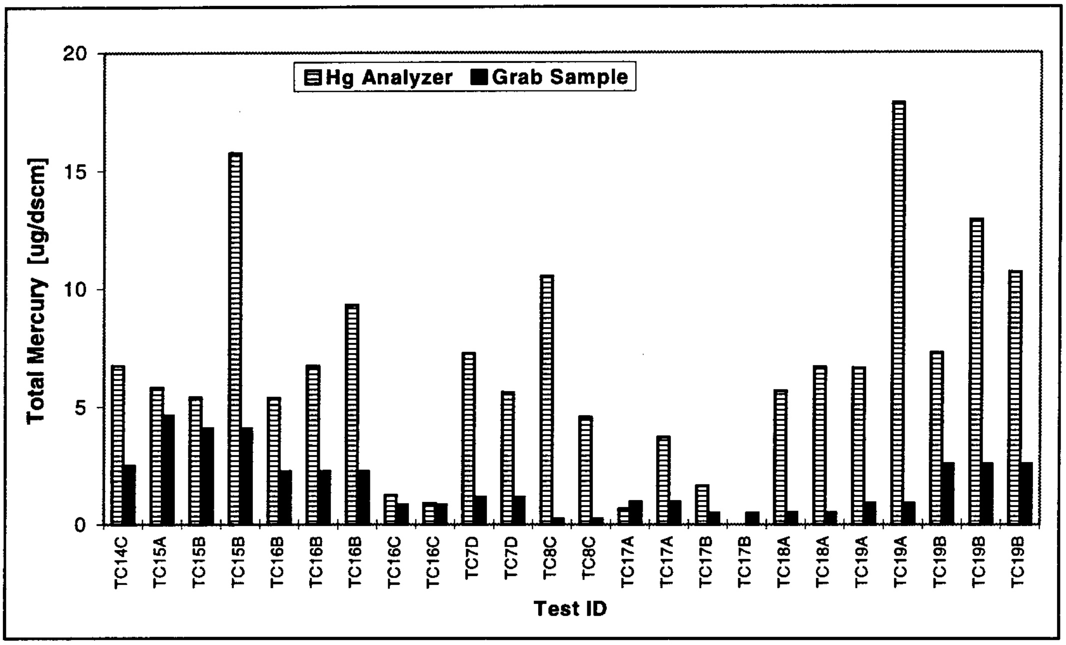


Figure 5.26 Comparison of Sample Train and On-Line Total Mercury Data

In Figure 5.27, the on-line mercury analyzer data are compared with the corresponding SO_2 values to illustrate the effect of SO_2 interference. In this figure, the mercury values show no apparent relation to the SO_2 values. By contrast, Figure 5.28 contains sample train data and shows an excellent relationship with SO_2 concentration. Most of the tests were done in pairs or triplicates at similar conditions. Therefore you would expect that changes in test conditions that affect SO_2 would also affect Hg. Figure 5.28 demonstrates this relationship and 5.27 does not. This indicates that the on-line mercury analyzer could not accurately discern the weak Hg signal from the strong SO_2 interference. The same comparisons were made with data from the elemental mercury analyzer and showed an even greater disparity. In some cases, values for elemental mercury were higher than those for total mercury.

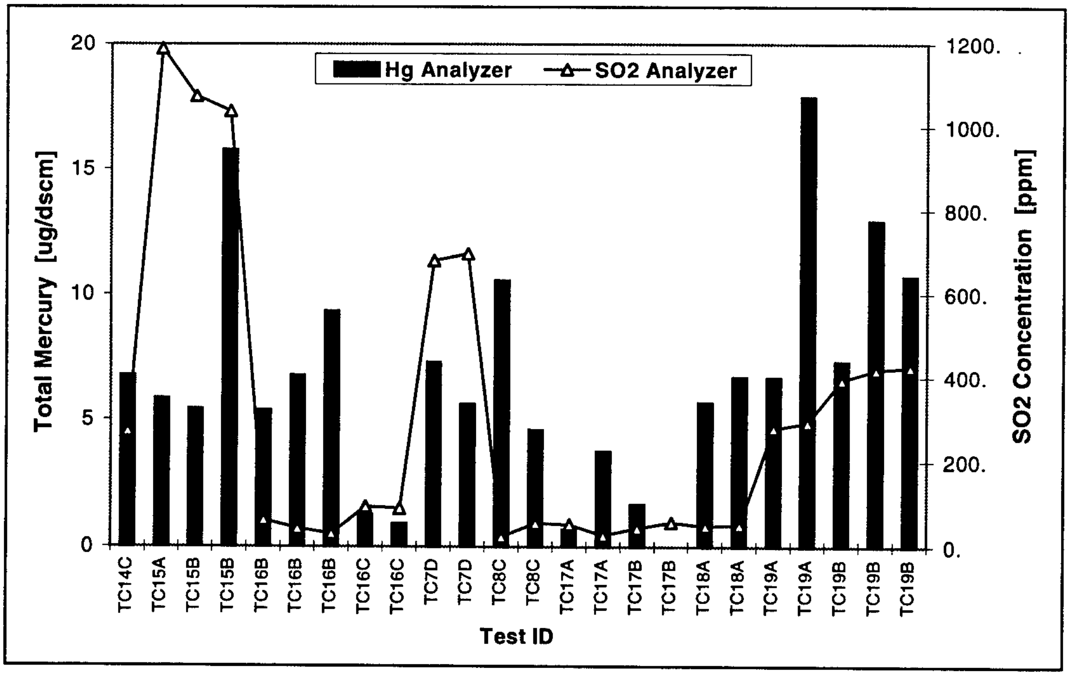


Figure 5.27 Comparison of On-Line Analyzer Total Hg Data and SO_2 Concentration

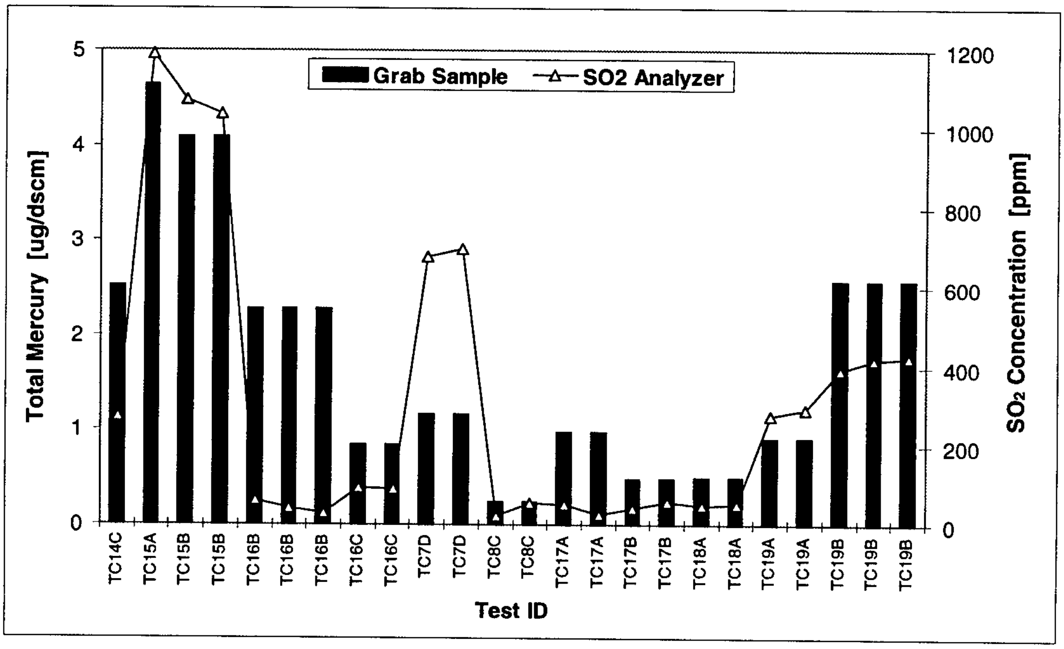


Figure 5.28 Comparison of Sample Train Mercury and SO_2 Concentration

CEDF Testing

Upon the completion of AECDP testing, data from the on-line mercury analyzer was analyzed and found to be compromised by SO_2 interference as shown above. Therefore, new correction curves were generated and further evaluation of the on-line mercury analyzer was performed in conjunction with a burner test program performed in the CEDF. The burner tests provided the opportunity to determine the effect of furnace operating parameters on mercury emissions, and to study on-line mercury analyzer operation at higher SO_2, particulate and mercury levels. Two burner designs were tested at various settings and operating conditions. Burner 1 was a commercial design and Burner 2 was developmental. The on-line mercury analyzer system was reconfigured to sample particulate-laden flue gas at the dry scrubber inlet. Unfortunaely, the short duration of each test (30 min) did not permit EPA or Ontario Hydro sampling.

The unburned carbon content in the fly ash, measured by the Loss On Ignition (LOI) test, was determined for each test condition. Flue gas components, SO_2, NO_x and CO, were continuously monitored and, later, compared to values from the on-line mercury analyzer to determine if combustion conditions impact mercury concentration and speciation. Of particular interest was the how Hg was affected by the unburned carbon content in the fly ash. Unfortunately, data analyses showed that the new correction curves still could not account for the high signal-to-interference ratio caused by the SO_2. Therefore, none of the data from the CEDF test will be presented, only a discussion of the on-line mercury analyzer performance and recommendations.

Operational Problems and Recommendations

During the course of the evaluation, several problems arose with respect to the analyzer design and operation.

Baseline Shift - During the burner tests, a sudden increase in the total Hg concentration was observed. After purging the on-line mercury analyzer with N_2 for several hours, a positive shift of about 11 μg/Nm^3 remained. Discussions with the analyzer company's personnel revealed that particulate bleedthrough and subsequent contamination of the analyzer glassware caused the shift. They indicated that high particulate, high SO_2, flue gas are the worst operating conditions for the analyzer.

Hg Spikes – Near the end of the burner tests, large spikes in the raw mercury signal (>400 μg/Nm^3) occurred when the analyzer returned to normal operation after an auto calibration or auto zero cycle. For large spikes, the analyzer did not recover completely before the next auto zero cycle (1 hour between cycles). This problem was traced to particulate bleedthrough and condensation in the heated sample line. Condensation occurred in the sample lines during auto zero or auto calibration because the sample gas stagnated in the lines when flow was terminated. When flow was restored, the condensate flowed into the reactor and released Hg absorbed in the condensate.

Auto Zero Timing - The maximum auto zero cycle duration is 99 seconds. During high SO_2/high Hg operation, this duration was not sufficient to obtain a true zero and subsequent measurements were in error. It is recommended that the auto zero cycle duration be increased.

Sample Line Insulation - The last 2 feet of inlet sample line and the sample lines to the reactor inlet were not insulated. These areas were subject to moisture condensation.

Sample Line Arrangement - While investigating the cause basekine shift noted above, it was found to disappear during an auto zero cycle, but not during an auto calibration cycle. The cause was determined to be the arrangement of the sample lines. Zero gas is introduced to the analyzer downstream of the reactor, chiller and demister, while calibration gas passes through the entire system. As a result, the span calibration was affected by particulate contamination while the zero calibration was not. Depending on the degree of contamination, a significant bias could be introduced to the signal. It is recommended that the zero gas be routed to pass through the entire system.

Gas Conditioning Traps - Several attempts were made to use gas conditioning traps, installed ahead of the analyzer, containing sodium hydroxide (NaOH) or gold. The purpose of the traps is to separate the signals created by the SO_2 and mercury. The NaOH trap is designed to remove all SO_2 from the sample so only mercury is measured. Similarly, the gold trap is designed to remove all mercury so only SO_2 interference is measured. However, several problems arose while using the traps that prevented proper siganl separation. These problems included:

1. During tests with the NaOH traps, excessive heat was generated due to the reaction with SO_2 and moisture. The heat melted plastic traps, and liquid carryover severely limited operating time with glass traps.

2. With both traps, there was uncertainty as to whether they were 100% efficient. In addition, it is not known whether mercury is affected by the NaOH trap.

3. On several occasions, data from tests with the traps in place did not agree with data from normal operation, or with data generated while creating the new SO_2 correction curves.

Detection Limit – During several tests, the mercury concentration at the wet scrubber outlet was near or below the stated detection limit of the on-line mercury analyzer (1 $\mu g/Nm^3$). For these cases, the mercury signal was completely lost in the SO_2 interference.

Conclusions

The on-line mercury analyzer system was tested during Phase II Series 2 of the AECDP Program and during a burner test program conducted in the CEDF. The test objective was to evaluate the system at conditions typical of a commercial coal-fired, utility application. The on-line mercury analyzer was operated over a wide range of conditions with flue gas from the inlet and outlet of a wet scrubber and from the inlet of a dry scrubber. On-line mercury analyzer measurements were compared to EPA Method 29 and Ontario Hydro sample train analyses as the basis of the evaluation. Based on this work, the following conclusions can be made:

> The analyzer system is fairly robust and requires little maintenance or observation during normal operation. Both analyzers are computer-controlled and feature auto zero and auto span calibration cycles.
>
> The analyzer system tended to overpredict mercury concentration at the wet scrubber outlet, and underpredicted mercury concentration at higher particulate and SO_2 concentrations. Results with the elemental analyzer were worse at the scrubber outlet, but probably because the mercury analyzer was operating near the stated detection limit.

In its current configuration, the on-line mercury analyzer system was unsuitable for this application due primarily to the extensive interference caused by high levels of SO_2. The on-line mercury analyzer did not perform well even at the reduced SO_2 concentration at wet scrubber outlet because the Hg/SO_2 ratio was too high to permit signal differentiation. Attempts to more accurately model SO_2 interference, resulted in improved performance, but further illustrated the fact that minor errors in the correction technique resulted in large errors in the calculated mercury values.

5.8.2 *Fourier Transform Infrared Spectrometry Analyzer*

An on-line Fourier Transform Infrared (FTIR) Spectrometry analyzer was used to measure concentrations of flue gas constituents at the inlet and outlet of the wet scrubber during the second test. The flue gas constituents measured included CO_2, CO, SO_2, NO, N_2O, NO_2, HCl and H_2O. The gas concentrations were measured using the extractive gas cell and gas analyzer software provided with the FTIR system. With this equipment, the infrared absorption spectra of the flue gas are measured and the concentrations of selected gases are determined in an error minimization routine.

The goals of the measurements were as follows:

- determine those gases that could be reasonably measured at the inlet and outlet of the wet scrubber,
- determine the operating characteristics, precautions and problems associated with continuous FTIR measurements of flue gas,
- determine the ability to measure HCl in flue gas using FTIR spectroscopy.

FTIR Equipment

The FTIR was operated as a continuous gas analyzer for most of the test period and was unattended for long periods of time. The liquid nitrogen-cooled photodetector for the FTIR has a rated "hold time" of eight hours and required replenishment at 6 to 8 hour intervals. Standardization with calibration gases was also typically performed at these or shorter intervals.

Instrument "zero" drift was quite low for all of the measured gases, but it was noticed that water vapor was difficult to purge. That is, after all other gases had been purged from the gas cell, residual water vapor was still evident. In retrospect, this residual water vapor signal was likely due to water absorption by the infrared windows (potassium bromide, KBr) in the gas cell and film deposits on the mirrors in the gas cell. Near the end of the test period the gas cell was cleaned, and the KBr windows were replaced. The shiny gold surfaces of the mirrors had dulled substantially indicating chemical attack by the acid gases. These problems are magnified by the high water vapor concentrations in the sampled flue gas.

Measurement Capability

At the outlet of the wet scrubber the water vapor concentration in the flue gas is on the order of 14% by volume and at the inlet it is on the order of 6% by volume. In contrast, the concentrations of some of the gases of interest are on the order of one to 300 ppm. Examples of these gases are HCl, CO, SO_2, N_2O, NO_2 and NO.

Measurements made on the raw (unprocessed flue gas) indicated that CO, CO_2, SO_2, and HCl could be measured simultaneously even at the high water vapor concentrations. These gases provide relatively strong absorption spectra at typical concentrations relative to the absorption spectra of the interfering water vapor. N_2O and NO_2 spectra are relatively weak compared to the water vapor so that accurate measurements could not be made at typical flue gas water vapor concentrations. Reasonable and repeatable measurements of NO could be made part of the time and were dependent in large degree on the amount of water in the flue gas and the accuracy of the spectral correction for water vapor. During the tests, the measured concentrations of NO, CO, CO_2 and SO_2 were in general agreement with the data from other gas analyzers.

HCl was not measured in significant quantities at the inlet or outlet of the wet scrubber. The concentration of HCl was expected to be low at the wet scrubber outlet, but the virtual non-detection of HCl at the wet scrubber inlet was surprising. In the lab, 100 ppm of HCl in N_2 is relatively easy to measure. Also, during initial trials of the FTIR on the CEDF, HCl concentrations of 35 to 40 ppm were measured in the flue gas sampled at the outlet of the convection pass.

After the AECDP tests were completed, a lab test was conducted to determine the effect of water vapor on the measurement of HCl. In the lab, a gas stream of 100 ppm HCl in N_2 was mixed with N_2 bubbled through a water bath. The water vapor gas line and mixture gas line were heated to prevent any condensation of the mixture. The temperature of the water bath and flow rates of the pure N_2 and HCl bottle gas were controlled so that the water vapor concentration in the final mixture could be controlled over a wide range. The FTIR sample cell was operated at 300°F.

It was found that if the temperature of all the sample lines was well above the water vapor dew point, the concentration of HCl could be accurately measured, even with high water vapor concentrations. However, as the sample line was cooled to near the dew point temperature, the HCl concentration at the FTIR gas cell would drop to near 0 ppm. This occurred over a very narrow temperature range (~5°F) for the heated sample lines. This type of on-off response indicates that only small amounts of liquid water (possibly only liquid films) are required to remove HCl from the gas stream.

During AECDP testing the sample lines were heated to near 300°F. However, at the flue, the sample line was always in contact with unheated metal fittings contained in a flange. The low metal temperatures at the flue penetration were probably low enough to cause a water film, and so remove the HCl from the flue gas before the measurement. Future measurements will require greater attention to the method of withdrawing the gas sample from the flue gas stream.

The most accurate measurements of the largest number of flue gas constituents can be made if the water content of the flue gas is reduced to about 1% or less, as is typical of the ice chest condensers upstream of most gas analyzers. Since all of the gases except HCl are relatively insoluble in water, this is a reasonable approach. Also, "dry" flue gas will require less maintenance of the gas cell and minimize chemical attack on the windows and mirrors. If the measurement of HCl concentration is needed, then the water vapor in the flue gas cannot be condensed.

Testing Results and Discussion

The flues at the AECDP wet scrubber are at static pressures ranging from about -5 in. WC to -19 in. WC below atmospheric. The flue gas was withdrawn from the flues using a standard gas sample pump located downstream of the FTIR gas cell. An O_2 analyzer was located downstream of the sample pump to insure that air infiltration to the sample lines did not dilute the sample. The gas cell was always operated at a temperature of 150 C (300°F) regardless of the sampling methodology, and a manometer was used to measure the gas cell pressure. This arrangement was selected to provide the shortest gas path with the fewest components upstream of the gas cell.

For most of the tests, a heated stainless steel tube equipped with an in-line particle filter was used to convey the gas from the flue to the gas cell. An ice chest to remove water vapor was normally located between the gas cell and the vacuum pump.

Operational Concerns and Recommendations

Although the FTIR has great capability for simultaneous concentration measurements of multiple gases, measurement in any flue gas is made more difficult by the presence of water vapor. The infrared spectra of water vapor overlaps, to some degree, all of the above-mentioned spectra with the exception of HCl. At the outlet of a wet scrubber, the water vapor concentrations are very high, so that measurements of some gases are no longer possible.

Water vapor has some very nonlinear spectra with very narrow line widths. The line widths are generally smaller than the spectral resolution of the FTIR, so small spectral shifts in the measurement can result in poor spectral subtraction. Similarly, for typical flue gas concentrations, the absorbance of water vapor (the interferant) can exceed the absorbance of an overlapping gas by a factor of 10. These two effects reduce the accuracy of the measurement, or can preclude the measurement of some gases.

The infrared spectra measured by the FTIR are summations of the contributions from all of the absorbing gases in the flue gas. Gases with overlapping spectra are separated by subtracting the contribution from one of the gases from the total spectra.

Most of the constituents of the flue gas that can be measured with the FTIR have very low solubilities in water, so that chilling and removing the water from the flue gas before the measurement is an obvious solution to the problem of spectral interference. For most of the testing at the wet scrubber this was not done in an attempt to measure HCl in the flue gas. HCl is highly soluble in water and would be effectively removed from the flue gas in the process of condensing the water vapor.

5.9 Phase II Test Series 2 Conclusions and Recommendations

5.9.1 Mercury Control

Immediate preservation of the Ontario Hydro impinger solutions with permanganate retards mercury loss during sample recovery. This modification resulted in improved agreement of total mercury between the Ontario Hydro and EPA Method 29 sampling methods. Use of the permanganate preservative is strongly recommended for future testing.

Reduction of flue gas temperature over the range of 250 to 300°F through the use of flue gas cooling or humidification did not influence ESP mercury removal on the basis of testing performed in Phase II Test Series I. As measured by Ontario Hydro sampling, the elemental mercury passed through the ESP unaffected. Similarly, changes in baghouse compartment temperature over the temperature range of 280 to 345°F did not affect total baghouse mercury control nor did it result in mercury enrichment on the particulate. In contrast to ESP operation, elemental mercury was oxidized to the more soluble form across the baghouse filtercake. The primary role of a conventionally operated baghouse toward the reduction of mercury emissions from a scrubbed utility power plant appears to be the conversion of elemental mercury over the fly ash filtercake. The combination of a baghouse and wet scrubber may have potential for total mercury emissions reduction due to the conversion of elemental mercury to a more soluble form. It should be noted, however, that the improvement in mercury control measured for the baghouse/wet scrubber combination was too large to be attributed solely to the conversion of elemental mercury across the baghouse. Differences in mercury control across the wet scrubber when preceded by an ESP versus a baghouse are discussed in subsequent sections of this report and will be evaluated in more detail in Phase III.

A gas flow distribution tray in the wet scrubber enhanced both SO_2 and total mercury emissions control over a wide range of L/G ratio and pH. The enhancement of SO_2 and total mercury control by the tray was pronounced at the lower L/G operating condition. The major contribution toward the lower mercury emissions was the decrease of soluble gas phase oxidized mercury emissions when the tray was installed. Elemental mercury emissions were generally unaffected by the tray configuration. In addition, SO_2 and mercury emissions from the tray tower were less variable than from the open tower at similar operating conditions. The better consistency in SO_2 and mercury emissions with the tray tower configuration relative to the open tower may be due to the reduction of flue gas channeling resulting from the tray. The reliance on open towers in the draft US EPA report, *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units - Interim Final Report*, may have contributed to the median mercury emissions control efficiency of only 17% for wet scrubbers.

Mercury control improved with increased L/G ratio for both the open and tray tower configuration. Emissions of oxidized mercury were reduced as the L/G ratio was increased. The slurry pH did not appear to have a significant impact on oxidized mercury emissions. Elemental mercury emissions from the wet scrubber were fairly consistent over the wide range of L/G ratio investigated. The exception was combined operation at low L/G and low pH, which increased elemental mercury emissions, based on Ontario Hydro sampling. The elimination of sampling bias due to the SO_2 in the flue gas with the Ontario

Hydro sampling method implies that the reduction of oxidized mercury to elemental mercury may be occurring in the aqueous phase of the scrubber.

Total mercury control was not measurably impacted by the switch from forced to natural oxidation for limited tests performed at a high L/G ratio. However, natural oxidation of the slurry provided elemental mercury emissions consistently lower than forced oxidation. There was an indication that the slurry chemistry may affect elemental mercury emissions from the scrubber. Additional tests addressing the impact of variable oxidation stoichiometry on mercury emissions are recommended.

The majority of the mercury captured in the wet scrubber ended up in the solid phase of the scrubber discharge. Extremely low quantities of mercury were generally measured in the FGD filtrate. The elevated levels of mercury detected in the absorber filtrate stemming from scrubber operation at low L/G, low pH conditions should be verified.

5.9.2 *Advanced Measurement Techniques*

Seefelder Messtechnik Mercury Monitor System

Evaluation testing was performed on the SMT mercury analyzer system during both Test Series 2 of the AECDP test program and an unrelated burner test program conducted in the CEDF. The primary objective of this work was to determine the operational ability of the SMT system with flue gas conditions both upstream and downstream of a wet scrubber unit. The evaluation testing was performed on both the Hg-Mat 2 total mercury analyzer and the Hg 2000 elemental mercury analyzer over a range of wet scrubber and burner operating conditions. The analyzer system is fairly robust in that it requires little maintenance or observation during normal operation. However, in its current configuration, the SMT analyzer system is not suitable for accurately measuring mercury concentrations in coal combustion-based flue gas. This is due primarily to the extensive interference caused by SO_2.

Fourier Transform Infrared Spectrometry Analyzer

Although the FTIR has great capability for simultaneous concentration measurements of multiple gases, measurement in any flue gas is made more difficult by the presence of water vapor. The infrared spectra of water vapor overlaps, to some degree, spectra of many flue gas components with the exception of HCl. At the outlet of a wet scrubber, the water vapor concentrations are very high, so that measurements of some gases are no longer possible.

Most of the constituents of the flue gas that can be measured with the FTIR have very low solubilities in water, so that chilling and removing the water from the flue gas before the measurement is an obvious solution to the problem of spectral interference. HCl is highly soluble in water and would be effectively removed from the flue gas in the process of condensing the water vapor. Therefore, it is difficult to monitor many flue gas components and HCl simultaneously with a FTIR.

6.0 PHASE II, TEST 3: COAL PROPERTY IMPACTS

The activity for Test Series 3 in Phase II represents work under Task 3 - Impacts of Coal Properties on Air Toxics Emissions - as outlined in the Phase II Management/Milestone Plan. The testing primarily addresses activity under Subtask 3.2 - Alternative Coal Tests. The objective of this task was to evaluate the sensitivity of air toxics emissions and flue gas treatment device capture efficiency to changes in coal properties. Sampling targeted the characterization of mercury and HCl emissions. The contribution to mercury emissions reduction from cleaning of the coal prior to combustion was evaluated by analyzing the raw and cleaned coal while measuring emissions from firing the cleaned coals. Two Ohio bituminous coals exhibiting a range of mercury and chlorine concentrations were selected for this test series. The variation of mercury speciation from firing the different coals and the impact of particulate emissions control equipment were quantified.

Previous operation has indicated that the distribution of mercury species present in the vapor phase is dependent on the coal properties and on interactions with fly ash in the particulate collection device. The distribution of mercury species at the FGD system inlet was measured with an ESP and alternately with a baghouse providing varying upstream particulate emissions control for each coal. The wet FGD system has been demonstrated to provide very high removal efficiency of oxidized mercury species at the selected operating conditions.

As reviewed in Section 5.0, mercury emissions control across the AECDP wet limestone scrubber was evaluated extensively in Test Series 2 of Phase II. The scrubber was operated over a broad range of liquid-to-gas ratios (L/G - 35-120 gal/kacf) and pH range (5.0-6.0) typical of commercial limestone slurry scrubbers. Mercury and SO_2 emissions control were measured with the scrubber configured as both a tray tower and as an open spray tower. Operation with the tray tower resulted in lower SO_2 and mercury emissions at all conditions relative to the open spray tower. SO_2 emission reductions ranged from 35-40% at the low pH, low L/G condition to 95-97% at the high pH, high L/G condition. Over the same range of operating conditions, mercury emissions reduction improved from 75% to 93%. The blend of Ohio 5/6 coals fired during Test Series 2 and the use of a baghouse to control particulate emissions upstream of the scrubber resulted in a high percentage of the vapor-phase mercury present as oxidized species at the scrubber inlet.

6.1 Objectives

The detailed objectives for Test Series 3 of Phase II are highlighted and summarized in the context of the overall plan for Phase II of the program.

Characterize the impact of coal properties on mercury emissions from a coal-fired boiler.

The coal chlorine content and ash characteristics are thought to affect partitioning between the solid and vapor phases and the ratio of mercury species in the vapor phase. Numerous researchers have observed high concentrations of oxidized mercury in utility flue gas when the coal had a high chlorine content. Two Ohio bituminous coals were selected to compliment the data obtained with the baseline Ohio 5& 6 coal. The mercury and acid gas emissions data were used to characterize the impact of key coal properties on mercury emissions by comparing measurement results for all three coals.

Expand existing project database on the effect of the particulate collection device on vapor-phase mercury speciation.

During Phase II Test Series 1, the distribution of mercury species measured downstream of the baghouse was significantly different than that measured downstream of the ESP for the program baseline coal. The elemental mercury fraction of the vapor-phase mercury was lower downstream of the baghouse. Intimate contact with catalytic reaction sites as the flue gas passes through the fly ash filter cake may provide for the oxidation of elemental mercury. Mercury speciation measurements downstream of the ESP and baghouse for the two additional coals were used to assess the impact of coal and fly ash properties on mercury speciation.

Quantify the impact of mercury speciation on wet scrubber mercury removal efficiency.

The distribution of mercury species at the scrubber inlet is believed to directly impact the mercury removal efficiency. The four combinations provided by firing two coals and upstream operation of the baghouse or ESP for each coal were expected to provide a range of elemental and oxidized mercury concentrations at the scrubber inlet. The wet scrubber was operated at a set of conditions benchmarked during the previous wet scrubber parametric tests. This permitted the comparison of mercury removal efficiencies for a total of five inlet mercury species distributions generated from actual combustion and process operations without doping mercury into the flue gas stream.

Examine wet scrubber slurry chemistry for possible correlation with mercury removal.

The results of the wet scrubber parametric tests indicate that the slurry chemistry may affect emissions of elemental mercury from the scrubber. The oxidation air stoichiometry in the limestone forced oxidation scrubber was varied from the baseline test conditions to alter slurry chemistry. The results from these few tests were compared with the Test Series II results to evaluate if slurry chemistry warrants further study in subsequent test programs.

Compare potential mercury emissions from raw coal with measured emissions from firing cleaned coals.

Coal cleaning is recognized as one cost-effective strategy for reducing mercury emissions from coal fired electric utility boilers. About 75 to 80% of the bituminous coal consumed by the power generation industry is cleaned to some extent.[40] Both of the coals selected for Test Series 3 were processed in commercial cleaning plants. Samples of the raw coal feed to the cleaning plants were analyzed for mercury and chlorine and the results compared with analysis of the as-fired coals. In addition, raw coal samples of the baseline Ohio 5/6 coal were analyzed for mercury. The mercury analyses of the raw coals were used to predict mercury emissions from firing the raw coal and the predicted emissions were compared with the measured emissions firing the cleaned coals.

6.2 Coal Selection

Review of the literature indicates that pre-combustion coal cleaning provides for some level of mercury emissions reduction. Coal cleaning as a means of trace metal emissions abatement has the advantages of relatively low cost, improved boiler efficiency, and the reduction of other emissions. Approximately 77% of eastern and Midwestern bituminous coal shipments are cleaned to meet customer specifications on heating value, ash, and sulfur content.[40] The average for Ohio coals is comparable at 69% based on 1995 reports from Ohio's coal preparation plants.[41] The average 21% reduction in the coal mercury concentration due to coal cleaning is based on the limited available data presented in Table 6.1[42]. Reported mercury removal due to coal cleaning is highly variable. No publicly available data on mercury reduction for cleaning Ohio coals was found. To establish mercury removal efficiencies attainable by coal cleaning for *commercially viable coals* as recommended by the U.S. EPA, Ohio coal should be included.

Mercury is generally reported to be associated with large dense minerals such as pyrite. Conventional cleaning techniques rely on the differences in density or surface properties to separate organic and inorganic coal components. Much of the mineral matter is liberated during conventional cleaning. On this basis, Finkelman predicted mercury reductions of 25-50% could be achieved by conventional coal cleaning[43]. The overall mercury removal average of 21% suggests that mercury removal by coal cleaning may not be governed by a simple mineral matter association. Akers and Dospoy compared the amount of mercury which could be removed by physical cleaning with the ash content of the coal[44]. Although a direct relationship was evident, the amount of mercury removal was both coal-specific and a function of the method of cleaning.

Table 6.1 Mercury Reduction by Conventional Coal Cleaning [42]

Seam	State	% Removal Mercury
C. Appalachian A		-11
C. Appalachian B		8.3
Illinois	IL	55
Illinois #6	IL	43
Illinois #6	IL	-8.3
Illinois # 2,3,5,	IL	17
Illinois # 2,3,5,	IL	42
Kentucky #11	KY	20
Kentucky #9 & #14	KY	13
L. Kittanning	PA	23
Pittsburgh	PA	20
Pittsburgh	PA	15
Pittsburgh	PA	7.7
Pittsburgh A	PA	27
Pittsburgh B	PA	36
Pittsburgh C	PA	7.1
Pittsburgh D	PA	-20
Pittsburgh E	PA	20
Pratt	AL	3.4
Pratt	AL	29
Pratt/Utley	AL	21
Sewickley	PA	0
Upper Freeport	PA	-200
Upper Freeport	PA	64
Upper Freeport	PA	60
Utley	AL	21
	Average	**21**

The Test Series 3 coals were selected on the basis of the mercury and chlorine contents of the as-fired coals, Ohio production, and use for power generation. To date, the majority of testing performed in Phases I and II of the AECDP has been with an Ohio 5/6 coal blend. Limited tests for mercury control across the dry scrubber/baghouse system were also conducted with Mahoning 7A coal in Phase II.

Chlorine is generally present between 200 - 2000 ppm in coal mined in the United States.[45] The chlorine content in coal from specific areas (Illinois, United Kingdom) can exceed 8,000 ppm. The average chlorine content in raw Ohio coal is approximately 750 ppm as reported by the Ohio Division of Geological Survey (OGS).[46] Chlorine concentrations up to 2200 ppm and as low as 35 ppm have been measured. The coal chlorine content has been reported to impact the ratio of oxidized to elemental mercury emissions from coal-fired boilers. Felsvang, Bloom, and Meij have all observed high concentrations of oxidized mercury in utility flue gas when the coal had high chlorine content[47,48,49]. These observations can be largely explained by equilibrium calculations for coal combustion systems[45]. The high level of oxidized mercury control measured across the wet scrubber in previous AECDP test series suggest that the coal chlorine content may, therefore, influence the mercury behavior in FGD systems.

The coal chlorine and mercury concentrations for the project test coal are presented in Figure 6.1 where the as-fired values are normalized to the Ohio averages based on raw coal analysis from the OGS. The baseline Ohio 5/6 coal contained average levels of chlorine. The Meigs Creek (No. 9) and Lower Freeport (No. 6A) coals were selected to provide a broader range of coal chlorine content based on historical analysis. The Meigs Creek coal was expected to provide a chlorine content significantly below the average for Ohio coals. However, the measured value of 660 ppm exceeded the expected value of around 200 ppm.

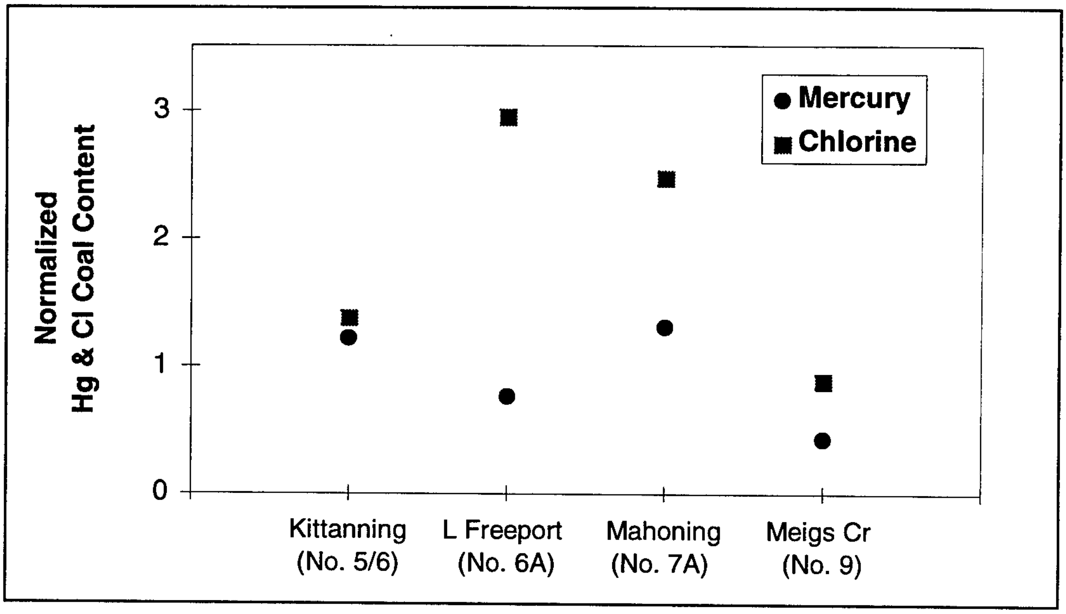


Figure 6.1 Comparison of Normalized Mercury and Chlorine Contents of Ohio Coals

The Meigs Creek and the Lower Freeport coals also have lower mercury concentrations in comparison to the previously evaluated Ohio 5/6 and Mahoning coals. The differences in the relatively low mercury content of the coals should not influence the chlorine concentration study on speciated mercury emissions. Table 6.2 summarizes the average as-fired mercury and chlorine contents of the AECDP Phase II test coals.

Table 6.2 Comparison of Mercury and Chlorine Concentration - AECDP Phase II Coals

Seam	**Mercury [ppm]**	**Chlorine [ppm]**
Ohio 5/6	0.25	1,100
Mahoning 7A	0.27	700
Lower Freeport 6A	0.16	2,180
Meigs Creek 9	0.09	660

The Ohio 1995 production statistics from the Ohio Department of Natural Resources, Division of Geological Survey for several major coal seams are compared in Figure 6.2.[41] The Pittsburgh (No. 8) coal was the most heavily mined seam, followed by the Clarion (No. 4), the Lower Kittanning (No. 6), and Meigs Creek (No. 9) seams. During 1997, the Ohio coals fired in the highest quantities at American Electric Power (AEP) included the Clarion, Meigs Creek , Pittsburgh, and Lower Freeport seams. The Ohio coals supplied in the largest volumes to Ohio Edison include the Pittsburgh, Lower Freeport, Upper Freeport, and Brookville seams.

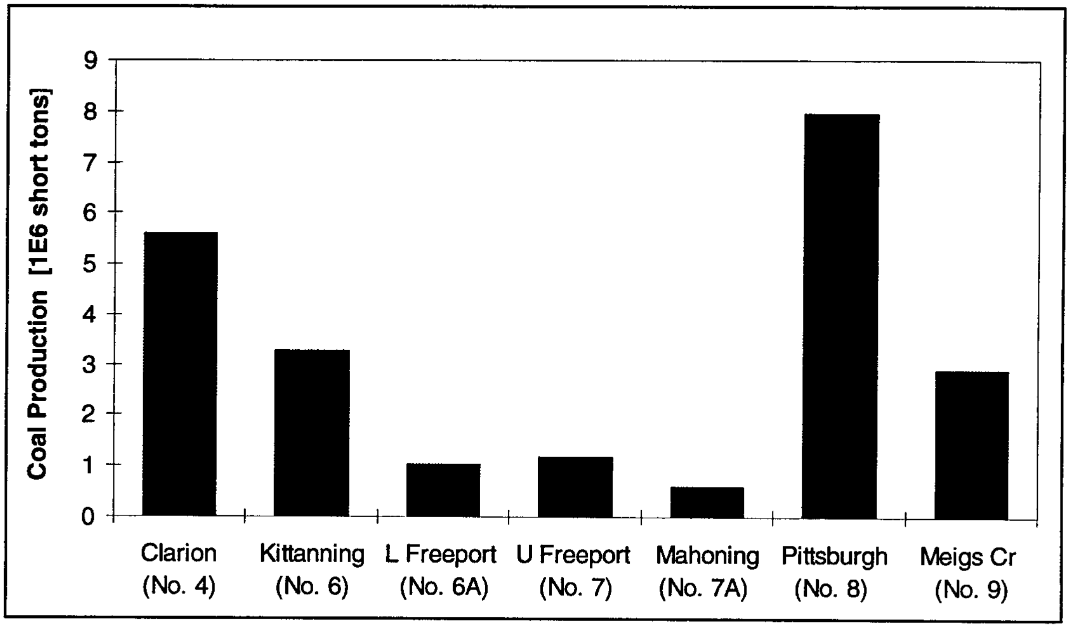


Figure 6.2 1995 Ohio Coal Production

The Lower Freeport and Meigs Creek coals met the project coal selection criteria. Both coals are representative of the mining and utility industries and provide a substantial range of mercury and chlorine coal contents. The selection of these coals (in addition to the previously tested coals) supports the research need specified in the final interim EPA report, *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units,* that more data is needed to verify the association between coal chloride concentration and mercury speciation[42]

6.3 Facility Operation

Two bituminous coals mined in Ohio, washed in commercial cleaning plants and fired in utility power boilers were fired in McDermott Technology's 100 MBtu/hr CEDF fitted with a B&W low-NO_x burner. The average flue gas properties with operation of the CEDF for the two test coals are summarized in Table 6.3. The SO_2 and O_2 measurements were taken at the scrubber inlet. The CO and NO_x measurements were made at the boiler convection pass outlet.

Table 6.3 - Flue Gas Composition

Flue Gas Component	Ohio 6A	Meigs Creek
NO_x, ppm	< 300	< 300
SO_2, ppm	1,610	2,960
CO, ppm	< 100	< 50
O_2, %	4.4	4.6
HCl, lb/10^{12} Btu	132,900	49,600
Particulate, lb/10^6 Btu	3.4	7.1

The HCl content of the flue gas was measured upstream of the wet scrubber using EPA Method 26A. For each coal, replicate HCl measurements at the ESP inlet, baghouse inlet and scrubber inlet were comparable with a percent relative standard deviation (PRSD) of approximately 2%. Uncontrolled measured emissions of 132,900 lb/trillion Btu (~180 ppm) were comparable to the predicted emissions (157,000 lb/trillion Btu) based on the Ohio 6A coal heating value and chlorine content. Uncontrolled measured emissions of 49,600 lb/trillion Btu (~65 ppm) were comparable to the predicted emissions (53,000 lb/trillion Btu) based on the Meigs Creek coal-heating value and chlorine content. The uncontrolled emissions were primarily detected in the vapor-phase at 99.3% and 97.5% for the Ohio 6A and Meigs Creek coals, respectively. On average, 97.9% of the total vapor-phase emissions were collected in the sulfuric acid impingers and the remaining 2.1% was collected in the NaOH impinger solutions for both coals. The percentage of the acid gas emissions collected in the NaOH impinger was consistent for the bituminous coals tested; the percent collected in the NaOH impingers averaged 2.6% for the Ohio 5/6 coal. Under the assumption that Method 26A accurately speciates, chlorine gas emissions from firing the Ohio 6A and Meigs Creek coals averaged 2.0 and 0.7 ppm, respectively.

6.3.1 Particulate Control Equipment

Key average operating conditions for the particulate control equipment are summarized in Table 6.4. The baghouse operating temperature was generally 40 to 50°F lower than the ESP operating temperature as a result of heat loss from the partial flow flue work. The baghouse was operated with GORE-TEX® membrane fabric bags. The bags were cleaned when the pressure drop across the baghouse reached the same value when operating with both coals.

Table 6.4 - Particulate Control Equipment Operating Conditions

	Ohio 6A	Meigs Creek
ESP		
SCA (ft^2/kacfm)	285	281
Inlet Temperature (°F)	359	379
Average Temperature (°F)	349	368
Average FGD Inlet Temperature (°F)	306	324
Baghouse		
Air-to-cloth ratio (ft/min)	4.0	4.0
Pressure drop (in. H_2O)	5.2	5.6
Inlet Temperature (°F)	328	332
Average Temperature (°F)	310	313
Average FGD Inlet Temperature (°F)	280	284

6.3.2 *Wet Scrubber*

The wet scrubber was operated at similar conditions for both the Ohio 6A and Meigs Creek coals. The scrubber operating conditions were selected to provide for comparison with the mercury and SO_2 results from Test Series 2. The scrubber was configured as a tray tower and operated as a limestone forced oxidation system at a constant superficial gas velocity. The nominal scrubber operating conditions are summarized in Table 6.5. The inlet flue gas temperature averaged 282°F for operation downstream of the baghouse and 314°F with scrubber operation downstream of the ESP. SO_2 removal efficiency averaged 96% for the Ohio 6A coal and 91% for the higher sulfur Meigs Creek coal.

Table 6.5 - AECDP Wet Scrubber Operating Parameters

Inlet Flue Gas Flow (acfm)	2050 acfm
Inlet Flue Gas Temperature (F)	275 - 325 °F
Nominal Slurry pH	5.4
Nominal L/G	125 - 130 gal/1000 acf
Oxidation Air Stoichiometry (mol O_2/mol SO_2 absorbed)	5 - 6 mol/mol
SO_2 Removal Efficiency	85 - 95%

6.4 Sampling and Analytical Procedures

Mercury emissions were measured at three locations - uncontrolled emissions from the CEDF, emissions downstream of the particulate collection equipment and emissions from the wet flue gas desulfurization (FGD) system. Mercury measurements were made using the Ontario Hydro method with the same sampling time, rate and KCl impinger sample preservation technique used in the second test series. The Ontario Hydro method was employed to provide an indication of the relative amount of oxidized mercury species and elemental mercury in the flue gas. EPA Method 29 was used to verify the total mercury emissions measured for both coals. Figure 6.3 presents a comparison of the average mercury concentration measured with the Ontario Hydro method to an EPA Method 29 check sample for each coal. The error bars shown in Figure 6.3 represent the range of mercury measurements at the boiler exit using the Ontario Hydro method. Mercury measurements with the two methods generally agree well with a slight high bias for the Ontario Hydro method.

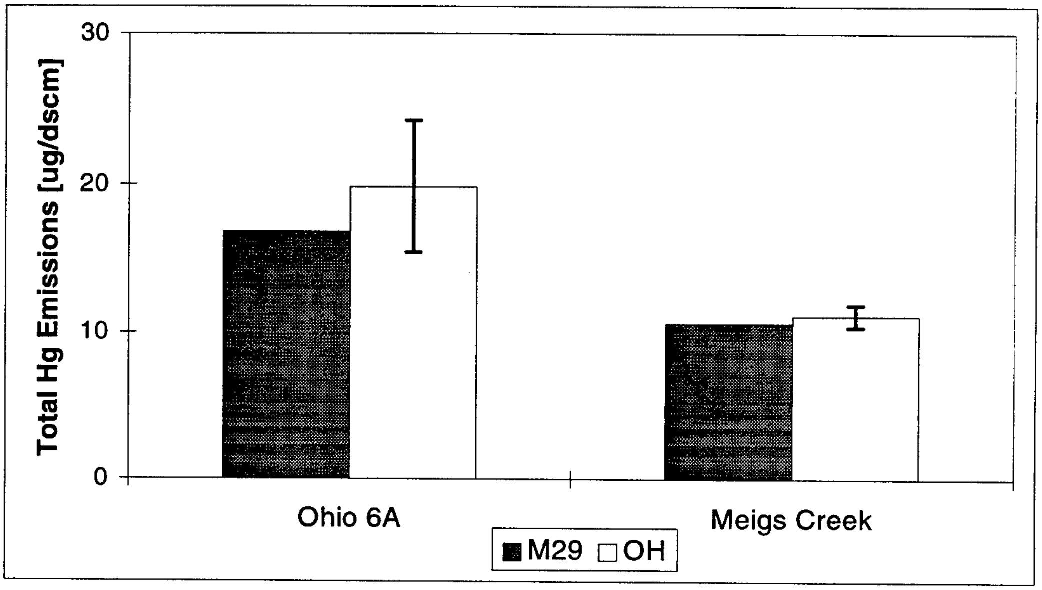


Figure 6.3 Comparison of Total Uncontrolled Mercury According to EPA Method 29 and Ontario Hydro Methods

6.5 Coal Cleaning

The coals characterized in Phase II were cleaned at three different commercial wash plants. The Meigs Creek coal was obtained from AEP's Muskingum Preparation Plant located in Cumberland, Ohio. The coal preparation circuit for the Meigs Creek coal consists of jigs, cyclones, centrifuges, and thickeners. The Lower Freeport coal was obtained from Harrison Mining which supplies the coal to Ohio Edison and AEP. Washing of the Lower Freeport coal is done on-site at Harrison Mining and involves the use of a heavy media washer, heavy media cyclone, and spirals. The Ohio 5/6 blend was provided by Holmes Limestone. Preparation included blending followed by crushing to a 4-inch top size, a water jig (1.55 specific gravity wash), and drying.

6.5.1 *Coal Cleaning Impacts*

The contribution of coal cleaning toward the reduction of mercury emissions from coal-fired electric utility boilers was examined. About 75 to 80% of the bituminous coal consumed by the power generation industry is cleaned to some extent. The Lower Freeport, Meigs Creek and Ohio 5/6 represent commercially cleaned coals, as did the Ohio 5/6 blend that was fired in Phase II Test II. The Ohio 5/6 Blend was fired in the SBS which has been shown to generate comparable levels and forms of mercury emissions to those from the CEDF.

Samples of the raw coal feed to the cleaning plants were analyzed for mercury and chlorine and the results were compared with analysis of the as-fired coals. Mercury emissions are affected by the coal composition and heating value in addition to the mercury concentration. The mercury analyses of the coals were used to predict mercury emissions from firing both the raw and cleaned coals, and the predicted emissions were compared with the measured emissions from firing the cleaned coals. Tables 6.6 through 6.8 summarize results of the coal analyses, emission predictions and measured emissions for each of the three coals. The average properties of the raw and cleaned coals and the corresponding percent reduction are presented to show the effects of cleaning.

Table 6.6 Impact of Coal Cleaning on Coal Composition and Mercury Emissions-Ohio 6A

Ohio #6A (CEDF)

Constituent	Raw	Washed	% Reduction
Ash (% dry)	21.71	6.73	69
Sulfur (% dry)	3.36	2.4	29
Chlorine (% dry)	0.187	0.218	-17
Chloride Predicted (lb/10^{12} Btu)	163404	157015	4
Btu/lb (dry)	11444	13884	-21
Btu/lb (MAF)	14618	14870	-2
Hg (ppm in coal)	0.3	0.16	47
Moisture.%	2.12	2.56	-21
Hg Predicted (lb/tr Btu)	26.22	11.52	56
Hg Actual (lb/tr Btu) - Ontario Hydro	N/A	13.79 ± 2.31	.
- M29	N/A	12.00	.

▨ Analysis performed by CONSOL, Inc.
Analysis performed by MTI

Table 6.7 Impact of Coal Cleaning on Coal Composition and Mercury Emissions-Meigs Creek

Meigs Creek #9 (CEDF)

Constituent	Raw	Washed	% Reduction
Ash (% dry)	24.54	13.54	45
Sulfur (% dry)	5.6	4.08	27
Chlorine (% dry)	0.064	0.066	-3
Chloride Predicted (lb/10^{12} Btu)	59802	53029	11
Btu/lb (dry)	10702	12446	-16
Btu/lb (MAF)	14183	14370	-1
Hg (ppm in coal)	0.14	0.09	36
Moisture %	2.12	3.12	-47
Hg Predicted. (lb/tr Btu)	13.08	7.23	45
Hg Actual (lb/tr Btu) - Ontario Hydro - M29	N/A N/A	8.06 ± 0.77 7.63	. .

▨ Analysis performed by CONSOL, Inc
░ Analysis performed by MTI

Table 6.8 Impact of Coal Cleaning on Coal Composition and Mercury Emissions-Ohio 5/6

Ohio 5/6 Coal Blend (SBS; Phase II-Test II)

Constituent	Raw	Washed	% Reduction
Ash (% dry)	12.9	5.83	55
Sulfur (% dry)	5.26	3.11	41
Chlorine (% dry)	0.128	0.137	-7
Chloride Predicted (lb/10^{12} Btu)	102090	100743	1
Btu/lb (dry)	12538	13599	-8
Btu/lb (MAF)	14394	N/A	
Hg (ppm in coal)	0.31	0.18	42
Moisture %	2.31	2.73	-18
Hg Predicted (lb/tr Btu)	24.73	13.24	46
Hg Actual (lb/tr Btu) - Ontario Hydro - M29	N/A N/A	12.48 ± 2.23 11.41 ± 2.57	. .

▨ Analysis performed by CONSOL, Inc.
░ Analysis performed by MTI

One test objective was to evaluate the effect of cleaning on the coal mercury and chlorine concentrations. Chlorine was enriched during cleaning for the bituminous coals indicating that chlorine concentrations are lower in the ash fractions than they are for the bulk raw coals. Coal cleaning produced a significant decrease in mercury concentration for all three coals, with mercury reductions ranging from 36 to 47 percent. As expected, sulfur also decreased as a result of cleaning for all three of the coals, with decreases ranging from 27 to 41 percent. Coal cleaning increases the heating value of coals providing an additional reduction in the actual emissions of these constituents (i.e. mercury, chlorine, and sulfur) since less mass of coal is fed to the boiler. This is reflected by the higher percentage reductions in predicted mercury and chloride emissions relative to reductions in the coal concentrations.

For the three Ohio coals evaluated, the reduction in mercury concentration from washing correlates with the percent reduction of ash (Figure 6.4). Based on these results, pre-combustion cleaning for mercury reduction in Ohio coals appears to be related to the efficiency of the ash removal. The complexity of the cleaning process was not observed to have an effect on the mercury removal beyond the efficiency of the ash removal. For comparison, the predicted reductions of mercury emissions resulting from the cleaning processes are also provided in Figure 6.4. The percent reduction in mercury emissions due to cleaning exceeds the percent change in the mercury coal content due to the higher heating value of the cleaned coals. The differences in the slopes of the two curves reflect the varied degrees of change in the coal heating value resulting from cleaning.

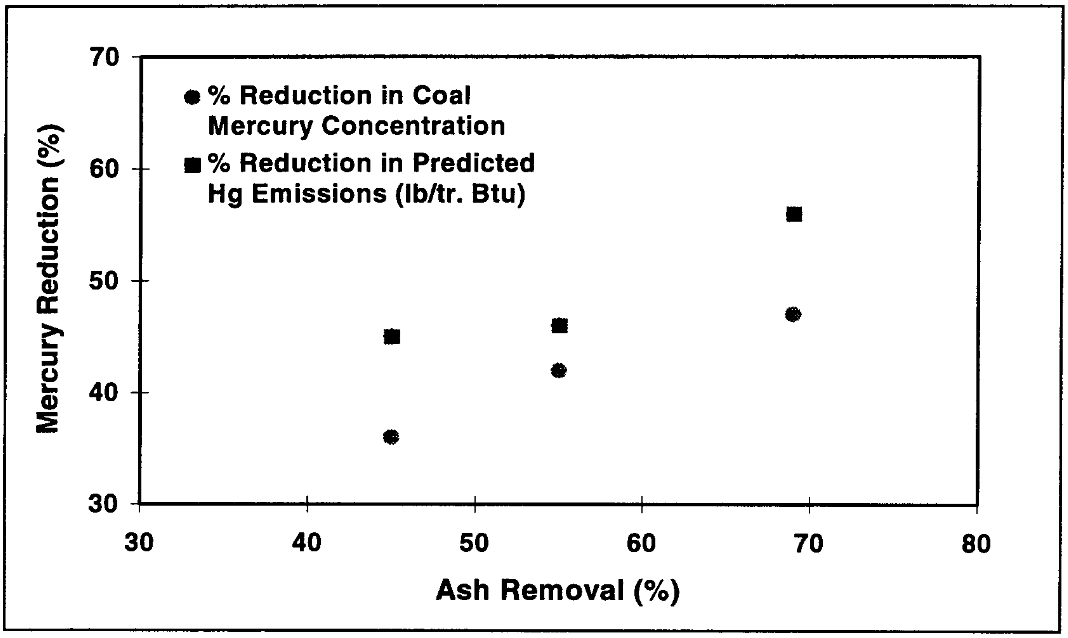


Figure 6.4 Effects of Coal Cleaning on Mercury Concentrations

Measured values of the mercury emissions were only obtained for the washed coals, as the raw coals were not fired to reflect commercial practice. The impact of coal cleaning on total mercury emissions was predicted on the basis of the raw and cleaned coal analysis. These predictions assume that mercury does not partition to the boiler ash and 100 percent of the mercury exits the furnace in the flue gas stream. (i.e., emission modification factor = 1). The effectiveness of the predictions is illustrated in Figure 6.5. Figure 6.5 compares the predicted and measured uncontrolled furnace emissions for each of the three coals. Measured emissions on the basis of Method 29 and Ontario Hydro sampling procedures are in agreement. The left half of the graph provides the results in units of lb/10^{12} Btu and the right half shows the values in µg/dscm. As can be seen, there is good agreement between the measured and predicted values for all of the coals tested.

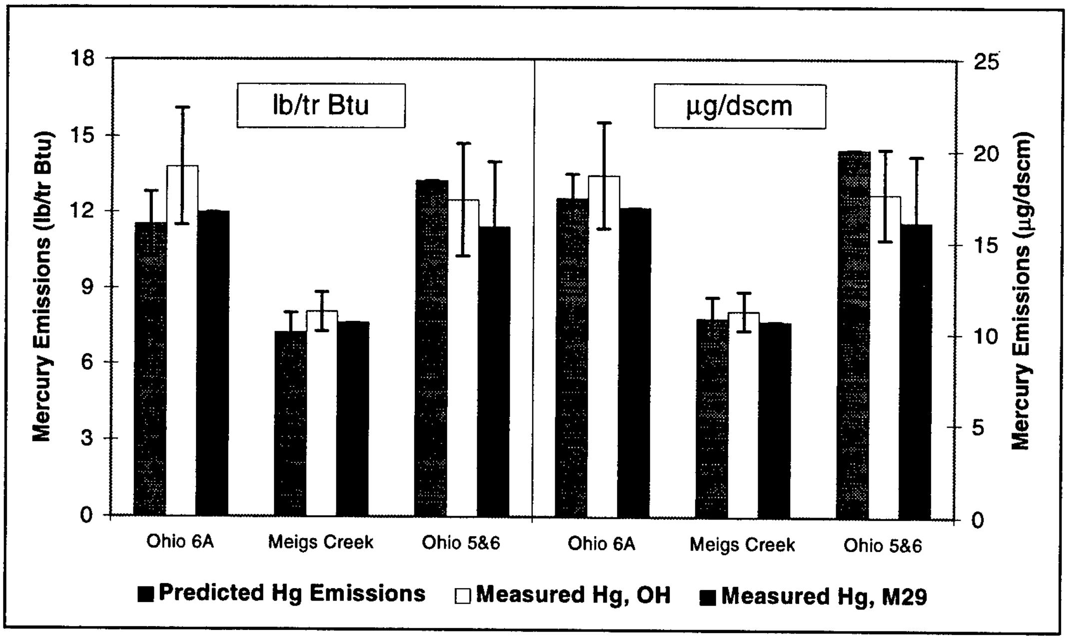


Figure 6.5 Summary of Predicted and Measured Uncontrolled Mercury Emissions - Three Coals

6.5.2 *Mercury Correlation to Coal Pyritic Sulfur*

In order to establish whether mercury is associated with the pyrite in coal, several of the washed coals fired in Phases I and II were analyzed for the various sulfur forms. The results are summarized in Table 6.9. For the three coals evaluated, the correlation of mercury and pyritic sulfur concentrations is poor. However, a tentative correlation exists between the mercury and organic sulfur in the washed Ohio test coals.

Table 6.9 Pyritic Sulfur and Mercury Content in Test Coals

	Phase I Ohio 5/6	**Phase II Ohio 5/6**	**Phase II Mahoning 7**	**Phase II Ohio 6A**
Pyritic, % as S	1.24	1.34	1.33	1.48
Sulfate, % as S	0.07	0.04	0.04	0.01
Organic, % as S	1.64	1.78	1.80	0.98
Mercury, ppm	0.24	0.25	0.27	0.17

6.5.3 *Coal Property Impacts on Mercury Speciation*

The spilt between particulate-and vapor-phase mercury and the distribution of vapor-phase mercury species is believed to be a function (in part) of the properties of the coal fired in the boiler. A primary coal constituent believed to affect mercury speciation is chlorine. The four bituminous test coals (i.e., Ohio 5/6 Blend, Mahoning 7, Ohio 6A, and Meigs Creek 9) were selected to provide a wide range of coal chlorine concentration. Uncontrolled mercury and acid gas emission measurements were conducted at the CEDF air heater exit for the Ohio 6A and Meigs Creek 9 coals during the third test series. The results were combined with those from previous testing to evaluate the effect of coal chlorine concentration on mercury speciation.

Figure 6.6 provides the percentages of mercury in the oxidized form based on the Ontario Hydro method as a function of the chlorine content of the coal. The data show essentially no trend of the coal chlorine concentration on the mercury speciation, with the exception that the portion of oxidized mercury emissions exceeded 76% for all four bituminous coals. The Meigs Creek 9 and Ohio 6A coals utilized in the third test series expanded the range of coal chlorine content in the test coals, but the Meigs Creek 9 coal did not provide a normalized chlorine ratio less than one as anticipated. Therefore, the curve does not cover the effect of chlorine concentrations significantly below the average for Ohio coals. Future selection of a bituminous coal with a chlorine concentration less than 400 ppm would be beneficial to complete the study of coal chlorine concentration on mercury speciation for Ohio bituminous coals.

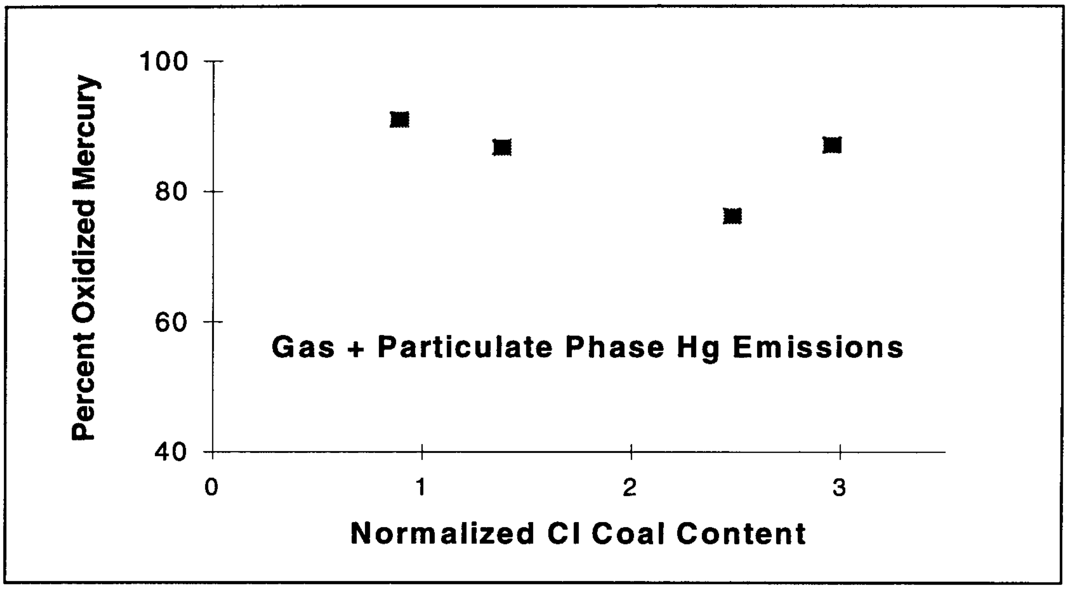


Figure 6.6 Oxidized Portion of Uncontrolled Mercury Emissions as a Function of Coal Chlorine Content

Conventional wisdom holds that the mercury adsorbed onto the particulate was originally in the oxidized form in the vapor state. Although the coal chlorine concentration did not trend with the vapor-phase oxidized mercury emissions, the relationship of the coal chorine content and percentage of mercury on the particulate was examined. This evaluation was performed to determine if increases in chlorine concentration would promote an increase in the fraction of mercury that partitions to the particulate phase. As can be seen from Figure 6.7, no relationship was found for the four test coals.

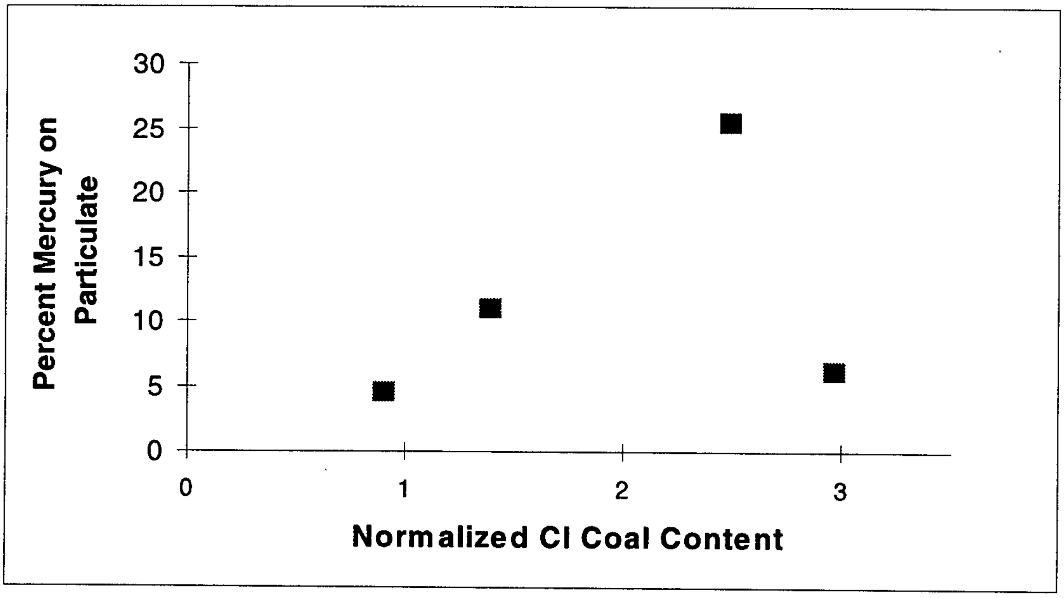


Figure 6.7 Percentage of Mercury on Particulate as a Function of Normalized Coal Chlorine Content

6.6 Equipment Performance

Particulate emissions from the ESP and baghouse for the Ohio 6A and Meigs Creek 9 coals are summarized in Figure 6.8. The ESP operating conditions were selected to provide a particulate loading of approximately 0.03 lb/10^6 Btu to the scrubber typical of commercial system operation. The ranges of particulate loading measurements for each coal/device combination are indicated in Figure 6.8. The particulate loading to the scrubber was significantly higher for the ESP/scrubber configuration. For the Ohio 6A coal, the particulate loading at the ESP inlet averaged 3.36 lb/10^6 Btu. The particulate loading at the ESP inlet averaged 7.07 lb/10^6 Btu for the higher ash Meigs Creek coal.

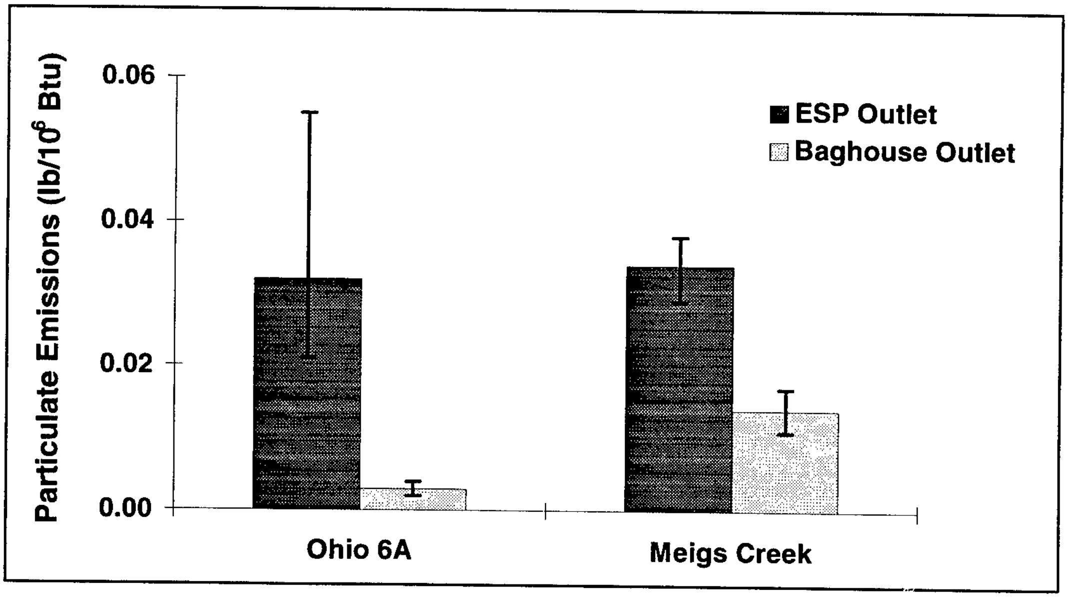


Figure 6.8 Particulate Emissions from ESP and Baghouse

The scrubber operating conditions were selected to provide for comparison with the results from Phase II Test Series 2. SO_2 removal efficiency averaged 96% for the Ohio 6A coal and 91% for the higher sulfur Meigs Creek coal. The scrubber was operated essentially as an open loop system with discharge of the system blowdown to control the solids loading in the recirculaton tank. This technique was used to provide a relatively constant dissolved chloride level in the absorber recirculating slurry of approximately 3,000 to 5,000 ppm despite a significant difference in chlorine concentrations in the scrubber inlet flue gas for the two coals.

6.6.1 Particulate Device Mercury Control

Particulate-Phase Mercury Control by ESP and Baghouse

The average reduction of particulate-phase mercury emissions across the ESP and baghouse for both coals is summarized in Figure 6.9. The mass emissions of particulate-phase mercury are significantly reduced by the particulate control equipment. Particulate mercury removal achieved by the ESP and baghouse exceeded 92% for the Ohio 6A and Meigs Creek coals. However, the concentration of mercury on the particulate collected in the flue gas sample train was generally higher at the particulate control device outlet than at the inlet as summarized in Table 6.10. This most likely reflects a higher concentration of mercury in the fine particulate, which penetrate the collection devices. This trend was also observed during the first test series.

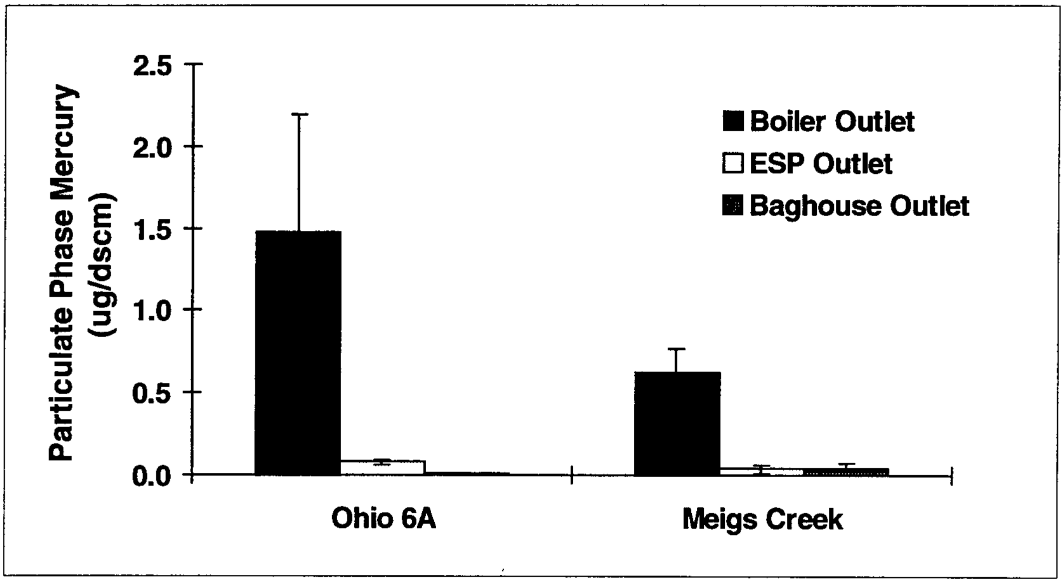


Figure 6.9 Particulate Mercury Emissions from ESP and Baghouse

Table 6.10 Particulate-Phase Mercury Emissions Summary

	Ohio 6A	Meigs Creek
Boiler Outlet		
Hg Concentration on Particulate (ppm)	0.27 ± 0.10	0.05 ± 0.01
Particulate Hg Mass Emissions (µg/dscm)	1.48 ± 0.69	0.63 ± 0.12
Average Fly Ash LOI @ 800 C (%)	5.04 ± 1.17	1.80 ± 0.16
ESP Outlet		
Hg Concentration on Particulate (ppm)	1.46 ± 0.57	0.63 ± 0.47
ESP Particulate Hg Mass Emissions (µg/dscm)	0.08 ± 0.02	0.04 ± 0.03
ESP Particulate Hg Control (%)	94.6	93.6
Baghouse Outlet		
Hg Concentration on Particulate (ppm)	1.11 ± 0.63	1.95 ± 0.45
Baghouse Particulate Hg Mass Emissions (µg/dscm)	0.006 ± 0.005	0.046 ± 0.020
BH Particulate Hg Control (%)	99.6	92.7

Partitioning of the total mercury emissions between the vapor-phase and the particulate-phase measured during AECDP Phase II tests is summarized in Table 6.11. The measured loss-on-ignition (LOI) at 800 °C of fly ash sampled isokinetically from the flue gas stream for each coal is noted. For the two coals evaluated in Phase II Test Series 3, higher particulate-phase mercury was measured on the higher LOI fly ashes. On average, approximately 12% of the total mercury was present on the particulate collected in the sampling train for the bituminous coals fired. For the relatively narrow range of low carbon carryover from the B&W low-NOx burners, the distribution of mercury between the vapor phase and the particulate did not appear to be strongly correlated with fly ash LOI.

Table 6.11 Partitioning of Uncontrolled Mercury Emissions for Bituminous Test Coals

Coal	Flue Gas Temperature (°F)	Total Mercury (µg/dscm)	Vapor- Phase (%)	Particulate-Phase (%)	Fly Ash LOI (%)
Ohio 5/6	333	17.6	88.8	11.2	2.5
Mahoning 7	328	22.3	74.4	25.6	5.7
Ohio 6A	342	20.1	93.8	6.2	5.0
Meigs Creek	358	11.2	95.2	4.8	1.8

However, when the range of carbon carryover is expanded to include results from other MTI test programs, U.S. DOE-FETC pilot-scale coal combustion tests with West Virginia Pittsburgh 8 bituminous coal and field sampling conducted by CONSOL on commercial boilers firing bituminous Illinois coal, a trend of increased particulate-phase mercury with unburned carbon (UBC) emerges.[12,13] The majority of the data in Figure 6.10 are from pulverized coal-fired boilers with the exception of the outlier of 35% UBC on fly ash generated by a cyclone boiler. As carbon carryover is associated with NO_x control and may be related to the mercury control across a particulate control devise, future tests will contribute to this database.

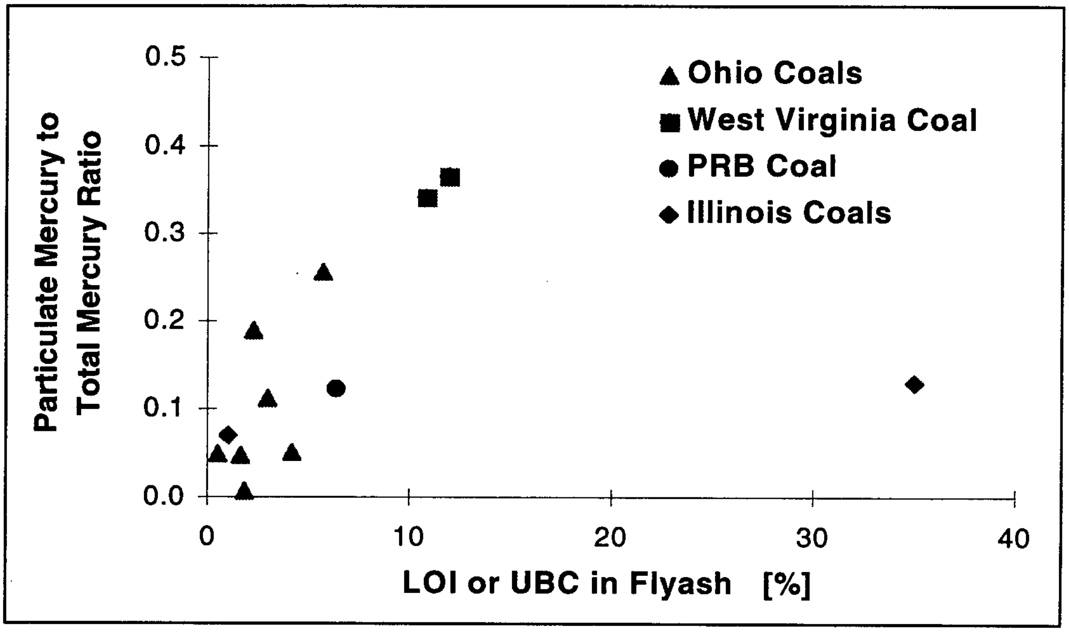


Figure 6.10 Impact of Carbon Carryover on Particulate Mercury Emissions

Impact of Particulate Control System on Vapor-Phase Mercury Speciation

The particulate emissions control equipment upstream of the FGD system may impact the speciation of mercury in the flue gas. Emissions measurements following the baghouse treating partial flue gas flow and an ESP processing the remaining bulk of the gas flow indicate a marked difference in mercury speciation. The fraction of the vapor-phase mercury measured as elemental mercury upstream and downstream of the particulate control equipment using the Ontario Hydro method for three coals is presented in Figure 6.11.

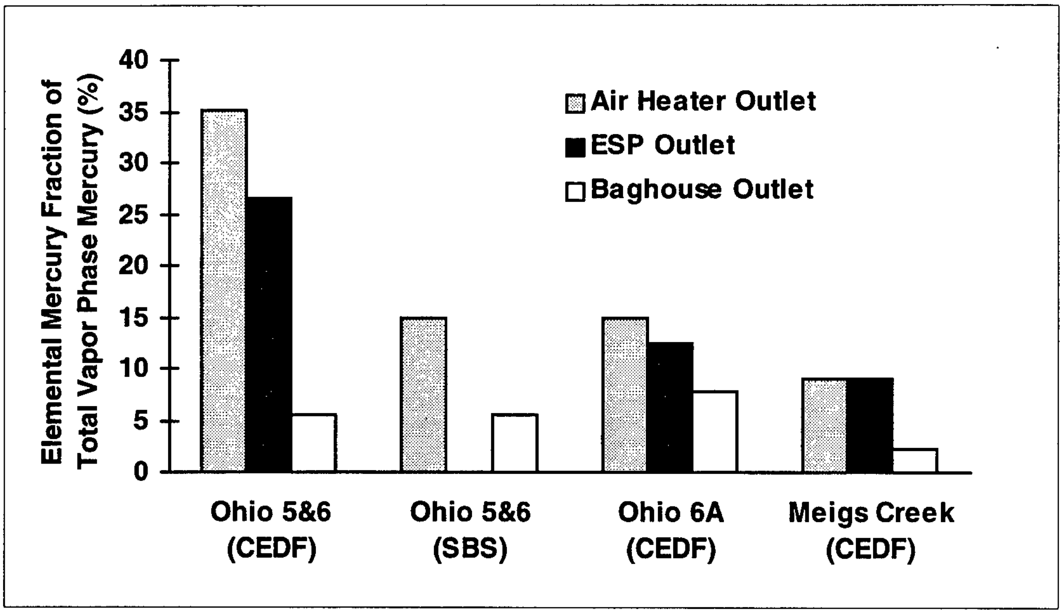


Figure 6.11 Impact of Particulate Control Equipment on Elemental Vapor-Phase Mercury Speciation

Figure 6.11 indicates that the Ohio 6A and Meigs Creek coal fly ash may also catalyze the conversion of elemental mercury to oxidized mercury species as the flue gas passes through the ash filter cake in the baghouse. In previous tests, the Ohio 5/6 fly ash oxidized elemental mercury to the more soluble form across the baghouse filtercake. Similar to operation with the Ohio 5/6 coal, significant species transformation was not generally observed across the ESP for the Ohio 6A and Meigs Creek coal fly ash. The total vapor-phase mercury concentrations were comparable before and after the particulate collection devices.

The ESP had a negligible impact on the elemental mercury concentration for both coals. The average baghouse outlet elemental mercury concentration was 46% lower than at the inlet for the Ohio 6A coal and 72% lower for the Meigs Creek coal. The average baghouse operating temperature (310°F) was similar for both coals. The extent of oxidation of elemental mercury is considerable for the Ohio bituminous coal evaluated; the baghouse outlet elemental mercury concentration was 65 to 70% lower than the inlet for the Ohio 5/6 coal at this common temperature.

Figures 6.12 and 6.13 show the changes in mercury speciation across the ESP and baghouse for the two test coals in Test Series 3. The range of the individual measurements is shown for each average mercury concentration plotted. A reduction in the average concentration of vapor-phase elemental mercury and an increase in oxidized mercury species across the baghouse were observed for both coals at a baghouse temperature of approximately 310°F. The consistent increase in oxidized mercury emissions measured with the Ontario Hydro method confirms that the oxidization of elemental mercury was occurring in the baghouse. Mercury speciation was comparable within the deviation of the measurements performed at the inlet and outlet of the ESP. The Meigs Creek coal data for the ESP configuration was especially consistent.

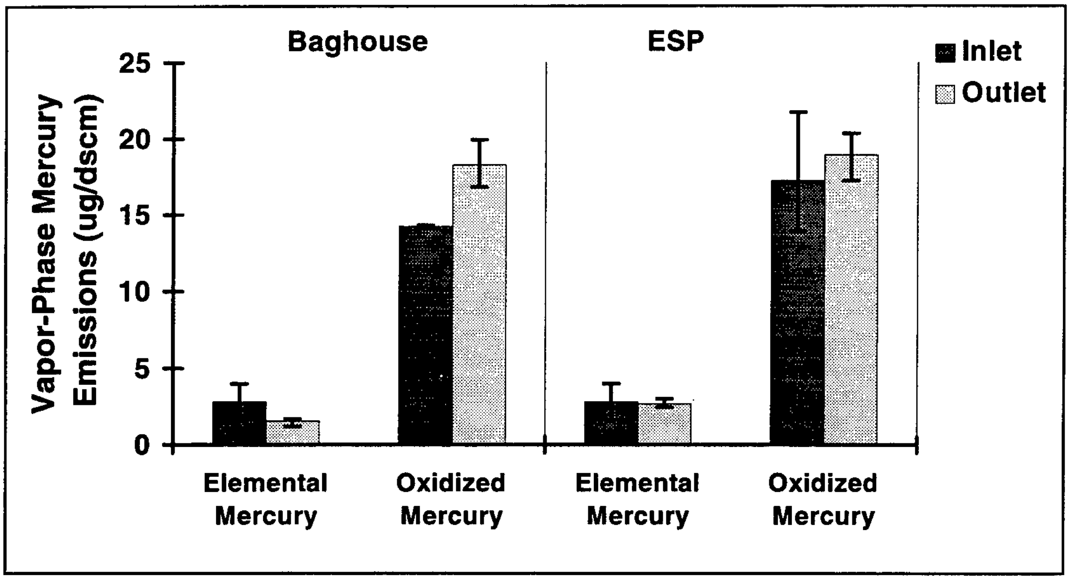


Figure 6.12 Impact of Baghouse and ESP on Vapor-Phase Mercury Speciation - Ohio 6A

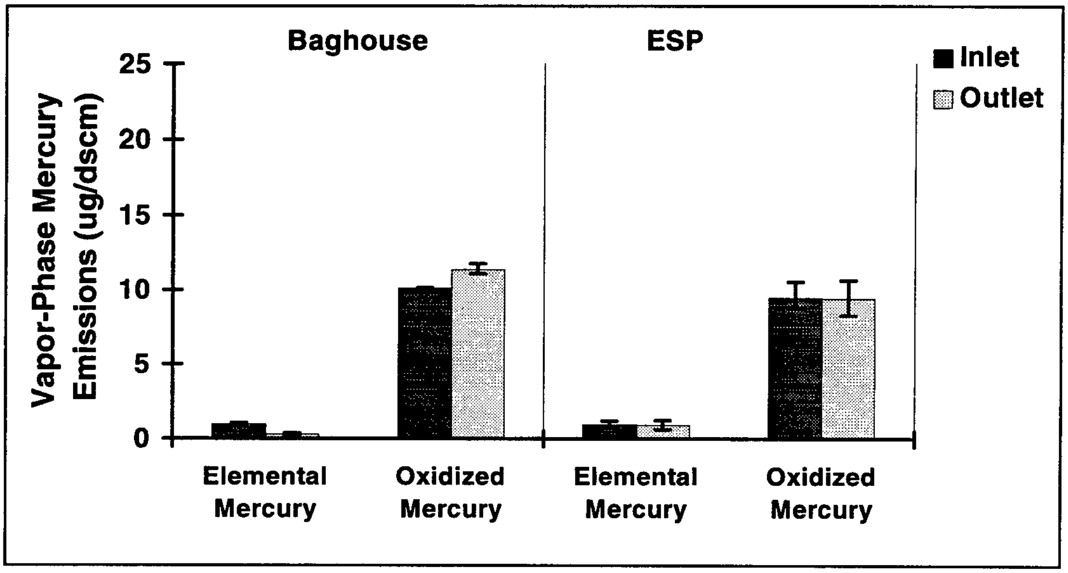


Figure 6.13 Impact of Baghouse and ESP on Vapor-Phase Mercury Speciation - Meigs Creek

The pronounced impact of the baghouse on vapor-phase mercury speciation observed relative to the ESP in these tests may be a function of more intimate contact between the flue gas and the fly ash as the gas passes through the filter cake. The 40 to 50°F flue gas temperature difference between the ESP and baghouse may also impact the relative speciation measured at the wet scrubber inlet.

The difference in the baghouse impact on mercury speciation observed for the two coals may be related to fly ash properties, flue gas composition, and baghouse operation. The baghouse operating conditions were similar for the two coals, but bag cleaning was more frequent for the Meigs Creek coal operation due to the higher ash loading. The Meigs Creek flue gas had a higher concentration of SO_2 and a lower HCl concentration than measured in the Ohio 6A flue gas.

Figures 6.14 and 6.15 are another way to look at the data presented at 6.12 and 6.13. All of the comments made above are valid for the following graphs. Figure 6.14 summarizes the total mercury measured at the inlet and outlet of the ESP for each of three coals, the partitioning of mercury between the particulate and vapor phases, and the distribution of mercury species in the vapor phase. Figure 6.15 summarizes the same information, only for the baghouse. The range bars represent the range of the triplicate or quadruplicate individual measurements from which the average total mercury emissions value is obtained. The average total mercury emissions reduction observed across the ESP is noted for each coal. It should be noted that the removal shown in Figures 6.14 and 6.15 is across the particulate control device only.

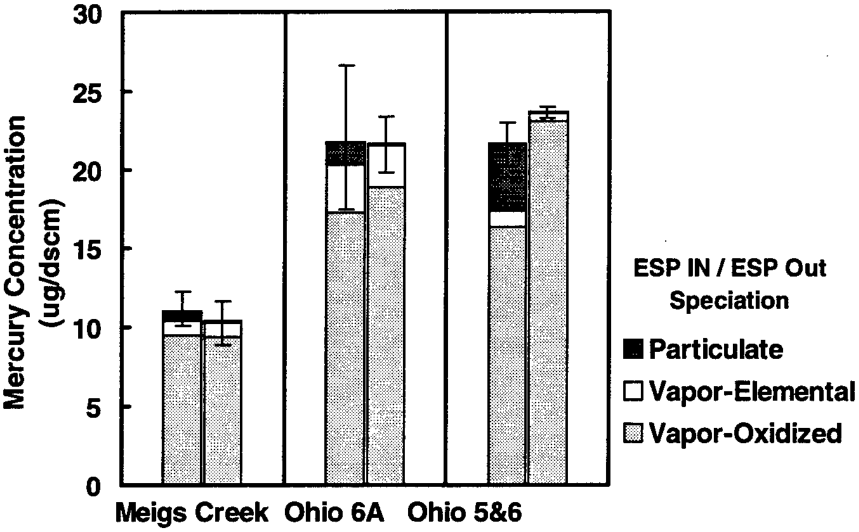


Figure 6.14 – ESP Mercury Measurements

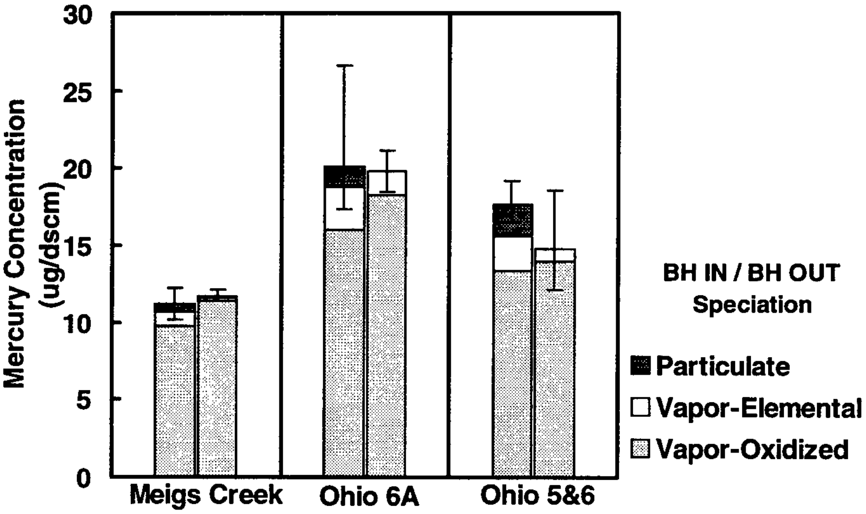


Figure 6.15 – Baghouse Mercury Measurements

The DOE has published data from commercial tests, which indicate an increase in the vapor-phase oxidized mercury concentration is possible across either an ESP or a baghouse based on EPA Method 29 measurements.[52] The most significant increases in oxidized mercury were associated with fly ashes having the highest SO_3, CaO and MgO concentrations in the ash for the test sites reported. The Fe_2O_3 content of these ashes was lower than the other sites. Investigation of the major constituents of the fly ashes produced in Phase II and those to be generated in Phase III for an association with the oxidation of elemental mercury is recommended for Phase III.

In the United States, ESPs are the dominant particulate emissions control systems installed at commercial coal-fired generating plants. The AECDP test data suggests that ESPs remove a significant portion of the particulate-phase mercury but have a limited impact on vapor-phase mercury. The data indicates that a baghouse used for particulate control can have a significant impact on the distribution of mercury species in the vapor phase. Vapor-phase mercury speciation is considered a key factor influencing mercury emissions control downstream of the particulate control equipment.

6.6.2 *Wet Scrubber Device Mercury Control*

FGD Total Mercury Removal Efficiency

The total (vapor and particulate-phase) mercury removal was measured across the scrubber as the scrubber was operated at the nominal conditions listed in Table 6.4. The average total mercury concentration at the inlet and outlet of the scrubber and the FGD system removal for each combination of coal and particulate control device is presented in Figure 6.16. The total mercury emissions control efficiency is noted beside the average outlet emissions bar. The range of mercury removals observed - 23% to 92% - is within the range of FGD system mercury removal reported in the literature.

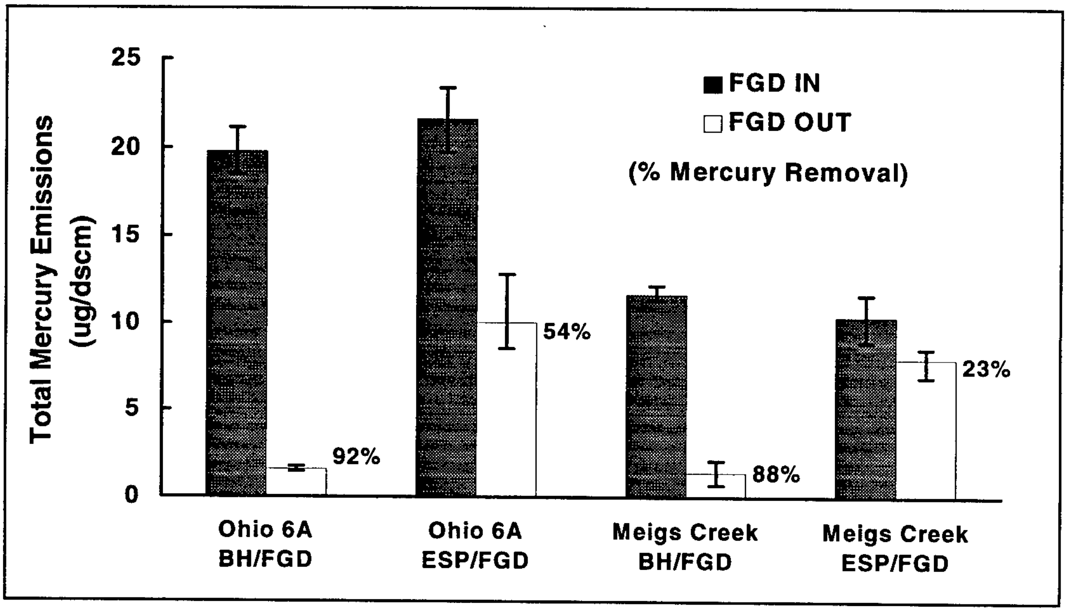


Figure 6.16 FGD Total Mercury Removal Summary

Total mercury emissions control across the scrubber for the same coal was influenced by whether the ESP or baghouse was used for upstream particulate emissions control. An apparent contribution towards improved mercury control results from a higher fraction of oxidized mercury in the flue gas. For the Ohio 6A and Meigs Creek coals, the scrubber was operated downstream of the baghouse first, and then downstream of the ESP for each coal to provide two levels of oxidized mercury at the scrubber inlet. Total mercury removal across the wet scrubber for the Ohio 5/6 coal blend is for the baghouse/wet scrubber configuration.

The measured difference in total mercury control by the scrubber can not be completely attributed to the change in the level of oxidized mercury at the scrubber inlet resulting from operation downstream of the two particulate control devices. Assuming the generally held belief that oxidized mercury is readily removed in the scrubber due to it's high solubility in water, a decrease of 7% in the level of oxidized mercury at the scrubber inlet would not be expected to reduce scrubber mercury removal efficiency by 74% as was observed for the Meigs Creek coal. Analysis of the mercury species distribution before and after the scrubber may provide further insight into the observed range of mercury emissions control performance for the wet scrubber.

Vapor-Phase Mercury Speciation Tracking Across Scrubber

The Ontario Hydro method was used to measure mercury speciation before and after the scrubber with the scrubber operated downstream of the ESP and the baghouse. The vapor-phase mercury speciation measurements are summarized in Figures 6.17 and 6.18 for each combination of coal and particulate/SO_2 emissions control system configuration. The averages of the triplicate inlet measurements are shown with range bars indicating the range of individual measurements.

For both coals, high efficiency oxidized mercury removal was obtained across the scrubber with the baghouse/FGD combination (Ohio 6A-97%, Meigs Creek-91%). On average, a reduction in elemental mercury emissions was also observed for both coals. The average concentration of elemental mercury at the scrubber outlet was 20% lower than at the inlet for the Ohio 6A coal and 7% lower for the Meigs Creek coal.

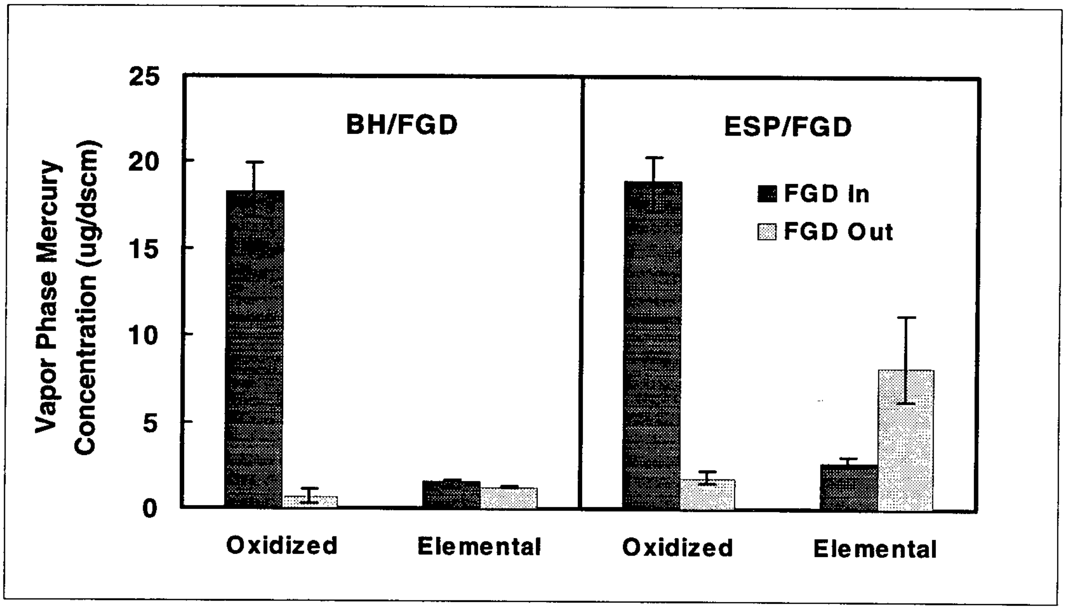


Figure 6.17 Mercury Speciation Across Scrubber - Ohio 6A

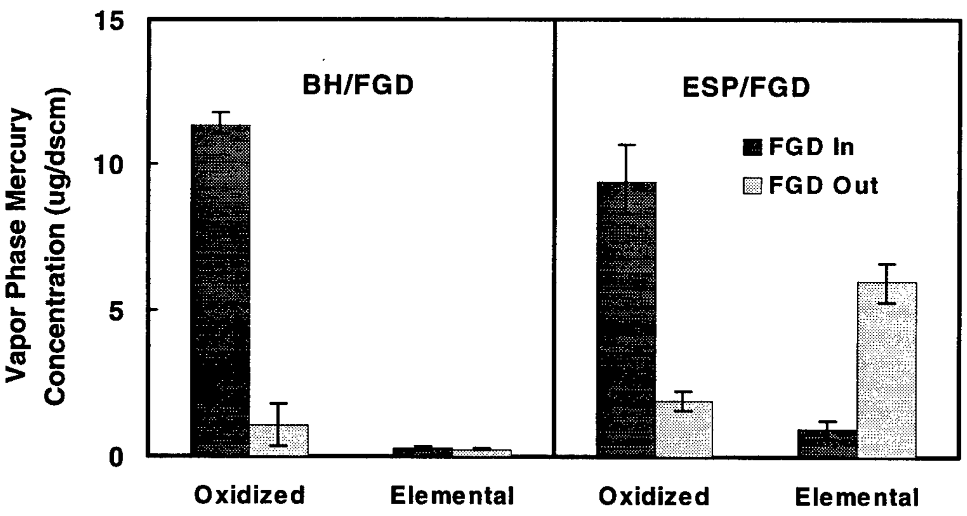


Figure 6.18 Mercury Speciation Across Scrubber - Meigs Creek

The impact of the scrubber on mercury speciation was distinctly different for the ESP/FGD system configuration. For both coals, reduction of oxidized mercury species emissions remained high (Ohio 6A - 91%, Meigs Creek - 80%) but was lower than the baghouse/FGD system. However, with the ESP/FGD configuration, emissions of elemental mercury were higher at the scrubber outlet than at the inlet for every measurement when the scrubber was operated at the nominal operating conditions. The higher elemental mercury at the scrubber outlet with the Meigs Creek coal was confirmed by triplicate measurements with a percent relative standard deviation (PRSD) of 11%. There was more variation in the Ohio 6A data resulting in a PRSD of 33%. The increased elemental mercury emissions offset the high efficiency oxidized mercury emissions reduction resulting in lower total mercury emissions control. The increase in elemental mercury emissions may be a result of the reduction of absorbed oxidized species in the scrubber and re-emission as vapor-phase elemental mercury. This explanation assumes that the speciation measurements at the scrubber inlet and outlet adequately reflect the actual speciation at these two locations. Or, the increase in elemental mercury may be an artifact of the Ontario Hydro sampling. The likelihood of an influence by a sampling bias may be related to the occurrence of different forms or concentrations of components in flue gas stream exiting a baghouse versus an ESP.

Figure 6.19 is another way to present the data found in Figures 6.17 and 6.18. Figure 6.19 provides the total removal and mercury speciation at the scrubber inlet and outlet for two process configurations. Only the baghouse was used for the Ohio 5 & 6 coal blend.

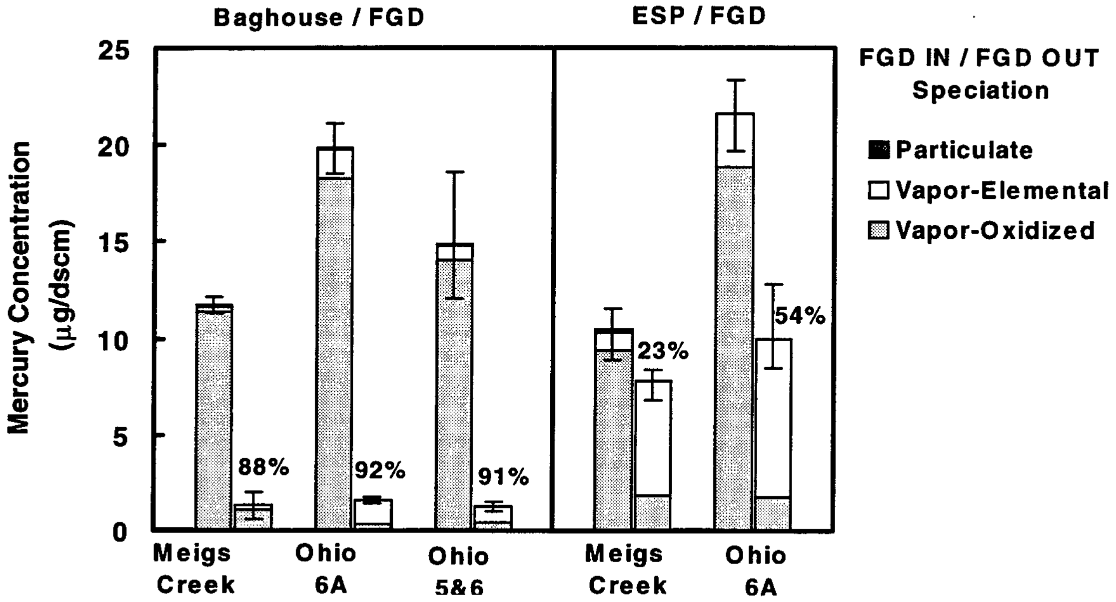


Figure 6.19 – Wet Scrubber System Mercury Removal and Speciation Summary

Operation of the ESP upstream of the scrubber results in several differences at the scrubber inlet relative to the baghouse/ESP combination. Key differences between the ESP and the baghouse that may individually or in combination impact mercury removal across the scrubber include:

- higher level of elemental mercury at the scrubber inlet,
- higher flue gas inlet temperature, and
- higher particulate loading.

Evaluation of the impact of these parameters on scrubber mercury removal is expected to continue in Phase III.

Particulate-Phase Mercury Tracking Across Scrubber

In Test Series 3, efficient particulate collection achieved by the ESP and baghouse limited the particulate-phase mercury to less than 0.5% of the total mercury concentration in the flue gas at the scrubber inlet. Particulate-phase mercury concentrations before and after the scrubber are summarized in Figure 6.20. In general, while still very low, the concentration of particulate mercury in the flue gas increased across the scrubber. This concentration increase may be due to the carry-over of fine gypsum particles from the scrubber containing a higher concentration of mercury than the fly ash at the scrubber inlet. The concentrations of mercury in the particulate at the scrubber inlet and outlet are compared in Figure 6.21. The mass loading of particulates at the scrubber outlet was generally comparable to or less than the loading at the scrubber inlet.

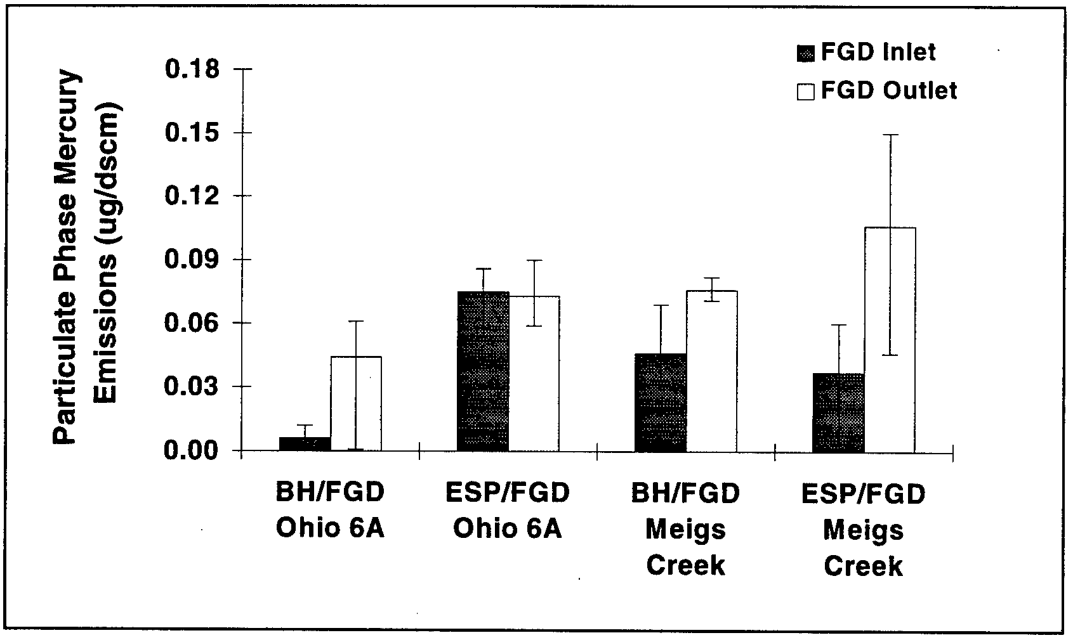


Figure 6.20 Particulate-Phase Mercury

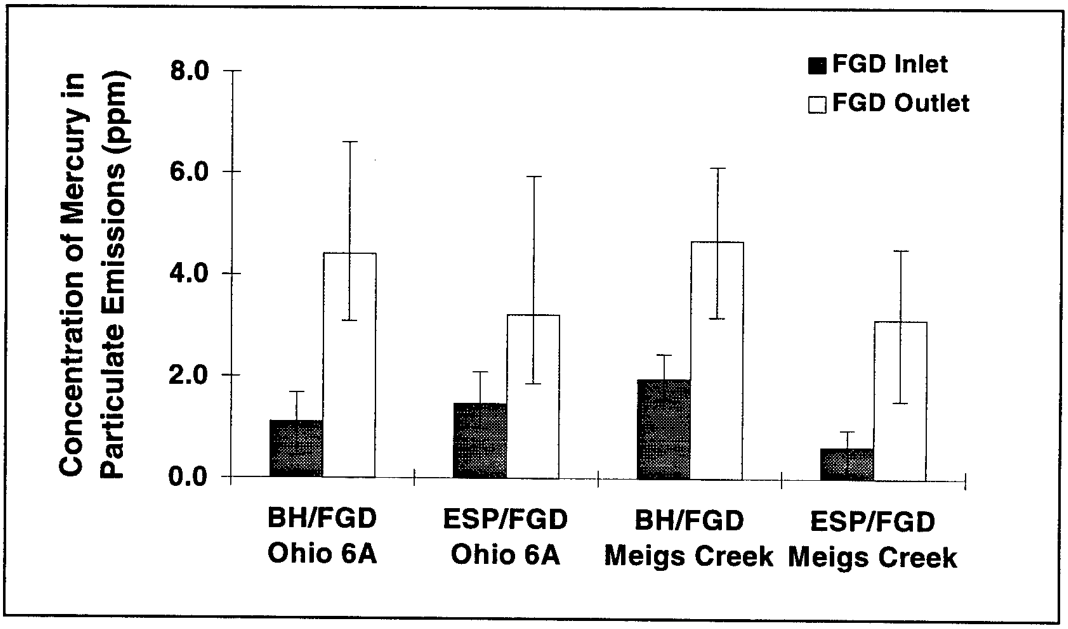


Figure 6.21 Comparison of Particulate-Phase Mercury Concentrations

However, the concentration of mercury measured in samples of gypsum filtered from a bulk slurry sample was typically less than that measured in the particulate in the flue gas downstream of the scrubber. The concentration of mercury measured in scrubber solids samples ranged from 0.08 to 1.0 ppm while the mercury concentration in particulates filtered from flue gas samples at the scrubber outlet ranged from 0.1 to 6.6 ppm. Therefore, gypsum carryover did not appear to contribute to the slight increase in particulate-phase mercury across the scrubber in Phase II Test Series 3.

Particulate-phase mercury accounted for 4% of the total mercury emissions following the scrubber for the baghouse/scrubber configurations, which exhibited high total mercury emissions control. The particulate-phase mercury averaged 1% of the total scrubber mercury emissions for the less efficient mercury control observed with the ESP/scrubber combination.

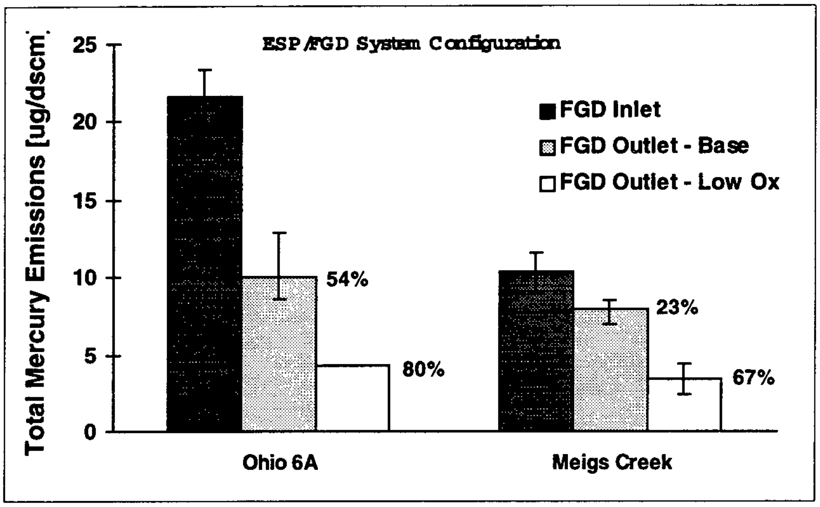


Figure 6.22 Impact of Oxidation Air Stoichiometry on Total Mercury Emissions

Impact of Scrubber Chemistry on Elemental Mercury Emissions

During the FGD parametric tests, it was observed that emissions of elemental mercury from the scrubber were generally lower when the scrubber was operated in the natural oxidation mode rather than as a forced oxidation system. A limited number of measurements were made in Test Series 3 to determine if the oxidation air stoichiometry could have an impact on elemental mercury emissions.

For the ESP/scrubber system, reducing the oxidation air stoichiometry resulted in a significant reduction in total mercury emissions from the scrubber as shown in Figure 6.22. For the Ohio 6A coal, mercury emissions reduction across the scrubber increased from 54% at the baseline operating conditions to 80% with operation at the lower air stoichiometry. Total mercury removal efficiency across the scrubber increased from 23% to 67% for the Meigs Creek coal.

The observed increase in mercury emissions control performance was largely a result of reduced elemental mercury emissions for both coals. Vapor-phase mercury speciation before and after the scrubber for the two scrubber operating conditions for each coal is summarized in Figure 6.23 and Figure 6.24. This limited test data indicates that in the limestone forced oxidation scrubber system, control of elemental mercury emissions may be related to the scrubber chemistry. One possible explanation for the improved performance is that altering the scrubber chemistry inhibited the reduction of oxidized mercury species absorbed from the flue gas and re-emission from the scrubber as elemental mercury.

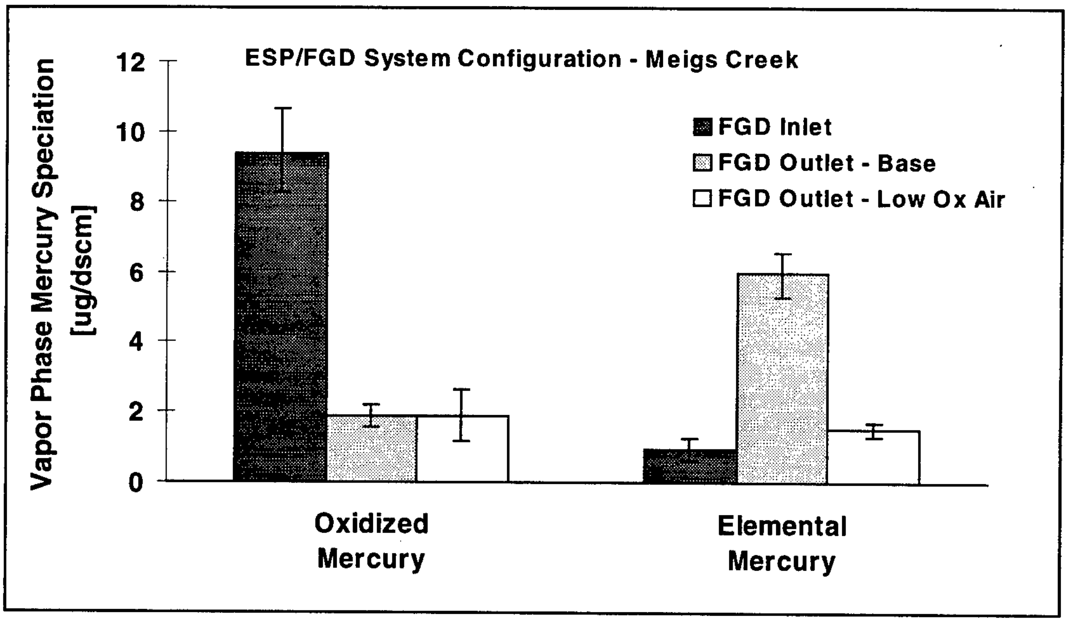


Figure 6.23 Impact of Oxidation Air Stoichiometry on Mercury Speciation - Ohio 6A

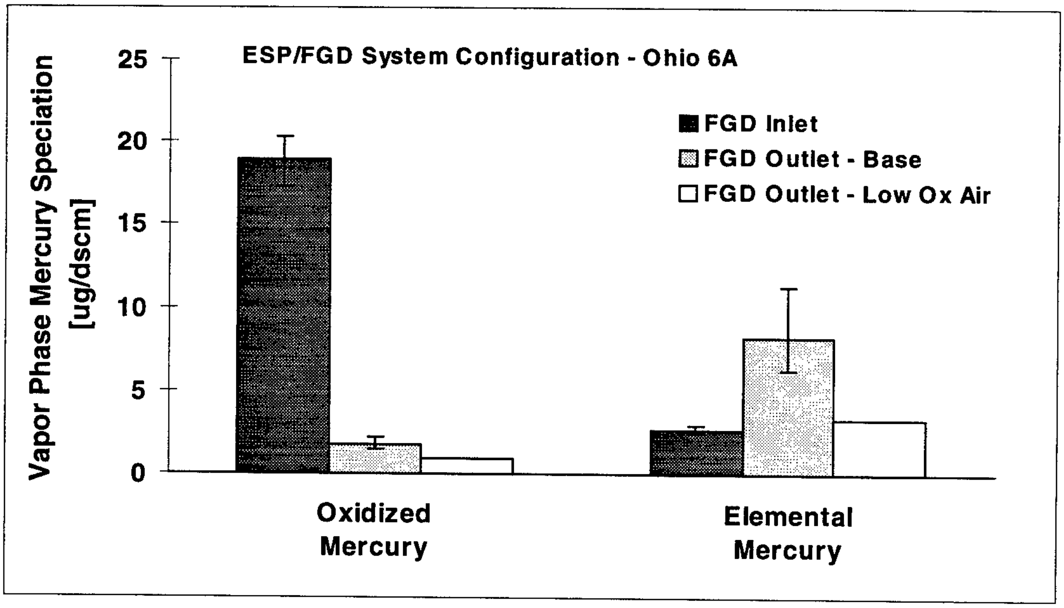


Figure 6.24 Impact of Oxidation Air Stoichiometry on Mercury Speciation - Meigs Creek

6.6.3 By-product Stream Evaluation

Analyses of the clarified recycle water and solid by-product were performed to quantify the amount of mercury in these primary scrubber outlet process streams. Samples were obtained approximately two hours after the initiation of the test conditions. Sampling and analysis was similar to the procedures followed in Test Series 2.

Table 6.12 summarizes the average mercury concentration detected in the outlet streams during conventional (high L/G) wet scrubber operation for the Ohio 6A and Meigs Creek coals. For comparison, the results from the Ohio 5/6 tests are included. For several of the test cases, extremely low quantities of mercury were measured in the FGD filtrate as typically reported in the literature. A greater portion of the mercury removed by the scrubber was regularly detected in the scrubber solid by-product. Of note are the substantial amounts of mercury detected in the liquid by-product relative to the solids for the Ohio 6A coal. Coal seam may influence the partitioning of mercury between the scrubber byproduct streams. Scrubber operation at borderline oxidation stoichiometries also resulted in elevated levels of mercury in the filtrate for both coals.

Table 6.12 FGD Process Stream Mercury Concentration - Conventional Operation with Tray

	Absorber Slurry [ppm]	**Absorber Filtrate [ppb]**
Phase I - Ohio 5/6	0.8	< 10
Ohio 5/6	2.7	0.7
Ohio 6A/BH	0.079	43
Ohio 6A/ESP	0.164	51
Meigs Creek/BH	0.293	< 0.5
Meigs Creek/ESP	0.280	7.2

6.6.4 Mercury Control Summary

In Test Series 3 of Phase II, tracking of mercury through entire utility coal utilization process including pre-combustion, combustion and post combustion processes for Ohio 6A and Meigs Creek coal was accomplished. To reflect the impact of the particulate device on mercury control in a wet scrubber, tracking of mercury from the coal source to the stack is provided for both the baghouse and ESP test configurations in Figures 6.25 through 6.28. For comparison, the abatement of mercury emissions for a utility plant equipped with a baghouse firing Ohio 5/6 coal is provided in Figure 6.29. The basis of comparison for mercury control in a wet scrubber is high L/G operation for SO_2 control greater than 90% for a range of high-sulfur coals.

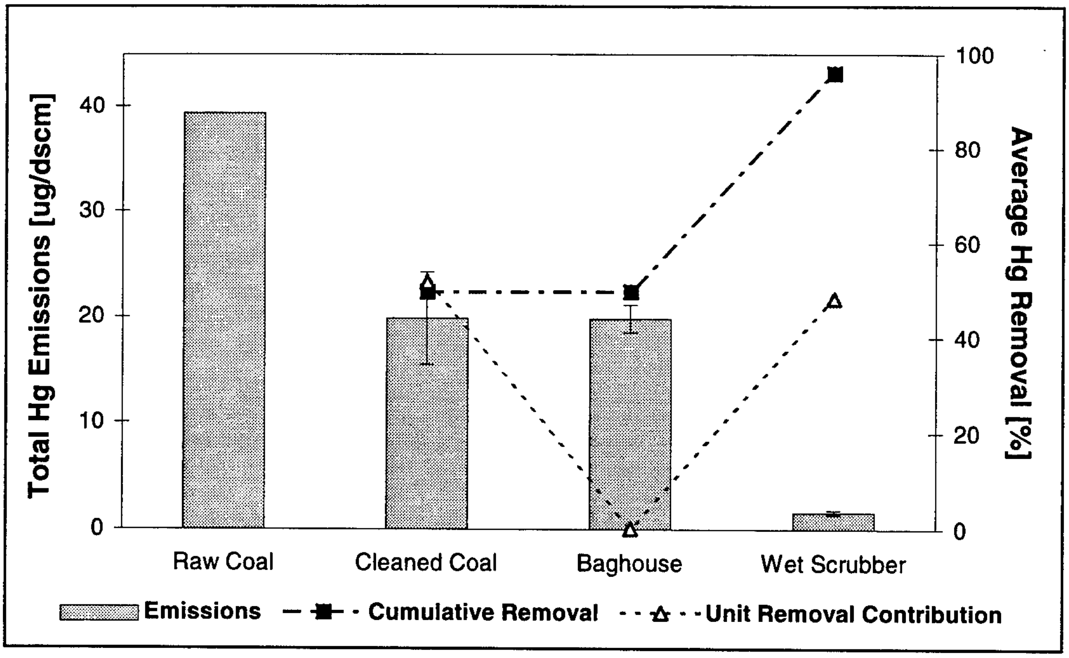


Figure 6.25 Mercury Emissions Reduction in a Utility Plant Equipped with a Baghouse - Ohio 6A Coal.

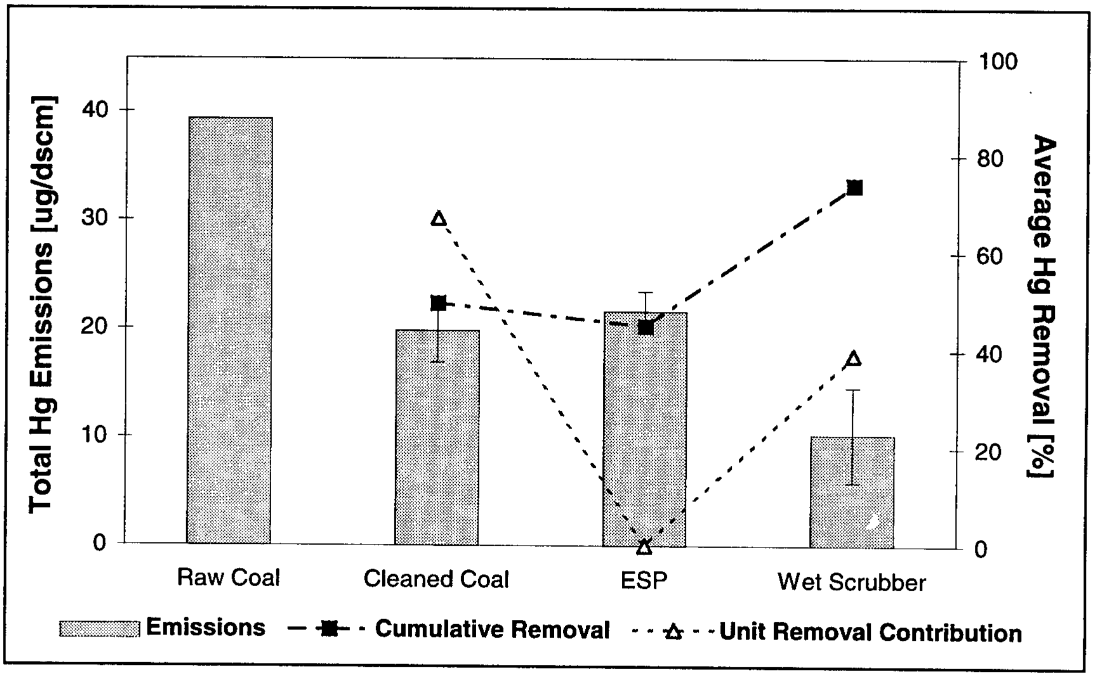


Figure 6.26 Mercury Emissions Reduction in a Utility Plant Equipped with an ESP - Ohio 6A Coal.

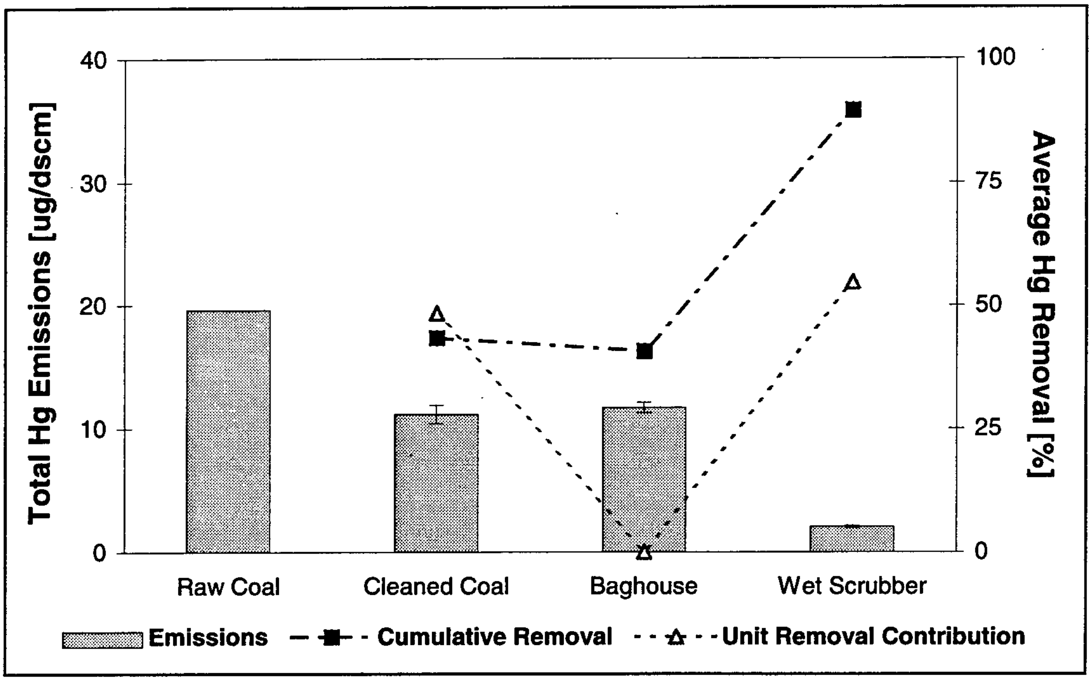


Figure 6.27 Mercury Emissions Reduction in a Utility Plant Equipped with a Baghouse - Meigs Creek Coal.

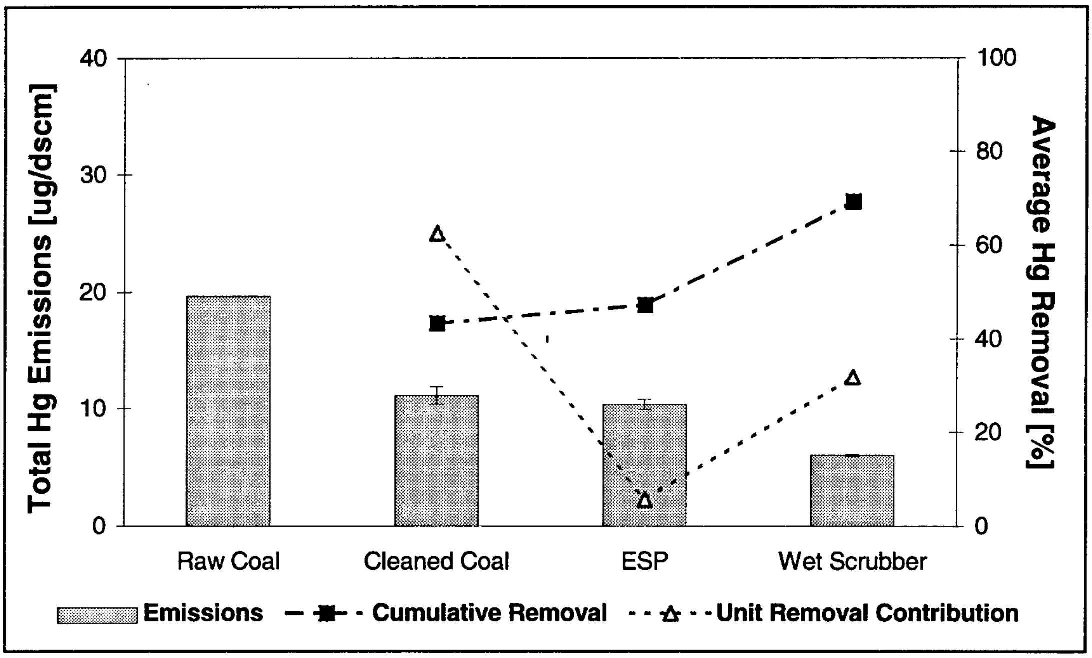


Figure 6.28 Mercury Emissions Reduction in a Utility Plant Equipped with an ESP - Meigs Creek Coal.

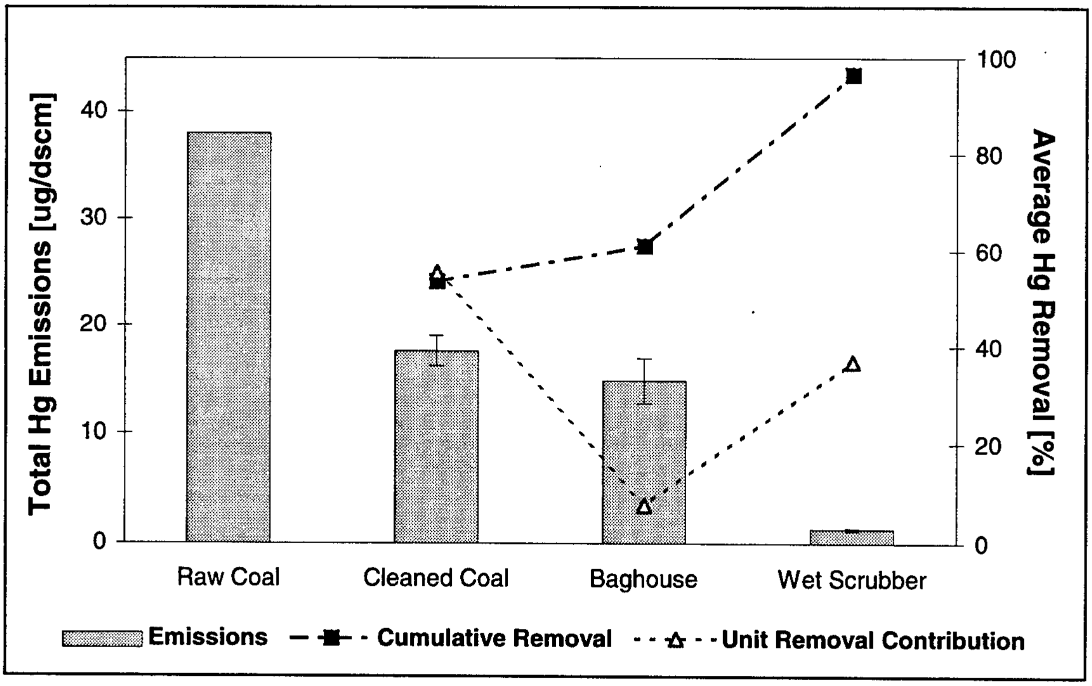


Figure 6.29 Mercury Emissions Reduction in a Utility Plant Equipped with Baghouse - Ohio 5/6 Coal.

6.7 Phase II, Test Series 3 Conclusions and Recommendations

Coal cleaning was evaluated as a method of reducing mercury emissions from coal-fired electric utility boilers. Approximately 75 to 80% of bituminous coal shipments are cleaned to meet customer specifications on heating value, ash, and sulfur content based on 1995 figures. The effect of coal washing on mercury and chlorine in both the coal and on emissions was examined for three Ohio bituminous coals. The cleaned coals were slightly enriched in chlorine by each cleaning process, indicating that chlorine is more concentrated in the bulk raw coal than in the ash fractions. Coal cleaning produced a significant decrease in mercury concentration for all three coals, with mercury reductions ranging from 36 to 47 percent. As expected, sulfur also decreased as a result of cleaning for all three of the coals.

For the three Ohio coals evaluated, the reduction in coal mercury content from washing correlated with the percent reduction of ash. Based on these results, pre-combustion cleaning for mercury reduction in Ohio coals appears to be related to the efficiency of the ash removal. The complexity of the commercial cleaning process or the extent of washing was not observed to have an effect on the mercury removal beyond the ash removal efficiency.

Several coal properties and combustion conditions were investigated for impacts on particulate partitioning and vapor-phase mercury speciation. These included the effect of unburned carbon on mercury partitioning, coal chlorine content on mercury speciation, and the association of mercury and pyritic sulfur in coal. On average, approximately 12% of the uncontrolled mercury was present on the particulate for the bituminous coals fired. For the narrow range of relatively low carbon carryover from the B&W low-NOx burners, the distribution of mercury between the vapor phase and the particulate did not strongly correlate with unburned carbon in the fly ash. As carbon carryover is associated with NO_x control and may be related to the mercury control across a particulate control device, future testing will contribute to this database. The coal chlorine content over the range of 650 to 2,200 ppm in the bituminous coals did not affect partitioning between the solid and vapor phases and the ratio of mercury species in the vapor phase. The correlation of mercury and pyritic sulfur content in three commercially ashed bituminous coals was poor. Continued investigation of coal constituents for correlations to particulate partitioning and vapor-phase mercury speciation is recommended.

Similar to the Ohio 5/6 coal, the Ohio 6A and Meigs Creek coal fly ash may also catalyze the conversion of elemental mercury to oxidized mercury species as the flue gas passes through the ash filter cake in the baghouse. In previous tests, the Ohio 5/6 fly ash oxidized elemental mercury to the more soluble form across the baghouse filtercake. Mercury species transformations were not generally observed across the ESP for the Ohio 6A and Meigs Creek coal fly ash as was the case for the Ohio 5/6 coal fly ash. Investigation of the major constituents of the fly ashes produced in Phase II and those to be generated in Phase III for a relationship to the oxidation of elemental mercury is recommended for Phase III.

A number of factors contributing to wet scrubber mercury emissions control performance were evaluated. Those factors observed to directly impact mercury control in a wet scrubber include:

- Ratio of mercury species in the inlet flue gas
- L/G
- Tower configuration
- Upstream particulate control device
- Fly ash properties
- Scrubber chemistry

Mercury control by a wet scrubber was independent of inlet mercury concentration, coal seam and slurry pH for testing performed with the Ohio bituminous coals. The coal chlorine content did not influence mercury control in the wet scrubber as anticipated by favoring the formation of oxidized mercury species in the vapor phase.

Significantly higher mercury control was obtained by the wet scrubber preceded by a baghouse when directly compared to an ESP/wet scrubber configuration. The ESP/wet scrubber system provided higher oxidized mercury emissions and elevated elemental mercury emissions relative to the baghouse/wet scrubber configuration. Increased levels of elemental mercury across the ESP/scrubber system partially contributed to low mercury control efficiency. The identification of alternative methods of modifying the inlet mercury speciation to improve mercury control of the commercially prevalent ESP/wet scrubber system is recommended. Due to the complex nature of the reactions occurring in wet scrubbers, additional efforts on understanding slurry chemistry impacts to prevent the reduction of absorbed oxidized mercury and re-emission of elemental mercury are recommended.

Mercury species and emissions were tracked through the entire utility coal utilization process including pre-combustion, combustion and post combustion processes for Ohio 6A and Meigs Creek coal. Total plant-wide reduction of mercury emissions with respect to the mercury concentration in the raw coal ranged from 69 to 97%. Operation with the baghouse upstream of the wet scrubber provided for at least 90% mercury emissions reduction with reference to the mercury content in three as-mined coals. Operation with an ESP upstream of the wet scrubber provided between 70 - 75% mercury emissions reduction with reference to the mercury content in two as-mined Ohio coals. The contribution of coal cleaning to the abatement of mercury emissions from the raw coal source exceeded 48% for the three coals and two test configurations. The contribution of a wet scrubber toward the abatement of mercury emissions was 23 – 92% mercury capture across the scrubber for the three coals and two particulate control test configurations.

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