

# ***Advanced Emissions Control Development Program***

## ***Phase III — Approved Final Report***

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## 1.0 REPORT SUMMARY

The primary 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. The project goal is to effectively control air toxic emissions through the use of conventional flue gas clean-up equipment such as electrostatic precipitators (ESPs), fabric filters (baghouses - BH), and wet flue gas desulfurization systems (WFGD). Development work concentrated on the capture of trace metals, fine particulate, hydrogen chloride and hydrogen fluoride, with an emphasis on the control of mercury.

The AECDP project 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). This report discusses results of all three phases of the AECDP project with an emphasis on Phase III activities.

Following the construction and evaluation of a representative air toxics test facility in Phase I, Phase II focused on characterization of the emissions of mercury and other air toxics and the control of these emissions for typical operating conditions of conventional flue gas clean-up equipment.<sup>1,2</sup> 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) particulate control devices (ESPs and baghouses) effectively remove the particulate-phase mercury, but the particulate-phase mercury was only a small fraction of the total for the coals tested, 3) wet scrubbing can effectively remove hydrogen chloride and hydrogen fluoride, and 4) wet scrubbers show good potential for the removal of mercury when operated under certain conditions, however, for certain applications, system enhancements can be required to achieve high removals when the scrubber is operated downstream of an ESP.

Phase III (Advanced Concepts and Comparison Coals) testing was directed at the development of enhanced air toxics emissions control strategies to further reduce the emissions of mercury. Phase III results further supported the findings of previous phases and demonstrated several methods of enhancing mercury control for both unscrubbed systems and systems equipped with WFGD. Results confirmed that the addition of sorbents can be used to significantly improve the capture of mercury in downstream particulate collection equipment. In addition, Phase III testing demonstrated three methods of minimizing the potential negative impact of an ESP on downstream control of mercury in WFGD systems. These methods included decreased oxidation air flow, the addition of H<sub>2</sub>S into the flue gas at the scrubber inlet, and the addition of EDTA into the absorber reaction tank.

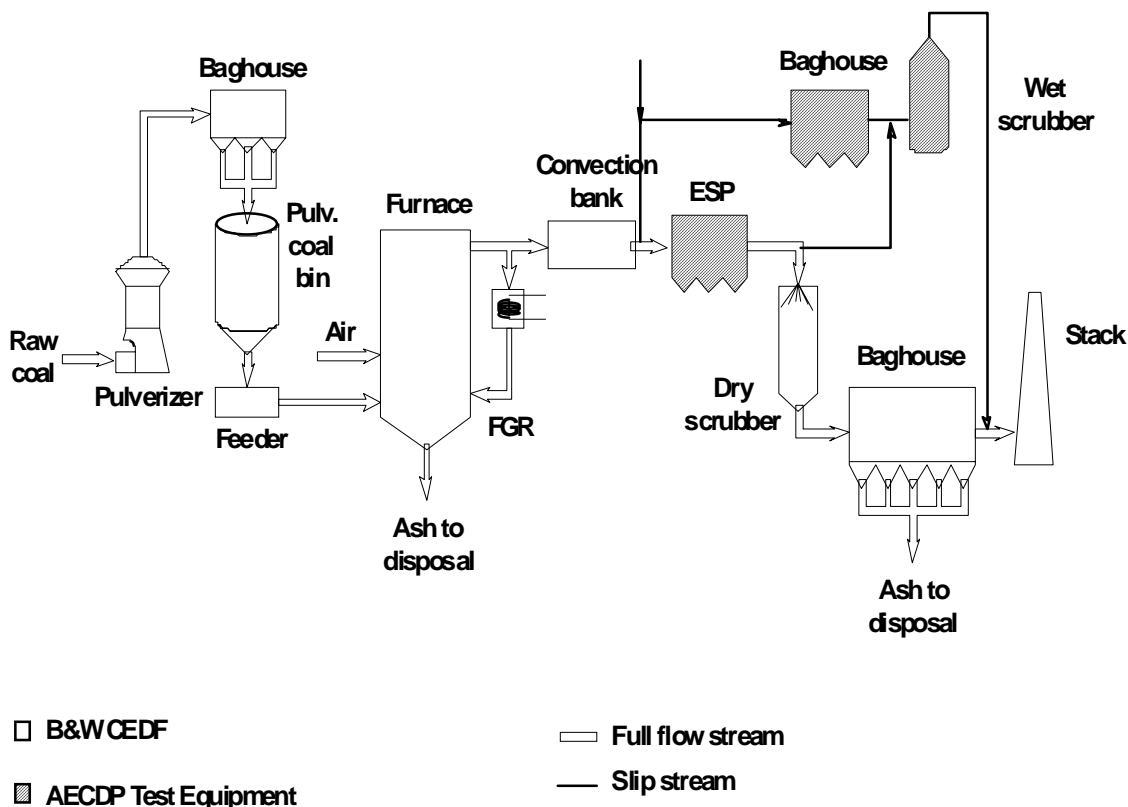
## 2.0 EXECUTIVE SUMMARY

The primary objective of the AECDP is to develop practical, cost-effective strategies for reducing the emissions of air toxics from coal-fired boilers. The project goal is to effectively control air toxic emissions through the use of conventional flue gas clean-up equipment such as ESPs, fabric filters (baghouse), and WFGD systems. Development work concentrated on the capture of trace metals, fine particulate, and hydrogen chloride and hydrogen fluoride, with an emphasis on mercury.

The AECDP project 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.<sup>1</sup> 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 an emissions database.

Air toxic benchmarking measurements were performed to quantify the air toxics emissions from the boiler and the back-end flue gas clean-up equipment. Air toxic emission verification was achieved through comparison of the air toxics emissions from the CEDF with the emissions predicted by the trace element content of 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), three series of tests were conducted.<sup>2</sup> The first two test series were directed at the development of air toxics control strategies, based on conventional particulate and SO<sub>2</sub> 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 Phase II.



**Figure 2.1 Clean Environment Development Facility Process Flow Diagram**

Phase III of the program (Advanced Concepts and Coal Comparisons) investigated advanced emissions control concepts primarily for the purpose of reducing vapor phase mercury emissions. Two different technical approaches were taken to address the two major segments of the coal fired utility market. These are:

- Scrubbed systems (primarily wet flue gas desulfurization) which represent about 25% of the coal utility market. The majority of these scrubbed systems consist of an ESP followed by a wet scrubber
- Unscrubbed systems which represent about 75% of the utility coal market. The majority of these systems consist of ESPs only.

Mercury species and emissions were tracked through the entire coal-utilization process, including pre-combustion, combustion and post-combustion processes for several Ohio coals. Commercial coal cleaning provided average mercury emission reductions of 42% compared to the raw coal. Particulate control devices (ESPs and baghouses) effectively remove the particulate-phase mercury, but the particulate phase mercury was only a small fraction of the mercury for the coals tested. A baghouse, which provides negligible control of vapor-phase mercury, can impact the speciation of the vapor-phase mercury in the flue, causing an increase in the oxidized mercury fraction.

Control of mercury by an ESP with upstream sorbent injection was demonstrated for two sorbents during Phase III testing. Injection of calcium based sorbents appears especially attractive when economics are considered. At limestone injection rates that provided calcium to sulfur ratios of 0.04 and 0.35 (sorbent to mercury ratios of 16,000 to 1 and 125,000 to 1 by mass), 41 % and 53 % removal of total mercury was achieved, compared to an 18% average removal for a baseline test with no sorbent injection. Carbon injection likewise provided improved control of mercury by an ESP, removing 53% of the total mercury in the flue gas, at an activated carbon to mercury ratio of 9,000 to 1 by mass. These sorbent injection tests were performed with an Ohio 5, 6, and 7 blend containing 0.269 ppm mercury on an as-fired basis.

Phase III testing related to FGD (flue gas desulfurization) systems focused on enhancing control of mercury across the wet scrubber when operated downstream of the ESP. Previous testing during Phase II consistently indicated less mercury removal for an ESP/WFGD system compared to a BH/WFGD system. Also, elemental mercury levels increased across the scrubber when an ESP was used upstream. Causes for these observations were hypothesized in the beginning of Phase III and corresponding methods for enhancing mercury control in the wet scrubber were tested. The hypotheses were based on the belief that the ESP can destroy gas phase species that would otherwise react with the mercury in the scrubber, and prevent the subsequent conversion of the oxidized mercury to the elemental form. These control methods were all developed with the goal of identifying low cost improvements in mercury control using existing equipment as much as possible.

Several enhancements were identified to improve control of mercury in a wet FGD system downstream of an ESP. The baseline data used for comparison with the enhancements showed 46% removal across the scrubber when preceded by an ESP when firing a blend of Ohio 5, 6, & 7 coals. Three enhancements were evaluated to determine their potential for eliminating the effect of the ESP on mercury control in the scrubber. These included reducing the oxidation air in the Absorber Reaction Tank (ART), introducing hydrogen sulfide ( $H_2S$ ) between the ESP and wet scrubber, and the addition of ethylenediaminetetracetic acid (EDTA). All three of these enhancements significantly improved mercury control across the wet scrubber and prevented increases in elemental mercury. Mercury removal increased to 80, 71, and 73% for the three enhancements, respectively. 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 for further reducing mercury emissions from utility stacks

Additional development is recommended to allow commercialization of the mercury control techniques demonstrated in this program. AECDP results encourage continued development of sorbent injection technology for unscrubbed systems, and technologies developed for enhanced mercury control in wet scrubbers. The next step for each of these technologies is optimization for a specific application followed by commercial demonstration.

### **Project Sponsors**

The Advanced Emissions Control Development Program is jointly funded by the United States Department of Energy's Federal Energy Technology Center, the Ohio Coal Development Office within the Ohio Department of Development, and Babcock & Wilcox— a McDermott company.

## **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

### 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 from 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 Air Toxics Regulatory Status

Title III of the CAA (Clean Air Act) established a list of 189 HAPs 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 EPA has been working with the U. S. DOE, the Electric Power Research Institute (EPRI), and the Utility Air Regulatory Group (UARG) to characterize air toxics emissions from existing power plants. Both the 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.

Risk assessment activities were performed including a screening assessment on all 67 of the hazardous air pollutants that could potentially be associated with coal fired power plants. Using conservative assumptions the list of HAPs of concern decreased to 12 priority HAPs associated with potential inhalation risks, and 4 priority HAPs with potential multipathway exposure risks. The internal EPA studies continued and the Mercury Study Report to Congress and the Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units – Final Report to Congress were issued.<sup>3,4</sup> These reports identified mercury as the HAP of primary concern and the EPA has deferred regulatory determination for mercury until additional information can be gathered. In addition to highlighting mercury, these reports identified residual concerns associated with arsenic and dioxins.

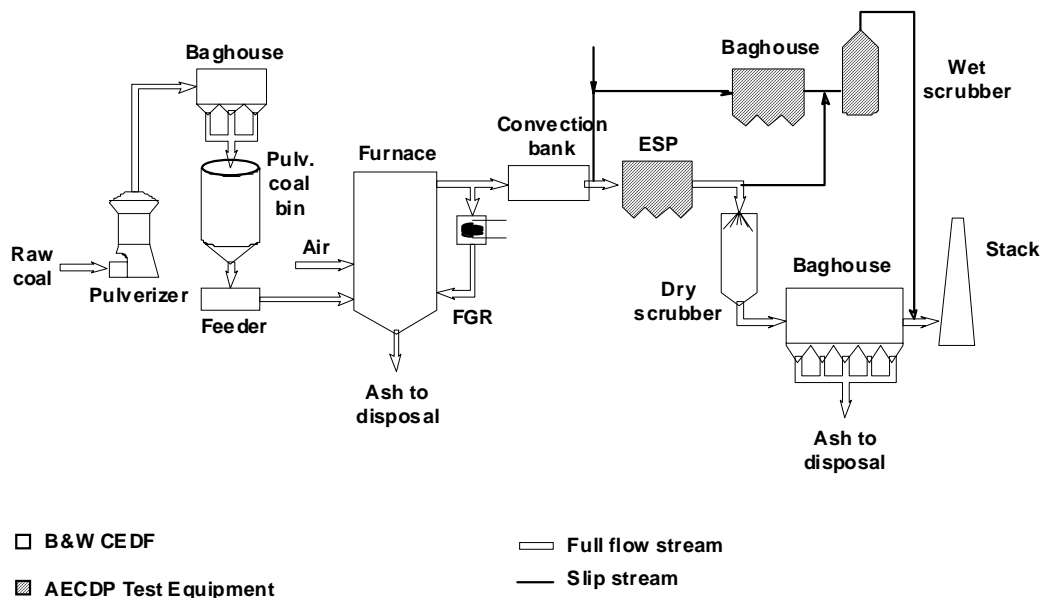
As a result of the need for additional information on mercury from coal fired boilers, the EPA has proposed an Information Collection Request (ICR). The goal of this request is to generate information through weekly sampling and analyses performed on the coals fired in all units over 25 megawatts in capacity. In addition, a subset of these units are to perform stack sampling on a quarterly basis to generate information on mercury concentration and speciation in the flue gas. These results will be combined with further EPA studies, and test data from on-going studies to aid the EPA in making regulatory decisions.

While the EPA's ultimate approach is uncertain, 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 was to develop practical strategies and systems for the simultaneous control of SO<sub>2</sub>, NO<sub>x</sub>, 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 ESPs, fabric filters (baghouses), and SO<sub>2</sub> removal systems such as wet scrubbers and various “clean-coal technologies”. This objective was achieved through extensive development testing in the state-of-the-art, 10 MW<sub>e</sub> equivalent, CEDF. The project has extended the capabilities of the CEDF to facilitate air toxics emissions control development work on “backend” flue gas clean-up equipment. Specifically, an ESP, a baghouse, and a wet scrubber for SO<sub>2</sub> (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 were 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 clean-up 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 was 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<sub>2</sub> scrubber) added to the CEDF. Baseline air toxics emissions and capture efficiency was established for each of the major flue gas clean-up devices: ESP, baghouse, and wet SO<sub>2</sub> 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<sub>2</sub> 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 was 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 was continued 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 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<sub>2</sub> scrubber — operate in a manner representative of commercial units.

The 10 MW<sub>e</sub> 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<sub>2</sub> removal with increased L/G ratio, improved SO<sub>2</sub> removal with increased tower velocity, and increased removal with increased spray zone height. Wet scrubber SO<sub>2</sub> removal performance was, as expected for a pilot unit, slightly lower than achieved by commercial systems (typically due to wall impingement).<sup>1</sup>

### 3.4.2 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 such as mercury, fine particulate (non-volatile trace elements), 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.

Measured air toxics emissions from the CEDF were compared to emissions predicted by the draft EPA EMFs and the EPRI particulate phase metal correlations.<sup>1,2</sup> 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 indicated that the HAPs generated by the CEDF are representative of commercial front-fired boilers firing bituminous coals.

## 3.5 Summary of Phase II Results

Phase II began on February 29, 1996, and ended on August 31, 1997. In Phase II (optimization of conventional systems), testing involved the development of air toxics control strategies based

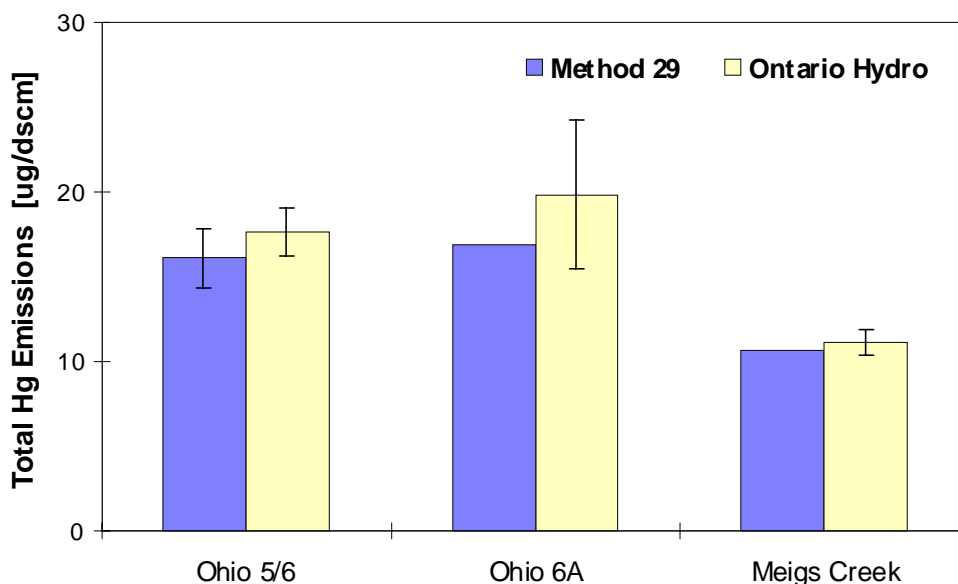
on conventional flue gas clean-up equipment.<sup>2</sup> Several Ohio steam coals were evaluated to provide data on the impacts of coal properties on mercury and acid gas emissivity, as well as to investigate the impacts of coal cleaning.

### 3.5.1 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 in these tests. Initially, total mercury emissions as measured by EPA Method 29 were higher than measured with the Ontario Hydro method. The use of the permanganate preservative during the Phase II resulted in improved agreement in 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 3.2.

### 3.5.2 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 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. Operating temperature, flue gas humidification, and baghouse fabric were evaluated as cost-effective means of reducing particulate and trace metal emissions.



**Figure 3.2 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.<sup>1,2</sup> Greater than 99% partitioning to the particulate phase 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 most of the trace metals. 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 from 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.

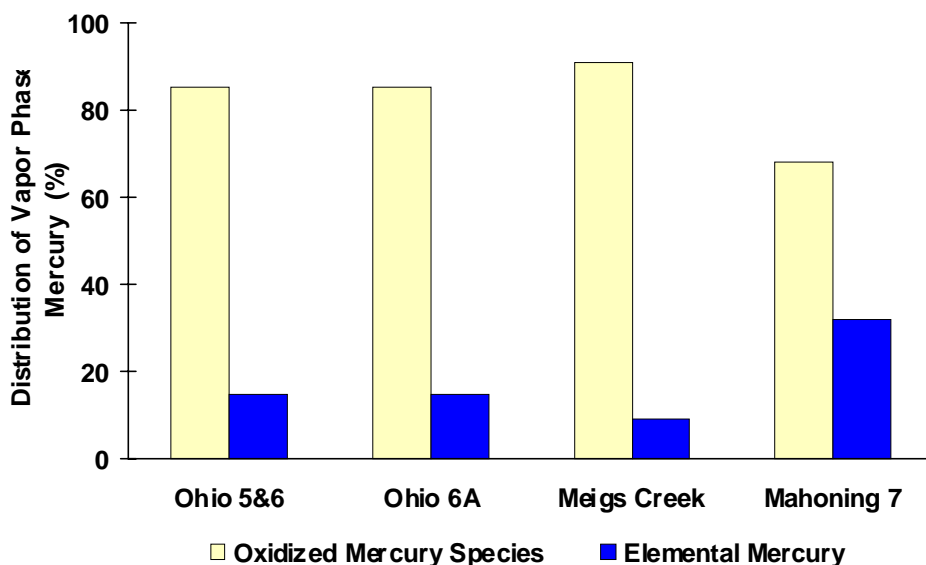
In anticipation of fine particulate (PM 2.5) regulations, the particle size distribution was measured to characterize particulate and unburned carbon emissions from a low-NO<sub>x</sub> burner. Analysis of the material collected suggest that the majority of the fine particulate (< 2.5 microns) emitted by the low-NO<sub>x</sub> burner was less than 0.5 micron, and 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. The majority of mercury removal can be attributed to the mercury adsorbed onto the particulate

entering the baghouse. 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. Over the range tested, temperature reduction did not affect total mercury emissions, although reduced baghouse temperature did favor the transformation of elemental mercury to an oxidized form.

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 3.3. However, once the flue gas passed through the baghouse, the proportion of elemental mercury was reduced. Two different baghouse fabrics, Ryton and GORE-TEX7, were evaluated for their impact on elemental mercury emissions. The elemental mercury emissions measured at the baghouse outlet were comparable between fabrics, suggesting that the transformation is primarily due to the bituminous coal fly ash. 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 has a high potential for total mercury emissions reduction due to the conversion of elemental mercury to a more soluble form.



**Figure 3.3 Characterization of Uncontrolled Mercury Emissions for Ohio Bituminous Coals**

However, ESP's are the dominant particulate emissions control systems installed at U.S. commercial coal-fired generating plants. The AECDP test data suggests that ESP's can remove most 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. Changes 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.

### **3.5.3 Flue Gas Desulfurization Devices**

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.

The relationship between wet scrubber SO<sub>2</sub> 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<sub>2</sub> control. Wet scrubber operating conditions that provided for low SO<sub>2</sub> control efficiency tended to also provide low mercury control for the bituminous coal-fired flue gas. Changes in wet scrubber operation to enhance SO<sub>2</sub> control, such as the installation of a tray or an increase in L/G, also improved mercury control. Extensive parametric testing was performed with the baghouse/wet scrubber system with the baseline Ohio 5/6 coal. The results of the parametric tests for WFGD control of mercury can be summarized as follows:

- Mercury control improved with increased L/G for the open tower and tray tower configurations 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.
- A gas flow distribution tray in the wet scrubber enhanced both SO<sub>2</sub> and total mercury emissions control over a wide range of L/G and pH, and provided more consistent data. The enhancement of SO<sub>2</sub> 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.
- 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.

- 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. Elemental mercury emissions from the wet scrubber were fairly constant over the wide L/G range investigated, and were generally unaffected by the tray configuration.

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<sub>2</sub> 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 low forced oxidation air stoichiometry.

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<sub>2</sub> removal. One 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 and larger contribution to the difference in total mercury control was the measurable increase in elemental mercury emissions across the scrubber when operated downstream of the ESP.

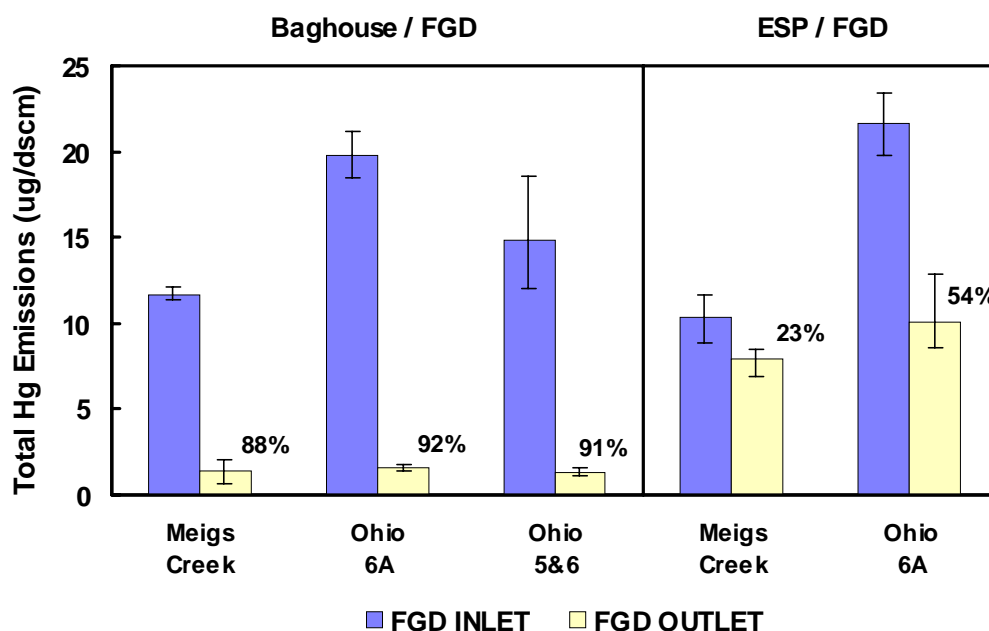


Figure 3.4 Summary of Wet Scrubber Total Mercury Control

### 3.5.4 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 in flue gas 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.

### **3.5.5 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<sub>2</sub> and lower mercury concentrations present in coal-fired flue gas. An on-line 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<sub>2</sub> 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 solubility 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.

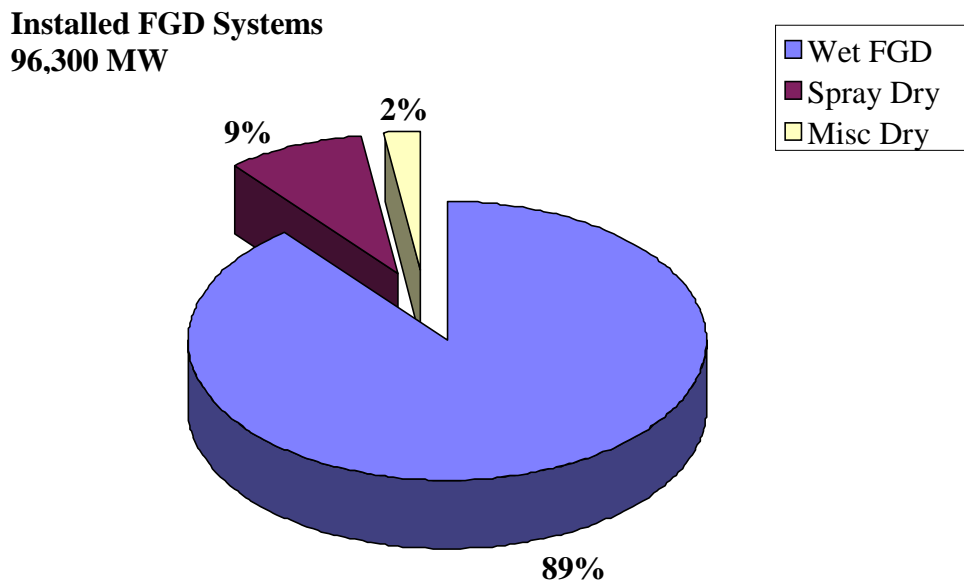
### 3.6 Utility FGD Population Study

An analysis of the available data for utility WFGD installations was done for several reasons:

- *To determine approximately the amount of mercury emitted by coal fired utilities and removed in utility WFGD systems.* Scrubbed systems comprise a relatively small percentage of the total generating capacity in the US. Estimating the current level of mercury removal for scrubbed systems can offer insight into the amount of mercury that can be captured on a national scale by increasing the number of scrubbed systems.
- *To determine the potential for improving the current level of mercury removal in scrubbed systems and the effect this improvement would have on mercury emissions levels.* Results from the previous phases of the AECDP program have identified potential areas for mercury removal improvement. By identifying improvements to mercury removal for these systems, utility emissions reductions can be approximated.

#### 3.6.1 Total Scrubbed Capacity in the U.S.

Currently in the US, 218 power-generating units representing approximately 96,300 MW of generating capacity are equipped with some type of FGD technology. As can be seen in Figure 3.5, the vast majority (89% of total generating capacity) of these are WFGD units. Specifically, 181 utility generating units, representing approximately 85,800 MW generating capacity, are equipped with WFGD systems. Of these, 165 units (80,300 MW) are equipped with either lime or limestone-based scrubbers.



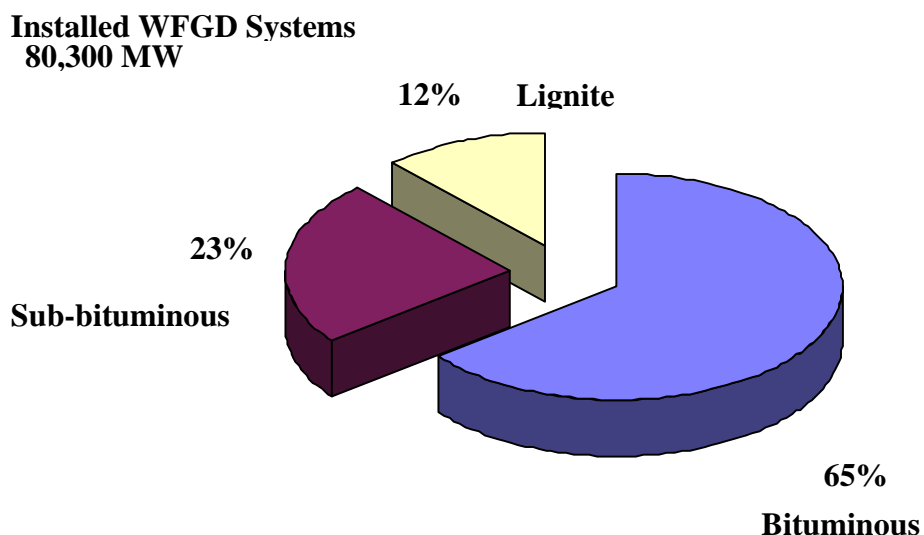
**Figure 3.5 Breakdown of FGD-Equipped US Generating Capacity**



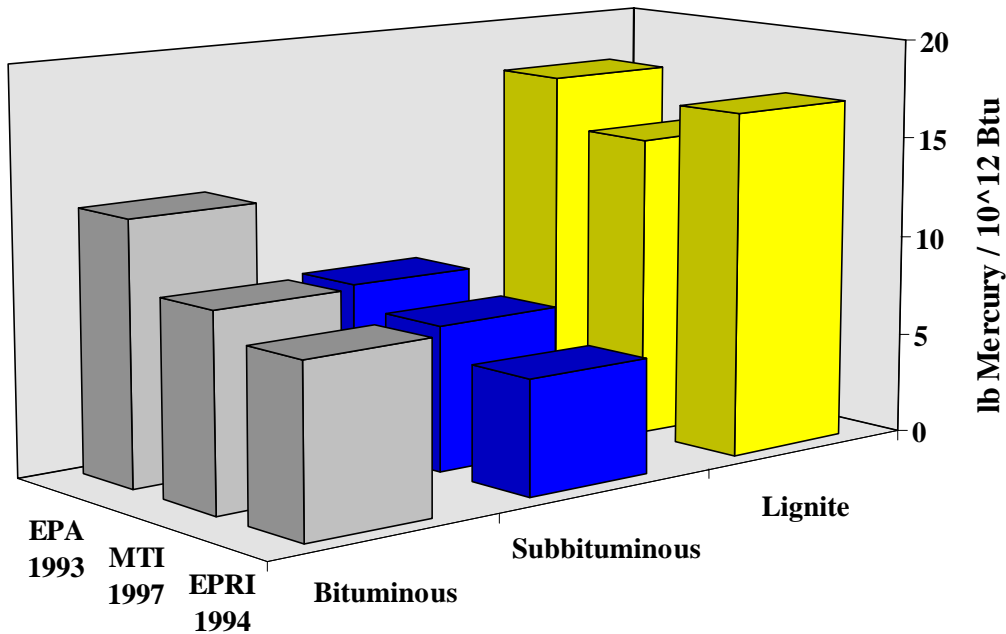
The primary focus of the AECDP program was on bituminous coal. In Figure 3.6, the US generating capacity equipped with WFGD systems is shown as a function of coal type. A large majority (65% of the scrubbed generating capacity) of these units are operated with bituminous coal, indicating that information gained from the AECDP program is applicable to the majority of scrubbed utility systems. Improvements to mercury capture identified in this program will be applicable to the largest segment of the scrubbed utility market, providing the greatest potential for reduction in mercury emissions on a national scale.

### 3.6.2 US Utility Mercury Emissions and Scrubber Performance

In order to determine the potential for improving utility WFGD mercury removal performance, it was first necessary to examine emission levels and current scrubber removal performance for the various coal types used in the US. In Figure 3.7, the predicted emission factors for bituminous, sub-bituminous and lignite coals with scrubbed systems are shown for various emissions studies. These emissions were predicted based various parameters including coal mercury concentration and heating value.

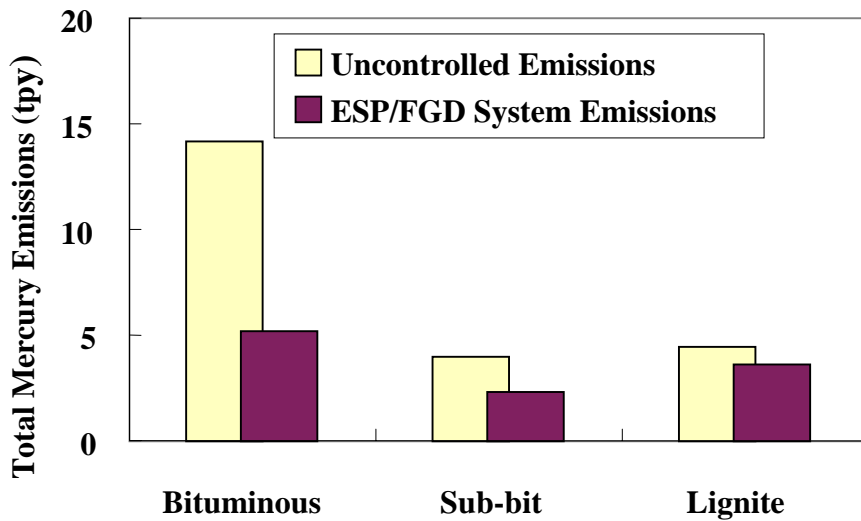


**Figure 3.6 Breakdown of US WFGD Systems by Coal Type**



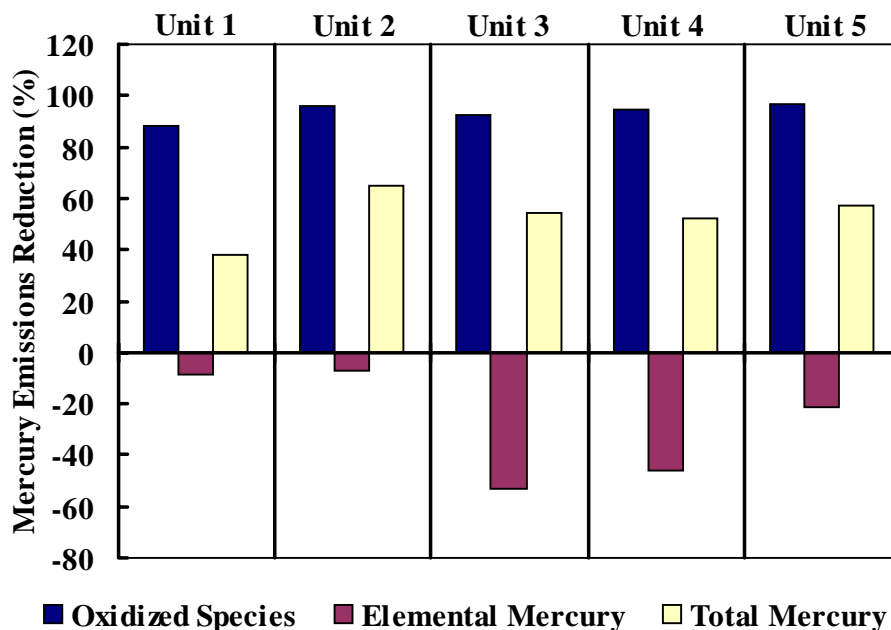
**Figure 3.7 Mercury Emissions Factors by Coal Type**

The MTI emission factors compare well with those of both EPA and EPRI, and were used for all subsequent calculations and analyses. These emission factors were then combined with available utility coal and generating data from the literature to obtain predicted mercury emissions on a mass basis. Likewise, WFGD mercury removal performance averages were determined from available data and used to determine scrubbed system emissions levels. In Figure 3.8 these mercury emissions, both uncontrolled and scrubbed, are shown (in tons/year) as a function of coal type. For this analysis, only WFGD systems located downstream of an ESP were included. By combining all three types of coals, the above data show that current US WFGD systems reduce mercury emissions by approximately 12 tons/year (from 23 to 11 tons/year).



**Figure 3.8 Mercury Emissions by Coal Type**

Various studies have shown that WFGD systems exhibit high removal performance of oxidized mercury species. However, these studies also show a “negative” removal of elemental mercury, thereby reducing the total mercury removal performance. This phenomenon is illustrated in Figure 3.9, which shows mercury removal performance for various commercial WFGD systems, as measured by the Ontario Hydro method. In each case high oxidized mercury removals and “negative” elemental mercury removals were observed.



**Figure 3.9 Commercial WFGD Speciated Mercury Removal**

As a final step in this study, the impact of alternative approaches to improving mercury removal was investigated. Because 75% of the current U.S. generating capacity is unscrubbed, it is important to have mercury control products available for both segments of the utility market in order to maximize mercury control. Enhanced mercury control concepts for the scrubbed market are discussed in more detail in Section 7.0; discussion of enhanced control for the unscrubbed market can be found in Section 6.0.

## 4.0 FACILITY DESCRIPTION AND OPERATING CONDITIONS

### 4.1 Facility Description

#### 4.1.1 Fabric Filter System

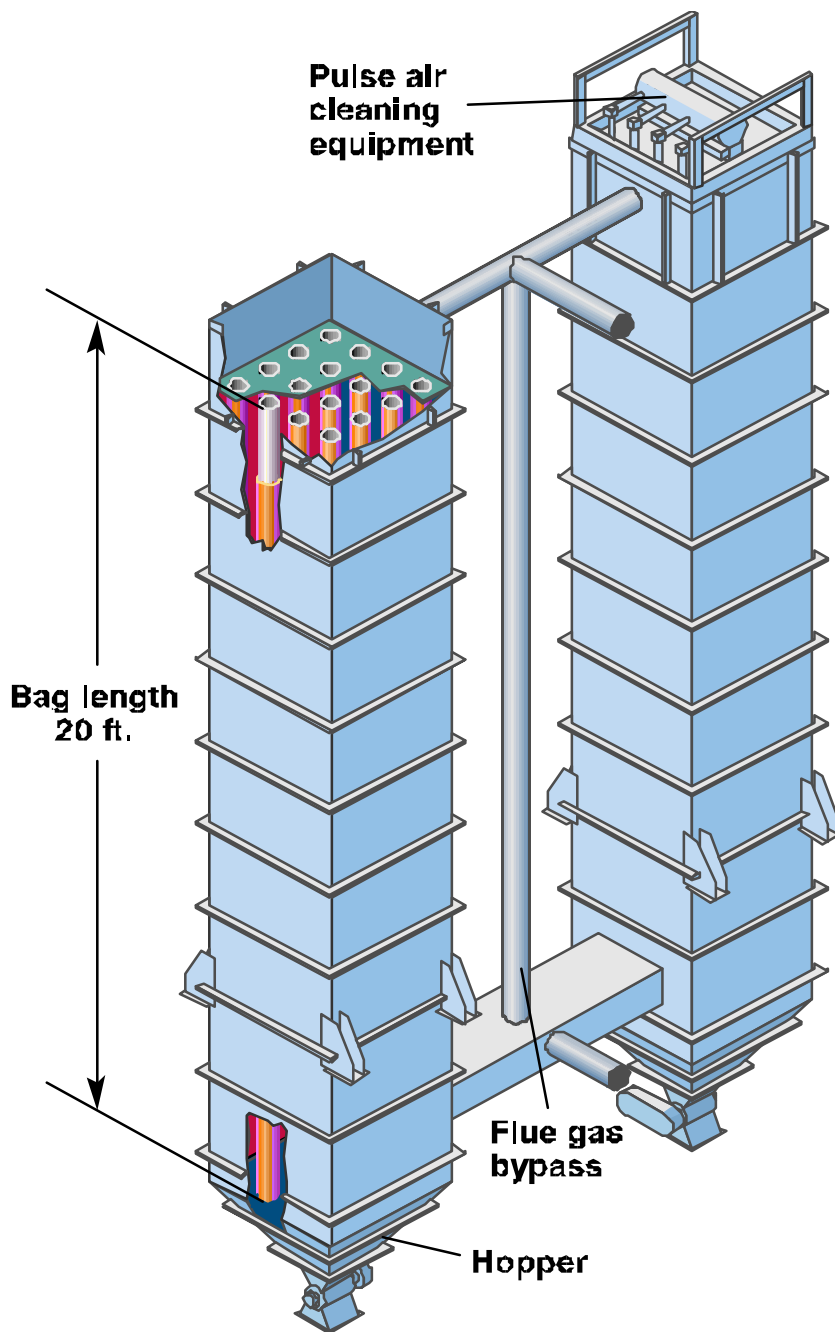
The fabric filter system (Figure 4.1) consists of a pulse-jet baghouse and fly ash disposal system. The fabric filter is designed for a flue gas slipstream from the CEDF of approximately 0.6 MW<sub>e</sub> equivalent.

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 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<sup>6</sup> 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/min              |
| Cleaning Method    | Pulse-jet; on-line or off-line |



**Figure 4.1 Pulse-Jet Baghouse**

The fly ash removed from the fabric filter bags falls into the baghouse hoppers. A rotary valve at the bottom of the hoppers transfers the ash to a vacuum ash handling system for transport to a disposal bin.

## **Wet Scrubber System**

The 0.6 MW<sub>e</sub> equivalent wet scrubber system includes the absorber tower, recirculation tank, reagent feed system, mist eliminator system, and slurry dewatering and disposal system. The absorber tower (Figure 4.2) is designed to simulate a vertical section down through a commercial reactor to accurately reproduce SO<sub>2</sub> 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.

The absorber consists of the absorber tower and slurry recirculation tank. The tower 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.

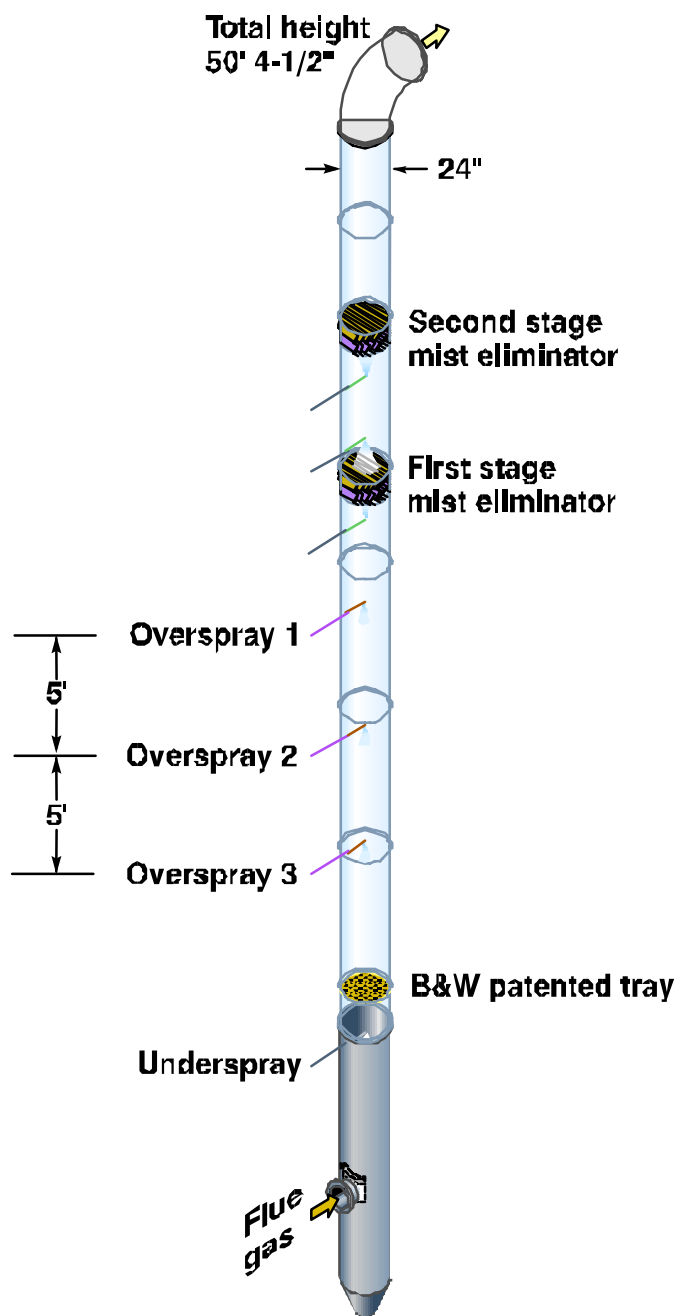
The wet scrubber is designed to process 5,062 lb/hr of flue gas with a SO<sub>2</sub> concentration of up to 6,000 ppm. The primary design characteristics for the wet scrubber system are summarized in the following table:

### **AECDP Wet Scrubber Design Summary**

|                                 |   |
|---------------------------------|---|
| Design limestone stoichiometry  | 1.1 mole Ca/mole SO <sub>2</sub> absorbed |
| Nominal SO <sub>2</sub> 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                          |

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<sub>2</sub> removal and air toxics collection in the wet scrubber. An air sparger system distributes clean air at the bottom of the absorber recirculation tank 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.

The reagent feed 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 directly 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<sub>2</sub> control for the variety of coals.



**Figure 4.2 Wet Scrubber**

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 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 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  $\text{SO}_2$  removal performance and the possible influence on air toxics capture.



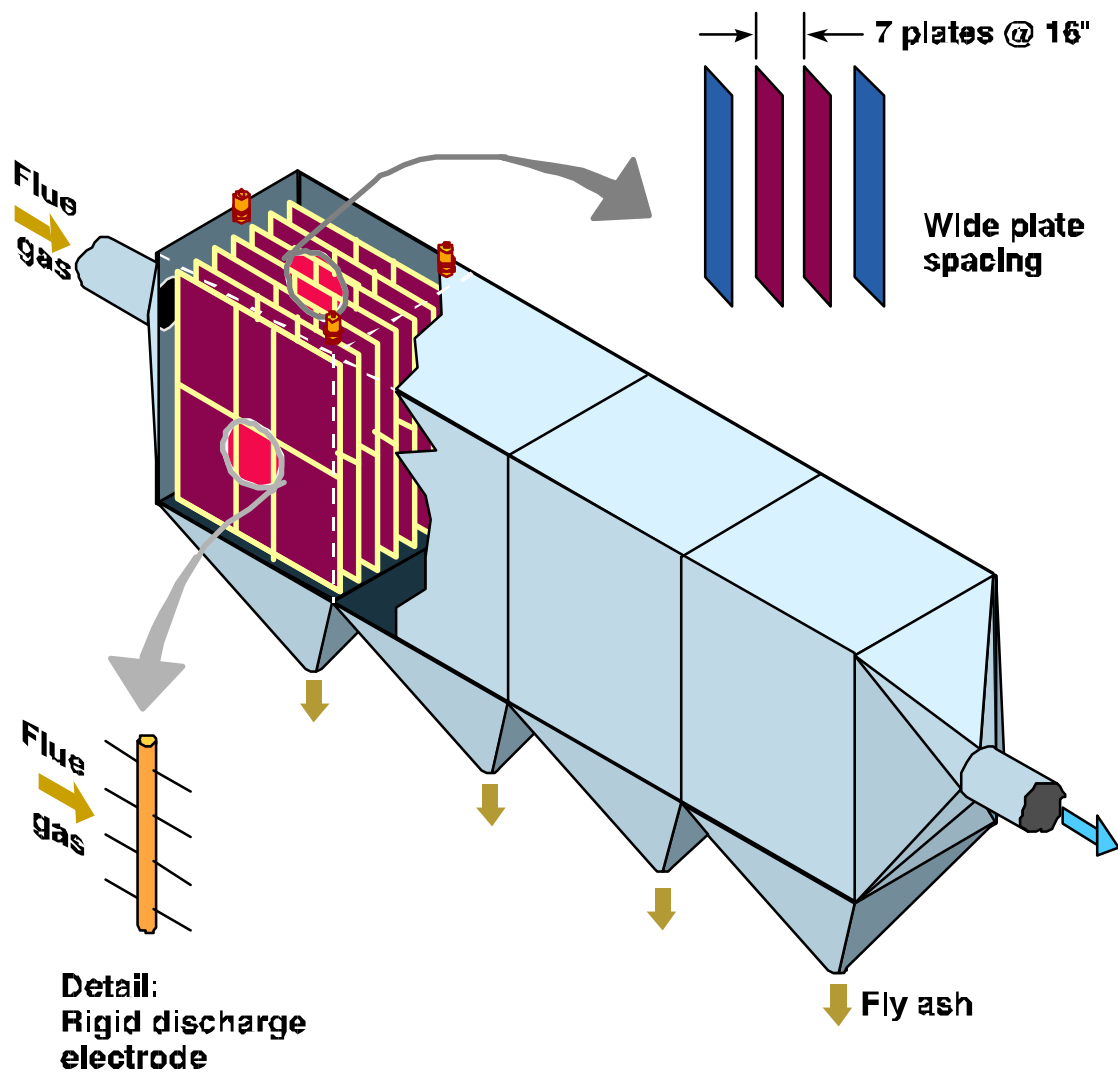
#### 4.1.2 Electrostatic Precipitator

The ESP (Figure 4.3) operates on the full flue gas flow (100 million Btu/hr, 10 MW<sub>e</sub> 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<sup>6</sup> 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 <sup>2</sup> /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                |



**Figure 4.3 Electrostatic Precipitator**

## **4.2 Phase III Test Objectives**

The testing completed in Phase I and Phase II of this project has provided data on the expected mercury emissions from Ohio coals and on the mercury removal performance of standard back-end flue gas clean-up equipment (electrostatic precipitator, baghouse and wet scrubber) operating at typical conditions. The objectives of the Phase III testing were to extend the mercury emissions database for coals and coal cleaning, and to investigate methods for improving the control of mercury emissions from coal burning power plants.

The primary objectives for the Phase III tests were:

- Advanced Mercury Control in Wet Scrubber Systems
- Mercury Control in Non-Scrubbed Systems
- Additional Coal Data for Data Library

## 4.2.1 Advanced Mercury Control in Wet Scrubber Systems

### 4.2.1.1 Resolve ESP/BH Differences seen in Phase II

In coal burning utility power plants, FGD equipment is preceded by an ESP or BH to provide particulate removal. The AECDP Phase II test results show that mercury emissions depend on the type of upstream particulate removal device. An FGD preceded by a BH consistently provided better mercury removal than an FGD preceded by an ESP, other FGD operating parameters being equal.

Mercury speciation data indicated that the BH provides some oxidation of elemental mercury, while similar data for the ESP shows no effect on the mercury speciation. Further, speciation measurements showed that with the BH/FGD equipment combination the FGD provided good removal of oxidized mercury while elemental mercury remained unchanged. With the ESP/FGD combination, the FGD provided good removal of the oxidized mercury while the elemental mercury concentration *increased*. The data indicated that with the ESP/FGD equipment combination the oxidized form of mercury captured by the FGD was converted to the elemental form and released back into the flue gas.

The majority of scrubbed utilities are represented by the ESP/FGD combination, and this combination provided the poorest total mercury removal. Pinpointing the source of the difference between these gas clean-up systems (BH/FGD and ESP/FGD) is important to the evaluation of techniques to reduce mercury emissions. In Phase III, tests were conducted to identify the characteristics of the particulate control devices (e.g., corona discharge, filter cake, etc.) that impact FGD mercury control and contribute to the observed differences in mercury removal performance across the FGD equipment.

### Improved Wet Scrubber Mercury Control

In Phase II tests of the ESP/FGD equipment combination, the oxidation air Stoichiometric Ratio (SR defined as moles of atomic oxygen per mole of SO<sub>2</sub> absorbed) in the scrubber was tested at normal (SR ~ 5) and very low (SR ~ 2) conditions to study the effect on mercury emissions from the scrubber. In forced oxidation systems, the oxidation air is used to convert calcium sulfite to calcium sulfate. Results showed that total mercury removal across the scrubber increased at very low oxidation air levels (i.e., high sulfite concentration), primarily because the conversion of oxidized to elemental mercury was reduced. When a baghouse was used, oxidation airflow had no effect on mercury removal, but this was expected given that the removal was already at a high level, and conversion of mercury from oxidized to an elemental form was not present to begin with.

The objectives in this phase were to more clearly define the oxidation air level that affects the improvement in mercury removal observed in previous tests, to identify the level of improvement that can be attained with commercial FGD systems, and to investigate the chemistry of mercury reactions in the FGD system. To accomplish these objectives, several oxidation air levels were tested, and tests with chemical additives were performed to investigate

the reaction chemistry of mercury in the limestone slurry. The additives that were selected for testing included H<sub>2</sub>S injection in the flue gas between the ESP and FGD, and the addition of EDTA to the scrubber slurry.

#### **4.2.2 Mercury Control in Non-Scrubbed Systems**

Conventional emissions control for the power generation industry can be classified as scrubbed or non-scrubbed systems. A majority of today's utilities do not have scrubbing systems for SO<sub>2</sub> emissions control, and so do not provide the level of mercury control that can be provided by FGD systems. Electrostatic precipitators are the most common means of high efficiency emissions control for these pulverized coal units.

Mercury control strategies for the substantial non-scrubbed utility market also need to be investigated. Currently, investigations of mercury removal in non-scrubbed systems have typically included ultra-high efficiency or modified particulate control devices and sorbent injection upstream of the particulate control device. For the AECDP Phase III test series, sorbent injection was investigated upstream of the electrostatic precipitator. The two types of sorbents investigated were furnace limestone injection and carbon injection upstream of the ESP.

#### **4.2.3 Additional Coal Data for Data Library**

One of the goals of this program has been to measure the uncontrolled emissions of pollutants from the combustion of coal, and to determine the emission factors based on the concentration of the pollutants in the coal. The uncontrolled emissions are those that exist at the outlet of the air heater and upstream of any pollutant removal device. In Phases I and II, uncontrolled emissions were measured for four different Ohio coal seams, including Ohio 5 and 6, Lower Freeport 6A, Mahoning 7A and Meigs Creek 9.

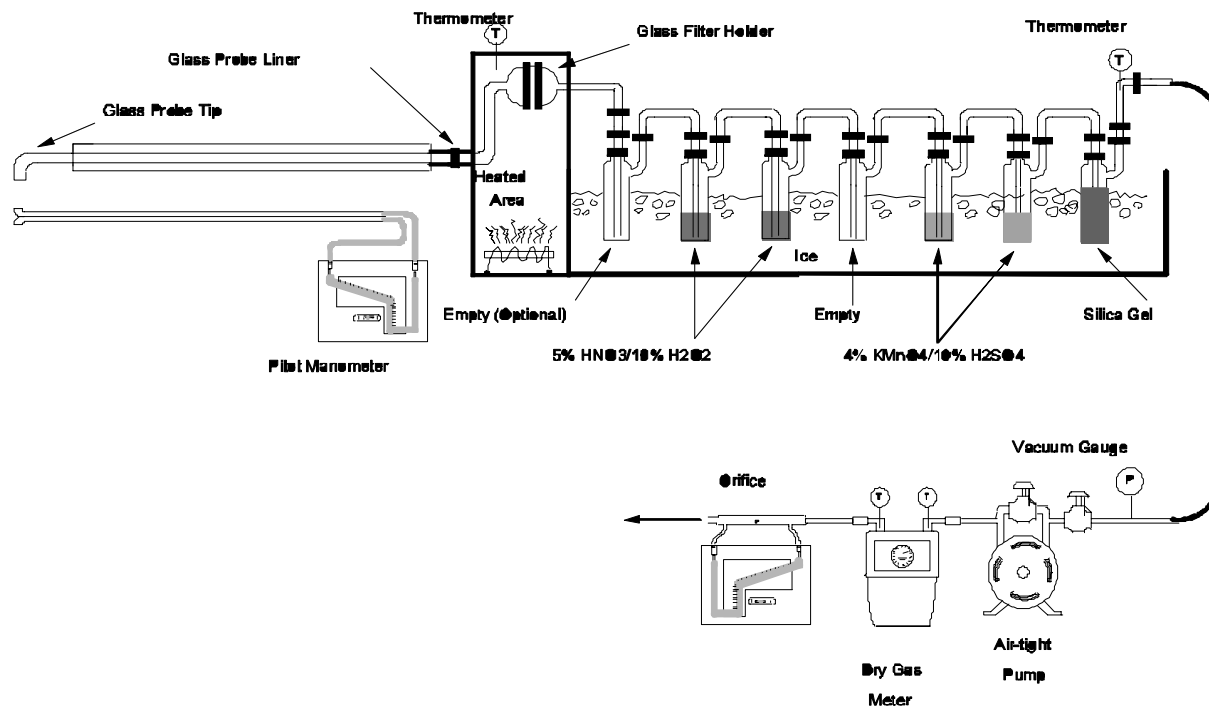
To expand this database, the uncontrolled emissions from two additional coals, a blend of Ohio 5, 6, and 7, and Clarion 4A, were measured. The Clarion 4A was tested only to characterize uncontrolled emissions. The Ohio 5/6/7 blend was tested for uncontrolled emissions and was also used as the test coal for other Phase III tests.

### **4.3 Sampling Procedures and Methods**

Flue gas 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 and II tests. With 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 elemental mercury resulting in an over-reporting of the oxidized mercury fraction. A schematic of the Method 29 sampling train is provided in Figure 4.4.

The Ontario Hydro method has been evaluated by several organizations as an improved measure of the elemental and oxidized mercury species compared to EPA Method 29. The Ontario Hydro technique was most frequently used in Phase III tests. With 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 of Hg. 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 4.4 Method 29 Sampling Train**

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. A summary of these modifications is given below:

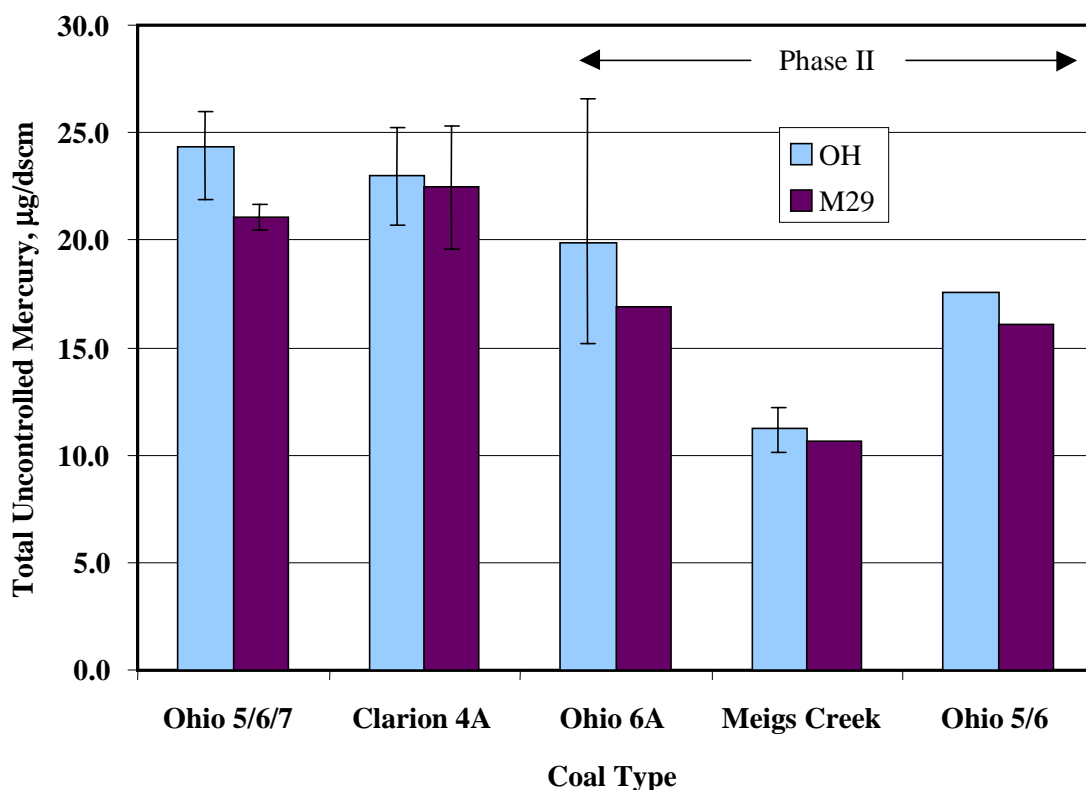
- Potassium permanganate ( $\text{KMnO}_4$ ) was added to the KCl impingers of the Ontario Hydro Method sampling train immediately after sampling to prevent the loss of oxidized mercury during recovery of the sample. The  $\text{KMnO}_4$  was added dropwise until the desired pink endpoint was achieved.
- 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  $\text{SO}_2$  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 sample flow rate, thereby reducing 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.

Mercury emissions were measured at three locations:

- at the outlet of the CEDF simulated economizer (and upstream of particulate control devices)
- downstream of the particulate collection equipment (and upstream of the FGD system)
- emissions from the wet FGD system.

The Ontario Hydro method was used to provide the relative amount of oxidized mercury and elemental mercury in the flue gas. EPA Method 29 was used to verify the total mercury emissions measured for both coals. Figure 4.5 presents the average uncontrolled mercury emissions measured with the Ontario Hydro method compared to the EPA Method 29 method for each coal from Phases II and III. The error bars shown in Figure 4.5 represent the range of the measurements for a given coal and measurement method. Mercury measurements with the two methods generally agree well with the Ontario Hydro method providing slightly larger measurements of total mercury.



**Figure 4.5 Comparison of Ontario Hydro and EPA Method 29 Sampling Methods**

Mercury emissions were the primary measurements of the Phase III tests. Trace metals (antimony, arsenic, barium, cadmium, chromium, cobalt, lead, manganese, nickel and selenium) were selectively measured by the Method 29 samples to provide additional data base information.

#### **4.4 Facility Operation and Performance**

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<sub>x</sub> burner. The average flue gas properties supplied by the CEDF for the two Phase III test coals are summarized in Table 4.1, along with the summary data from the Phase II CEDF-fired coals. The SO<sub>2</sub> and O<sub>2</sub> measurements were taken at the scrubber inlet. The CO and NO<sub>x</sub> measurements were made at the boiler convection pass outlet.

**Table 4.1 Average Flue Gas Composition Provided by the CEDF**

| Flue Gas Component                  | Phase II Coals |             | Phase III Coals |            |
|-------------------------------------|----------------|-------------|-----------------|------------|
|                                     | Ohio 6A        | Meigs Creek | Ohio 5/6/7      | Clarion 4A |
| NO <sub>x</sub> , ppm               | < 300          | < 300       | < 300           | < 300      |
| SO <sub>2</sub> , ppm               | 1,610          | 2,960       | 1,808           | 2,239      |
| CO, ppm                             | < 100          | < 50        | < 150           | < 100      |
| O <sub>2</sub> , %                  | 4.4            | 4.6         | 4.9             | 4.6        |
| HCl, lb/10 <sup>12</sup> Btu        | 132,900        | 49,600      | 90,800          | 19,300     |
| Particulate, lb/10 <sup>6</sup> Btu | 3.4            | 7.1         | 5.5             | 5.9        |

The HCl content of the flue gas was measured upstream of particulate control devices using EPA Method 26A. Measured uncontrolled emissions for both the Phase II and Phase III coals were comparable to the predicted emissions based on the coal heating value and chlorine content. A summary of the comparisons is shown in Table 4.2.

**Table 4.2 Flue Gas HCl Emission Comparison**

| Coal Type   | HCl Emissions, lb/10 <sup>12</sup> Btu |           |
|-------------|--|-----------|
|             | Measured                               | Predicted |
| Ohio 6A     | 132,900                                | 157,000   |
| Meigs Creek | 49,600                                 | 53,000    |
| Ohio 5/6/7  | 90,800                                 | 98,800    |
| Clarion 4A  | 19,300                                 | 36,600    |

The uncontrolled emissions of HCl were primarily partitioned to the vapor phase. Vapor phase percentages for the Phase III coals were 99.6% (Ohio 5/6/7) and 99.4% (Clarion 4A). Similar results were observed for the Phase II coals (99.3% - Ohio 6A and 95.7% - Meigs Creek).

### ***Particulate Control Equipment***

Key average operating conditions for the baghouse and electrostatic precipitator are summarized in Table 4.3. The baghouse operating temperature was generally 30 to 40°F lower than the ESP operating temperature as a result of heat loss from the partial flow flue work. As in Phase II, the baghouse was operated with GORE-TEX® membrane fabric bags. The bags were cleaned when



the pressure drop across the baghouse reached its upper limit. The same set point was used for Phase II and Phase III baghouse operation.

**Table 4.3 Particulate Control Equipment Operating Conditions**

|                                      | <b>Ohio 5/6/7</b> | <b>Clarion 4A</b> |
|--------------------------------------|-------------------|-------------------|
| <b>ESP</b>                           |                   |                   |
| SCA (ft <sup>2</sup> /kacfm)         | 268               | 258               |
| Inlet Temperature (°F)               | 342               | 359               |
| Average Temperature (°F)             | 331               | 342               |
| Average FGD Inlet Temperature (°F)   | 278               | 303               |
| <b>Baghouse</b>                      |                   |                   |
| Air-to-cloth Ratio (ft/min)          | 4.0               |                   |
| Pressure Drop (in. H <sub>2</sub> O) | 5.2               |                   |
| Inlet Temperature (°F)               | 321               |                   |
| Average Temperature (°F)             | 300               |                   |
| Average FGD Inlet Temperature (°F)   | 267               |                   |

Particulate loading and removal performance for the ESP and baghouse are summarized in Table 4.4. Emissions levels for both the ESP and baghouse were below the New Source Performance Standard of 0.03 lb/10<sup>6</sup> Btu.

**Table 4.4 Particulate Emissions Summary**

|   | <b>Ohio 5/6/7</b> | <b>Clarion 4A</b> |
|---|-------------------|-------------------|
| <b>ESP</b>                              |                   |                   |
| Inlet Loading (lb/10 <sup>6</sup> Btu)  | 5.4               | 5.9               |
| Outlet Loading (lb/10 <sup>6</sup> Btu) | 0.015             | 0.016             |
| Particulate Removal (%)                 | 99.72             | 99.74             |
| <b>Baghouse</b>                         |                   |                   |
| Inlet Loading (lb/10 <sup>6</sup> Btu)  | 5.8               |                   |
| Outlet Loading (lb/10 <sup>6</sup> Btu) | 0.006             |                   |
| Particulate Removal (%)                 | 99.90             |                   |

### ***Wet FGD Equipment***

The wet scrubber (abbreviated WFGD) was operated at the same conditions throughout Phase III as shown in Table 4.5. The only parameter that was varied was oxidation air stoichiometry. During Runs P3-4 and P3-5 the oxidation air was purposely decreased to study the effect of slurry chemistry on mercury removal. Variations in pH were caused by upsets to scrubber chemistry, such as blinding, or by the addition of chemical additives like EDTA and DBA (dibasic acid). The large range in the inlet SO<sub>2</sub> concentration was caused by natural variations in the coal sulfur content. Overall, the scrubber operated very smoothly throughout Phase III.

**Table 4.5 Phase III Wet Scrubber Operating Parameters**

|   |             |
|---|-------------|
| Nominal Slurry pH                       | 5.4         |
| Range                                   | 4.9 - 6.1   |
| Nominal L/G Ratio, gal/kacf             | 120         |
| Range                                   | 109 - 125   |
| Nominal Tower Velocity, fps             | 9.0         |
| Range                                   | 8.8 - 10.1  |
| Nominal Spray Flux, gpm/ft <sup>2</sup> | 66          |
| Upper-Spray Header Flow (3), gpm each   | 60          |
| Under-Tray Spray Header Flow, gpm       | 20          |
| Oxidation Air Stoichiometry, mol/mol    | 1.9 - 10.1  |
| Inlet SO <sub>2</sub> , ppm             | 1525 - 2490 |
| SO <sub>2</sub> Removal Efficiency, %   | 89 - 99     |

### **4.5 Quality Assurance Program Management**

Phase III of the AECDP Project was performed in accordance with the Research and Development Division (R&DD) STANDARD PRACTICE Quality Program. This program is registered to International Standard ISO 9001:1994. This program is the baseline operating level designation for normal business practices within R&DD. The program is specified in the Quality Management Manual and implemented by the Standard Practice Manual.

The project workscope is defined by way of project planning with the result being an agreement with the customer at the outset of the project. Changes to the workscope are also agreed upon with the customer. Accordingly, project records are maintained throughout the testing program to provide a historical account of all significant activities. The calibration of all measurement standards and measuring and test equipment used within the R&DD is controlled in order to

ensure that measurements made are quantifiable and reproducible in terms of nationally recognized standards.

The Quality Assurance organization exercises general surveillance over projects conducted according to STANDARD PRACTICE. Internal audits are planned and conducted to verify the implementation and effectiveness of the internal quality system.

Project records are available for customer review at the R&DD. The retention of these records is in accordance with McDermott Technology, Inc. policy (minimum five years) or as specified by customer requirements, applicable codes, standards, or specifications.

The R&DD STANDARD PRACTICE quality assurance program is well recognized as an outstanding base quality program for research work by such organizations as the U.S. DOE, U.S. DOD, EPRI, Gas Research Institute and many others. Application of the Quality Management Manual ensured a high level of quality assurance on this project. Examples of some of the project areas that benefited from this quality assurance program in Phase III include the maintaining and use of technical procedures, calibration of instrumentation, and control of project materials, to name a few.

## 5.0 COAL CHARACTERISTICS AND UNCONTROLLED EMISSIONS

In Phase II of the AECDP Program the effects of coal properties and coal cleaning on mercury emissions were investigated. This effort was continued in Phase III, and in addition, the uncontrolled trace element emissions of the selected coals were characterized in order to expand the emissions database on Eastern bituminous coals.

Coal washing/cleaning is a common practice for upgrading bituminous coal. The primary purpose of coal cleaning/washing is to remove ash and sulfur associated with dense mineral matter in the raw coal, thereby providing a higher grade of coal. It has been shown in the literature and demonstrated in Phase II that washing can also remove significant amounts of mercury from the coal. Similarly, the uncontrolled trace element emissions of several Ohio coals and the removal of these elements in particulate control devices was investigated in Phase II. These efforts were continued in Phase III for two additional Ohio coals, with an emphasis on mercury.

### 5.1 Coal Selection

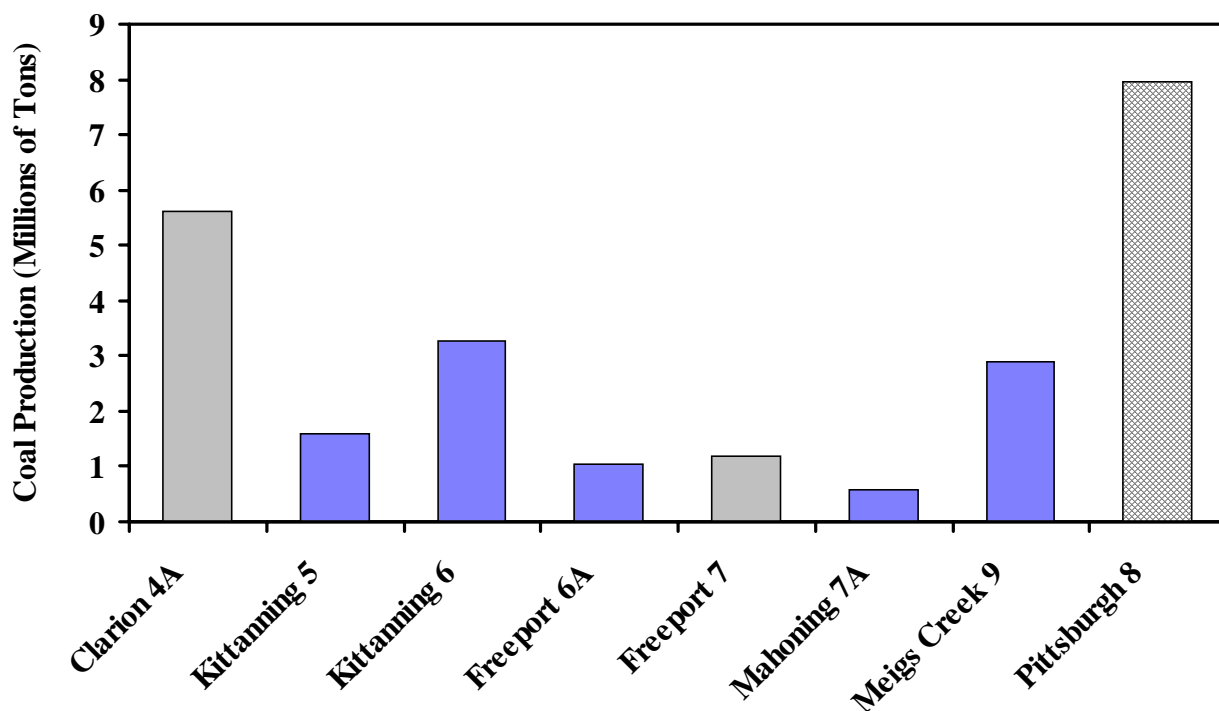
Throughout the AECDP test program coal selection has been guided by two selection principles:

- The coal is mined in quantity
- The coal is fired by Ohio utilities

Along with these, the other factors that influenced coal selection in Phases I and II are:

- A range of coal sulfur contents that is representative of coals burned by Ohio utilities.
- A range of chlorine concentration to determine the affect of chlorine, if any, on the speciated forms of mercury.
- A range of coal types that provide a database of uncontrolled air toxics emissions for Ohio coals.

Figure 5.1 shows the eight most highly mined Ohio coals based on tonnage.<sup>5</sup> The coals tested in Phases I and II of this program are indicated by the dark colored bars. Although heavily mined in Ohio, the Pittsburgh #8 coal (indicated by crosshatch) has been studied extensively at other laboratories across the country<sup>6,7</sup>, and therefore was not selected for Phase III testing. The two remaining coals in Figure 5.1 are the Clarion 4A and the Ohio #7 (Freeport) coals. A review of published data indicated that the mercury and other trace metal concentrations of these coals were similar to other Ohio coals.<sup>8</sup>



**Figure 5.1 Annual Production of Ohio's Eight Most Heavily Mined Coals**

At the time of purchase the Ohio #7 was a premium low-sulfur coal and was not available as a “stand alone” raw coal. Rather it was blended in various percentages with other coals to achieve desired overall properties (sulfur content for example). At the time of purchase the Ohio #7 coal was blended with Ohio #5 and #6 to achieve sulfur concentrations of about 2.8%. A slightly higher fraction of Ohio #7 coal was included in the blend for this test, resulting in an average sulfur content of about 2.5 %. The blended percentages of the Ohio #5, #6, and #7 coals were in the approximate ratio 30%/30%/40%, respectively.

## **5.2 Comparison of Raw & Cleaned Coals**

In Phase II the effect of coal washing on the concentration of mercury, ash and sulfur was examined to determine the amount of mercury removed and to determine if the mercury was preferentially associated with either the ash or the sulfur.<sup>2</sup> This effort was continued and expanded in Phase III. Samples of the raw coal were obtained from the coal supplier before washing. Washed coal samples were obtained either from the trucks as they arrived on site, from the local coal pile or from the coal stream leading to the CEDF coal preparation equipment. Additionally, “as-fired” samples of pulverized coal were obtained from the transport piping between the pulverizer and the pulverized coal bunker.

Table 5.1 shows the concentration of ash, sulfur, chlorine and mercury, and the heating value of the raw (unwashed) and the “as-fired” (washed and pulverized) coal for the Ohio 5/6/7 and Clarion 4A coals. As expected, the concentration of ash and sulfur in the coal decreases and the heating value increases as a result of coal processing. Processing of the raw coal removed over

half of the mercury in the Ohio 5/6/7 coal blend and about one-quarter of the mercury in the raw Clarion 4A coal. The chlorine concentration for both coals increased on a mass basis.

The percentage change in the selected constituents and heating values for the Phase III coals are shown in Table 5.2 along with the comparable data for the Phase II coals. The percentage reduction in ash, sulfur and mercury from coal processing for the Phase II coals is similar to that measured in Phase II. The increase in chlorine concentration and heating value due to washing the coal measured in Phase III is also similar to that in Phase II.

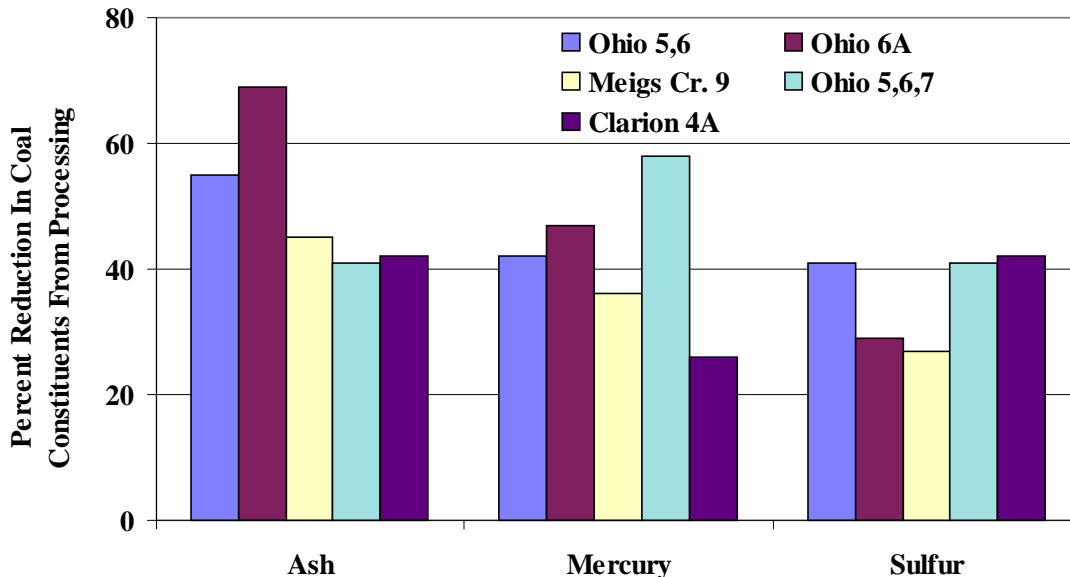
**Table 5.1 Effect of Coal Washing on the Coal Heating Value and Various Constituents.**

| Constituent        | Ohio 5, 6, 7 Blend |          | Clarion 4A |          |
|--------------------|--------------------|----------|------------|----------|
|                    | Raw                | As Fired | Raw        | As Fired |
| Ash (% , dry)      | 15.62              | 9.14     | 15.69      | 9.08     |
| Sulfur (% , dry)   | 4.47               | 2.5      | 3.91       | 2.74     |
| Chlorine (% , dry) | 0.085              | 0.112    | 0.039      | 0.045    |
| Btu/lb (dry)       | 12001              | 13117    | 12801      | 12908    |
| Hg in coal (ppm)   | 0.636              | 0.269    | 0.218      | 0.162    |

**Table 5.2 Percent Change in Coal Constituent Concentrations and Heating Value for the Phase III and Phase II Coals**

| Constituent          | Phase III   |            | Phase II |             |          |
|----------------------|-------------|------------|----------|-------------|----------|
|                      | 5,6,7 Blend | Clarion 4A | Ohio 6A  | Meigs Cr. 9 | Ohio 5,6 |
| Ash (% , dry)        | -41         | -42        | -69      | -45         | -55      |
| Sulfur (% , dry)     | -44         | -30        | -29      | -27         | -41      |
| Chlorine (% , dry)   | +32         | +15        | +17      | +3          | +7       |
| Btu/lb (% , dry)     | +9          | +0.8       | +21      | +16         | +8       |
| Hg in coal (% , dry) | -58         | -26        | -47      | -36         | -42      |

Figure 5.2 shows the total reduction in each of three coal constituents for the Phase II and Phase III coals. The reduction in mercury concentration is similar to the reductions in ash and sulfur. However, because of limitations in sampling the coal and the relatively small number of measurements, a specific trend of mercury reduction with either the ash or the sulfur cannot be made. The average reductions in ash, mercury, and sulfur for the 5 coals are 50.4%, 41.8%, and 34.2%, respectively.



**Figure 5.2 Effect of Coal Cleaning on the Ash, Mercury and Sulfur Content of the Coal**

### **5.3 Trace Element Uncontrolled Emissions**

The fate of trace elements contained in the coal and released (vaporized) during the combustion process depends on many factors including the physical properties of the element. A trace element may be retained on fly ash and remain in the boiler as bottom ash, or be carried by the flue gas to the back end of the boiler. The vapor phase of the element may condense on relatively cold heat transfer surfaces in the convection pass, on the particulate carried by the flue gas, or remain in the vapor state.

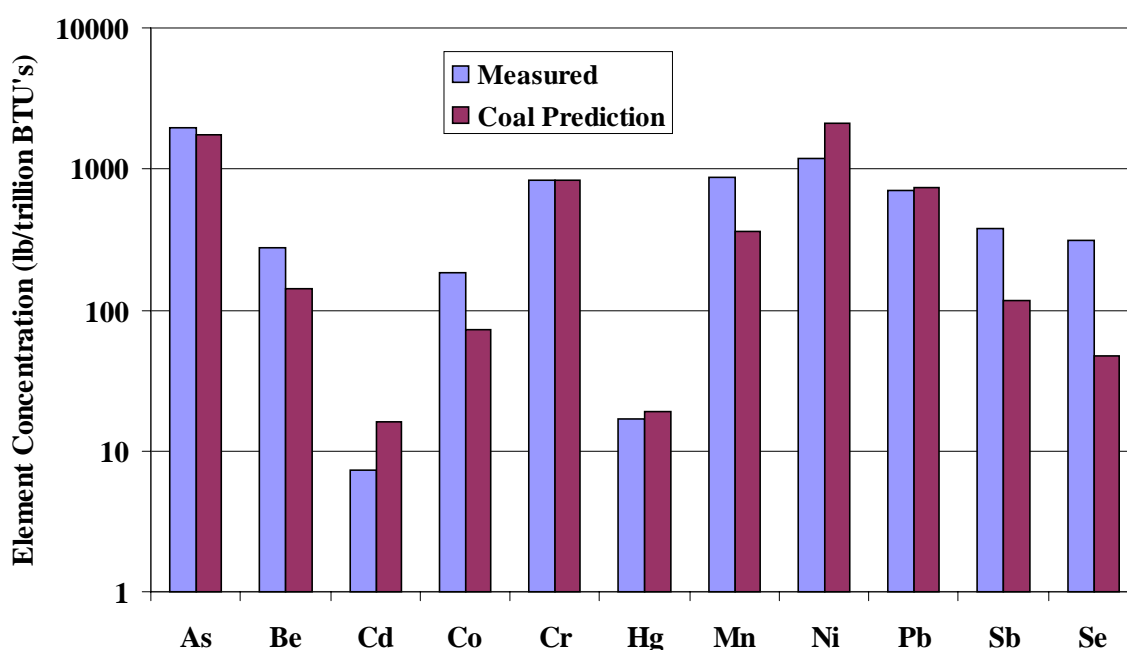
Previous testing by EPRI and the US EPA has resulted in the formulation of EMF's or emission factors that represent the fraction of the element mass flow entering the boiler with the coal that is emitted from the boiler upstream of flue gas clean-up equipment.<sup>9,10</sup> The boiler emission factor reflects the total mass flow of the element leaving the boiler (vapor phase and particle phase) and is dependent on the type of boiler (e.g., wall fired, tangential, cyclone).

As in previous test Phases, the uncontrolled emissions of trace elements were measured in Phase III for the Ohio 5/6/7 blend and the Clarion 4A coals. These measurements were made upstream of the ESP or upstream of the baghouse, depending on the particulate removal device in service at the time of measurement.

The concentrations of chlorine and fluorine were measured using EPA Method 26. Trace metals other than mercury were measured using EPA Method 29 exclusively. Total mercury was measured using both Method 29 and the most recent version of the Ontario-Hydro technique

(permanganate preservative). These sampling and analytic methods provide both vapor phase and particle phase concentrations of the elements, and the concentration of the speciated forms of vapor phase mercury.

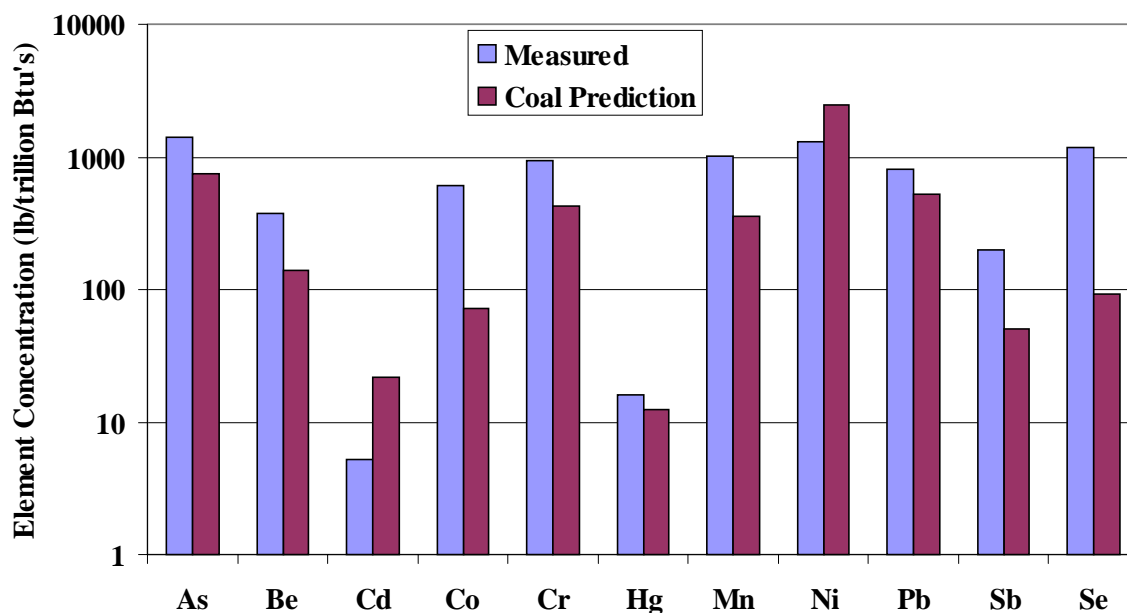
The measured concentrations of trace elements in the flue gas (vapor + particulate) are shown in Figure 5.3 for the Ohio 5/6/7 coal blend. Also shown are the maximum flue gas concentrations based on coal analyses. With the exception of Hg, the flue gas data are the average of a duplicate set of Method 29 measurements. The estimated flue gas concentrations are based on a single analysis of a composited coal sample. The flue gas mercury concentrations are the averages of the Method 29 and multiple Ontario-Hydro measurements, and the estimated concentration is based on multiple analyses of the coals.



**Figure 5.3 Measured Uncontrolled Trace Element Concentrations for the Ohio 5/6/7 Blend and Predictions Based on Coal Concentrations**

Figure 5.3 shows that the concentration of the trace elements varies widely from element to element, and that the measured concentrations in the flue gas are scattered about the concentrations estimated from the coal analyses. Figure 5.4 shows the data for the Clarion 4A, and the same trends are observed in this figure.





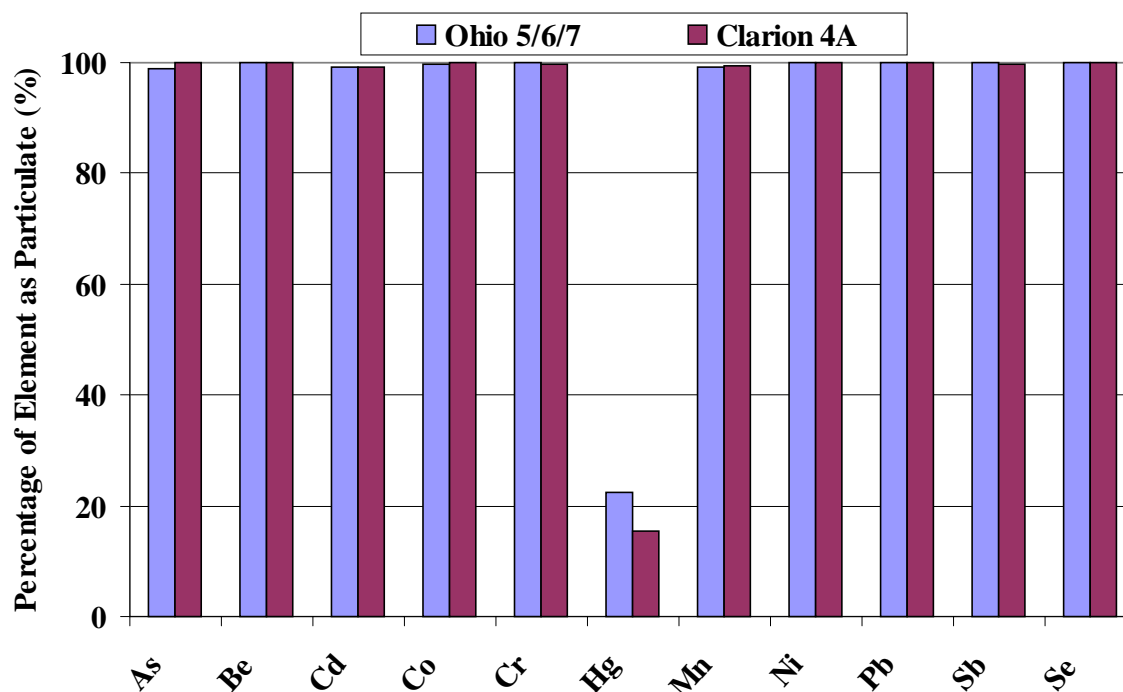
**Figure 5.4 Measured Uncontrolled Trace Element Concentrations for the Clarion 4A Coal and Predictions Based on Coal Concentrations**

Comparison of Figures 5.3 and 5.4 shows that the trace element concentration in the flue gas for the two coals is very similar. This is evident both in the relative concentration of the elements as well as the absolute concentrations. Also, the absolute concentrations of the trace elements for the Ohio 5/6/7 and Clarion coals are very similar to those measured in Phases I and II.

The trace elements in the flue gas shown in Figures 5.3 and 5.4 are contained in both the vapor and solid particulate phases. Figure 5.5 shows the fraction of the elements contained in the particle phase for the two coals tested. With the exception of mercury, over 99% of the element concentration is contained in the particle phase. Elements that are contained almost exclusively in the particle phase are effectively controlled by particulate removal devices.

#### **5.4 Mercury Partitioning and Speciation**

Uncontrolled emissions of mercury are partitioned between the particulate and vapor phases, and the vapor phase mercury typically exists in both the elemental ( $\text{Hg}^0$ ) and oxidized ( $\text{Hg}^{++}$ ) forms. EPA Method 29 is currently the EPA approved sampling procedure for determining metals



**Figure 5.5 Trace Element Partitioning to the Particle Phase for the Ohio 5/6/7 and Clarion 4A Coals**

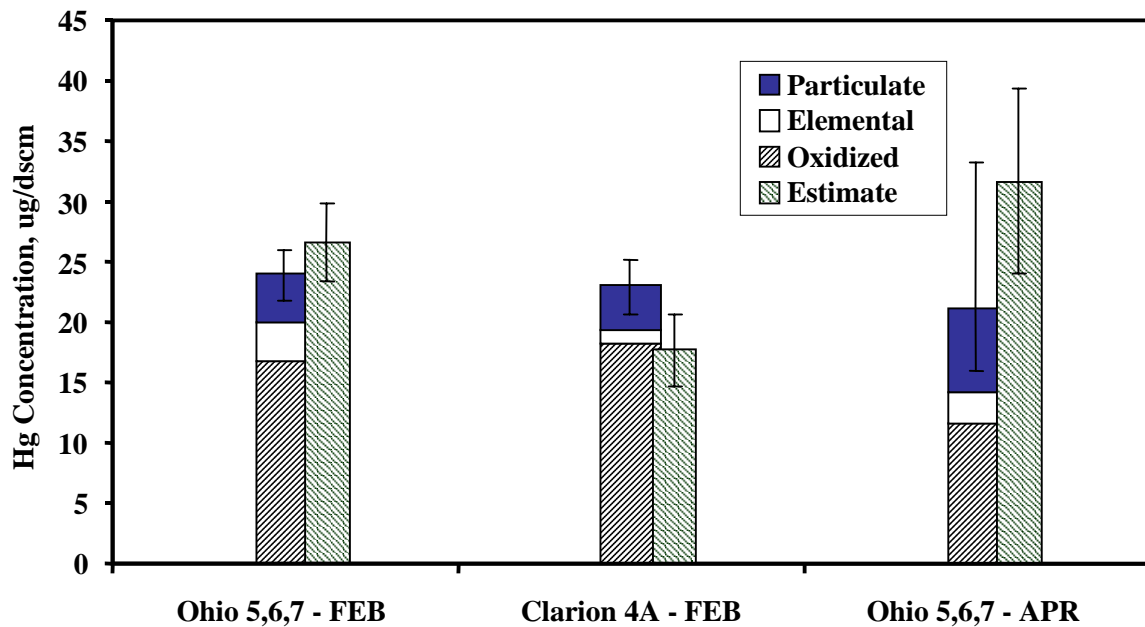
(including total mercury) in flue gas. The Ontario-Hydro method using permanganate preservative is currently the accepted technique for measuring the speciated forms of mercury.

### **Mercury Partitioning**

Phase III testing consisted of two 4-day test campaigns. The Ohio 5/6/7 and Clarion 4A coals were burned during the first week of testing, while only the Ohio 5/6/7 was burned in the second week of testing. The uncontrolled emissions were determined from Ontario Hydro and Method 29 measurements for tests in which there was no sorbent injection.

The mercury partitioning into the particle and vapor phases are shown in Figure 5.6 for each of the coals and for each of the two test campaigns. The data shown are the average of Ontario-Hydro measurements of uncontrolled emissions in tests without sorbent injection. Also shown in this figure is the estimated total mercury concentration in the flue gas based on the mercury concentration in the coal. The range bars indicate the maximum and minimum values contained in the average concentration.

The total uncontrolled emissions of mercury for the Ohio 5/6/7 coal during the two test periods averaged about 23 µg/dscm, and are about 5 µg/dscm less than the estimated emissions based on coal mercury concentration. The variability in the measured gas concentration and the estimated



**Figure 5.6 Measured Uncontrolled Mercury Emissions and Estimated Emissions From Coal Analyses for Phase III Tests**

gas concentration are both greater in the second week of testing than in the first week. The total mercury emissions of the Clarion 4A coal is about 18  $\mu\text{g}/\text{dscm}$  and is about 5  $\mu\text{g}/\text{dscm}$  greater than the estimate based on coal mercury concentration.

Figure 5.7 compares the mercury partitioning (vapor and particle phases) of the Phase III coals with that of the Phase II coals. To account for the variation of total mercury in the coals, the particle and vapor phase fractions are shown as percentages of the total mercury. The fraction of mercury in the particle phase ranges from a low of 5 % for the Miegs Creek coal to 28 % for the average Ohio 5/6/7 blend. The mercury partitioning of the Clarion 4A coal and for the first week of testing with the Ohio 5/6/7 coal are about the same as those measured for Phase II coals. The particle phase mercury fraction for the April tests of the Ohio 5/6/7 blend is larger than for the February test and is about the same percentage as was measured for the Mahoning 7A coal.

Figure 5.8 shows the relationship between the fraction of mercury in the particle phase and the unburned carbon in the fly ash. This figure identifies the data from Phase I and II coals, and the Phase III coals as well as data from the literature.<sup>2,11,12</sup>

The data indicates a general trend of increasing particle phase fraction of mercury with increasing unburned carbon. The scatter in particle phase mercury fraction for values of unburned carbon less than 5% is quite large, which indicates that other variables may affect the

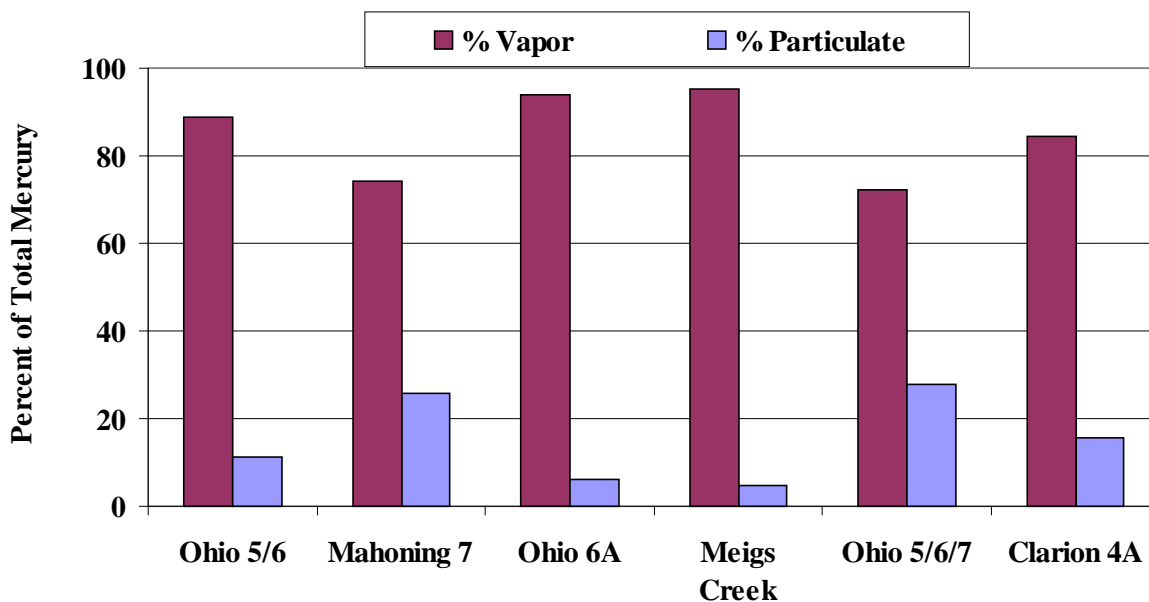


Figure 5.7 Partitioning of Uncontrolled Mercury Emissions For Six of the AECDP Test Coals

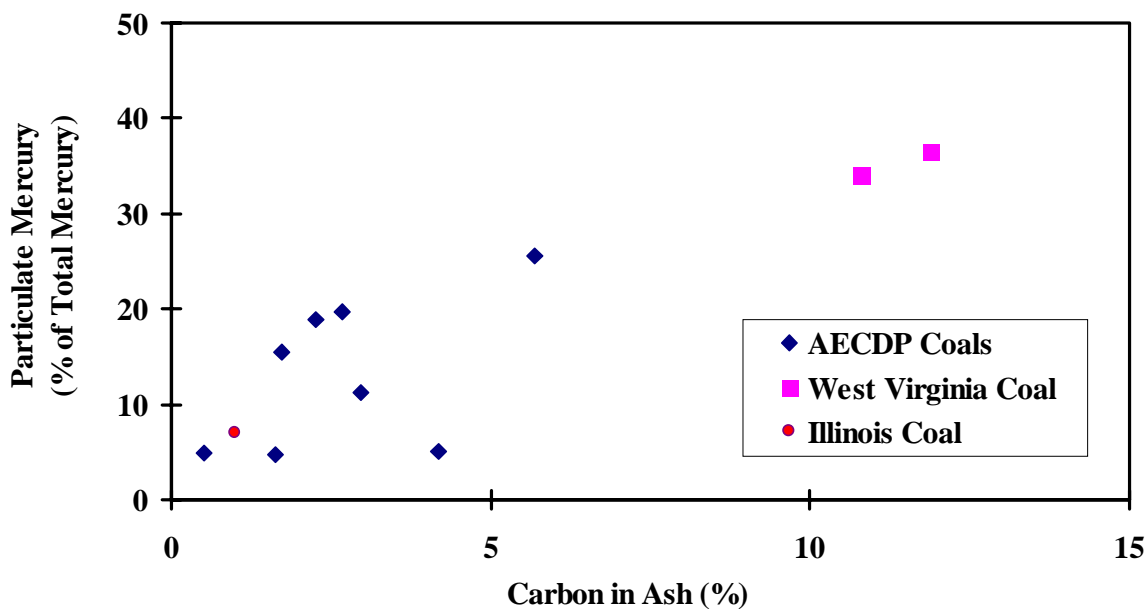


Figure 5.8 Dependence of Particulate Mercury on Carbon in the Fly Ash

particle phase mercury content at low average values of unburned carbon. Examples are combustion conditions or the variation in other coal constituents that affect mercury partitioning.

### **Mercury Speciation**

Vapor phase mercury in flue gas can exist in either the elemental form ( $\text{Hg}^0$ ) or oxidized form ( $\text{Hg}^{++}$ ). The form of the mercury in the flue gas may affect the ultimate fate of the mercury after reaching the atmosphere. The methods available for removal of mercury from the flue gas also depend on the form of the mercury.

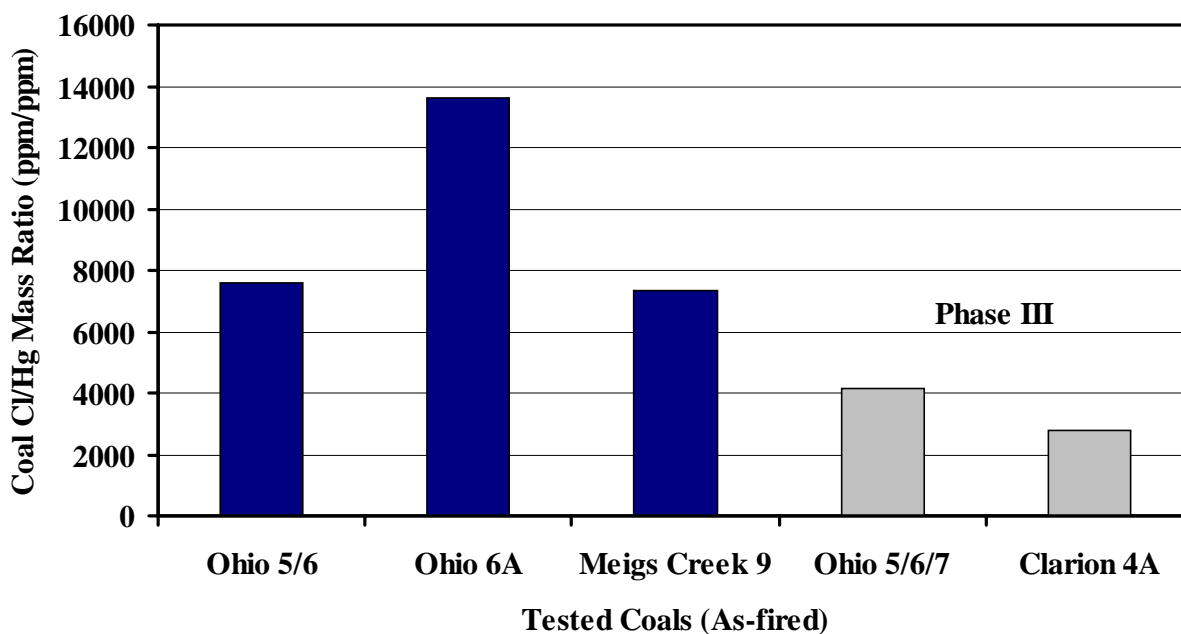
The ionic form of mercury in flue gas is typically considered to be  $\text{HgCl}_2$ , and is relatively soluble in aqueous solutions. It has been shown to be effectively removed in wet scrubbers. The elemental form of mercury is essentially insoluble in aqueous solutions. Removal methods for elemental mercury typically involve adsorbents or amalgam formations with metals, and are estimated to be significantly more costly than for the removal of ionic mercury.

It has been shown that the concentration of chlorine in the flue gas can affect the relative concentration of oxidized and elemental mercury<sup>13</sup>. That is, coals with high chlorine concentration would tend to produce more of the oxidized (mercuric chloride) form of mercury and less of the elemental form. This is one explanation for the tendency of western coals to produce relatively higher fractions of elemental mercury in the vapor phase.

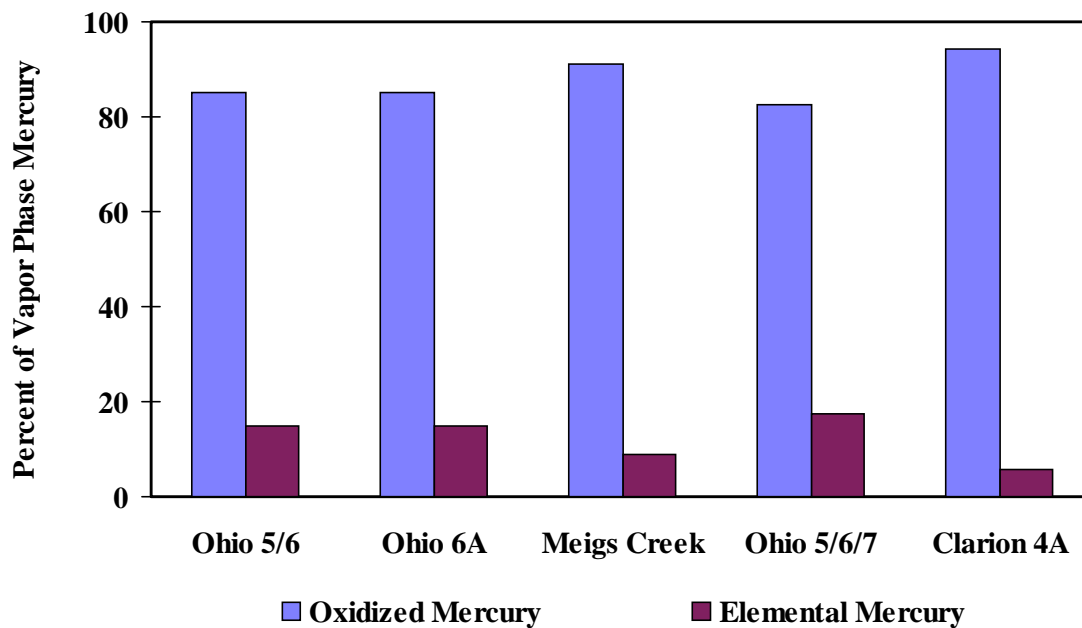
In Phase II, one of the coals was selected based on the relatively low reported chlorine concentration in an attempt to further investigate this effect. This was not achieved because the “as-received” coal had chlorine and mercury concentrations similar to other Ohio coals. Figure 5.9 shows the chlorine-to-mercury concentration ratio in the coal for the Phase II coals and for the coals tested in Phase III. The concentration ratio for the “as-fired” Phase II coals (washed and pulverized) ranged from about 8,000 to 14,000, while the concentration ratio for the Phase III coals ranged from about 3,000 for the Clarion 4A to 4,000 for the Ohio 5/6/7. The Phase III coals had the lowest chlorine/mercury mass ratio of any of the coals tested.

The speciated components of mercury in the flue gas are shown in Figure 5.10 for Phase II, Test 3 and for the Phase III coals. The fraction of the total vapor phase mercury in the ionic form is relatively consistent for all of the coals shown, ranging from about 83% to 95%.

These data, along with those in Figure 5.9 indicate that mercury speciation is unaffected by chlorine content over for the range of coal chlorine concentrations tested. It also must be kept in mind that for the coals tested the chlorine concentration was at least three orders of magnitude greater than the mercury concentration. These high concentrations of chlorine may mask any affect that chlorine has on the speciated fractions of mercury.



**Figure 5.9 Range of Coal Chlorine-to-Mercury Mass Ratios Tested in the AECDP Program**



**Figure 5.10 Vapor Phase Mercury Species in Eastern Bituminous Coals**

## 5.5 Conclusions

Predicted emissions of mercury based on the coal analyses were in good agreement with the measured values. The average predicted emissions for the Ohio 5/6/7 blend were greater than the average measured concentration by about 5 ug/dscm, while predictions for the Clarion 4A were about 5 ug/dscm less than measured.

Approximately 69% of Ohio 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 the two Phase III coals. Both cleaned coals were slightly enriched in chlorine, indicating that chlorine is more concentrated in the bulk raw coal than in the ash fractions for these coals. Coal cleaning produced a decrease in mercury concentration for both coals, with mercury reductions of 58% and 26% for the Ohio 5/6/7 blend and the Clarion 4A, respectively. For the Phase II and Phase III coals the contribution of coal cleaning to the abatement of mercury averaged 42%. This average reduction in mercury content of the coal due to the washing process is greater than sulfur, but less than the ash.

Partitioning - On average, approximately 20% of the uncontrolled mercury emissions were present on the particulate for the Phase III coals. The data from the Phases I, II, and III indicate a strong tendency for increased particle phase mercury with unburned carbon.

The coal chlorine contents for the “as-fired” Ohio 5, 6, & 7 blend and Clarion 4A coals were 1120 and 450 ppm, respectively. The five bituminous coals evaluated in Phases II and III covered a range of coal chlorine content of 450 to 2,200 ppm. The ratio of chlorine to mercury in the coal ranged from 3,000 to 14,000 for the Phase II and III coals. Over this range chlorine concentration did not have an observable affect on mercury partitioning or speciation

The trace metal concentrations in the Phase III coals were similar in magnitude to those measured in previous phases. Also, most of the trace elements were partitioned to the particulate phase, which may be removed by particulate control devices.

## **6.0 PARTICULATE CONTROL AND UNSCRUBBED SYSTEMS**

Approximately seventy-five percent of today's coal-fired power plants are not equipped with FGD systems. These systems most often control particulate emissions with ESPs. With possible mercury emissions regulation for the electric power industry pending, it is imperative to have appropriate cost-effective mercury capture technologies available for both the unscrubbed power plant market and the wet scrubber market.

All three phases of the AECDP project included trace element control across conventional particulate control devices such as ESPs and baghouses. This work is summarized in section 6.1. In Phase III of the AECDP project, limestone and carbon sorbent injection were tested for their mercury capture capabilities. The sorbent injection work is presented in sections 6.2 and 6.3. Section 6.4 briefly discusses methods that are being investigated by others for mercury capture in unscrubbed systems. These and subsequent sections of the report address post-combustion control of mercury emissions, while the pre-combustion contribution from coal cleaning was discussed in section 5.

### **6.1 Particulate Control Device Performance Summary**

#### **6.1.1 Trace Metal Removal**

Conventional baghouses and ESPs have demonstrated high collection efficiencies for metals with low to medium volatility that condense on or form fine particulate. These metals include arsenic, barium, beryllium, cadmium, cobalt, chromium, manganese, nickel, lead, antimony, and selenium. Many of the trace compounds are enriched in the smaller fly ash particles because of the high surface area for deposition by condensation. While this size dependence results in some species being less efficiently removed than the fly ash in the particulate collection device, the removal of trace metals is strongly related to overall particulate collection efficiency.

Numerous field studies have identified "particulate-phase" metals that tend to associate with fly ash particles and are well controlled by particulate control technologies.<sup>14,15</sup> This behavior was confirmed in the Phase I AECDP tests.<sup>1</sup> Comparison of the average removal efficiencies measured across the baghouse and ESP during Phase I and II are provided in Figure 6.1 and Table 6.2

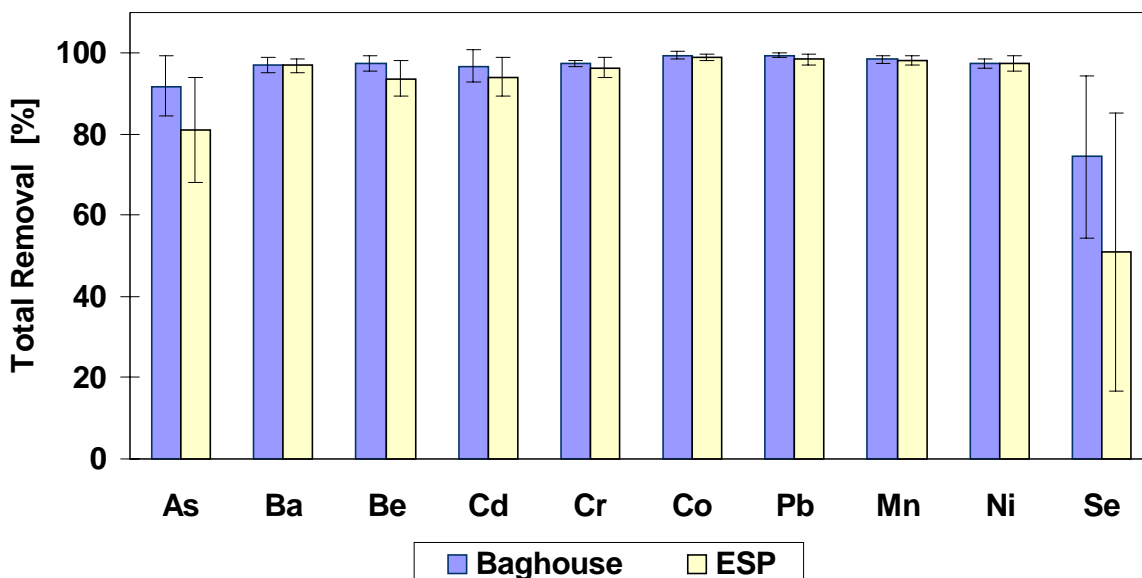
Similar levels of trace element control across the particulate control devices were observed during Phases I and II with the exception of the more volatile elements: arsenic, cadmium, and selenium. The higher level of particulate metal control achieved by the baghouse (in Phase II) can generally be attributed to the overall lower particulate emissions from the baghouse compared to the ESP. Baghouse particulate emissions averaged 0.003 lb/MBtu corresponding to an average particulate removal efficiency of 99.93%. ESP particulate emissions averaged 0.011 lb/MBtu corresponding to an average particulate removal efficiency of 99.72% during typical operation.



The variability in the control of the trace metals across the particulate devices (over a range of operating conditions) is illustrated in Figure 6.1. The metals exhibiting the highest variability in removal efficiency were arsenic and selenium. These metals 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.

**Table 6.1 Comparison of Particulate Device Trace Element Control<sup>2</sup>**

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

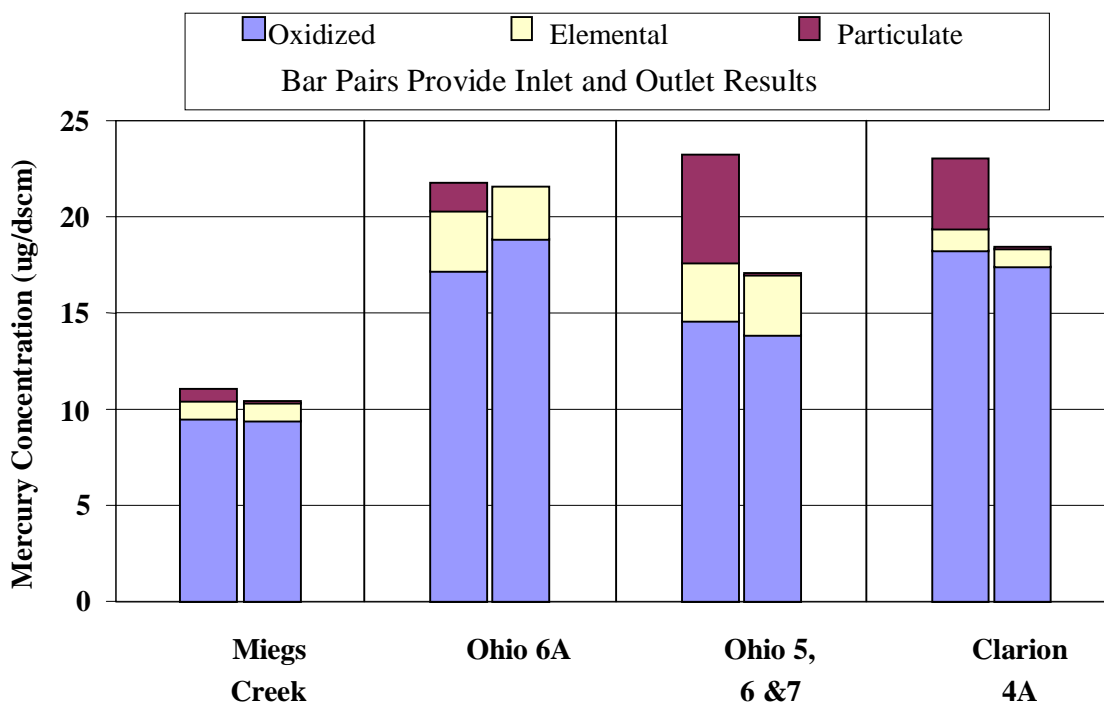


**Figure 6.1 Phase II ESP and Baghouse Trace Metal Removal Efficiency<sup>2</sup>**

## 6.1.2 Mercury Control Across Conventional ESPs and Baghouses

In Phase II it was shown that conventional particulate control equipment can remove nearly all of the particulate phase mercury. However, the vapor phase mercury passes through the devices essentially uncontrolled.<sup>2</sup> This data was confirmed in Phase III.

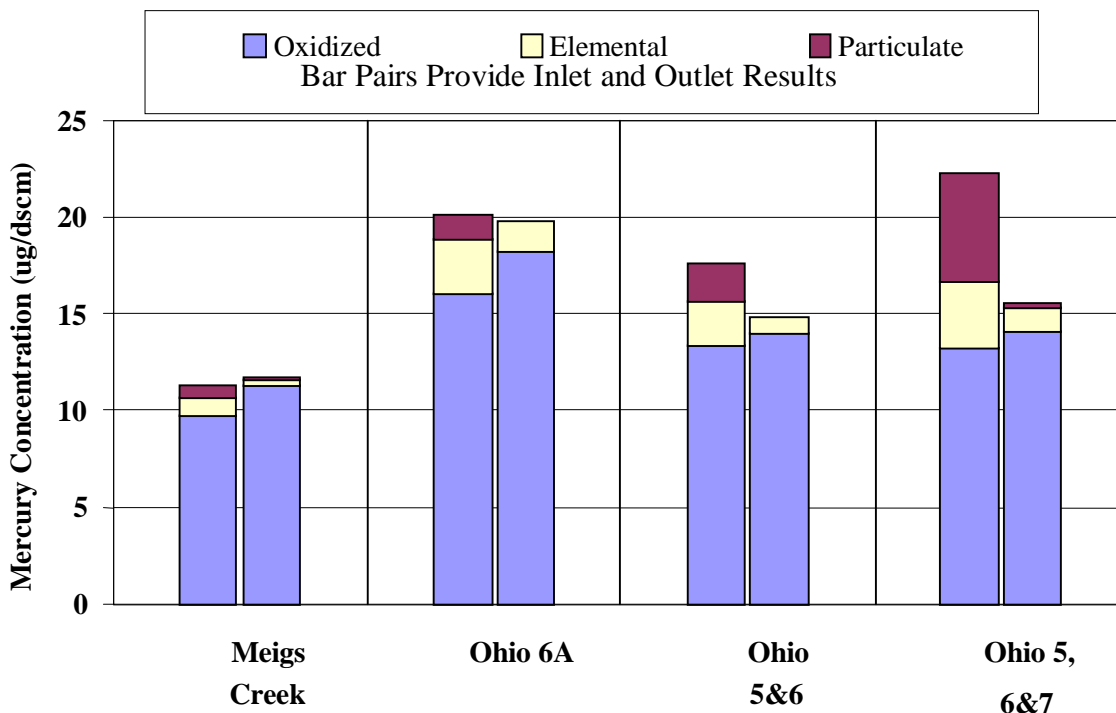
**Electrostatic Precipitator** - In this program, mercury emissions control by the ESP was measured for several Ohio high-sulfur bituminous coals. The ESP was operated at flue gas inlet temperatures ranging from about 325EF to 350EF. Figure 6.2 summarizes the mercury measured at the inlet and outlet of the ESP for four coals. This figure shows the partitioning of mercury between the particulate and vapor phases, and the distribution of mercury species in the vapor phase. Data for this figure were measured using the Ontario Hydro Method with triplicate measurements. Comparison of the mercury concentrations at the inlet and outlet of the ESP show that the particle phase mercury is effectively removed from the flue gas, while the vapor phase mercury passes through the ESP uncontrolled. The ESP provided limited reduction in total mercury emissions.



**Figure 6.2 AECDP Phase II Mercury Removal by the ESP**

Although most of the particulate phase mercury was removed from the flue gas, the inlet mercury consisted of mostly vapor phase mercury. Figure 6.2 indicates that the ESP had little impact on the concentration of elemental mercury in the flue gas. Most of the observed variation in the total mercury measured reflects variation in the measured quantity of oxidized mercury in the vapor phase.

**Baghouse** - The effect of a pulse-jet baghouse on mercury emissions was evaluated for four Ohio high sulfur bituminous coals. In these tests, the baghouse was operated at temperatures ranging from 300EF to 350EF. The partitioning and speciation of mercury at the inlet and outlet of the baghouse is presented in Figure 6.3. As with the ESP, the average total mercury reduction across the baghouse was minimal for each coal. Nearly total control of the particulate phase mercury was measured. In contrast to the ESP, the concentration of elemental mercury in the vapor phase was reduced across the baghouse, while that of the oxidized mercury in the vapor phase increased.

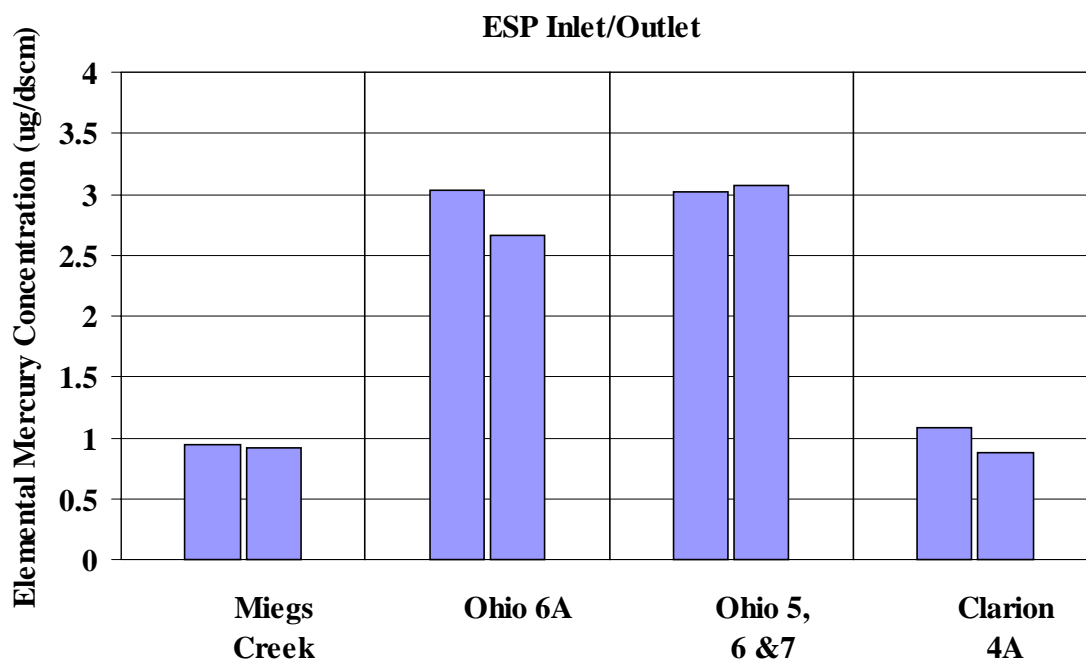


**Figure 6.3 Mercury Removal by a Pulse-Jet Baghouse**

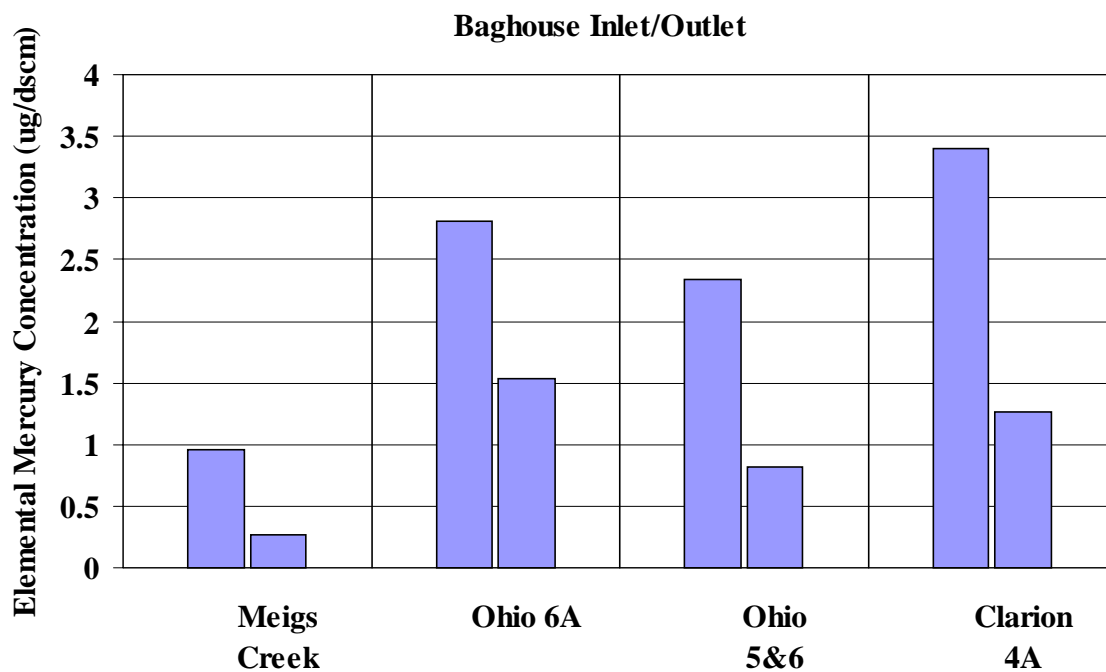
### 6.1.3 Mercury Control Across Conventional ESPs and Baghouses – Phase III

Figures 6.4 and 6.5 show the elemental mercury concentration in the flue gas at the inlet and outlet of the ESP and baghouse, respectively. The data in Figure 6.4 shows that elemental mercury remained essentially the same across the ESP for all coals. The data in Figure 6.5 consistently shows reductions in elemental mercury across the baghouse

It is recognized that the absolute concentrations of elemental mercury for the coals tested are relatively low so that changes in mercury concentration are more difficult to evaluate. However, the consistency of the results for repeat tests and for multiple coals adds to the significance of these findings.



**Figure 6.4 Elemental Mercury Concentration at the Inlet and Outlet of an ESP for Four Ohio Coals**



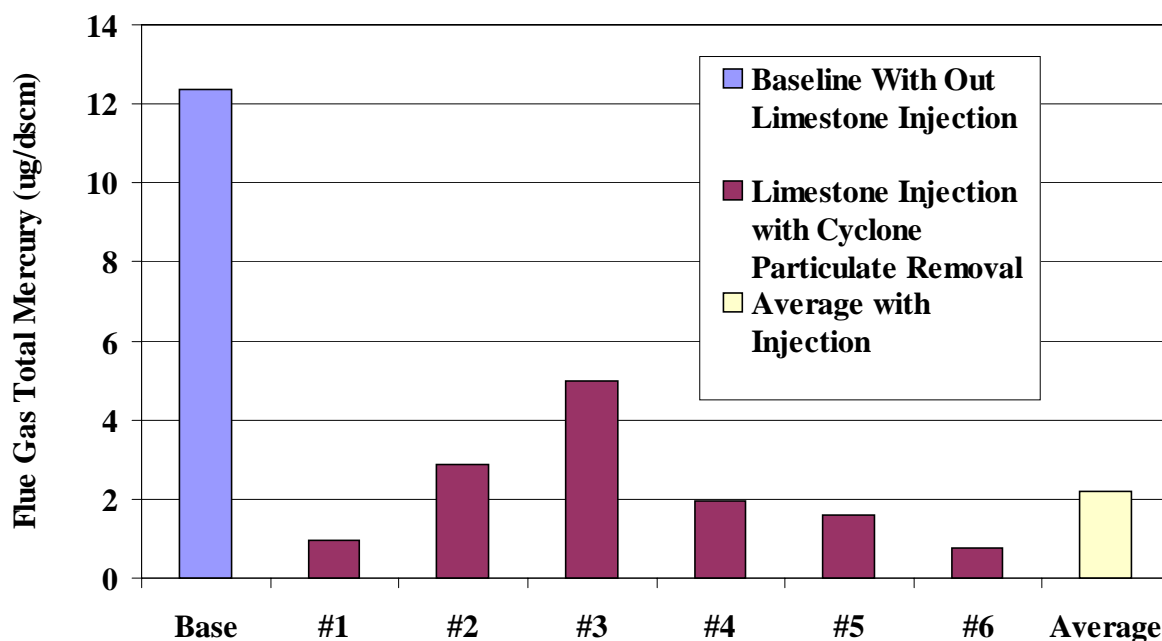
**Figure 6.5 Elemental Mercury Concentration at the Inlet and Outlet of a Baghouse for Four Ohio Coals**

## 6.2 Limestone Injection for Mercury Control

### 6.2.1 Background

The potential for substantial flue gas mercury removal using furnace limestone injection was seen during Babcock & Wilcox/McDermott Technology, Inc.'s Combustion 2000 – Low Emission Boiler System program<sup>16</sup>. The overall goal of the Combustion 2000 program was to dramatically improve environmental performance and thermal efficiency of conventional coal-fired power plants. Furnace limestone injection was used as a unit operation in the Enhanced Limestone Injection Dry Scrubbing System (E-LIDS<sup>TM</sup>). In this test program limestone was injected in the upper furnace at a temperature of about 2200EF. The Combustion 2000 Ca/S ratio was set at 1.40 mol/mol to achieve ultra-high SO<sub>2</sub> removal (a requirement of that project). An 80% efficient cyclone separator was then used to collect the fly ash and calcined lime just upstream of a dry scrubber. At this location the flue gas temperature was approximately 325EF.

Flue gas mercury concentration was measured downstream of the cyclone separator before limestone injection (baseline condition) and for six tests after limestone injection was started. Ontario Hydro measurements of the total flue gas mercury concentration for the baseline and the six limestone injection tests are shown in Figure 6.6. Note that the data are shown as single point measurements in addition to the average for the six runs that were made at a Ca/S ratio of 1.4 mol/mol. The data show that the mercury concentration in the flue gas is substantially reduced by the limestone injection and subsequent particulate removal with a cyclone separator. On average, mercury in the flue gas was reduced by 82%.



**Figure 6.6 Combustion 2000 Furnace Limestone Injection Mercury Removal  
Ca/S = 1.40 mol/mol and Mechanical Cyclone Separator Used for Particulate Control**

The particulate collection device used in these tests was a mechanical cyclone separator with only 80% particulate collection efficiency. It would be expected that a conventional particulate removal device (ESP or baghouse) with particulate removal efficiencies of 99+% would also provide an increase in mercury removal.

Work conducted by the US EPA and Acurex Environmental Corporation (funded by the State of Illinois, ICCI) also indicated that the injection of calcium based sorbents into flue gas could result in significant removal of mercury.<sup>17,18</sup> They examined the high temperature/short gas-phase residence time removal of mercury using injection of lime while burning an Illinois #6 coal. The lime was injected as a slurry at a Ca/S of 2.0 mol/mol at 968°C (1775°F). Under these conditions 77% of the total mercury was removed from the flue gas (Table 6.2). Based on these results they concluded, “injection of lime in the high temperature regions of coal-fired processes upstream of air pollution control systems can efficiently transfer mercury from the gas to the solid phase.”

**Table 6.2 Furnace Lime Injection by EPA/Acurex for Mercury Control<sup>16</sup>**

| Test                           | Total Concentration | Gas Phase Portion | Solid Phase Portion |
|--------------------------------|---------------------|-------------------|---------------------|
| Coal Combustion Baseline       | 5.7 µg/dscm         | 100%              | 0%                  |
| Coal Combustion Lime Injection | 8.0 µg/dscm         | 23%               | 77%                 |

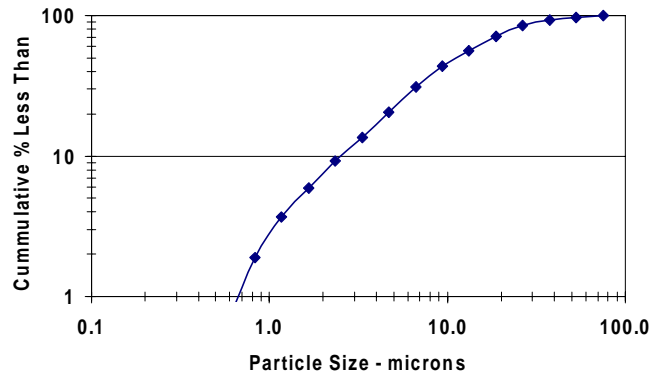
Based on the test results from the B&W/MTI Combustion 2000 project and the EPA/Acurex ICCI project it was determined that furnace injection of calcium-based sorbents was a potential method for mercury removal from power plants without scrubbing systems.

### 6.2.2 Limestone Characteristics and Test Parameters

The limestone chosen for the Phase III AECDP tests was a high purity ( $\text{CaCO}_3 > 95\%$ ) limestone purchased from Akrochem in Akron, Ohio. This sorbent was the same as used during the B&W/MTI Combustion 2000 tests. Table 6.3 and Figure 6.7 show the limestone particle size distribution. The limestone's particle size characteristics included a mass mean diameter ( $D_{43}$ ) of 15.42 microns, Sauter mean diameter ( $D_{32}$ ) of 5.61 microns, and a surface area of  $1.07 \text{ m}^2/\text{cm}^3$ .

**Table 6.3 and Figure 6.7 Limestone Particle Size Distribution**

| <b>Limestone Size Distribution</b> |                                |                       |
|------------------------------------|--------------------------------|-----------------------|
| MMD ( $D_{43}$ ) = 15.42 microns   |                                |                       |
| SMD ( $D_{32}$ ) = 5.61 microns    |                                |                       |
| <b>Size<br/>(microns)</b>          | <b>Cumulative<br/>Mass (%)</b> | <b>% In<br/>Range</b> |
| 75.00                              | 100.00                         | 2.40                  |
| 53.03                              | 97.60                          | 5.17                  |
| 37.50                              | 92.43                          | 7.94                  |
| 26.52                              | 84.49                          | 13.85                 |
| 18.75                              | 70.64                          | 14.50                 |
| 13.26                              | 56.14                          | 12.46                 |
| 9.38                               | 43.68                          | 12.74                 |
| 6.63                               | 30.94                          | 10.30                 |
| 4.69                               | 20.64                          | 7.04                  |
| 3.31                               | 13.61                          | 4.42                  |
| 2.34                               | 9.19                           | 3.24                  |
| 1.66                               | 5.95                           | 2.27                  |
| 1.17                               | 3.68                           | 1.79                  |
| 0.83                               | 1.89                           | 1.22                  |
| 0.59                               | 0.67                           | 0.67                  |



Limestone feed rates previously tested in the Combustion 2000 program were set based on stoichiometry ratios consistent with  $\text{SO}_2$  capture. Although these feed rates also provided for substantial mercury removal, they result in additional operating difficulties because of the increased solids loading in the convective heat transfer region of the boiler. For this reason, limestone feed rates were selected for these tests that represented relatively low Ca/S ratios yet quite high Ca/Hg ratios. Lower Ca/S ratios provide the obvious economic benefit of reduced reagent cost, and also result in convection pass solids loading only slightly greater than that from the fly ash.

Two limestone flow rates were tested. The flow rates chosen for the limestone injection tests were 200 lb/hr ( $\text{Ca/S} = 0.35 \text{ mol/mol}$ ) and 25 lb/hr ( $\text{Ca/S} = 0.04 \text{ mol/mol}$ ). An injection temperature target of 2100 to 2300 °F was chosen as the optimum range to calcine the limestone ( $\text{CaCO}_3$ ) into lime ( $\text{CaO}$ ). It was assumed that  $\text{CaO}$  would be more reactive with mercury as it is with  $\text{SO}_2$ , because of the increased surface area and reactivity.

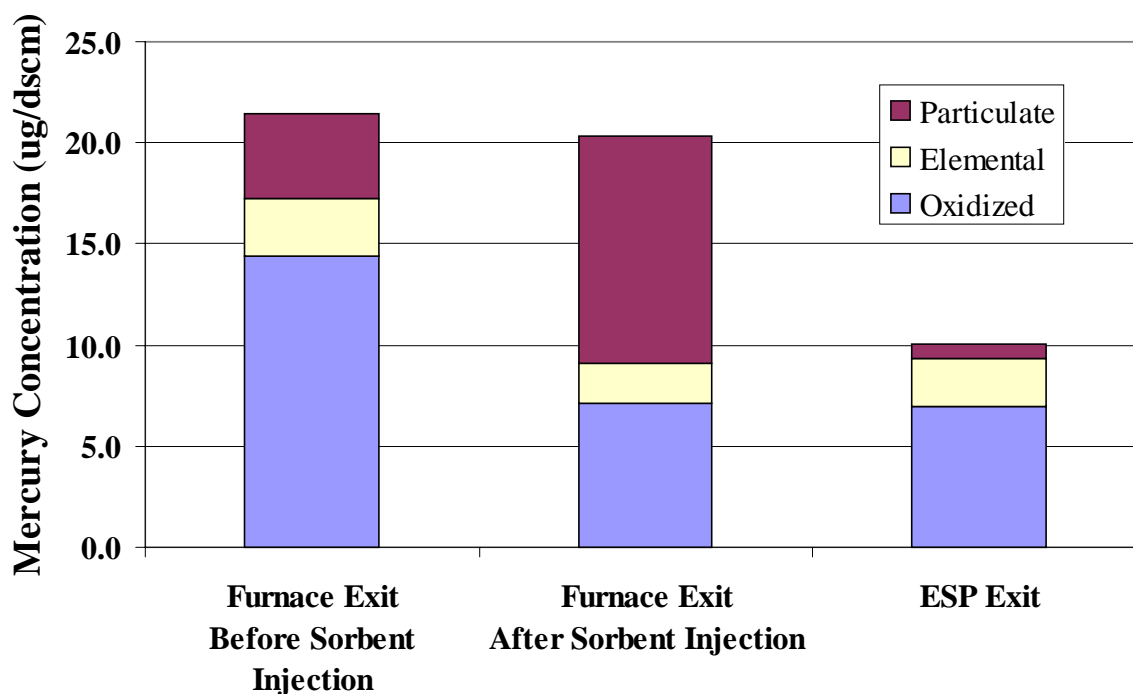
The ESP was operated for particulate control during the limestone injection tests. The ESP inlet flue gas temperature was 350 °F. Mercury concentrations were determined at the inlet and outlet of the ESP with triplicate Ontario Hydro measurements. One set of triplicate measurements was performed prior to sorbent injection to provide a baseline set of comparison data.

### 6.2.3 Limestone Injection Mercury Capture Results

Figure 6.8 shows the mercury partitioning and speciation for three sets of mercury measurements:

- ESP inlet without limestone injection (baseline)
- ESP inlet with limestone injection of 200 lb/hr
- ESP outlet with limestone injection of 200 lb/hr

As shown in Figure 6.8, the total mercury in the flue gas at the ESP inlet with and without limestone injection is about the same. Limestone injection substantially increases the particle phase mercury, thereby substantially reducing the vapor phase oxidized mercury. The particle phase mercury is then effectively removed by the ESP, providing an overall mercury removal of 53% compared to the baseline condition. Without limestone injection, mercury removal would correspond to the particle phase mercury at the ESP inlet and would be at most 17%. The increased removal provided by limestone injection appears to be a result of the capture of oxidized mercury by the CaO particulate (onto or into the particulate phase) and the subsequent removal of the particulate in the ESP. Limestone injection at a rate of 200 lb/hr (Ca/S of 0.35) had no apparent effect on the elemental mercury.

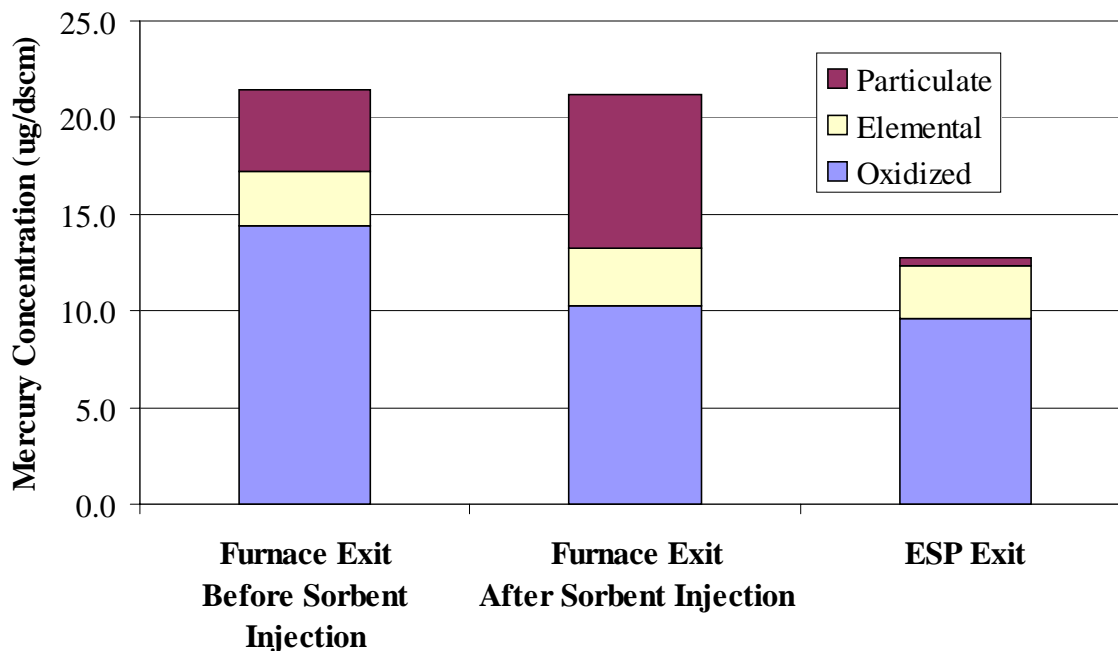


**Figure 6.8 Limestone Injection Mercury Capture at Ca/S = 0.35**

Figure 6.9 shows a similar set of data for a limestone feed rate of 25 lb/hr. This figure shows the same trends as Figure 6.8. Limestone injection increases the particle phase mercury while decreasing the oxidized vapor phase mercury. Compared to the baseline mercury concentration without injection, limestone injection at 25 lb/hr provided 41% mercury removal across the ESP.

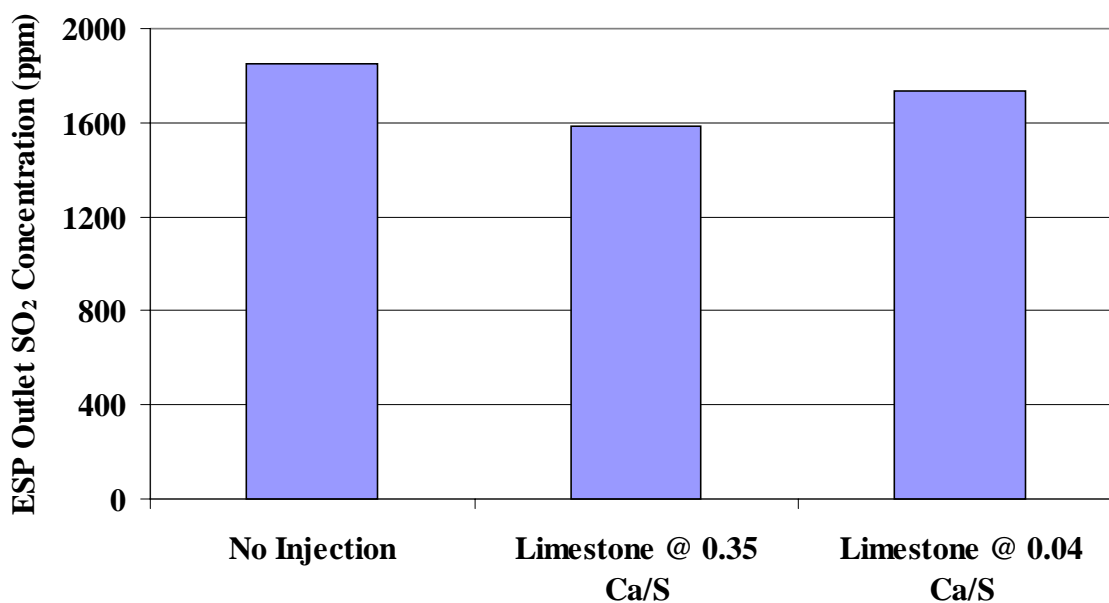


The mercury removal appears to be a result of the reduction of oxidized mercury (onto or into the particulate phase) and the subsequent removal of the particulate in the ESP. Limestone injection at a Ca/S of 0.04 had no effect on the elemental mercury.



**Figure 6.9 Limestone Injection Mercury Capture at Ca/S = 0.04**

Other benefits associated with the use of limestone injection for mercury control include an incremental amount of SO<sub>2</sub> removal and a high probability for SO<sub>3</sub> removal. The SO<sub>2</sub> concentration in the flue gas without limestone injection and at the two injection flow rates is shown in Figure 6.10. An SO<sub>2</sub> removal of 15% was achieved at a limestone Ca/S of 0.35 mol/mol (200 lb/hr) and a removal of 7% at a limestone Ca/S of 0.04 (25 lb/hr). Although these removals are relatively small, it may provide a utility with an SO<sub>2</sub> trim, or simply provide additional margin on operation (adjust operating conditions or SO<sub>2</sub> credits).



**Figure 6.10 SO<sub>2</sub> Removal During Limestone Injection Tests**

Data was not obtained for SO<sub>3</sub> removal during the AECDP tests. However, work done at Babcock & Wilcox/McDermott Technology, Inc., and by other investigators indicates that furnace injection of a calcium-based sorbent can effectively remove SO<sub>3</sub>, a PM<sub>2.5</sub> precursor, from the flue gas. Reducing the SO<sub>3</sub> concentration in the flue gas reduces the flue gas acid dewpoint and the risk of corrosion. This provides the potential for additional heat recovery by the air heater and the associated increase in thermal efficiency. Operation at reduced air heater gas temperatures may also increase mercury removal. Removal of SO<sub>3</sub> from the flue gas may also cause slightly reduced performance of an ESP.

### **6.3 Carbon Injection for Mercury Control**

#### **6.3.1 Background**

Injection of activated carbon into the flue gas is a method of mercury control that is currently used for municipal solid waste (MSW) plants.<sup>19,20</sup> With reported mercury removals of more than 90 percent, activated carbon injection is effective for the control of mercury in MSW plants and medical waste combustors (MWCs).<sup>21</sup> Its effectiveness on a wide range of power plants, however, is still uncertain. The major unknown is the effectiveness of carbon injection at typical power plant mercury concentrations, which are usually one to two orders of magnitude lower than those in MWCs. The gas conditions and mercury species found at the two types of facilities are also significantly different. Preliminary studies on utility flue gas have indicated that carbon injection can be used to remove mercury from coal-fired flue gas.<sup>22,23</sup>

Activated carbon tests were conducted by EPRI and Radian at EPRI's Environmental Control Test Center (ECTC) in 1994 burning an Eastern U.S., medium-sulfur coal.<sup>24</sup> The study

investigated the effects of carbon injection rate and flue gas temperature on mercury removal from flue gas. The activated carbon was injected at 350 °F upstream of an ESP. Results of the EPRI/Radian study are presented in Table 6.4 below. Note that the mercury values are for the vapor phase mercury only. From these results they concluded that without carbon injection, essentially no vapor-phase mercury was removed across the ESP and the total vapor phase mercury removal was only about 25% for a carbon-to-mercury ratio of 10,000:1.

**Table 6.4 EPRI/Radian Vapor Phase Mercury Removal Data for Carbon Injection Upstream of an ESP<sup>24</sup>**

| Test ID                     | Run | Inlet Hg(0)<br>μg/Nm <sup>3</sup> | Inlet Hg(II)<br>μg/Nm <sup>3</sup> | Total Inlet Vapor<br>μg/Nm <sup>3</sup> | Hg(0) Removal (%) | Hg(II) Removal (%) | Total Hg Removal (%) |
|-----------------------------|-----|-----------------------------------|------------------------------------|---|-------------------|--------------------|----------------------|
| <b>Baseline</b>             | 1   | 0.95                              | 14.00                              | 14.95                                   | NC                | NC                 | NC                   |
| <b>Baseline</b>             | 2   | 0.58                              | 9.20                               | 9.77                                    | 0                 | 2                  | 2                    |
| <b>Baseline</b>             | 3   | 0.59                              | 9.47                               | 10.06                                   | -5                | 8                  | 7                    |
| <b>Average for Baseline</b> |     |                                   |                                    |   | <b>-3</b>         | <b>5</b>           | <b>5</b>             |
| <b>3000:1</b>               | 1   | 0.28                              | 9.75                               | 10.03                                   | 2                 | 12                 | 12                   |
| <b>3000:1</b>               | 2   | 0.29                              | 8.96                               | 9.25                                    | 5                 | 1                  | 1                    |
| <b>3000:1</b>               | 3   | 0.43                              | 8.54                               | 8.97                                    | 40                | 5                  | 6                    |
| <b>Average for 3000:1</b>   |     |                                   |                                    |   | <b>16</b>         | <b>6</b>           | <b>6</b>             |
| <b>10000:1</b>              | 1   | 0.85                              | 9.49                               | 10.34                                   | 58                | 20                 | 23                   |
| <b>10000:1</b>              | 2   | 1.04                              | 8.81                               | 9.85                                    | 74                | 17                 | 23                   |
| <b>10000:1</b>              | 3   | 0.94                              | 9.21                               | 10.15                                   | 55                | 23                 | 26                   |
| <b>Average for 10000:1</b>  |     |                                   |                                    |   | <b>62</b>         | <b>24</b>          | <b>24</b>            |

A research program co-funded by EPRI and Public Service Electric and Gas (PSE&G), with ADA Technologies as a subcontractor, evaluated the potential of particulate collection devices to reduce mercury emissions through carbon injection. The tests were performed at the Hudson Generating Station in Jersey City, New Jersey.<sup>25</sup> The plant burns a low-sulfur bituminous coal. Results from these tests are shown in Table 6.5. Two types of activated carbon were tested; American Norit's Darco FGD and an experimental carbon identified as AC-1.

**Table 6.5 EPRI/PSE&G Hudson Station  
Mercury Removal using Carbon Injection Upstream of an ESP**

| <b>Sorbent</b> | <b>Injection Rate<br/>C/Hg ratio</b> | <b>Collection<br/>Temperature (°F)</b> | <b>Total Hg Removal<br/>Range (%)</b> |
|----------------|--------------------------------------|--|---------------------------------------|
| <b>None</b>    | 0                                    | 255                                    | 3                                     |
| <b>None</b>    | 0                                    | 268 – 278                              | 0                                     |
| <b>Norit</b>   | 11500:1                              | 240 – 255                              | 13 – 17                               |
| <b>Norit</b>   | 20000:1                              | 240 – 255                              | 41 – 42                               |
| <b>Norit</b>   | 45000:1                              | 220 – 235                              | 76 – 83                               |
| <b>Norit</b>   | 27000:1                              | 275 – 280                              | 14 – 38                               |
| <b>Norit</b>   | 45000:1                              | 270 – 275                              | 28 – 35                               |
| <b>AC-1</b>    | 18000:1                              | 240 – 250                              | 33 – 45                               |
| <b>AC-1</b>    | 45000:1                              | 240 – 250                              | 56 – 58                               |
| <b>AC-1</b>    | 29000:1                              | 280                                    | 28                                    |

The data indicate a distinct reduction in total mercury removal efficiency with increased temperature. The maximum mercury removal achieved was 83% at 221 °F in the ESP with a Norit C/Hg ratio of 45000:1. Full-scale ESP operation at this low temperature is not practical however, due to potential problems with acid condensation. The highest mercury removal achieved at the higher temperature range was 35% at 272 °F and a carbon C/Hg ratio of 45000:1.

Because of the current interest in activated carbon injection for mercury control, one test was conducted during the Phase III AECDP project. These results were used for comparison against results obtained by others as well as for comparison against the furnace limestone injection data.

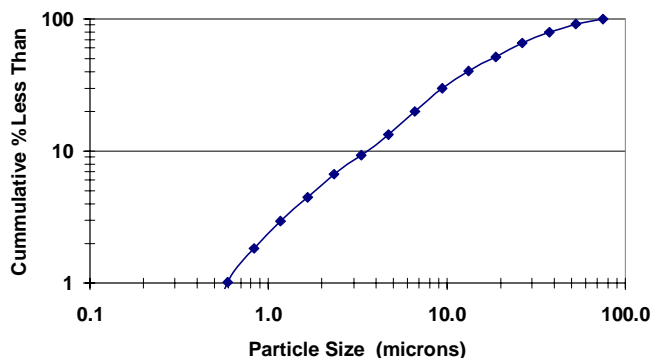
### **6.3.2 Carbon Sorbent Characteristics and Test Parameters**

The activated carbon selected for the injection tests was a lignite-based activated carbon obtained from Norit Americas (commercially known as Darco FGD carbon). Table 6.6 and Figure 6.11 show the carbon particle size distribution. The carbon's particle size characteristics included a mass mean diameter ( $D_{43}$ ) of 22.9 microns, Sauter mean diameter ( $D_{32}$ ) of 7.08 microns, and a surface area of  $0.85 \text{ m}^2/\text{cm}^3$ .

The carbon was injected upstream of the ESP. The injection temperature was approximately 400°F and the ESP inlet temperature was about 345°F. The carbon flow rate was approximately 14 lb/hr which is equivalent to a carbon-to-mercury (C/Hg) mass ratio of 9000:1.

**Table 6.6 and Figure 6.11 Carbon Particle Size Distribution**

| <b>Carbon Size Distribution</b> |                                |                       |
|---------------------------------|--------------------------------|-----------------------|
| MMD ( $D_{43}$ ) = 22.9 microns |                                |                       |
| SMD ( $D_{32}$ ) = 7.08 microns |                                |                       |
| <b>Size<br/>(microns)</b>       | <b>Cumulative<br/>Mass (%)</b> | <b>% In<br/>Range</b> |
| 75.00                           | 100.00                         | 8.65                  |
| 53.03                           | 91.35                          | 11.63                 |
| 37.50                           | 79.73                          | 13.45                 |
| 26.52                           | 66.28                          | 14.41                 |
| 18.75                           | 51.86                          | 11.63                 |
| 13.26                           | 40.24                          | 10.47                 |
| 9.38                            | 29.77                          | 9.80                  |
| 6.63                            | 19.97                          | 6.73                  |
| 4.69                            | 13.24                          | 3.92                  |
| 3.31                            | 9.32                           | 2.66                  |
| 2.34                            | 6.66                           | 2.20                  |
| 1.66                            | 4.45                           | 1.50                  |
| 1.17                            | 2.95                           | 1.13                  |
| 0.83                            | 1.83                           | 0.82                  |
| 0.59                            | 1.01                           | 0.74                  |
| 0.41                            | 0.27                           | 0.27                  |



### 6.3.3 Carbon Injection Mercury Capture Results

Particulate and vapor phase mercury species were measured at the inlet and outlet of the ESP during the carbon injection test, and are shown in Figure 6.12. Also shown in this figure are baseline mercury concentrations measured before any injection tests. Compared to the baseline condition, carbon injection at 14 lb/hr (C/Hg = 9000:1 by mass) resulted in a total mercury removal of 53%. The removal appears to be a result of the capture of oxidized mercury (onto or into the particulate phase) and then the subsequent removal of the particulate in the ESP. Carbon injection at a C/Hg of 9000:1 under the operating conditions discussed above had no effect on the elemental mercury.

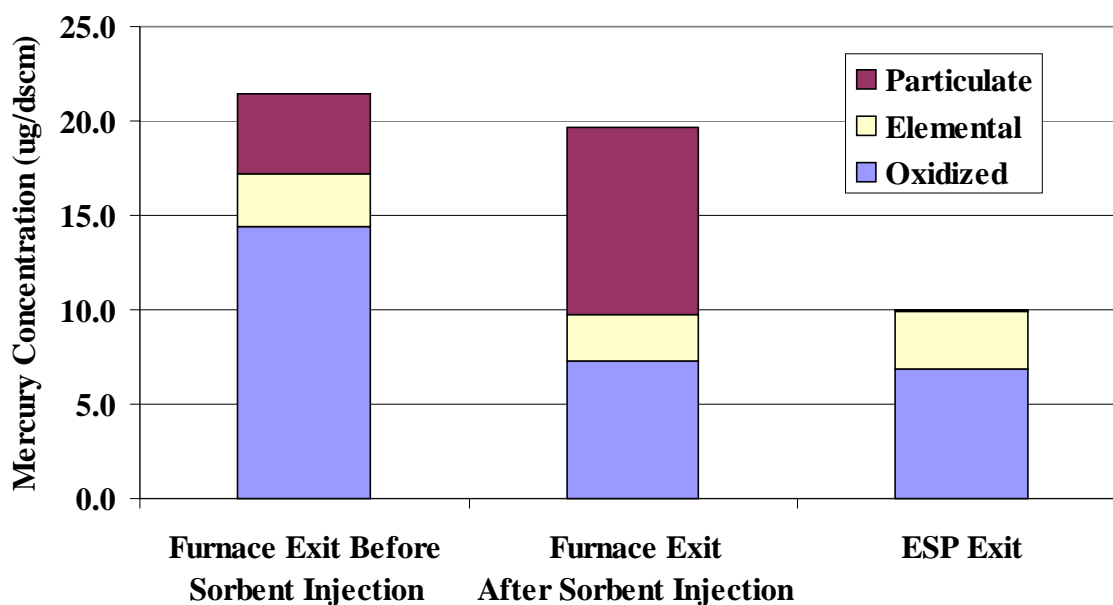


Figure 6.12 Carbon Injection Mercury Capture at C/Hg = 9000:1

#### 6.4 Limestone and Carbon Injection Summary

The test results for limestone and carbon injection show that significant amounts of mercury can be removed through the use of sorbents. Table 6.7 provides a summary of the operating conditions for the three tests.

Table 6.7 shows that the carbon injection had the lowest sorbent/Hg mass ratio but provided a mercury removal equivalent to the high flow limestone test. The difference in sorbent/mercury ratios for these two tests is about a factor of 8. This indicates that activated carbon is a more effective sorbent than limestone on a mass basis. However, activated carbon typically costs over an order of magnitude more than limestone, and therefore, based on these tests, limestone is more effective on a sorbent cost basis.

Table 6.7 AECDP Sorbent Injection Operating Conditions Summary

|                       | Limestone | Limestone | Carbon  |
|-----------------------|-----------|-----------|---------|
| Flow Rate, #/hr       | 200       | 25        | 14      |
| Ca/S mass ratio       | 0.35      | 0.04      | ---     |
| Sorbent/Hg mass ratio | 125,000:1 | 16,000:1  | 9,000:1 |
| Injection Temp, °F    | 2200      | 2200      | 400     |
| ESP Temp, °F          | 350       | 350       | 345     |
| Total Hg Removal      | 53%       | 41%       | 53%     |

## 6.5 Other Unscrubbed Mercury Removal Systems

Other methods or sorbents for mercury removal in unscrubbed systems have been investigated and reported in the literature. Provided below is a summary of several of these methods and technologies, which can be compared to limestone injection.

Other approaches to mercury control that are under investigation and may be applicable to unscrubbed utility systems include:

- Injection of other non-carbon sorbents.
- Injection of impregnated carbons and unburned carbon
- Advanced particulate control device designs

***Non-Carbon Sorbents*** - Examples of other sorbent test programs for mercury control include:

- Acurex and the U.S. EPA have conducted bench-scale, packed bed studies of a mixture of fly ash and hydrated lime (advanced silicate, also known as Advacate) as well as Advacate sorbents with chemical additives for mercury removal.<sup>18</sup> This work is being performed in combination with hydrated lime and carbon tests for comparison. Results have shown that the injection of Advacate sorbents give similar mercury removals as carbon based sorbents.
- The University of Cincinnati is investigating silicon and titanium based sorbents for mercury capture in a program funded through the Ohio Coal Research Consortium (OCRC).<sup>26</sup>
- Dravo Lime is using Sorbalit for mercury control. Sorbalit is produced by mixing lime with surface-activated substances such as activated carbon or lignite coke, and sulfur-based components in a proprietary process.

In comparison with furnace limestone injection, virtually all of the other sorbents being investigated are more costly and are not as near to commercial development. Furnace limestone injection allows for a very low-cost sorbent to be used in small amounts for modest mercury control (40 – 60%).

***Activated Carbons*** - The injection of activated carbon into the flue gas of municipal solid waste plants has been shown to be an effective way to control mercury emissions (often >90% removal). Many organizations have been investigating the use of activated carbon for utility mercury control. The investigations have also included impregnated carbons such as those tested at the Energy and Environmental Research Center (EERC) at the University of North Dakota<sup>27</sup> as well as unburned carbon in utility coal fly ash.<sup>28</sup>

The effectiveness on a wide range of power plants is uncertain, however. The major unknown is the effectiveness of carbon injection for the concentrations of mercury species that are formed in a power plant. Mercury concentrations in flue gas from coal fired utilities are typically one to two orders of magnitude lower than those in municipal solid waste plants. Successful use of

activated carbon for electric utilities may depend on type of fuel and mercury speciation. Although some data has been published, the data is limited. It has also been shown that activated carbon is an expensive sorbent for mercury control.

**Advanced Control Devices** - Other areas of investigation include the enhancement of electrostatic precipitators for fine particulate and air toxics control<sup>29</sup>, development of an electrostatically enhanced core separator for particulate air toxics control<sup>30</sup>, and a patented Corona Discharge Reactor (Environmental Elements Co.).<sup>31</sup> The technology employs a corona glow discharge to oxidize elemental mercury. A glow discharge is similar to one produced in a fluorescent light bulb. The oxidized mercury is easier to capture after being exposed to the Corona Discharge Reactor. For application to unscrubbed ESP systems, this approach would require a mercury capture device downstream of the Corona Discharge Reactor.

## 6.6 Unscrubbed Systems Results Summary

### Particulate Control Devices

- Conventional particulate control devices such as electrostatic precipitators and baghouses do a good job of removing non-volatile trace metals that condense onto the particulate in the flue gas and then are removed by the particulate collection device. 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 higher level of particulate control by the baghouse compared to the ESP.
- Particulate-phase mercury is well controlled by ESPs and baghouses (>90%) while burning eastern bituminous coals.
- Total vapor phase mercury passes through conventional ESPs and baghouses uncollected in the tested temperature range of 325 – 375°F.
- Elemental mercury passes through the ESP unchanged, but it is partially converted to oxidized mercury across the baghouse. Radian has also reported elemental mercury conversion across different baghouse fabrics and different fly ashes.<sup>32</sup> This has significance to wet scrubber mercury control and is covered in section 7.
- Injection of limestone and carbon sorbents at modest flow rates followed by a particulate removal device provided effective control of mercury in flue gas.
- The sorbent injection tests indicate that furnace limestone sorbent injection provides more cost-effective control of mercury emissions than carbon injection in terms of sorbent costs.
- Mercury speciation data for both the limestone and carbon injection test indicated that the oxidized mercury is captured by the sorbent, while the elemental form of mercury remains unchanged.



## 7.0 MERCURY REMOVAL BY WET FGD

As was discussed in Sections 5 and 6, heavy metals tend to partition to the particulate phase, with the exception of mercury. Unlike most of the other trace metals, mercury tends to remain in the vapor phase at relatively low temperatures and does not readily condense onto fly ash particles. Therefore, it cannot be collected with the fly ash as easily as the other metals. Additionally, mercury can exist in its oxidized ( $\text{Hg}^{++}$ ) or elemental ( $\text{Hg}^0$ ) form, and each is affected differently by subsequent pollution control equipment.

Because of the wide difference in solubility,  $\text{Hg}^{++}$  is relatively easy to capture in a wet scrubber while  $\text{Hg}^0$  is difficult. The relative amount of each species formed upstream of the wet scrubber depends on several factors such as coal characteristics, combustion variables, the type of particulate collector used, and other factors.

AECDP Phase II results indicated that an ESP, as used by most utilities, can affect the process chemistry so that a portion of the  $\text{Hg}^{++}$  is reduced to  $\text{Hg}^0$  within the wet scrubber and then emitted with the flue gas. Figure 7.1 shows the mercury concentration at the scrubber inlet and outlet for several different coals. Tests employing the ESP had a higher  $\text{Hg}^0$  concentration at the outlet than at the inlet even though no difference could be discerned in the inlet gas. This section describes the results of tests designed to study and possibly mitigate this phenomenon.

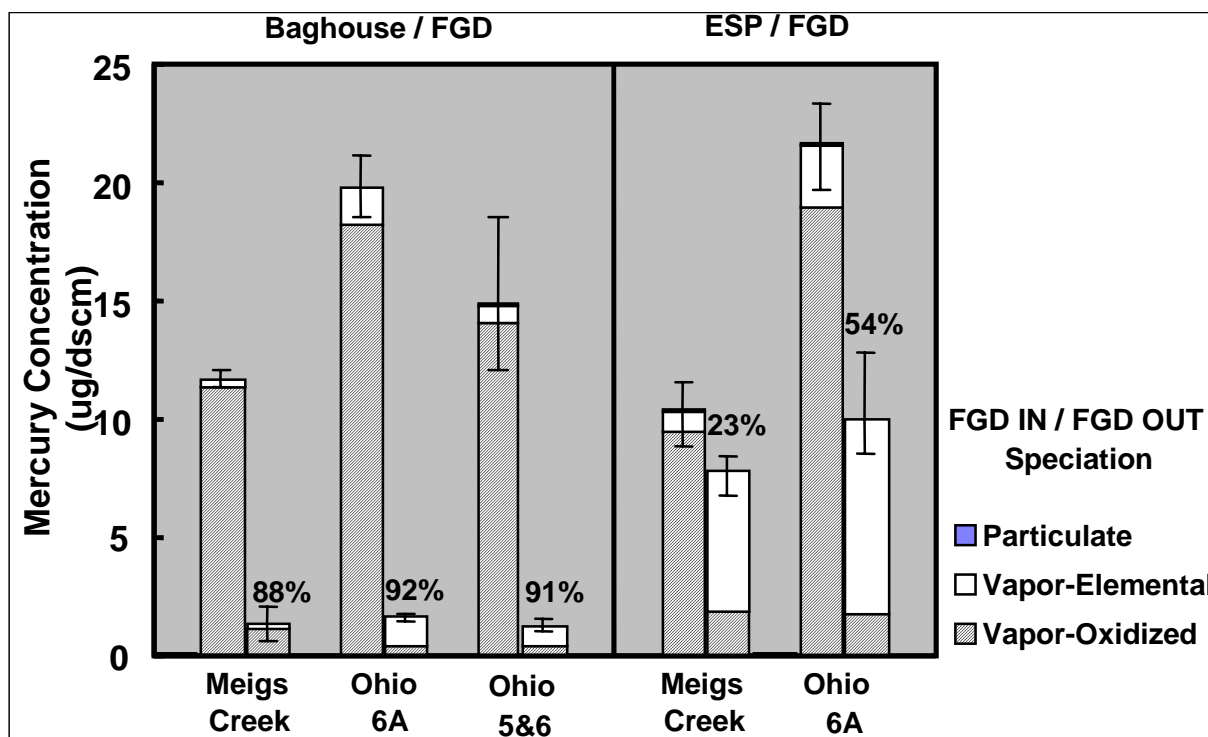


Figure 7.1 Effect of Particulate Control Device on WFGD Hg Removal – Phase II

Three approaches were taken to identify the cause of the difference in scrubber mercury removal for the ESP/WFGD system versus the BH/WFGD system. Background for the selected approaches is as follows:

- The mercury captured by a wet scrubber is predominantly in the oxidized form. Even though this form is quite soluble, analysis of slurry filtrate and solids showed that essentially all mercury ended up in the solid phase. This indicates that the aqueous phase  $\text{Hg}^{++}$  forms a relatively insoluble compound that deposits with the slurry solids. One such compound is mercuric sulfide.
- A brief test conducted in Phase II indicated that decreasing the amount of oxidation air to the reaction tank eliminated the conversion of  $\text{Hg}^{++}$  to  $\text{Hg}^0$ . Decreasing the oxidation air also increased the concentration of sulfites in the slurry.
- These observations indicate that a sulfide donating species could be responsible for the ultimate sequestration of mercury in the solids, and that ESP operation inhibits or removes that species. They also indicate that, in the absence of the sulfide donating species, a competing reaction that reduces the oxidized mercury to elemental becomes more predominant. Transition metals were suspected to play an active role in these reactions since they can act as catalysts and/or reactants for reducing oxidized species.

A program was developed to test different aspects of the above scenario consisting of the following phases:

- The ESP and BH were tested in various configurations to identify which device was responsible for the difference in mercury removal across the wet scrubber. It is possible that the ESP had a negative effect on mercury removal, or that the baghouse had a positive effect.
- The affect of oxidation airflow on scrubber chemistry was studied in greater detail.
- Scrubber chemistry was altered by the addition of chemicals to the reaction tank or to the inlet flue gas. It was hypothesized that  $\text{H}_2\text{S}$  was being destroyed by ozone created in the ESP. Therefore,  $\text{H}_2\text{S}$  was added to the inlet flue gas as a sulfide donating species to react with the mercury. In another test, a chelating agent was added to the reaction tank to sequester transition metals and prevent them from interfering with the mercury reactions.

More detailed descriptions of these tests and the test results are provided in the following sections.

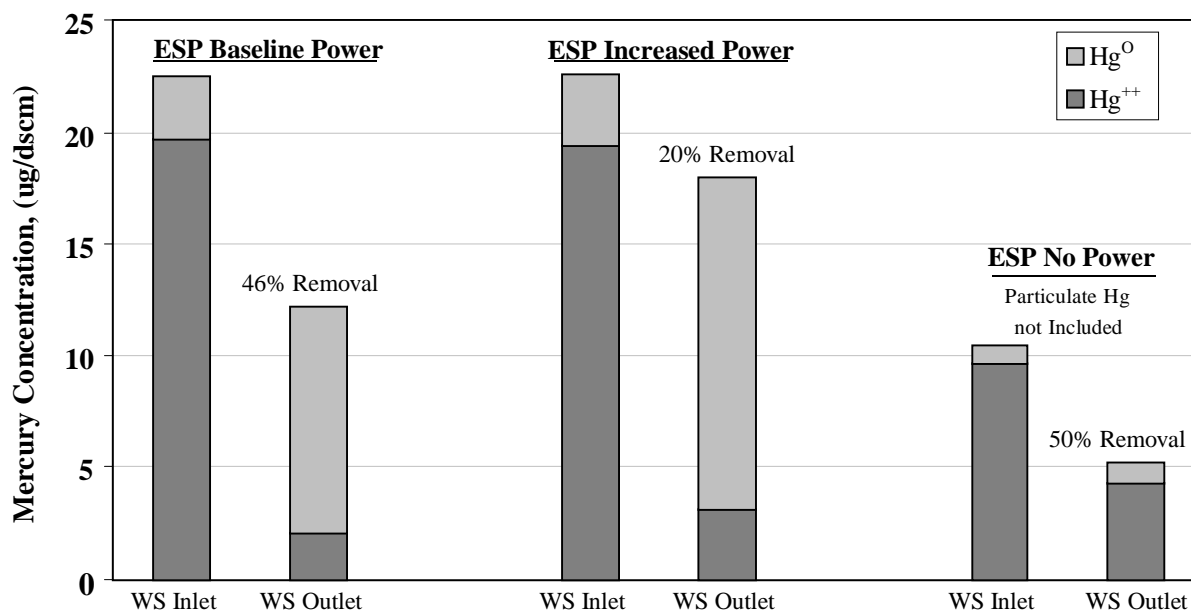
## **7.1 Effect of ESP Power on WFGD Mercury Removal**

The purpose of this test series was to investigate the effect of ESP operating power on wet scrubber mercury removal. All previous tests that showed conversion of  $\text{Hg}^{++}$  to  $\text{Hg}^0$  across the

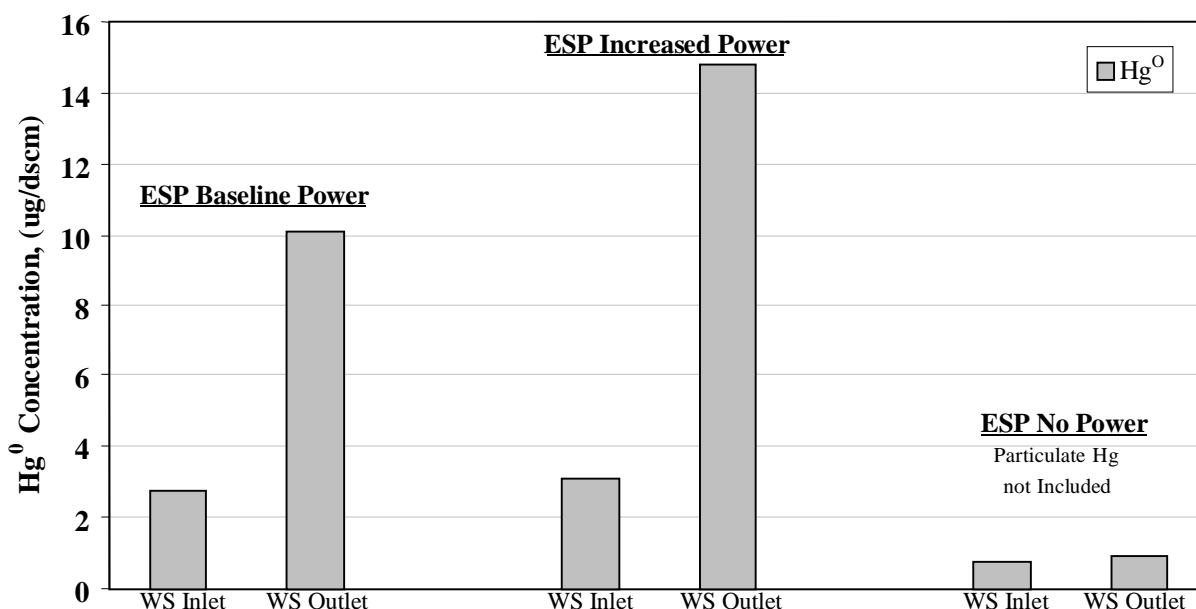
wet scrubber had been performed at a single ESP operating voltage. These tests were conducted to determine if this observed effect would change with the ESP power level.

For baseline operation, the ESP was operated with three of the four fields in service, and the power was set to maintain outlet particulate loading at 0.02 to 0.03 lb/MBtu (i.e., within the NSPS limit). These baseline conditions were not chosen to simulate any particular utility application. Two runs were conducted, with triplicate measurements of mercury at the inlet and outlet of the wet scrubber for each. In the first run, ESP voltage was increased by 60% above the baseline voltage. In the second run, ESP power was turned off.

Figure 7.2 shows the vapor-phase mercury concentration of  $Hg^{++}$  and  $Hg^0$  measured at the wet scrubber inlet and outlet for the three different ESP operating conditions. The vapor-phase mercury refers to the portion of the mercury associated with the gas-phase and excludes that portion associated with the particulate. Since the wet scrubber results were measured downstream of the particulate control device, very little particulate-phase mercury was measured. Figure 7.3 shows only  $Hg^0$  for the same three ESP conditions as those in Figure 7.2. The figures clearly show that the operating voltage of the ESP has a direct, negative impact on the wet scrubber mercury performance. The proportion of  $Hg^{++}$  and  $Hg^0$  at the wet scrubber inlet is the same for all three tests. However, for the high power test, the amount of  $Hg^0$  significantly increased across the wet scrubber. The elemental mercury remains constant for the no power test, which is the observed behavior when the scrubber is preceded by the baghouse. This indicates that the electric field affects some component of the flue gas, which, in turn, has a negative impact on wet scrubber chemistry. Since mercury is present in such small quantities, it is likely that the active component of the flue gas is also present in small quantities, like  $H_2S$ , for example.



**Figure 7.2 Effect of ESP Operating Voltage on WFGD Performance**



**Figure 7.3 Effect of ESP Operating Voltage on  $Hg^0$**

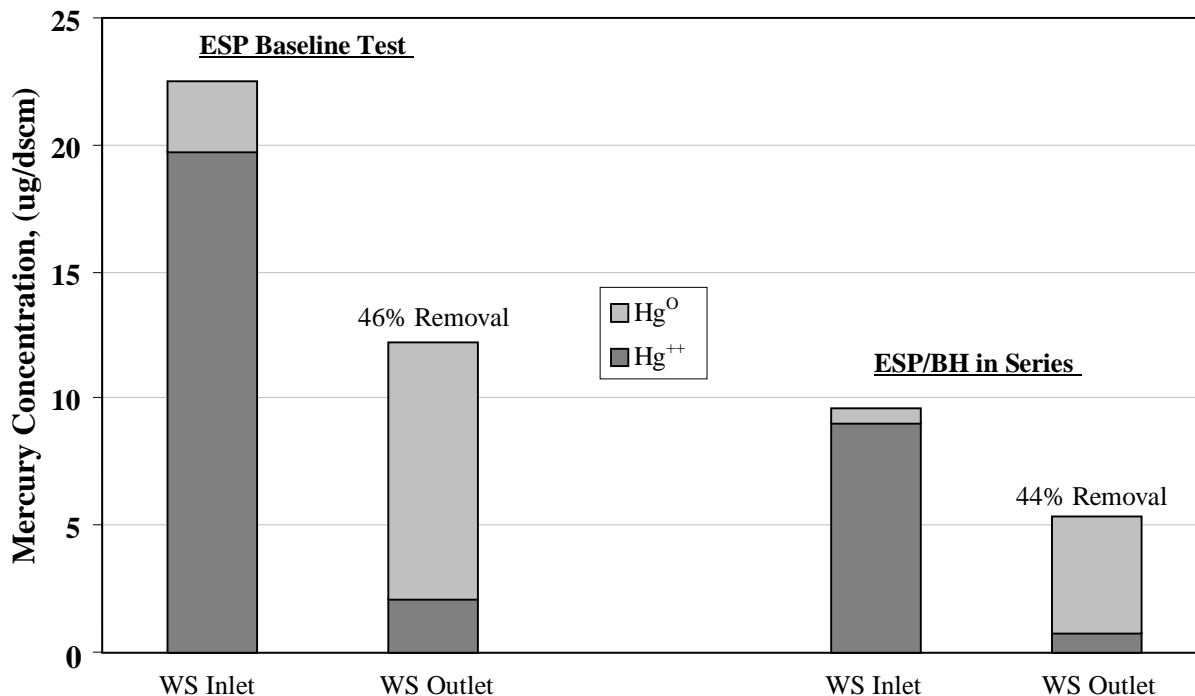
## 7.2 Particulate Collector Effect on WFGD Hg Removal

The next test also was performed to investigate whether the ESP had a negative effect on scrubber mercury removal or if the baghouse had a positive effect. A new section of flue work and a valve were added to the facility to allow clean flue gas from the ESP to flow through the baghouse before entering the wet scrubber. In this way, any positive improvement in the baseline ESP/WFGD performance could be attributed to the baghouse filter cake. Conversely, if poor mercury removal were still achieved by this arrangement, it would indicate that the baghouse provided no enhancement to scrubber mercury removal.

Particle laden flue gas was routed through the baghouse until a suitable filter cake deposited on the bags, as measured by the baghouse pressure drop. Cleaned gas from the ESP was then routed through the baghouse and wet scrubber and a two-hour sampling run was begun. Between the runs, the filter cake was removed by pulse cleaning, and a new filter cake was allowed to deposit before beginning a repeat run.

Figure 7.4 compares the total gas-phase mercury concentration at the scrubber inlet and outlet for the ESP baseline test and the test with the ESP and BH in series. The total mercury is further divided into its elemental and oxidized portions. The figure shows that the total amount of gas-phase mercury entering the scrubber was much less in the ESP/BH test than in the ESP baseline test. Mercury concentration at the scrubber inlet naturally varied over time, probably due to slight changes in the coal and the combustion process. However, the proportion of each mercury species remained relatively constant. A comparison of the elemental mercury for each test shows that it increased substantially across the wet scrubber for both test configurations. Also,

the total mercury removal was about 45% in both cases. A large portion of the oxidized mercury was still converted to elemental mercury regardless of whether a BH was used in series with the ESP. Therefore, it was concluded that the ESP was having a negative impact on scrubber performance.



**Figure 7.4 WFGD Performance with the ESP and BH in Series**

### 7.3 Effect of Oxidation Air on WFGD Hg Removal

During Phase II of this project, it was discovered that wet scrubber mercury removal efficiency could vary with the quantity of oxidation air supplied to the ART. For the ESP/WFGD system, reducing the oxidation air stoichiometry resulted in a significant reduction in total mercury emissions from the scrubber as shown in Figure 7.5. For the Ohio 6A coal, mercury removal across the scrubber increased from 54% at the baseline operating conditions to 80% when operating at the lower air stoichiometry. Similarly, scrubber mercury removal increased from 23% to 67% for the Meigs Creek coal.

The observed improvement in scrubber mercury removal was largely a result of reduced elemental mercury emissions for both coals. To illustrate how the different mercury species was affected by oxidation air, Figure 7.6 and Figure 7.7 show the same data as Figure 7.4 broken down by the mercury species. Low oxidation air must somehow inhibit the reduction of oxidized mercury, or provide a species needed to sequester the oxidized mercury in the slurry.

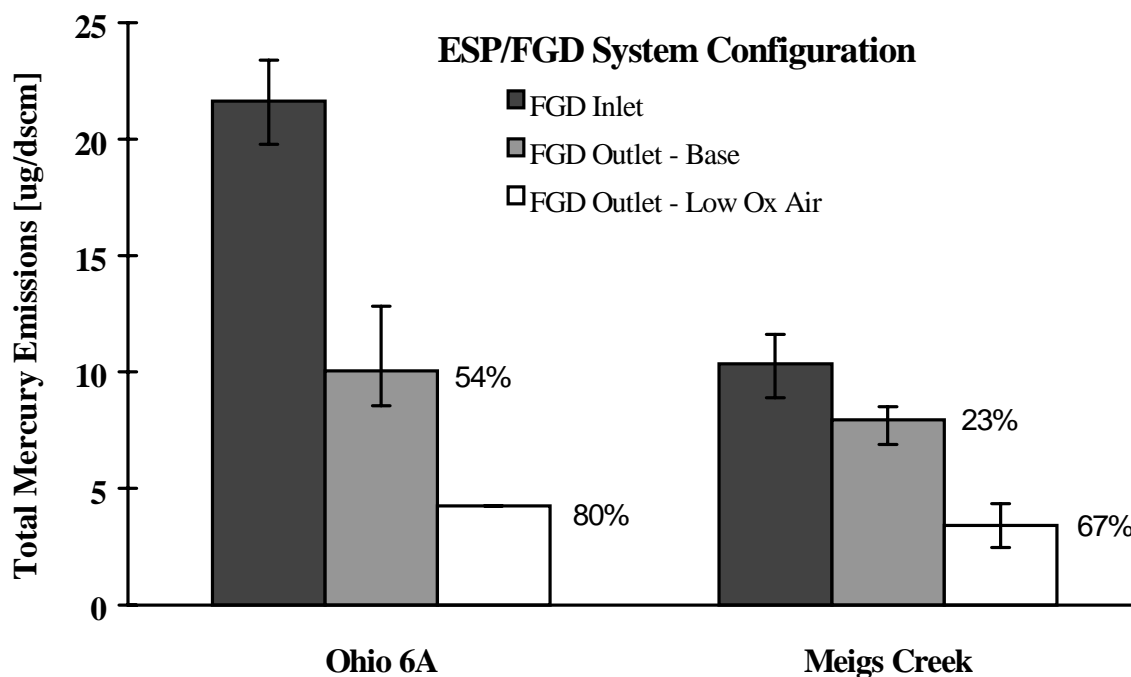


Figure 7.5 Effect of Oxidation Air on Total Mercury Emissions – Phase II

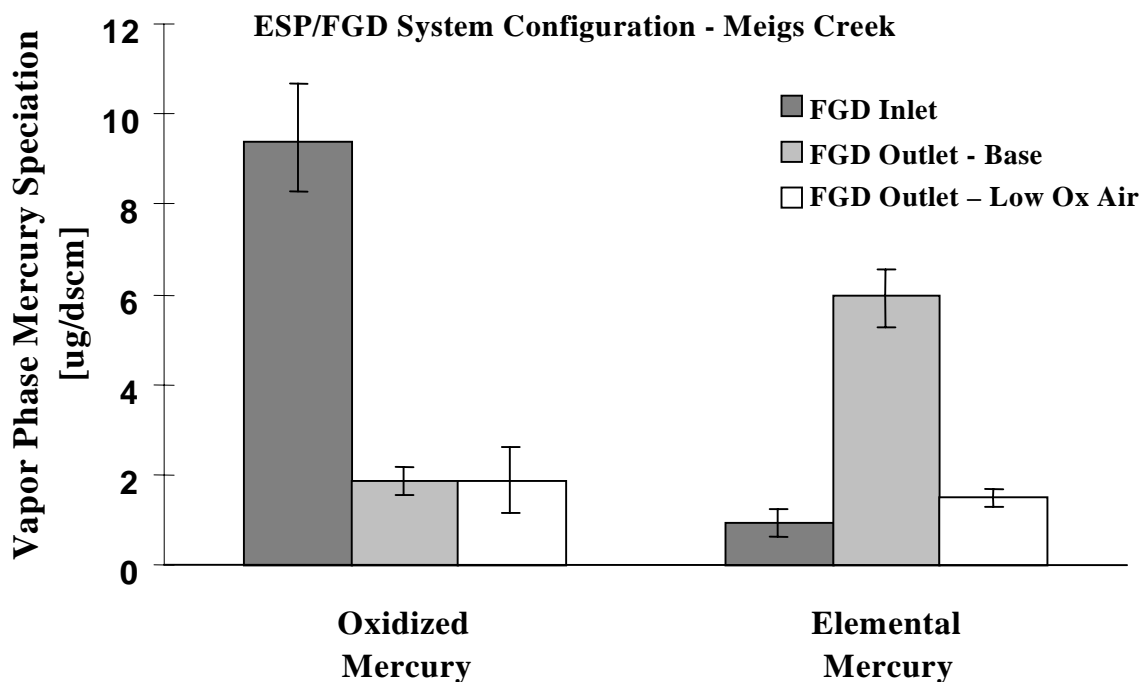
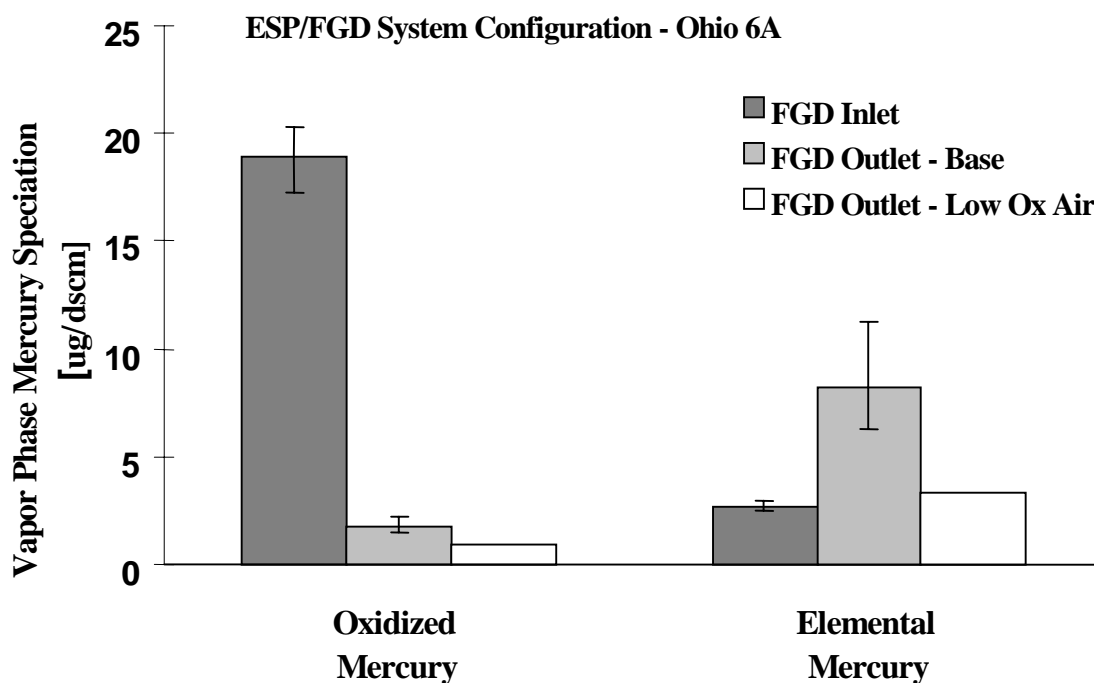


Figure 7.6 Effect of Oxidation Air on Mercury Speciation – Meigs Creek

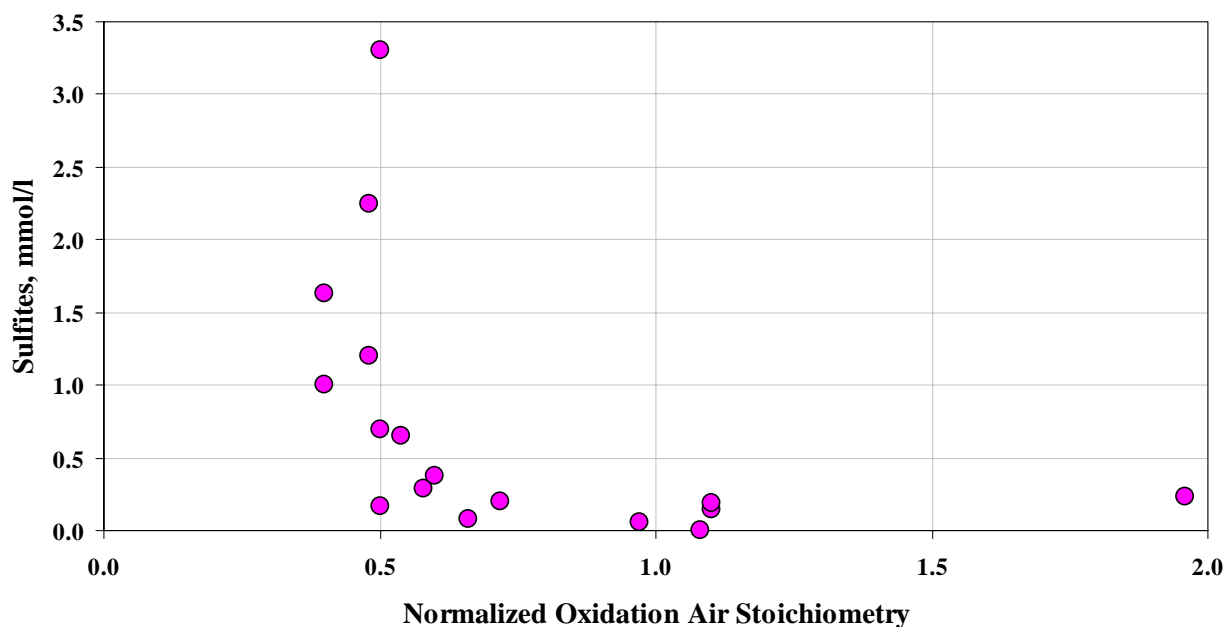


**Figure 7.7 Effect of Oxidation Air on Mercury Speciation – Ohio 6A**

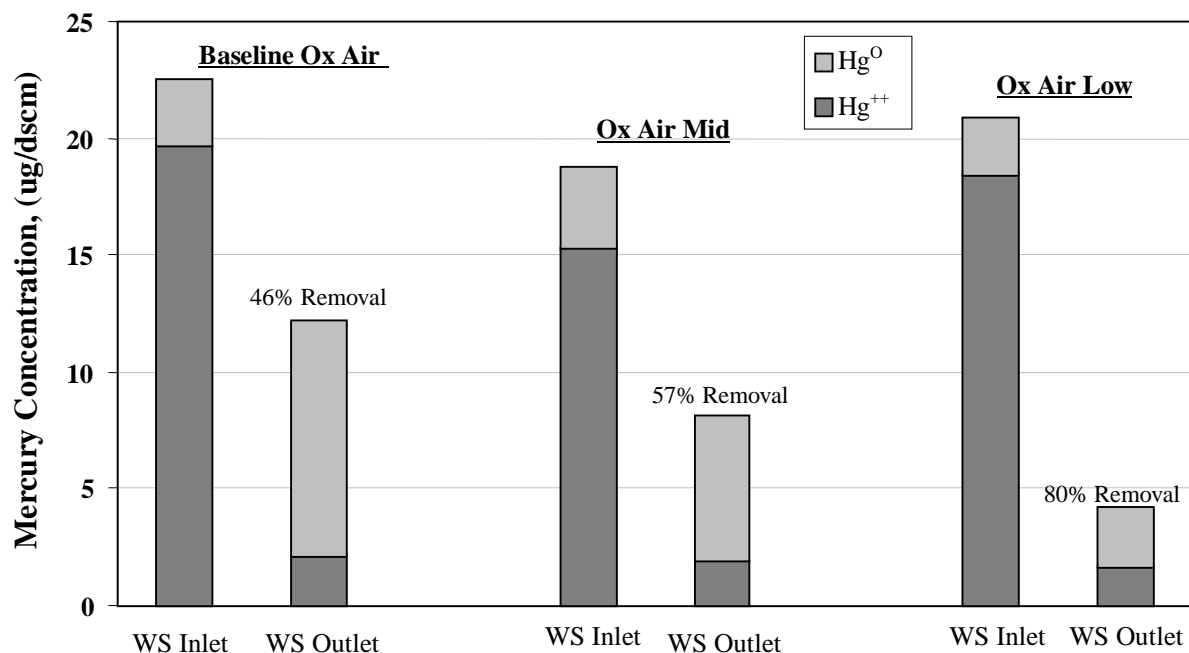
In Phase III, the effect of oxidation air on mercury capture was expanded into several runs at intermediate levels of oxidation air. Each of these tests employed an ESP for particulate control. To monitor the effect of reduced oxidation air on scrubber chemistry, slurry grab samples from the ART were analyzed for sulfite concentration. Figure 7.8 shows how the ART sulfite concentrations are affected by oxidation air stoichiometry. At a normalized oxidation air stoichiometry (NOAS) above 0.7, sulfite concentration remained below 0.25 mmol/l. Below a NOAS of 0.7, the sulfite concentrations increase rapidly and at a NOAS of 0.5, sulfite concentrations as high as 3.3 mmol/l were measured.

Figure 7.9 compares wet scrubber inlet and outlet mercury concentration for the base case and the runs at a mid- and low-level of oxidation air. The bars include the elemental and oxidized fractions of the total vapor phase mercury. The relative amounts of oxidized mercury at the inlet and outlet did not change significantly for the three tests. However, the amount of oxidized mercury converted to elemental decreased as the oxidation air decreased. This point is further illustrated in Figure 7.10 that shows only the elemental mercury for the three tests. For the baseline test, elemental mercury increased by 265% across the wet scrubber. This improved to a 76% increase for the second test, and only 2% for low oxidation air test. Total gas-phase mercury removal improved from 46% for the base case to 80% for the low oxidation air case. These normalized oxidation air stoichiometry results show a strong relationship between oxidation air and wet scrubber mercury removal for an ESP/WFGD system. This demonstrates that scrubber chemistry can affect mercury removal and suggests a possible and simple way for utilities to improve mercury removal performance. However, the level to which any utility can reduce

oxidation air will be highly site specific and will depend on several factors such as scaling considerations and gypsum purity requirements.

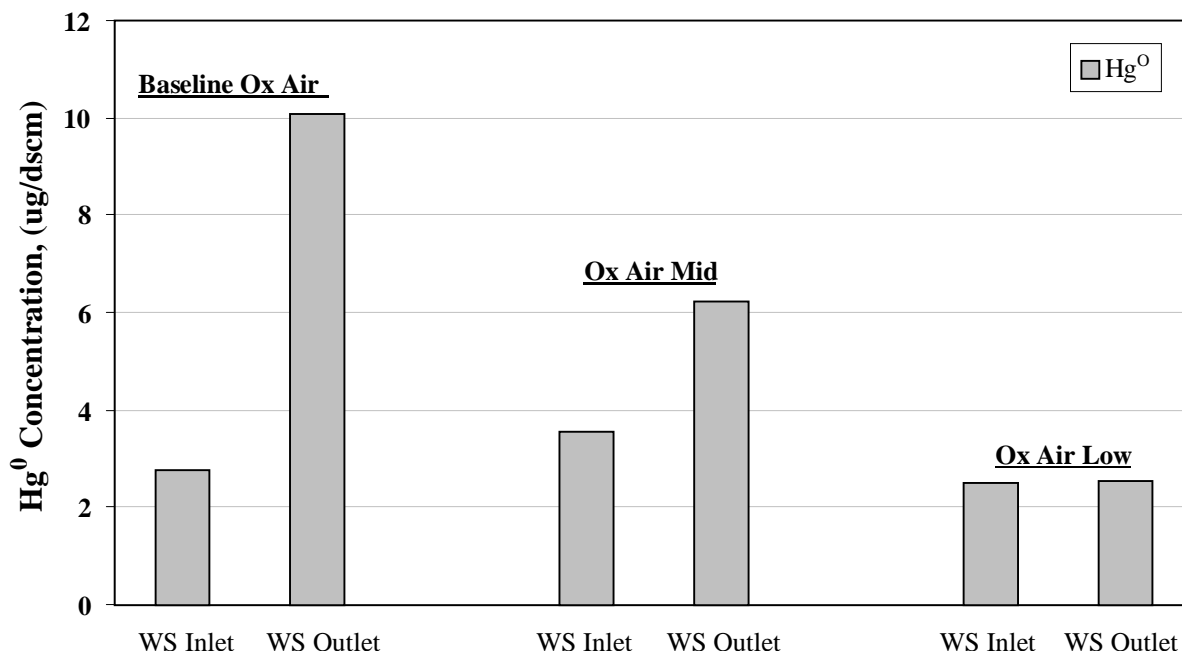


**Figure 7.8 Effect of Oxidation Air on WFGD Slurry Sulfite Concentration**



**Figure 7.9 Effect of Oxidation Air on WFGD Performance**





**Figure 7.10 Effect of Oxidation Air on  $Hg^0$**

#### **7.4 Effect of Chemical Additives on WFGD Hg Removal**

Another set of tests was performed to investigate the use of additives to prevent the conversion of  $Hg^{++}$  to  $Hg^0$  and thereby improve wet scrubber mercury removal. Tests were performed (triplicate runs for each) to evaluate the effect of  $H_2S$  injection into the flue gas, and EDTA addition to the scrubber slurry. The  $H_2S$  was chosen as a possible sulfide donating species that could assist in capturing oxidized mercury. The EDTA was selected to sequester transition metals and prevent them partaking in the mercury reactions.

##### **7.4.1 $H_2S$ Injection**

The  $H_2S$  injection system consisted of four, 140 standard cubic feet gas cylinders. Each cylinder contained 0.8% hydrogen sulfide ( $H_2S$ ) in nitrogen. The cylinders were connected, one at a time, to an existing, welded  $SO_2$  injection line. Mixing was accomplished with a gas disperser consisting of a perforated tube that spanned the width of the flue.

A critical flow orifice was connected directly to the outlet of the  $H_2S$  regulator. Flow through the orifice was controlled by manually setting the orifice pressure to a predetermined value. The system was designed to provide an  $H_2S$  concentration of about 2 ppm in the flue gas entering the scrubber.

Figure 7.11 shows the gas-phase mercury concentration of  $Hg^{++}$  and  $Hg^0$  measured at the wet scrubber inlet and outlet for the ESP baseline and  $H_2S$  injection tests. Gas-phase wet scrubber mercury removal increased with the addition of  $H_2S$  from 46% to 71%. This increase was due

mainly to a decrease in the conversion of  $\text{Hg}^{++}$  to  $\text{Hg}^0$ . This is more clearly shown in Figure 7.12 that shows only  $\text{Hg}^0$ . Elemental mercury increased by 265% across the wet scrubber in the ESP baseline test, and decreased by 13% during the  $\text{H}_2\text{S}$  injection test.

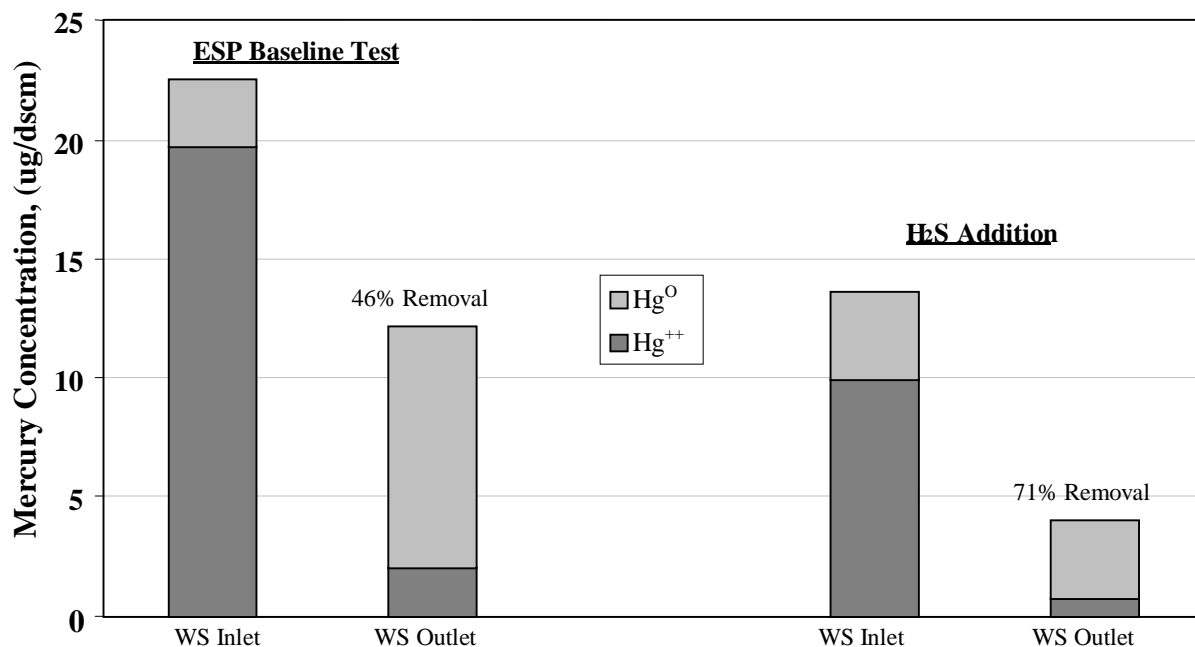


Figure 7.11 Effect of H<sub>2</sub>S Injection on WFGD Mercury Performance

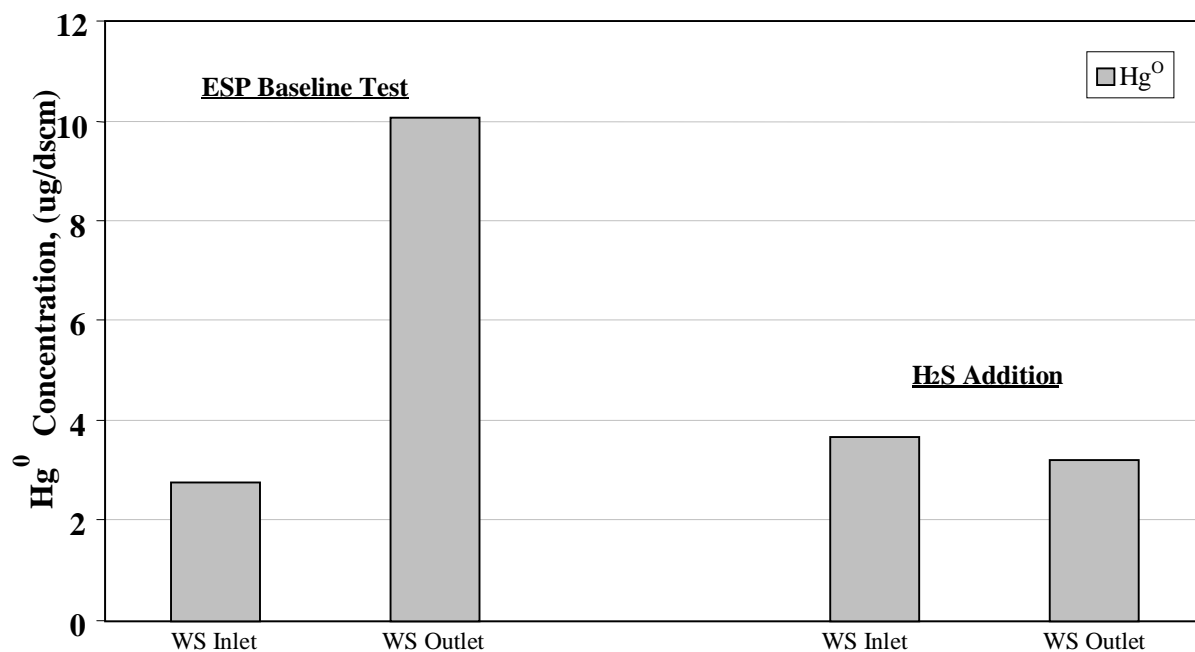


Figure 7.12 Effect of H<sub>2</sub>S Injection on WFGD Outlet Hg<sup>0</sup>

### 7.4.2 EDTA Addition

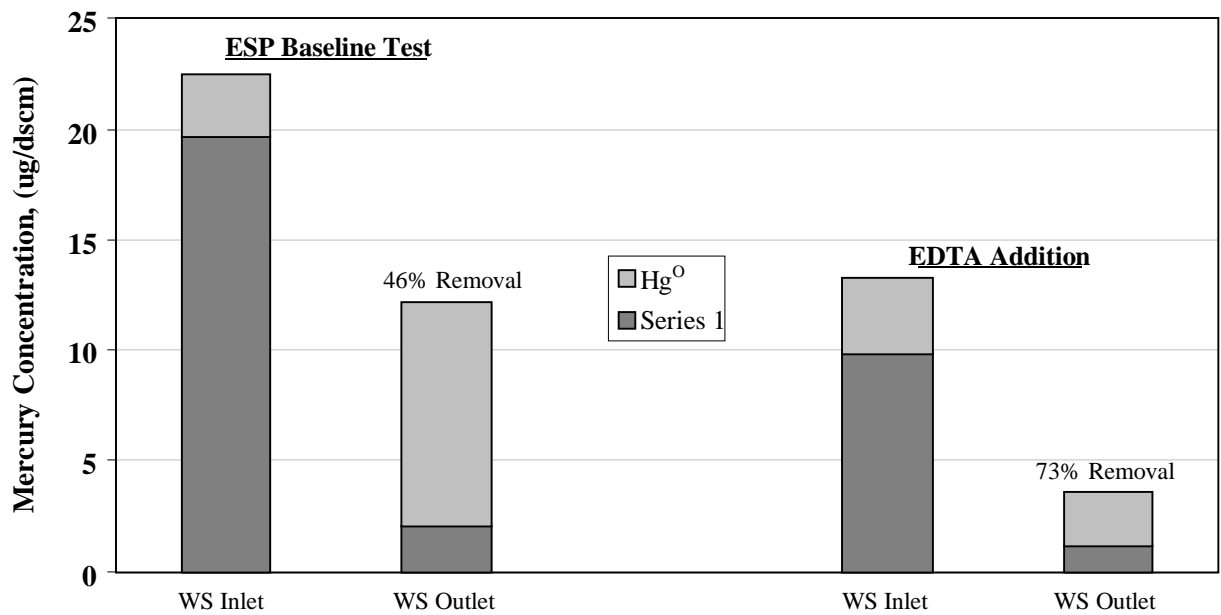
Chelating agents, such as EDTA, are known to sequester transition metals, which prevents them from taking part in chemical reactions. Transition metals may act as a catalyst in the conversion of  $\text{Hg}^{++}$  to  $\text{Hg}^0$  in the wet scrubber. EDTA is also employed by a few utilities with inhibited oxidation systems because it prevents sulfites from oxidizing to sulfates. This effect was also seen during this test in which the sulfite concentration jumped from a typical value of 0.2 mmol/l to 3.5 mmol/l immediately after EDTA was added. Sulfite concentration soon settled between 1.0 and 1.5 mmol/l and remained there for the duration of Phase III tests. This indicates that the EDTA concentration remained sufficiently high to affect scrubber chemistry.

In the thick chemical soup that describes wet scrubber slurry, the action of a chelating agent could not be predicted. Therefore, an excess of EDTA was added to the ART to ensure that all possible catalysts were sequestered. Eleven pounds of EDTA were added in a single batch prior to the start of the run. This is equivalent to about 1300 ppm EDTA. It was expected that the EDTA concentration would diminish over time as water was purged from the system along with the waste solids, but this was desirable so that the effect of EDTA concentration could be observed.

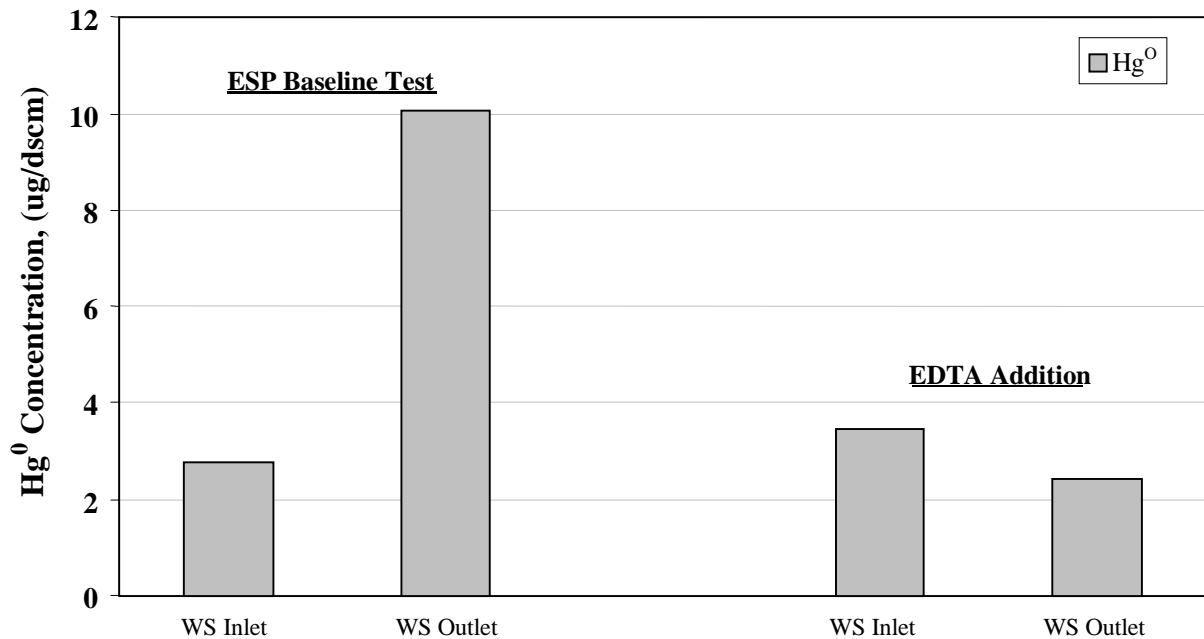
Figure 7.13 shows the gas-phase mercury concentration of  $\text{Hg}^{++}$  and  $\text{Hg}^0$  measured at the wet scrubber inlet and outlet for the ESP baseline and EDTA addition tests. Gas-phase wet scrubber mercury removal increased from 46% to 73% with the addition of EDTA. This improvement was due mainly to a decrease in the conversion of  $\text{Hg}^{++}$  to  $\text{Hg}^0$  as illustrated in Figure 7.14. Elemental mercury increased by 265% in the ESP baseline test and decreased by 29% during the EDTA addition test.

After the EDTA test was completed, sorbent injection tests (Section 6.0) were conducted. Although specific wet scrubber tests were not conducted during this time period, the mercury concentration at the outlet of the wet scrubber was continually monitored. Figure 7.15 shows the gas-phase mercury concentration of  $\text{Hg}^{++}$  and  $\text{Hg}^0$  measured at the wet scrubber inlet and outlet for the ESP baseline and for the four tests after EDTA addition. Gas-phase wet scrubber mercury removal remained high for all these tests and ranged from 70% to 76% as compared to 46% for the baseline test. This was due mainly to a decrease in the conversion of  $\text{Hg}^{++}$  to  $\text{Hg}^0$  as illustrated in Figure 7.16. Elemental mercury increased by 265% in the ESP baseline test and decreased by 3% to 31% after EDTA addition. This indicates that sufficient quantities of EDTA remained in the system to affect scrubber mercury removal, and that the amount of EDTA added at the start of this test series was probably too much.

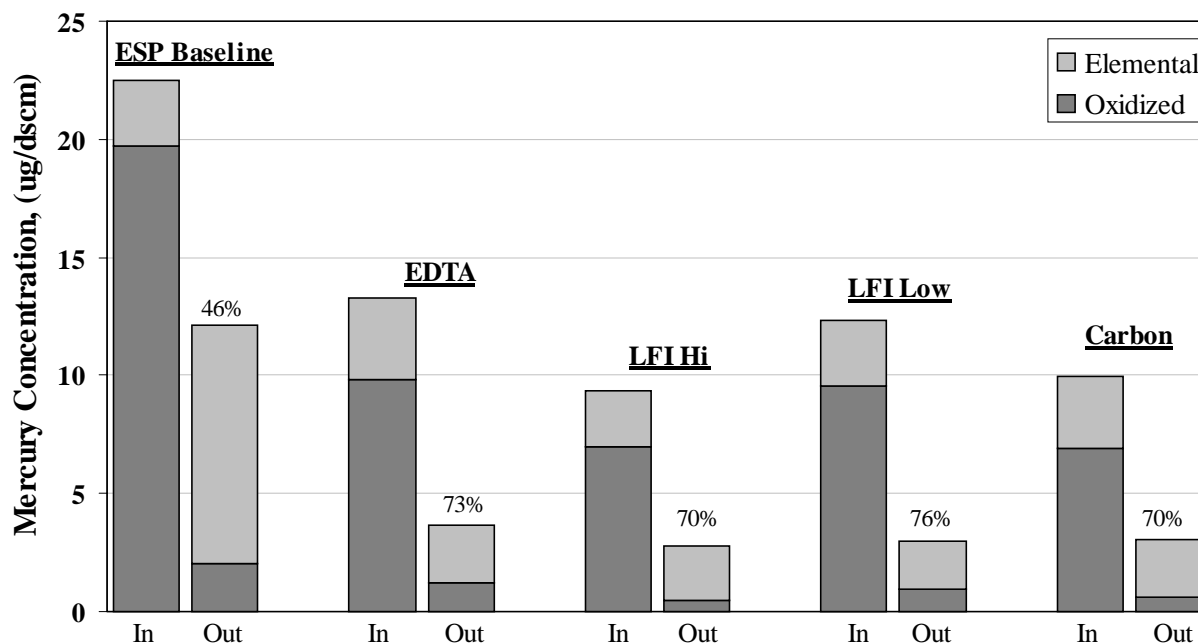
There are many types of chelating agents available and further research is needed to determine the most effective and economical agent, as well as the optimum concentrations. However, this test demonstrated that such a system is feasible and effective at preventing the conversion of oxidized mercury to the elemental form in the ESP/WFGD configuration.



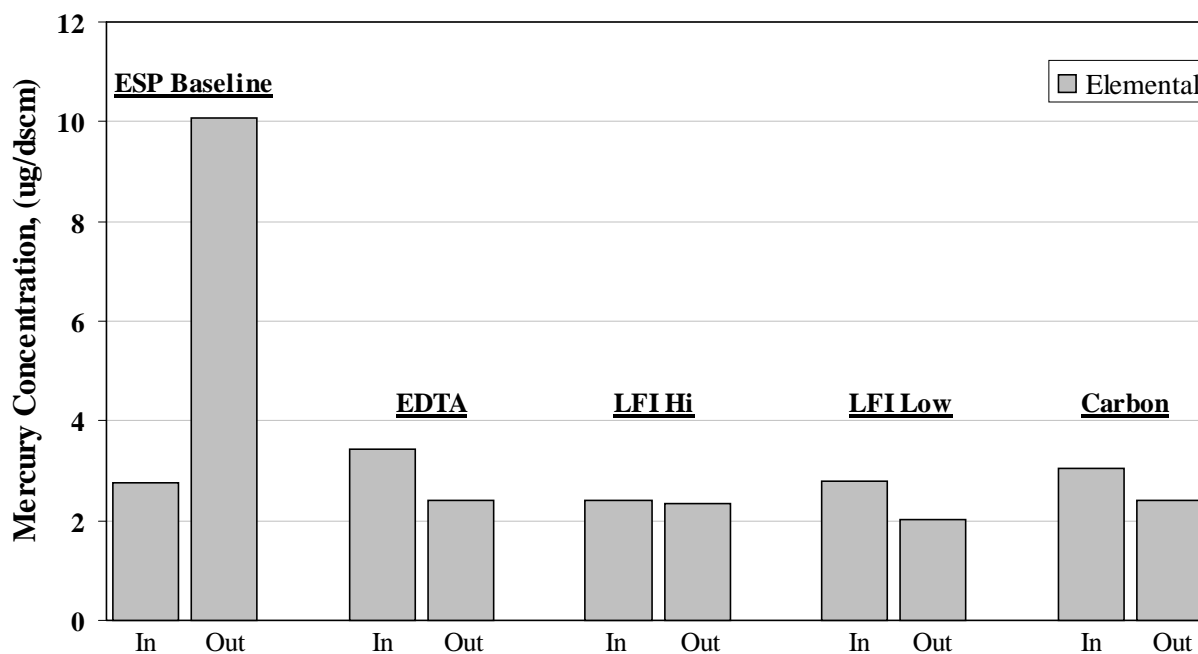
**Figure 7.13 Effect of EDTA on WFGD Performance**



**Figure 7.14 Effect of EDTA on  $\text{Hg}^0$**

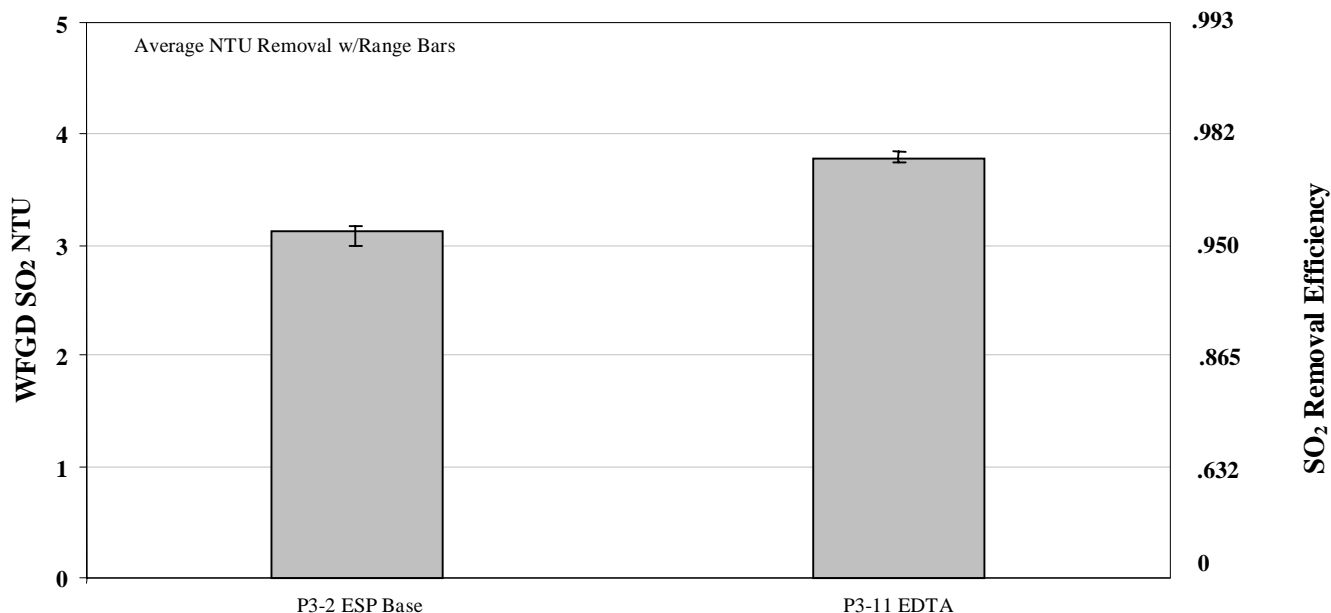


**Figure 7.15 Effect of EDTA on WFGD for Tests after EDTA Addition**



**Figure 7.16 Effect of EDTA on Hg<sup>0</sup> from WFGD for Tests after EDTA Addition**

An unexpected result of the EDTA test was an improvement in the scrubber SO<sub>2</sub> removal performance. Figure 7.17 shows wet scrubber SO<sub>2</sub> removal for the ESP baseline test and the EDTA test. The average SO<sub>2</sub> Normalized Transfer Units (NTU) increased from 3.1 for the baseline test to 3.8 for the EDTA test. This makes the use of chelating agents even more attractive to utilities. However, more tests are needed to determine the optimum concentration that produces the positive effect on SO<sub>2</sub> removal and whether the use of EDTA diminishes the resale value of the gypsum byproduct. Note that the NTU removals are from a transform of the efficiency by the equation  $NTU = -\ln(1 - \text{SO}_2 \text{ removal efficiency})$ . Efficiency is provided on the right side for comparison.



**Figure 7.17 Effect of EDTA on WFGD SO<sub>2</sub> Removal**

## 7.5 WFGD Transient Hg Mass Balance

A transient mass balance was performed around the wet scrubber ART based on the measured flows and concentrations of mercury entering and leaving the wet scrubber system. These include the flue gas flow, the limestone feed into the ART and the hydroclone underflow (blowdown) stream leaving the ART. The mass balance for unsteady state operation can be expressed by:

$$\text{Input} - \text{Output} = \text{Accumulation}$$

In the case of mercury, the input term is an expression of the rate of absorption of mercury from the gas and particulate phases to the aqueous phase and mercury that enters the ART with the limestone feed. This can be expressed mathematically as:

$$\text{Input} = \left[ G' \cdot y'_{Hg} \cdot 10^{-6} \cdot \frac{\epsilon_{Hg}}{100} \right] \frac{g}{\text{min}} \cdot \frac{60 \text{ min}}{hr}, \quad g/hr \quad (1)$$

where:  $G'$  = Flue gas flow rate at the wet scrubber inlet, DSCM/min.

$y'_{Hg}$  = Total Hg concentration at the wet scrubber inlet,  $\mu\text{g}/\text{DSCM}$

$\epsilon_{Hg}$  = Total wet scrubber mercury removal efficiency, %

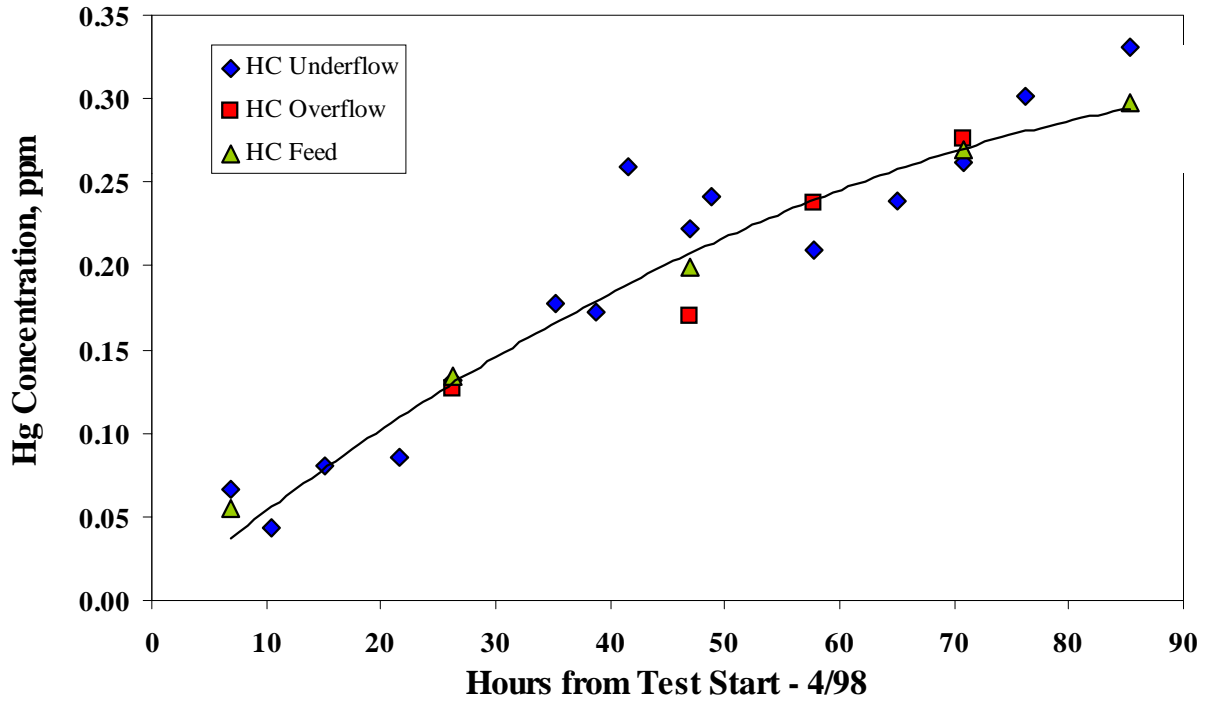
The output term in the mass balance consists of the hydroclone discharge rate and mercury concentration of the discharged slurry and the mercury exiting the scrubber system with the flue gas. Also, because the hydroclone is only operated for short periods to control the solid concentration in the ART, the flow rate used in the output term is an average flow rate calculated over the duration of a test. The rate of mercury rejection from the system is then:

$$\text{Output} = F_s \cdot X_{Hg} \cdot 10^{-6}, \quad g/hr \quad (2)$$

where:  $X_{Hg}$  = Hg concentration in the ART, ppm

$F_s$  = Average hydroclone flow rate, g/hr

Figure 7.18 shows the concentration of mercury in the slurry streams entering and leaving the hydroclone as a function of test time. The increasing mercury concentration with time indicates that a steady state mercury concentration in the ART was not reached during the weeklong test. Also, comparison of the mercury concentrations from the three slurry streams shows that within the scatter of the data, the hydroclone overflow and underflow are essentially the same and equal to the concentration in the ART.



**Figure 7.18 Measured Total Hg Concentration in the Hydroclone Streams**

The accumulation term in the unsteady state mass balance is expressed as:

$$\text{Accumulation} = \frac{d(M_s \cdot X_{\text{Hg}}) \cdot 10^{-6}}{dt}, \text{ g/hr} \quad (3)$$

where:  $M_s$  = Mass of slurry in the ART, g

The mass of slurry in the ART is assumed to be constant and equal to:

$$M_s = (1075 \text{ gal} \cdot SG_s \cdot 8.34 \text{ lb/gal} \cdot 454 \text{ g/lb}) \cdot 10^{-6}, \text{ g} \quad (4)$$

where: 1075 = Average volume of the ART Tank, gal  
 $SG_s$  = Specific Gravity of the ART Slurry (typical = 1.108)

Then, the transient mass balance then becomes:



$$C_1 = C_2 X_{Hg} + C_3 \frac{dX_{Hg}}{dt} \quad (5)$$

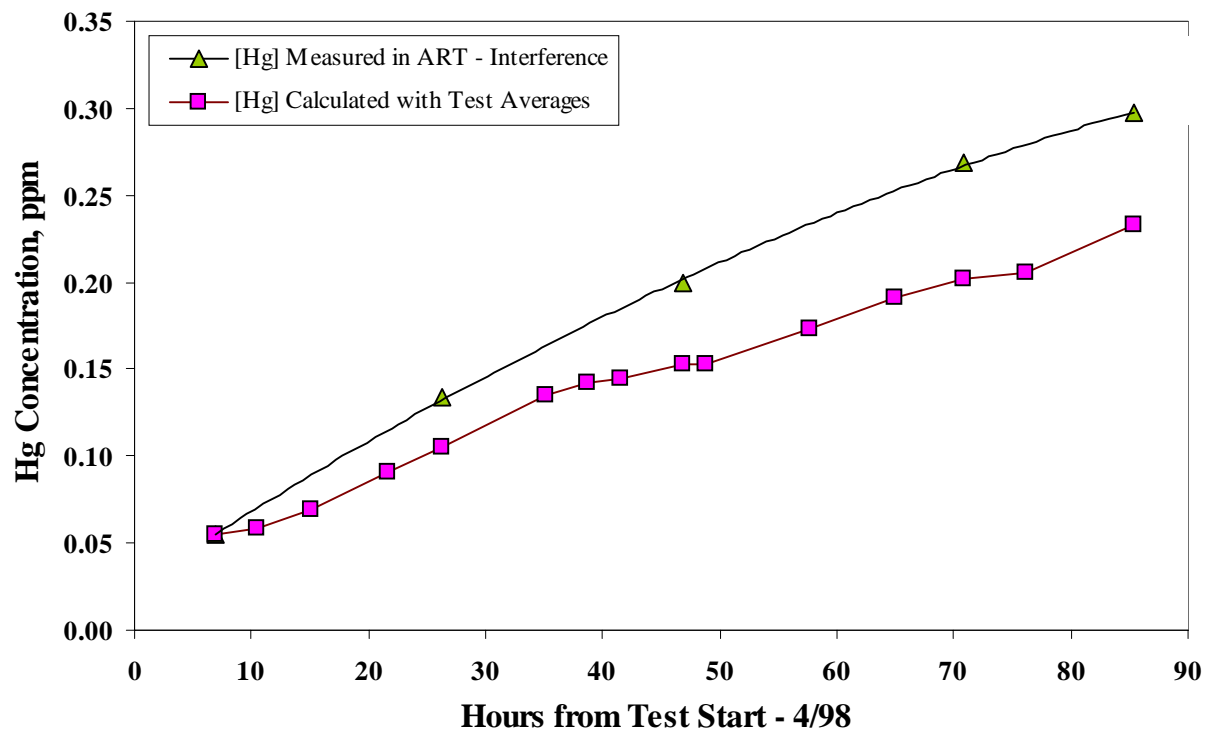
where:  $C_1 = G' \cdot y'_{Hg} \cdot \epsilon_{Hg} \cdot 60 / 100 \cdot 10^{-6}, \quad g / hr$   
 $C_2 = F_s \cdot 10^{-6}, \quad g / hr$   
 $C_3 = 1075 \cdot SG_s \cdot 8.34 \cdot 454 \cdot 10^{-6}, \quad g$

Equation 5 can be integrated and simplified to give the ART slurry concentration as a function of time:

$$X_{Hg_2} = \frac{C_1}{C_2} \left( 1 - e^{-\frac{(t_2-t_1)}{C_3/C_2}} \right) + X_{Hg_1} e^{-\frac{(t_2-t_1)}{C_3/C_2}} \quad (6)$$

In Equation 6, the initial mercury concentration of the slurry in the ART is due to mercury contained in the limestone and gypsum used to initially charge the ART.

Equation 6 can be used to predict the mercury concentration of the ART slurry based on known and measured variables. The ***predicted*** concentration of mercury in the ART as a function of time is shown in Figure 7.19 along with the ***measured*** concentrations of mercury in the ART. The measured ART mercury concentration at the end of the test was 0.297 ppm while the calculated value using Equation 6 was 0.232 ppm. This gives a mercury mass balance closure of 78% which is within the limits of the analytical techniques. Equation 6 was also used to calculate a steady state ART mercury concentration of 0.392 ppm. The equation predicted that the system would require about 400 hours of operation to reach steady state.



**Figure 7.19 Transient Mass Balance Predictions**

## 7.6 WFGD Result Summary

In Phase II, it was observed that type of particulate collector affected WFGD mercury removal. With an ESP, a large portion of the oxidized mercury entering the scrubber was converted to elemental mercury and escaped with the flue gas. This effect was not seen when a baghouse was used.

In Phase III, this phenomenon was repeated. Therefore, tests were identified to evaluate the roles of both the ESP and baghouse in WFGD mercury control. First the ESP power was increased and mercury measurements were made for comparison with the baseline results. The data showed further increase in elemental mercury across the downstream WFGD system as a result of the increased ESP power, and the total mercury removal dropped to 20% compared to 46% for the baseline condition. Next a test was conducted in which the flue gas was passed through the ESP and then the baghouse. The baghouse had no effect on the overall scrubber mercury removal. A large portion of the oxidized mercury was still converted to elemental mercury. Therefore, it was concluded that the ESP was having a negative impact on scrubber performance.

Three approaches were identified for enhancing the control of mercury across a WFGD system when an ESP is used for particulate collection. These approaches included confirmation of the effects of reduced oxidation airflow that was tested in Phase II, the addition of trace quantities of  $H_2S$  downstream of the ESP and the addition of EDTA to the slurry in the ART. All three of these approaches meet the criteria that calls for low cost solutions utilizing existing emissions control equipment as much as possible.

The positive effect of reducing oxidation air observed in Phase II was reproduced in Phase III. Gas-phase wet scrubber mercury removal increased from 46% to 80% when oxidation air stoichiometry was reduced to about 50% of its normal operating level. This improvement was due to a decrease in the amount of oxidized mercury converted to elemental mercury across the wet scrubber. Elemental mercury *increased* across the wet scrubber by 265% for the baseline test, and by only 2% for reduced oxidation air test.

The use of both  $H_2S$  and EDTA as additives proved successful in controlling the conversion of oxidized mercury to the elemental form, and enhancing the control of mercury in the WFGD system. When  $H_2S$  was added to the flue gas downstream of the ESP (at about 2 ppm) the mercury control improved from 46% to 71% and the elemental mercury concentration remained relatively constant across the scrubber. Similarly the addition of EDTA the ART slurry eliminated the conversion of oxidized mercury to the elemental form, and the total mercury removal increased to 73%.

## 8.0 ADVANCED MEASUREMENT TECHNIQUES

A Jerome mercury analyzer was used during the second week of Phase III testing in an attempt to monitor the vapor phase mercury concentration in the flue gas. The purpose of this effort was to provide relatively rapid feedback on changes in mercury concentration that occurred as a result of changes in operating conditions of the flue gas clean-up equipment. Data from the analyzer was not intended as a mercury measurement, but rather as an indicator of change.

The Jerome mercury analyzer, made by Arizona Instruments, Inc. was developed to measure elemental mercury in ambient air. The instrument measures the change in the electrical resistance of a gold coil due to the formation of a mercury-gold amalgam. The unit is relatively small and contains a sample pump, filters and valves to sample ambient air.

The Jerome mercury analyzer has a low-limit sensitivity of about 5 ng of mercury. That is sufficiently low that mercury concentrations typical of flue gas (1 to 20 ug/dscm) can be measured by sampling at reasonable flow rates (~ 2 lpm) for reasonable times (~ 2 to 3 minutes). This type of analyzer is sensitive only to elemental mercury. Ionic mercury must first be reduced to the elemental form before measurement.

There are several advantages to this type of Hg analyzer. The zero point reference, or initial condition, is measured immediately before each measurement, and so is not susceptible to long term drift. The total amount of mercury collected during a measurement can be controlled by adjusting the sample time or the sample flow rate. It is insensitive to SO<sub>2</sub>, which is the most common interferent with mercury analyzers that use atomic absorption.

The gold coil resistance is sensitive to several other acid gasses, primarily HCl and N<sub>2</sub>O. Oxygen must be present in the sample gas stream, and the sample gas must be non-condensing. To avoid these problems and to permit control of the total quantity of mercury collected for analysis, the mercury was collected onto a gold coil dosimeter. The dosimeter was then heated to release the captured mercury into the Jerome analyzer.

To measure the concentration of both elemental and ionic mercury, flue gas was sampled through either of two sets of impingers. One set consisted of high purity water followed by a drop out impinger for removing HCl. The second set consisted of a solution of stannous chloride or sodium borohydrite for reducing ionic mercury to the elemental form, and to remove HCl. Dosimeters for collecting the mercury were attached to the outlet of the dropout impinger.

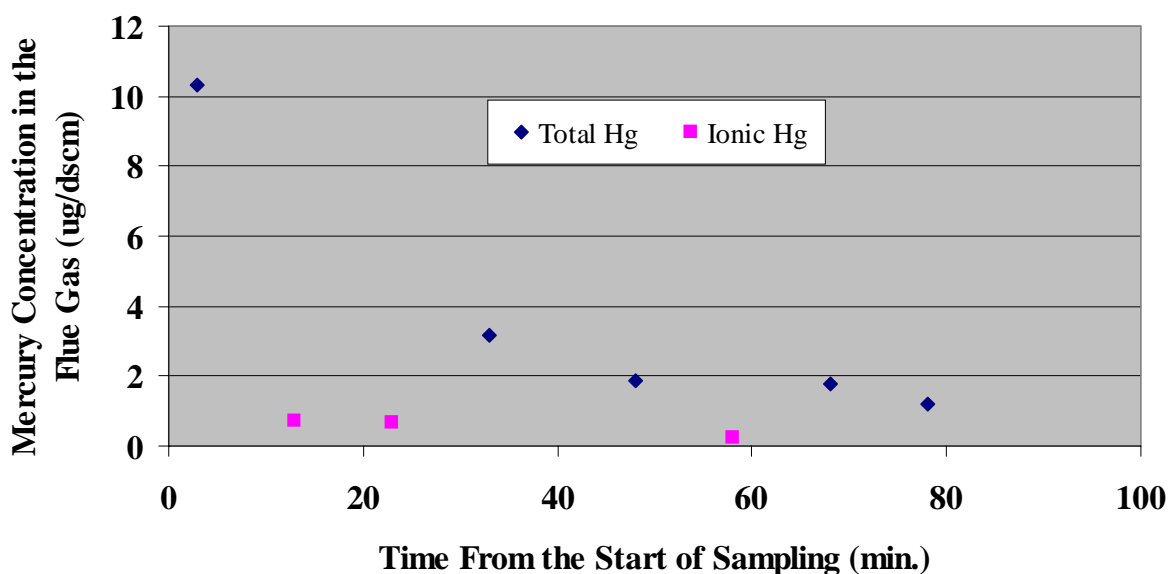
The concentrations of mercury measured using this procedure were uniformly low compared to expected concentrations but were repeatable and indicated the correct trends. Two possible sources of error were identified. First, it was observed during these tests that condensation from the flue gas was forming upstream of the first aqueous impinger. Although elemental mercury is essentially insoluble in tap water, it can be retained in water with a low pH, typical of flue gas condensation. Secondly, although the sample lines had previously been used for mercury sampling, they were not specifically cleaned before this test. It is possible that the lines had become contaminated over time.

To determine if condensation/sample lines had affected the data, a second set of measurements were made after completion of the scheduled Phase III tests. The long trace heated sample lines were replaced by short lengths of Teflon tubing (4 feet) that were cleaned with acetone and nitric acid. Fresh solutions were prepared in clean impingers.

The measured concentrations of mercury during this abbreviated test are shown in Figure 8.1 as a function of total sample time. The initial measurements of both the elemental and total mercury are in good agreement with Ontario Hydro measurements of vapor phase mercury concentrations conducted at the conclusion of the Phase III tests. The figure also shows that the measured concentration of ionic mercury rapidly decreased with sample time.

Since the water and  $\text{NaBH}_4$  solutions would not be consumed this rapidly, the decrease is probably due to flue gas condensate that formed in the sample tubes just upstream of the impingers.

The results in Figure 8.1 indicates that the Jerome analyzer has the capability to provide representative measurements of mercury in flue gas provided that the analyzer is presented with a representative sample. In this test, errors introduced in sampling and sample conditioning easily exceeded errors associated with the accuracy of the instrument.



**Figure 8.1 Change in Measured Mercury Concentration as a Function of Sampling Time**

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## 10.0 ACRONYMS

|                      |   |
|----------------------|---|
| AECDP                | Advanced Emissions Control Development Program    |
| ART                  | Absorber reaction tank                            |
| B&W                  | Babcock & Wilcox                                  |
| BH                   | Baghouse  |
| CAA                  | Clean Air Act as amended in 1990                  |
| CEDF                 | Clean Environment Development Facility            |
| DBA                  | Dibasic acid                                      |
| DOE                  | Department of Energy                              |
| ECTC                 | Environmental Control Test Center                 |
| EERC                 | Energy and Environmental Research Center          |
| EDTA                 | Ethylenediaminetetracetic acid                    |
| E-LIDS <sup>TM</sup> | Enhanced Limestone Injection Dry Scrubbing System |
| EMF                  | Emission modification factors                     |
| EPA                  | United States Environmental Protection Agency     |
| EPRI                 | Electric Power Research Institute                 |
| ESP                  | Electrostatic precipitator                        |
| FCEM                 | Field Chemical Emissions Monitoring               |
| FGD                  | Flue gas desulfurization                          |
| FTIR                 | Fourier Transform Infrared                        |
| HAP                  | Hazardous air pollutant                           |
| ICR                  | Information Collection Request                    |
| LFI                  | Limestone Furnace Injection                       |

|       |  |
|-------|--|
| MSW   | Municipal solid waste                  |
| MTI   | McDermott Technology, Inc.             |
| MWC   | Medical waste combustor                |
| NOAS  | Normalized oxidation air stoichiometry |
| OCDO  | Ohio Coal Development Office           |
| OCRC  | Ohio Coal Research Consortium          |
| PSE&G | Public Service Electric and Gas        |
| R&DD  | Research & Development Division        |
| SMT   | Seefelder Messtechnik                  |
| SR    | Stoichiometric Ratio                   |
| UARG  | Utility Air Regulatory Group           |
| WFGD  | Wet flue gas desulfurization           |