

Introduction to the Air & Waste Management Association's 29th Annual Critical Review



Pratim Biswas

Several agencies and researchers have suggested a plausible link between anthropogenic sources emitting mercury, its bioaccumulation in the food chain, and its adverse effects on human and animal health. The need to better understand the key scientific issues associated with emissions inventory, control technology, fate and transport in the environment, and health effects has

also been recognized by researchers and policy-makers. This year's Critical Review will discuss the recent, ongoing, and planned studies to address the issues related to the presence of mercury in the environment.

An emissions inventory compiled by the U.S. Environmental Protection Agency (EPA) (EPA, 1998) identifies emissions from combustion as the largest single source category (80% of the total), with coal combustion the largest fraction (72.3 tons per year in the United States, 46% of the total) in this category. The reported total emissions of mercury from all sources in the United States was 158 tons per year during 1994–1995. Nriagu and Pacyna (1988) have estimated global anthropogenic emissions of vapor phase mercury to range between 1,000 and 6,000 tons per year. There has been discussion associated with the data compiled, and the Critical Review mentions issues related to the development of an accurate inventory, along with two new data-collection initiatives by the EPA: the Toxic Release Inventory and the Information Collection Request.

The Critical Review then discusses mercury control technology, beginning with a review of data on mercury removal in conventional pollution control equipment (electrostatic precipitators, fabric filters, wet and dry flue gas desulfurization scrubbers) and NO_x control systems. This is followed by a review of optimization/modification of conventional control equipment for mercury removal efficiency (e.g., converting elemental mercury to oxidized mercury, followed by scrubbing). Finally, the review explains new technologies being developed at the pilot-scale specifically

designed for mercury removal, along with a comparison of costs for mercury control.

The paper next examines the issue of mercury transport in the environment, to establish a link between mercury releases and concentrations in the ambient air, soil, water, and sediments. It elucidates the need to account for the chemistry of mercury and the development of accurate wet and dry deposition models. A review of a proposed field study in the Great Lakes region to quantify the relative contribution of the various sources to ambient levels of mercury is discussed.

The ultimate motivation of these studies is to relate the emissions inventory, control technology, and models of mercury transformation and fate to how ambient levels of mercury affect human health. All forms of mercury are known to be toxic and exhibit different health effects. In the 19th century, the neurological disorder induced by mercury exposure from the leather tanning process was known as "mad hatter's disease." Widely cited incidents from accidental acute exposure in this century include the Iraqi grain and the Minamata Bay incidents. Recent studies in the Seychelles and Faroe Islands set out to determine the existence of an association between exposure levels of pregnant women to methylmercury and the postnatal neurological development of their children. Because these studies have both contradictory and controversial data, the National Academy of Science will review all data on health effects during an 18-month effort. The review will aid in understanding the results of the collected data and provide insight on the lower threshold of mercury in fish and what impact, if any, the data will have on potential regulations. The Critical Review summarizes these points as they relate to mercury emissions from combustion sources.

Led by Thomas Brown, a team of researchers from the U.S. Department of Energy's Federal Energy Technology Center has prepared the 1999 Critical Review, entitled "Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate." The report's primary authors are Brown, Dennis N. Smith, Richard A. Hargis, Jr., and William J. O'Dowd.

The A&WMA Critical Review Program Committee welcomes your participation at the 92nd A&WMA

Annual Meeting in St. Louis and attendance at the Critical Review presentation on June 23, 1999, at 1:30 p.m., in the America's Center, Room 231. In addition to Brown's presentation of the review, a panel consisting of experts from academia, industry, and government will participate in a lively discussion. The panel will include the Critical Review Committee Members listed below, and Dr. Connie Senior of PSI Technologies, Dr. Dennis Laudal of the University of North Dakota's Energy and Environmental Research Center, independent consultant Dr. James Craner, and Dr. James Kilgroe of EPA. Audience members are also welcome to present their thoughts, and those not able to attend may respond in writing. The discussants' presentations, public responses, and the authors' final thoughts on the subject will be published in a later issue of the *Journal of the Air & Waste Management Association*.

REFERENCES

Nriagu, J.O.; Pacyna, J.M., *Nature* **1988**, 333, 134.

U.S. Environmental Protection Agency, *Mercury Study Report to Congress*, EPA-452/R-97-003; Office of Air Quality Planning and Standards and Office of Research and Development, Washington, DC, 1998.

Critical Review Committee Members

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Due to the voluminousness of this year's Critical Review, only the abstract, introduction, and conclusions are being published in this issue of the *Journal*. The entire 1999 Critical Review can be viewed and printed out from the A&WMA Web site (www.awma.org); copies can be obtained by contacting A&WMA at (412) 232-3444, ext 3179, or by emailing gcosby@awma.org. It will also be distributed at the Association's 1999 Annual Meeting in St. Louis, MO, June 20–24.

Mercury Measurement and Its Control: What We Know, Have Learned, and Need to Further Investigate

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ABSTRACT

Based on the available evidence of health effects, the U.S. Environmental Protection Agency (EPA) has been evaluating the need to regulate mercury releases to the environment. In response to the congressional mandates in The 1990 Clean Air Act Amendments (CAAA), the EPA has issued the Mercury Study Report and the Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units Report. In spite of the enormous effort represented by these reports, as well as the efforts of both the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI), in conducting the field measurement programs that form the basis for these reports, a definitive answer on the need for mercury regulation has not been found. However, the EPA, as well as other regulatory agencies and health researchers, have suggested a "plausible link" between anthropogenic sources emitting mercury and the methylation, bioaccumulation in the food chain, and adverse health effects in humans and wildlife.

Policy-makers have recognized that regulations must be based on good science and that a number of issues still remain. These issues can generally be grouped into four main categories: emissions inventory, control technology, fate of releases, and health effects. This paper will discuss recent, ongoing, and planned studies to address the remaining issues regarding the presence of mercury in the environment, with an emphasis on those studies that are directly related to the DOE/Federal Energy Technology Center's (FETC) programmatic effort.

The emissions inventory contained in the EPA Mercury Study Report addresses known anthropogenic sources of mercury to the environment for 1994–1995. Emissions from combustion are the largest single source category. Within this source category, combustion of coal accounts for the largest fraction. While the DOE/FETC does not necessarily agree with all the assumptions made in the EPA estimate, it is obvious that coal combustion is a significant source of mercury. In fact, the data used to estimate coal combustion emissions were based largely on field studies conducted under the DOE and EPRI programs. In conducting these studies, individual sites were selected

to give a good cross section of the U.S. boiler population, conventional control equipment, and coal types. Issues related to the development of an accurate inventory are discussed here, along with two new data-collection initiatives by the EPA: the Toxic Release Inventory (TRI) and Information Collection Request (ICR).

The discussion of mercury control technology begins with a review of data on mercury removal in conventional pollution control equipment [electrostatic precipitators (ESPs), fabric filters (FFs), and wet and dry flue gas desulfurization (FGD) scrubbers], and NO_x control systems. Fuel switching, used as an SO₂ compliance strategy, can also have an effect on mercury emissions. Next, optimization/modification of conventional control equipment for mercury removal efficiency (e.g., converting elemental mercury to oxidized mercury followed by scrubbing) is reviewed. Finally, new technologies being developed at the pilot scale specifically designed for mercury removal are discussed, along with a comparison of costs for mercury control.

A link between releases of mercury and concentrations in the ambient air, soil, water, and sediments must be established to evaluate the benefits of various control strategies. For mercury contained in stack gases, dispersion modeling must be combined with plume chemistry and wet and dry deposition models. The contribution of sources to local, regional, and global pools of mercury must be quantified. A review of a proposed field study that will be conducted this year in the Great Lakes region to quantify the relative contribution of the various sources to ambient levels of mercury is also provided.

This brings us full circle to the motivation to develop an emissions inventory, control technology, and models of mercury transformation and fate. How ambient levels of mercury affect human health forms the impetus for regulation and control. The effects of mercury on human health have been recognized for some time. In the 19th century, the neurological disorder induced by mercury exposure from the leather tanning process was known as "mad hatter's disease." Widely cited incidents from accidental exposure during this century include the Iraqi grain and the Minamata Bay incidents. Although these were

acute exposures, the EPA established a lower threshold limit for mercury in fish muscle at 0.5 parts per billion (ppb), based on the observations of the Iraqi episode.

The most recent health study has raised some uncertainty over the link of health effects to chronic, low-level exposures. The purpose of the studies in the Seychelles and Faroe Islands was to determine the existence of an association between exposure levels of pregnant women to methylmercury and the postnatal neurological development of their children. Because these studies have both contradictory and controversial data, the National Academy of Sciences (NAS) will review all data on health effects during an 18-month effort. The review will aid in understanding the results of the collected data, provide insight on the lower threshold of mercury in fish, and what impact, if any, will the data have on potential regulations. The paper summarizes these points as they relate to mercury emissions from combustion sources.

EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE), through the Federal Energy Technology Center (FETC), manages the largest funded program in the country for developing (1) an understanding of mercury emissions, (2) measurement of these emissions, and (3) control technology (-ies) for these emissions for the U.S. coal-fired electric generating industry. DOE has initiated, or has collaborated with other government and industrial organizations in, these and other efforts relating to mercury and other hazardous air pollutants (HAPs), also known as air toxics. One of DOE's first reports on trace elements in coal was conducted from 1976 through 1978 by researchers at DOE's Pittsburgh Energy Technology Center (PETC, now FETC) and the Pittsburgh Mining Operations of the Department of the Interior's Bureau of Mines. The report was completed less than two years after DOE was formed, and 13 years before Title III of the 1990 Clean Air Act Amendments was enacted (Cavallaro et al., March 1978).

This work was conducted at PETC facilities years before the terms "hazardous air pollutants" and "air toxics" came into vogue. The work indicated, from 10 different coal beds, that most of the trace elements of interest are concentrated in the heavier specific gravity fractions of the coal, and, therefore, are associated with the mineral matter. It was speculated that the removal of the mineral matter should result in significant trace element reductions ranging up to 88% (Cavallaro et al., March 1978).

Since that time, many collaborative efforts on trace element research (focused on mercury) have been realized between DOE/FETC and EPA, the U.S. Geological Survey (USGS), the Electric Power Research Institute (EPRI), the utility industry, other government agencies at both the federal and state levels, and other U.S. and foreign

research organizations. Most efforts in trace element research have been conducted in this decade, and many of the most important efforts in the understanding of mercury have been conducted during the last six years.

EPRI and DOE/FETC collaborated on the sampling and analyses of a possible 189 listed HAPs resulting from coal combustion and indicated by EPA as potentially impacting our ecosystems and human health. The combined EPRI and DOE/FETC efforts provided comprehensive HAPs assessments from over 30 different coal-fired power plants in the United States to the EPA for both of their congressionally mandated reports: the Mercury Study Report and the Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units—Final Report to Congress (EPRI, 1994; U.S. DOE, 1996).

Through an interagency government review process, DOE/FETC and DOE's Policy Office were also involved with some of the results of the data and conclusions contained in these two reports. With FETC managing the largest mercury control program, the Mercury Study Report stressed during the review period that for the promising technologies, "Given the relative low maturity level of these technologies, commercial deployment is still at least several years away, and will be strongly dependent on the results of the Phase II efforts." The EPA report also stated, "Before any of the technologies are fully realized for utility application, the fundamental mechanisms of the flue gas and mercury chemistries during the combustion and post-combustion conditions, along with the various interactions with the different types of fly ash must be understood" (Brown, T.D., 1997; EPA, 1997).

Phase II, as referred to in the above paragraph, is part of DOE/FETC's Advanced Emissions Control Technology "Mega PRDA Program" (PRDA is a Program Research and Development Announcement). During Phase I of the program, 11 of the 17 awarded contracts were related to mercury understanding and control. Work was initiated in October 1995 and completed in July 1997. The efforts encompassed two years of laboratory- and bench-scale testing and evaluation of several approaches for controlling the emission of mercury from coal-fired utility boilers. During a down-selection process, FETC selected six Phase II proposals (two-to three-year efforts) to further investigate and develop fine particulate and mercury control technologies and concepts. These research projects constitute the most comprehensive program both in the United States and worldwide regarding coal-fired utility boiler systems.

This research focuses on developing potential technologies for mercury emission reduction from utility plants and is aimed at either adding some type of sorbent technology to adsorb the mercury, improving the mercury capture effectiveness of existing pollution control

technology, or using new technology for mercury control. There are other DOE/FETC initiatives that also address research areas related to mercury. The FETC in-house research and development (R&D) program conducts HAPs and mercury measurement and controls R&D for both conventional and advanced coal-fired power systems. The Small Business Innovative Research Program (SBIR), the University Coal Research Program (UCR), and the Jointly Sponsored Research Program (JSRP) at the University of North Dakota Energy and Environmental Research Center (UNDEERC or EERC) have many focused areas in mercury measurement and control R&D for the coal-fired utility industry.

Through interagency government review processes, DOE/FETC has also been involved with the review and comment on EPA initiatives regarding the Toxic Release Inventory (TRI) and the Information Collection Request (ICR) for mercury concentration determinations in the various coals utilized in the utility industry and for mercury flue gas speciation measurements, which represent a cross-section of the coal-fired utility industry. There are issues related to the reporting threshold limits EPA has indicated for cobalt, vanadium, mercury, and dioxin and furan compounds for the utility industry. FETC has been involved in all the aspects of the EPA ICR, from coal sampling for mercury concentrations to the quality assurance and quality control of both the coal and flue gas mercury measurements.

These and other programs and projects initiated by DOE/FETC, and in collaboration with outside participants, are detailed in this report. The information includes data from the initial comprehensive assessments of HAPs, mercury speciation method developments, and the efforts of DOE/FETC and their contractors regarding the understanding of mercury and its control across a highly variable coal-fired utility industry. This review describes

- (1) the diversity in coal composition;
- (2) the species of mercury in flue gas resulting from combustion;
- (3) the ability to measure mercury speciation;
- (4) factors influencing mercury speciation and adsorption or other capture mechanisms; and
- (5) the technical and economic mercury issues for coal-fired utility boiler systems.

The technology breakthroughs made by the DOE/FETC contractors are detailed, along with the implications of these results on mercury control for the utility industry. In addition, research efforts conducted by other organizations are discussed. The report also examines the potential need for regulations and a schedule for recommending them before the ICR initiative is completed, before making determinations on mercury reporting thresholds under the TRI initiative, and, most importantly, before the National Academy of Sciences (NAS) has com-

pleted its study on the somewhat conclusive, but controversial, mercury-related health studies conducted on the inhabitants of the Faroe and Seychelles Islands. The NAS is mandated by Congress to provide a report on the human reference dose level for mercury.

The impact of existing flue gas cleanup systems and mercury concentrations in coal that is supplied to the electric utilities require improved understanding before any regulatory decision is made. The EPA ICR should elucidate many of the uncertainties. To illustrate instances where these knowledge gaps are closing, the following examples are provided. Data that would not require a 90% reduction of mercury emissions for individual plants and utilities. For instance, data collected by DOE/FETC and EPRI contractors are indicating that mercury removals for plants equipped with wet flue gas desulfurization (WFGD) systems are between 50 and 65% of the mercury, which includes the particulate-bound mercury. The vapor phase represents 80–95% of the oxidized mercury in the flue gas prior to scrubbing by the WFGD. The oxidized mercury gets into the environment sooner as a result of local deposition, but the plants with the highest concentrations of oxidized mercury in the flue gas utilize WFGD systems (e.g., Ohio Valley plants firing medium- to high-sulfur bituminous coals).

The EPA ICR will provide additional data on mercury removal from WFGD systems and from other air pollution control devices used in the utility industry. On a mass basis, over one-third of the coal utilized in this country is from the Powder River Basin (PRB) and other subbituminous coals. Many full-scale characterization studies conducted by DOE/FETC contractors on power plants firing PRB coal indicate between 20 and 30% mercury capture associated with electrostatic precipitators; and on average 50–60% mercury capture at plants equipped with baghouses, with 90% mercury capture being observed.

A sensitivity analysis for mercury emission control has been performed to examine how control options may impact the diverse U.S. power plant population. The first option, shown in Figure ES-1, considers setting a cap on emissions of 0.03 tons of mercury emitted per million tons of coal consumed. At this level of control, about 10% of the U.S. power plants that have low mercury emissions come under the cap with little or no additional controls needed. For about half of the total coal consumption, less than 40% additional control would be required. On about 10% of the total coal consumption, fairly significant control would be required, ranging from 66 to 85% reduction from the existing emissions level. The remaining 30% of power plants would require approximately 40 to 67% mercury emissions reduction. The overall reduction in mercury emissions from the national mercury emissions inventory estimate for the reference year of 1996 is about 50%.

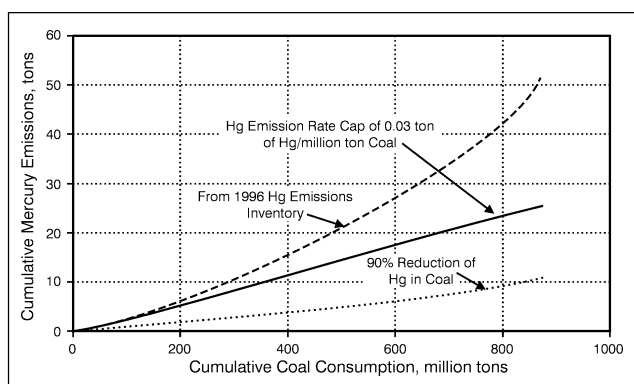


Figure ES-1. 1996 mercury emissions and control scenarios (Smith, D.N. 1999).

In the second option, a 90% reduction of mercury contained in the mined coal is considered. This scenario credits mercury removal from coal preparation and existing power plant controls toward an overall 90% reduction goal. Approximately 60% of the coal consumed would require controlled reduction between 80 and 90%. Nearly 98% of the coal consumed would require reductions of at least 50%. The overall reduction in mercury emissions from the national mercury emissions inventory estimate for the reference year of 1996 is about 80%.

This sensitivity analysis demonstrates that mercury control options are highly dependent on the existing power plant's operating characteristics and design. As stricter control options are considered, the flexibility to achieve these reductions begins to diminish.

Mercury control technology availability should not be the driving force behind any regulatory decision for mercury emissions from coal-fired power plants. Control technology availability has an impact, but the need for control, based on health impacts, must be a driver. The Seychelles studies provided data to calculate a mercury reference dose (MRD) of 0.5 $\mu\text{g Hg/kg-bw/day}$ (grams of mercury per kilogram of body weight per day). This is in comparison to EPA's calculated 0.1 $\mu\text{g Hg/kg-bw/day}$ MRD, from the acute exposure with the Iraqi contaminated grain incident. The Agency for Toxic Substances and Disease Registry (ATSDR) has recently indicated a mercury reference dose (MRD) or mercury risk level (MRL) of 0.3 $\mu\text{g Hg/kg-bw/day}$ based upon the Seychelles Island studies. If an MRL of 0.3 $\mu\text{g Hg/kg-bw/day}$ limit was indicated by NAS from their 18-month study, it is estimated that 90% or more of the state fish advisories would not be required. This alone may be the most dramatic factor impacting the level of control required under any regulatory determination process.

The NAS study and the agency's subsequent submission of a report should provide information on the reference dose level. DOE/FETC and EPRI support of industry's progress in advancing the state-of-the-

art understanding of mercury measurements and control in the utility industry, is thought to enhance any future regulatory process or requirement by the sound science achieved through these investigations.

DOE/FETC, in collaboration with EPA, EPRI, and USGS, is developing a program to demonstrate the most promising mercury control technologies at larger- or full-scale at different coal-fired utilities. DOE will issue a solicitation before the end of fiscal year 1999 (September 30, 1999). The solicitation will ask for proposals to scale up the promising technologies and will require contractor and industrial cost sharing. These demonstrations need to be completed before any regulatory decisions can be made based on sound science. There are many engineering and technical issues that need to be addressed before mercury control is implemented in the utility industry.

INTRODUCTION

The 1990 Clean Air Act Amendments (CAAA) brought about a new awareness regarding the potential impact or health effects of stationary source emissions. A possible 189 pollutants were identified as hazardous or toxic; these pollutants have collectively become known as "air toxics." Of the 11 titles contained in the CAAs, Title III, Hazardous Air Pollutants (HAPs), has promoted some of the most interesting and exciting research, as well as eventual development of many databases on air toxic emissions from all industrial stationary sources in the United States.

The specific provisions under Title III of the CAAs regarding electric steam generating units were comprehensively addressed by DOE/FETC and EPRI in their collaborative air toxic characterization programs. Their work concluded that many of the air toxics from coal-fired utilities are "not a concern to the environment and human health." There still exist, however, uncertainties regarding arsenic, chromium, nickel, dioxin, and furan compounds, and most importantly, mercury emissions from coal-fired utility boilers. (U.S. EPA HAPs Report, 1998)

The work, initiated by DOE/FETC and EPRI in 1990 and continued through 1997, provided most of the data used as the basis for EPA's conclusions regarding air toxic emissions from coal-fired utility boilers. The results of the studies and the input to the knowledge base regarding these emissions are discussed below. The assessment of toxic emissions, with a focus on mercury, has continued since 1993.

Conventional particulate control devices used in the utility industry capture the majority of the trace elements (Sb, Be, Cd, Cr, Co, Pb, Mn, Ni, and, in most cases, As) and compounds of these elements indicated on the CAAA HAPs list to levels exceeding 95% and as high as 99.99%. The obvious elements not collected at high efficiencies were Hg, Se, and, in some cases, As. Approximately 65% of the utility power plants only utilize an electrostatic

precipitator (ESP); 10% utilize only a fabric filter (FF); and the remaining 25% utilize a combination of an ESP and wet FGD systems.

It has been determined that the high removal of the trace elements/compounds is independent of coal rank, boiler configuration, concentrations in the coal and subsequent flue gas, and conditions before and within the air pollution control devices (APCDs). The nonvolatile nature of these elements augments their association with the particulate matter being collected from 99.0 to 99.99% in the various particulate control devices (ESPs and FFs). The remaining low levels of particulate matter and associated trace elements are effectively removed across wet FGD systems. (EPRI, 1994; U.S. DOE Report, 1996) Table 1 gives the emission factors of these elements from the DOE/FETC program from 1993 and the results from past studies on trace element emissions from coal-fired boilers.

A detailed examination of the available data from coal-fired power plants was conducted recently. (Senior, C. L., et al., 1997) Data reviewed included the EPRI and DOE-sponsored studies as well as data from the scientific literature. Again, most of the HAPs (Cd, Co, Cr, Ni, Pb, Be, Mn, and Sb) showed uniformly high capture efficiency in all types of APCDs studied to date. Not only was the capture efficiency for these elements high, but it fell within 2 standard deviations of the average particulate matter capture efficiency for the particular device.

Three elements (As, Se, and Hg) exhibited capture efficiencies in the air pollution control devices that were significantly less than the particulate matter collection efficiency. An in-depth look at the data suggests that this is because these elements either are concentrated in the sub-micron particulate or are in a gaseous form.

Both the type of coal and the type of APCD seemed to have an impact on arsenic and selenium capture in coal-fired power plants. Subbituminous coals and lignite coal have large amounts of calcium in the ash that can react with arsenic and selenium. Average capture efficiencies for arsenic depended on coal type: 98.9% for subbituminous coals, 99.6% for lignite coals, and 96.3% for bituminous coals. Selenium is a volatile element in the flame and shows low-capture efficiencies in coal-fired power plants. Average capture efficiencies were strongly dependent on coal type: 98% for subbituminous coals, 62% for lignite coals, and 44% for bituminous coals. For both elements, the amount captured in ESPs was significantly less than that in fabric filters. This points to an interaction between arsenic, selenium, and calcium in the large fly ash particles in sub-bituminous coals and lignites. A significant fraction of selenium may be emitted in the gas phase as suggested by the low capture efficiency (35% on average) for selenium in plants burning bituminous coals and employing ESPs.

Improvements to the conventional particulate control devices have increased the collection of the particulate even for particles less than 2.5 μm and have further reduced the trace elements/compounds well below the detection limits of the state-of-the-art multi-metals sampling and analytical technique (EPA Method 29). In addition, the development of new retrofit and novel particulate control devices for new installations have also shown the improvement in the collection efficiencies of the particles less than 2.5 μm , with a corresponding reduction of the potentially hazardous trace elements. Based on DOE/FETC and EPRI findings from their comprehensive HAPs measurements, Table 2 indicates lower calculated emissions or reduction of trace elements of concern as particulate collection efficiency is increased.

For the reference year of 1997, the uncontrolled emissions from U.S. coal-fired power plants was calculated to be 105,000 tons. However, on average, the particulate matter capture efficiency on a mass basis for the utility industry was estimated to be 99%. Therefore, it was calculated that the coal-fired utility industry removes more than 103,900 tons of trace elements with the fly ash. Trace element removals associated with higher particulate removals for a 600-MWe coal-fired power plant are also presented in Table 2. This is extremely important for the toxic release inventory (TRI) that the utilities must compile. The TRI is a public database that may cause some concern owing to the high levels of trace elements from coal combustion (i.e., fly ash being landfilled). Of course, utilities

Table 1. Emission factors (lbs/trillion btu).

Trace Element	DOE	Literature
Antimony	0.1 - 2.4	NA
Arsenic	0.1 - 42	1 - 860
Beryllium	0.1 - 1.4	1 - 32
Cadmium	0.1 - 3.0	1 - 490
Chromium	0.1 - 51	10 - 5000
Manganese	1.1 - 22	30 - 2400
Mercury	0.5 - 14	1 - 22
Nickel	0.3 - 40	1 - 2500

Table 2. Effect of control level on emissions.

Control Level	1997 Total U.S., 900 million tons of coal, dry basis	600-MW Plant 3 million tons
Uncontrolled Emissions	105,000 tons*	353 tons
99% Control	1,050 tons	3.5 tons
99.9% Control	105 tons	700 lb
99.99% Control	10.5 tons	70 lb
99.999% Control	1.05 tons	7 lb

*Assuming 117 mg/g total nonvolatile trace elements in coal, including Sb, As, Be, Cd, Co, Cr, Pb, Mn, and Ni. Mean value from 1993 DOE Study.

with fabric filters will remove more of the trace elements with the increase in particulate collection efficiency. Figure 1 compares field data on the distribution of trace elements/compounds of these elements for a fabric filter and an ESP installed on the boilers firing a subbituminous and bituminous coal, respectively. While the trace elements found in the two boilers are different, the higher efficiency particle collector (i.e., fabric filter) has the lowest emission rates for the trace elements. While mercury is a small percentage of the air toxic generated in the combustion process and only represents a small fraction of the emissions, some consider mercury an issue owing to its persistence and propensity for bioaccumulation.

Capture efficiency for particulate of 99.0 to 99.99% is achievable in the utility industry with fabric filters, while 99.999% is possible with new technologies developed under DOE funding (e.g., ADA Technologies additives; UNDEERC Advanced Hybrid Particle Collector; ABB's modifications to ESPs, including flue gas cooling in conjunction with pulsed energization; Environmental Element's Laminar Flow ESP; and Particle Agglomerator) (Durham et al., 1997; Miller, 1997; ABB et al., 1997; Feldman, P., et al., 1997; and Helfrich et al., 1997). EPRI's Compact Hybrid Particulate Collector (COHPAC), a high air-to-cloth-ratio, pulse-jet fabric filter downstream of an underperforming ESP, also can collect particles at 99.99% when combined with an ESP (Miller, R.L., et al., 1997; Browning et al., 1997).

The improvements and enhancements to conventional particulate control devices and novel concepts will enable effective collection of particles below 2.5 μm . The effective collection below this size also enables high efficiency collection of the trace elements and compounds (As and Se) and other HAPs associated with this particle size range. Work continues on reducing emissions of primary fine particulate below 2.5 μm through the many projects sponsored by DOE, EPRI, and EPA.

Most of the recent focus of these institutions involves developing an understanding of mercury and its various

forms, while funding and performing research and development for technologies or strategies for controlling mercury in coal-fired utility boilers in case regulations are required.

Based on the available evidence of health effects, EPA has been evaluating the need to regulate mercury releases to the environment and has issued the Mercury Study and the Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units reports. In spite of the enormous effort represented by these reports, as well as the efforts of both the DOE/FETC and EPRI, in conducting the field measurement programs that form the basis for these reports, a definitive answer on the need for mercury regulation has not been found. However, EPA, as well as other regulatory agencies and health researchers, have suggested a "plausible link" between anthropogenic sources emitting mercury and the methylation, bioaccumulation in the food chain, and adverse health effects in humans and wildlife.

Policy-makers have recognized that regulations must be based on good science and also that a number of issues still remain. These issues can generally be grouped into four main categories: emissions inventory, control technology, fate of releases, and health effects. As previously stated, this review will discuss recent, ongoing, and planned studies to address the remaining issues regarding the presence of mercury in the environment, with an emphasis on those studies that are directly related to the DOE/FETC's programmatic effort.

The emissions inventory contained in the EPA Mercury Study Report addresses known anthropogenic sources of mercury to the environment for 1994 through 1995. Emissions from combustion are the largest single source category. Within this source category, combustion of coal accounts for the largest fraction. While DOE/FETC does not necessarily agree with all the assumptions made in the EPA estimate, it is obvious that coal combustion is a significant source of mercury. In fact, the data used to estimate coal combustion emissions were based largely on field studies conducted under the DOE and EPRI programs. In conducting these studies, individual sites were selected to give a good cross-section of the U.S. boiler population, conventional control equipment, and coal types. Issues related to the development of an accurate inventory are discussed here, along with two new data-collection initiatives by the EPA: the Toxic Release Inventory (TRI) and Information Collection Request (ICR).

Developing effective mercury control technologies in coal-fired utility applications is extremely difficult if researchers can not determine the amount, vapor phase speciation (elemental versus oxidized mercury), and particulate-bound mercury. Total mercury (Hg) concentrations in

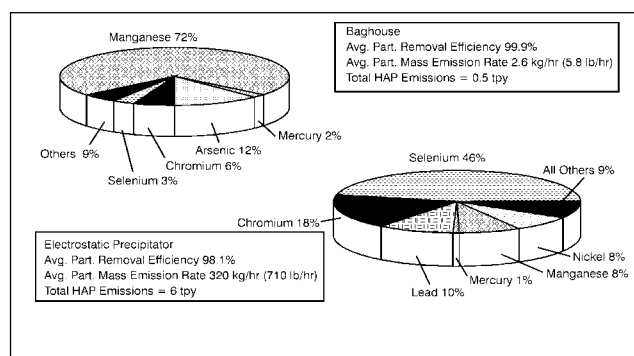


Figure 1. Distribution of trace elements identified as HAPs (U.S. DOE, September 1996).

coal, based on data collected since 1993, are relatively constant across the U.S. (20 to 120 parts per billion on a weight basis, or ppbw) with more than 75% of the coals having concentrations below 100 ppbw. There are a few exceptions with some concentrations being between 200 and 300 ppbw. However, when the different ranks of coal are fired in utility boilers, there is substantial variation in the concentrations of elemental mercury (Hg^0) versus oxidized mercury (Hg^{2+}) as measured at the inlet to the particulate control device. The percentage of Hg^0 varies from 10 to >90% indicating that speciation is very dependent on coal type. The chemical species of Hg formed during the combustion process and post-combustion conditions vary significantly from one plant to another, exacerbating the effective control of Hg across the utility industry.

While combustion conditions vary, the subsequent fly ash, carbon in the ash, and vapor-phase constituents can also play a major role in determining the percentage of the Hg chemical species formed. Understanding the rate-controlling mechanisms (i.e., transport, equilibrium, and kinetics) will not only aid in predicting the Hg species formed, but, eventually, will aid in optimizing existing air pollution control devices (APCDs) for Hg removal. Kinetics may play more of a role on the form of Hg than anticipated. Effective removal is dependent on the species of Hg present in the flue gas. For example, Hg^{2+} is water soluble and is less volatile compared to Hg^0 . Reducing the temperature of the flue gas and utilizing wet scrubbing could result in increased Hg^{2+} removal.

The discussion of mercury control technology begins with a review of data on mercury removal in conventional pollution control equipment [electrostatic precipitators (ESPs), fabric filters, wet and dry flue gas desulfurization (FGD) scrubbers], and NO_x control systems. Fuel switching, used as an SO_2 compliance strategy, can also have an effect on mercury emissions. Next, optimization/modification of conventional control equipment for mercury removal efficiency (e.g., converting elemental mercury to oxidized mercury followed by scrubbing) is reviewed. Finally, new technologies being developed at the pilot-scale specifically designed for mercury removal are discussed, along with a comparison of costs for mercury control.

This year's Critical Review addresses mercury speciation, mercury measurement, mercury emissions inventory, and mercury control technology development in the following sections:

- Emissions Inventory*
- Mercury Measurement and Mercury Control Technology Development*
- Mercury and Its Speciation*
- Mercury Speciation and Its Measurement*
- Factors Influencing Mercury Speciation and Adsorption Control Technology Investigations and Development for*

- Coal-Fired Utility Applications*
- Mercury Control Sensitivity*
- Recent R&D and Emerging Mercury Control Technologies for Coal-Fired Utility Boiler Systems*
- Coal Preparation or Coal Cleaning*
- Activated Carbon and other Sorbent Injection Technologies for Mercury Capture*
- Enhancing Mercury Capture in Flue-Gas from Utility Wet Desulfurization (WFGD) Systems*
- Other Innovative Approaches for Mercury Control in the Coal-Fired Utility Industry*
- Cost of Mercury Control*
- Conclusions and Recommendations on Mercury Measurement and Control*

EMISSIONS INVENTORY

Mercury cycles in the environment as a consequence of both natural and human activities. The annual global cycling of mercury in the earth's atmosphere amounts to about 5000 tons. It is estimated that 4000 tons are the consequence of anthropogenic activities (EPA Mercury Study Report to Congress, 1998). The United States emits about 3% of the global anthropogenic emissions of mercury amounts to some 150 tons annually. Within this context, the U.S. coal-fired power generation, the largest source of mercury emissions as a class of industrial activity, contributes approximately one-third, or 50 tons, annually. Other large source emitters include municipal waste combustors, which emit nearly 20% and medical waste incinerators which emit nearly 10% of all U.S. anthropogenic emissions (U.S. EPA White Paper, 1998).

As a consequence of the large natural emissions of mercury to the atmosphere and the difficulty in accurately measuring anthropogenic emissions, these emissions and their subsequent influence on terrestrial deposition and uptake in the food chain are subjects of significant uncertainty. It is not the intention of this critical review to examine all of the shortcomings associated with developing a mercury emission inventory for the complete range of mercury emission sources but rather to focus on the largest contributor to anthropogenic mercury emissions in U.S. coal-fired power plants.

In this section, the DOE/FETC's interest in developing an improved understanding of mercury behavior as it relates to coal-fired power generation is briefly reviewed. This is followed by the results of emission inventory development that came from the FETC's collaborative efforts with the EPA, EPRI, and other public and private sector organizations. Finally, the continuing efforts to improve our understanding of mercury emissions from coal-fired power plants are reviewed.

During the 1990s, DOE, in collaboration with the EPRI, conducted field studies of commercial coal-fired

power plants that still serve as a seminal data source on mercury behavior in coal-fired power plants. The results from these field tests provided a basis for the EPA to estimate emissions of mercury in documents such as the Mercury Study Report to Congress.

Coal-Fired Power Plants

Coal-fired power plants are the predominant type of power generation in the United States. Electric utility sales to consumers totaled 3140 billion kWh in 1997, which was up 1.4% from 3098 billion kWh in 1996 (EIA, *Electric Power Annual 1997*, Vol. 2, 1998). Coal-fired electricity generation accounted for 1737 billion kWh in 1996 and increased to 1788 billion kWh in 1997. Recently, coal-fired generation accounted for 56% of total generation. Coal consumption at U.S. electric utilities increased from 875 million tons in 1996 to 900 million tons in 1997.

The characteristics of the coal-fired power plant that most greatly influence mercury emissions are the mercury content of the as-fired coal, the type of burner(s) on the plant, the boiler operating conditions, the design and operation of any particulate collection devices, and the design and operation of any flue gas treatment systems. In the following section, each of these power plant characteristics is discussed as it pertains to recent experience.

Coal Use at Electric Utilities

Coal consumption at electric utilities has increased constantly since 1991 with the largest increases occurring in the past few years. The coal quality is depicted in Table 3 (EIA, *Cost and Quality of Fuels for Electric Utility Plants*, 1996).

The coal-producing states providing the largest amounts of coal to electric utilities are Wyoming, Kentucky, and West Virginia. Using the method established by the EPA in the *Electric Utility Report to Congress*, a detailed estimate of annual mercury emissions can be made from available data sets that characterize the coal-fired power generation industry in 1996.

Review of Estimating Method: Mercury Content in Coal

Mercury concentration data for U.S. coal deposits are extensively covered by the U.S. Geological Survey's (USGS) COALQUAL database (Toole-O'Neil et al., 1999). COALQUAL contains analyses of approximately 7500 full-bed core and channel samples each representing the entire thickness of a coal bed. Table 4 summarizes the mercury concentration data on a state-level basis. The table has been constructed by using the complete set of samples provided in the COALQUAL database with the exception of the samples that did not provide complete proximate analysis of the coal.

In general, the median mercury concentration in the coal is lower than the mean concentration. From a statistical viewpoint, if the sampling distribution of mercury concentration has a strong central tendency (most of the distribution area is under a single peak), then the median is a good estimator of the central value. The median fails as an estimator only if the area under the tails is large, while the mean fails if the first moment of the tails is large. For the mercury concentration distributions in a given state, the mean value appears to provide the most suitable representation.

In some cases, the variability of mercury concentration at the state level is very significant and brings into question the ability to use state-level values of mercury content in coal as a proxy for coal-fired power plant operations. Several underlying assumptions diminish the ability to confidently estimate mercury inventories using this procedure. The degree to which the coal samples represent the mining operations is problematic. Many of these samples have been collected more than two decades ago and, in some cases, were obtained from abandoned mines. Furthermore, the variability of mercury within a given coal mine can be considerable and may distort the "composite average" mercury content of coal delivered to end users.

Table 3. Origin of coal by state, 1996 (nameplate capacity of 50 MW or more).

State of Origin	Quantity million tons	Higher Heating Value, Btu/lb	Weight % Sulfur	Weight % Ash
Alabama	16.8	12,319	1.13	12.0
Arizona	11.0	10,948	0.53	9.6
Colorado	21.7	10,988	0.45	8.2
Illinois	42.4	11,322	2.29	8.8
Indiana	23.9	11,087	2.43	9.4
Kansas	0.2	12,054	2.59	10.2
Kentucky	117.4	12,200	1.65	10.2
Louisiana	3.2	6,954	0.96	12.2
Maryland	3.1	12,594	1.55	12.5
Missouri	0.6	11,053	3.73	14.6
Montana	35.4	9,094	0.51	6.5
New Mexico	24.1	9,401	0.71	19.9
North Dakota	23.6	6,593	0.72	9.3
Ohio	24.8	11,819	3.56	10.8
Oklahoma	0.1	13,064	3.11	7.0
Pennsylvania	47.2	12,530	1.79	11.5
Tennessee	2.9	12,504	1.24	10.5
Texas	51.3	6,434	1.00	15.7
Utah	18.7	11,641	0.47	10.2
Virginia	14.5	12,818	1.05	10.2
Washington	4.5	7,895	0.71	15.5
West Virginia	101.8	12,419	1.47	11.1
Wyoming	268.9	8,650	0.35	5.4
Imported	4.7	11,797	0.63	5.8
Total	862.7	10,263	1.10	9.2

Table 4. Mercury content in coal from COALQUAL database.

State of Origin/Rank	Higher Heating Value, Btu/lb	Mean Hg Conc., ppmw	Median Hg Conc., ppmw	Hg Conc. Sample Variance, ppmw
Alabama/bit	12,575	0.22	0.18	0.028
Alaska/sub	7,756	0.06	0.05	0.002
Arizona/sub	10,834	0.04	0.05	0.000
Arkansas/lig	6,220	0.33	0.24	0.075
Colorado/bit	11,250	0.06	0.03	0.005
Colorado/sub	9,527	0.06	0.05	0.003
Illinois/bit	11,605	0.09	0.08	0.002
Indiana/bit	11,386	0.10	0.08	0.006
Iowa/bit	9,937	0.16	0.14	0.010
Kansas/bit	12,014	0.17	0.14	0.019
Kentucky/bit	12,595	0.16	0.11	0.024
Louisiana/lig	7,955	0.12	0.12	0.000
Maryland/bit	12,788	0.33	0.18	0.160
Missouri/bit	10,839	0.17	0.15	0.016
Montana/lig	6,701	0.13	0.10	0.017
Montana/sub	8,124	0.08	0.06	0.003
Montana/bit	6,790	0.23	0.23	0.003
New Mexico/sub	9,297	0.06	0.04	0.005
North Dakota/lig	6,265	0.14	0.11	0.017
Ohio/bit	11,948	0.20	0.17	0.022
Oklahoma/bit	13,135	0.23	0.13	0.084
Pennsylvania/bit	12,759	0.27	0.20	0.069
Tennessee/bit	13,364	0.15	0.10	0.024
Texas/lig	7,628	0.17	0.14	0.018
Utah/bit	10,061	0.09	0.05	0.011
Virginia/bit	13,580	0.11	0.07	0.009
Washington/sub	7,417	0.29	0.11	0.206
West Virginia/bit	13,247	0.16	0.10	0.034
Wyoming	8,544	0.10	0.08	0.008

The impact of coal cleaning is significant and has been reviewed in Appendix D of the EPA's Utility Report to Congress as well as a recent article on mercury concentration in coal (Toole-O'Neil et al., 1999). In the Utility Report to Congress, a cleaning factor was applied to the USGS COALQUAL mercury concentrations for bituminous coals from Alabama, Iowa, Indiana, Kansas, Kentucky, Maryland, Missouri, Ohio, Oklahoma, Pennsylvania, Utah, Virginia, and West Virginia. This cleaning factor, 0.79, suggested a 21% removal of mercury prior to coal combustion as a result of coal cleaning.

Toole-O'Neil et al. (1999) evaluated the tendency of coal cleaning to preferentially remove mercury. Of the 24 cases of coal cleaning cited in this report, the average decrease in mercury concentration was 37% on an energy basis and ranged from 12 to 78% for individual cases. On a mass basis, the average mercury reduction from coal cleaning was 30%, which indicates a coal cleaning factor of 0.70, a lower value than that used by the EPA.

Review of Mercury Inventory Estimating

Method: Emission Modification Factors (EMFs)

Flue gas cleanup systems and other operational strategies imposed at the power plant have a variable impact on the emissions of mercury. Therefore, an emission modification factor (EMF) was developed by EPA that reflects the ratio of the mercury emissions after installation of a particular subsystem or unit process to the mercury emissions that would be realized if 100% of the mercury entering the subsystem or unit process were left in the flue gas. Table 5, modified from a table in the Electric Utility Report to Congress, qualitatively describes the impact power plant operations have on mercury emissions.

The carbon adsorption system is the only system deliberately installed to control mercury emissions. This and other mercury control options, to be discussed later, are expensive to implement. One reason for the expense is that large flue gas volumes must be treated to capture a very small amount of mercury; typical mercury concentrations in untreated flue gas are in the low parts-per-billion range. The mercury in the flue gas can be characterized as being in two forms: oxidized or elemental. The ability of systems to capture mercury is dependent, in part, on the species of mercury in the flue gas, as evidenced in Table 5.

Environmental equipment used to control pollutants emitted from coal combustion flue gas must meet local, state, and federal regulations. The trend in these regulations is to tighten requirements for new sources of pollution as well as to require retrofit of existing power generating equipment with environmental controls. A modern power plant is typically equipped with a high efficiency baghouse (FF) or ESP for particulate removal, staged-combustion burner configurations for low-NO_x emissions, and postcombustion flue gas treatment devices for NO_x and SO₂ control. Examples of the latter devices are selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) technologies for NO_x control and high efficiency FGD scrubbers for SO₂ control. Additionally, advanced coal-fired power generation technologies are evolving from cooperative efforts between DOE and industry, such as those being demonstrated in the Clean Coal Technology Program. Technologies, such as the integrated gasification combined cycle (IGCC) and pressurized fluidized-bed combustion (PFBC), are capable of producing electricity more efficiently than a conventional pulverized-coal combustion power plant. These advanced power systems are also equipped with very high efficiency gas clean-up technologies.

Many of the existing coal-fired power generation facilities do not include modern flue gas treatment systems, however. In 1996, the net dependable capacity of U.S. coal-fired power generation was about 300 billion watts (GW), of which nearly 75 GW (25%) had conventional

Table 5. Power plant operations affecting mercury emissions.

Power Plant Configuration and Operations Strategy	Effect on Mercury Emissions	
	Primarily Oxidized Mercury	Primarily Elemental Mercury
Conventional Coal Cleaning	Decrease in emission (highly coal specific)	
Fuel Switching: Coal to Gas	Decrease in emission	
ESP	Some decrease in emission	Some decrease in emission
FF	Some decrease in emission	Greater decrease in emission
Scrubber	Decrease in emission	No effect
Spray Dryer/FF	Some decrease in emission	Limited decrease in emission
	Carbon Adsorption System	Decrease in emission (based on pilot-scale studies)

scrubbing technology for controlling SO₂. However, much of the remaining capacity has met regulatory requirements for SO₂ emissions through use of low sulfur coals, by fuel switching or by co-firing low-sulfur fuels, such as natural gas or biomass.

EMFs: Coal Combustion

Coal combustion results in the production of hot gases and particles that are typically contained in a radiant furnace operating at temperatures exceeding 2000 °F (1093 °C). Most of the mercury entering the furnace is rapidly volatilized and moves through the convective section and economizer of the boiler island before exchanging heat in the air preheater. The extent to which mercury is removed from the flue gas is severely limited because of the extreme temperatures associated with this portion of the power plant.

Numerous combustion configurations are used in the electric utility industry. More recently, combustion modifications have occurred in existing coal-fired power plants, principally as a result of NO_x control requirements associated with Title IV of the CAAA. NO_x emissions are primarily accomplished with low-NO_x burners (LNBS), which have lower capital requirements than SCR or SNCR, but do not generally have the capability to achieve ultralow emission rates. The applications of LNBS are limited at present to dry bottom boiler configurations.

The burner-type distribution for coal-fired power plants is provided in Table 6. This distribution is broken into coal consumption patterns, capacity distribution, and number of boilers. The largest segment of the population (80%) is comprised of tangential- and opposed-firing burners. Measurements of mercury entering and leaving these systems have been conducted at least once for every firing configuration listed in Table 6. Additionally, the mercury removal process within the boiler island has also been measured for most of the LNB configurations that are present at electric utilities. Even though some of the firing configurations, such as cyclones, are not likely to be built in the future, they still are

often a dominant portion of the fleet of steam-electric generation plants existing today and will likely exist well into the next century.

As mentioned, in 1996, the utility industry consumed approximately 875 million tons of coal having an energy content of about 18 quads (quadrillion Btu, 10¹⁵) producing 1,737 billion kWh of electricity while emitting 5.5 million tons of NO_x. The composite NO_x emission rate from coal-fired power generation is

0.61 lb/MMBtu, which contrasts with recent New Source Performance Standards (NSPS) of about 1.35 lb/MWh or 0.15 lb/MMBtu. Tables 7 and 8 give the distribution of NO_x emission rates as a function of current boiler and firing configuration for uncontrolled and controlled NO_x emissions. Mercury emissions can be affected by changes in burner configuration that accommodate reduced NO_x formation. Relatively drastic changes in coal-fired combustion systems will be realized as the CAAA continue to be implemented into the next decade, and this should be taken into consideration as mercury control measures are scrutinized.

Electric utilities are in the process of meeting Phase II requirements of Title IV of the CAAA. Based on the EPA's final rule making for Phase II, the projected reductions based on boiler configuration are:

Boiler Type	NO _x Reduction, tons/year
Dry Bottom Wall-Fired	90,000
Tangentially Fired	30,000
Cell Burner	420,000
Cyclone (>155 MWe)	225,000
Wet Bottom (>65 MWe)	80,000
Vertically Fired	45,000
Total	890,000

Table 6. Firing-type distribution for coal-fired power plants (1996).

Firing Type	Coal Consumption, million tons	Net Dependable Summer Capacity, GW	Number of Boilers
Front	82.1	33.9	254
Tangential	393.3	128.5	424
Opposed	314.5	107.5	203
Vertical	7.7	3.5	28
Cyclone	68.0	22.4	86
Other	9.0	3.1	40
Total	874.7	299.0	1035

Table 9 provides a listing of coal-fired power plant mercury EMFs developed by the EPA for various firing configurations. Values close to 1 are expected owing to the high temperatures in the boiler. Those values much less than 1 are counter-intuitive and are suspect. For example, the value of 0.41 for opposed-fired, dry bottom boilers, without NO_x controls, can be compared with the value of 0.81 for opposed-fired, dry bottom boilers with NO_x controls. Because NO_x control would be expected to cause lower, not higher, mercury emissions, the data on which the 0.41 value was based were reviewed. In this case, the emissions for a large segment of the boiler population (36% on a capacity basis) are based on test data from one plant in the EPA's development of EMFs for this firing configuration. In addition, the firing system for this plant had a special configuration (cell burner) that represents less than 30% of the total population in this class. The impact of very limited data on developing an emission inventory for mercury will be discussed in the Emissions Inventory section.

EMFs: Flue Gas Cleaning

Flue gas cleaning systems can be grouped into two major classifications: particulate control systems and flue gas treatment systems for SO₂ control. Particulate from coal-fired power plants is principally controlled with either an ESP or a FF. Table 10 lists the major particulate control systems employed at coal-fired power plants.

The vast majority of particulate control at coal-fired electric utility plants is accomplished with cold-side ESP.

Table 7. Normalized power plant distribution - uncontrolled systems (1996).

Firing Method	Cell	Cyclone	Wall	Tangential	Vertical
Capacity	0.13	0.17	0.25	0.41	0.02
Coal Consumption	0.15	0.16	0.24	0.42	0.02
NO _x Emissions	0.20	0.26	0.24	0.26	0.03

Table 8. Normalized power plant distribution - controlled systems (1996).

Firing Method	LNB	LNBO	LNCf	LNCB	Other	OFA
Capacity	0.40	0.13	0.32	0.02	0.02	0.11
Coal Consumption	0.41	0.11	0.31	0.02	0.03	0.11
NO _x Emissions	0.42	0.12	0.30	0.02	0.02	0.10

LNB - low-NO_x burner.

LNBO - low NO_x burner with over-fire air.

LNCf - low NO_x concentric firing (tangential systems).

LNCB - low NO_x cell burner.

Other - combustion modifications.

OFA - over-fire air.

Table 9. EPA mercury EMFs.

EMFs for Coal-Fired Power Plants	Mercury EMF
Front-Fired Dry Bottom without NO _x Control	0.94
Tangentially Fired Dry Bottom with NO _x Control	0.92
Tangentially Fired Dry Bottom without NO _x Control	0.81
Opposed-Fired Dry Bottom with NO _x Control	0.81
Vertically Fired Dry Bottom with NO _x Control	0.78
Opposed-Fired Dry Bottom without NO _x Control	0.41
Cyclone-Fired Wet Bottom without NO _x Control	0.93
Cyclone-Fired Wet Bottom with NO _x Control	0.54

It is interesting to note, however, that coal-fired power stations built over the past several years have installed a significant amount of FF baghouses. The "other" particulate matter control systems are principally comprised of hot-side ESPs (where control occurs upstream of the air preheater) and mechanical devices, such as cyclones and multiclones. Table 11 shows the estimated mercury emission factor for each particulate control device.

The distribution of SO₂ flue gas clean-up devices by amount of coal burned (in all coal-fired power generation plants in the United States in 1996) is provided in Table 12. It can be seen that the predominant SO₂ removal control device is WFGD.

The "other" sulfur control strategies are mainly fuel switching and a small amount of sorbent injection and regenerable SO₂ control. The predominant means of SO₂ control is switching from high- to low-sulfur coal.

Table 13 gives the modified mercury emission rates for power plants equipped with flue gas treatment controls.

The EMFs for scrubbers used by the EPA may be biased low. The 1994 geometric mean EMF was 0.66, indicating an average removal efficiency of 34%. More recent data have been compiled that show a higher average removal efficiency (see Table 14), at least for units firing bituminous coals. As shown in this table, the more recent data give a geometric mean mercury removal for such units of 51%, or an EMF of 0.49. The geometric mean EMF for the combined bituminous and lignite units shown in Table 14 is 0.59. The two units burning lignite coal listed in the table showed much lower mercury removal efficiencies (<5%). This is not surprising considering the fact that lignite coals tend to generate elemental rather than oxidized mercury in the flue gas. Therefore, it is apparent that a separate EMF should be used for each coal type. If the data used by the EPA previously are separated by coal type, the geometric mean EMF would be 0.55 for bituminous coal. Excluding the bituminous coal data would result in a geometric mean EMF of 0.70 for the other coal types. This EMF was calculated from the

Table 10. Particulate control systems for coal-fired power plants (1996).

Particulate Control	Coal Consumption, (million tons)	Net Dependable Summer Capacity (GW)	Number of Boilers
Cold-Side ESP	650.2	226.7	777
FF	67.2	19.3	74
Particulate Scrubber	14.6	4.0	10
Other	142.8	49.0	174
Total	874.7	299.0	1035

lignite and subbituminous coal data in Table C-19 of the EPA Utility Report and two additional data points from more recent data.

Mercury Emissions Inventory

An inventory of mercury emissions from fossil fuel-fired power plants was prepared by EPA in the Utility Report to Congress. The base year for this inventory was 1994. For coal-fired electric utility power plants, the total emission inventory for the United States was estimated to be 51.34 tons. Coal consumption at electric utility plants during 1994 was 817.3 million tons (Electric Power Monthly, EIS, 1998). More recent data of annual coal consumption that contain sufficient detail on coal quality is available for 1996, where consumption rose to 874.7 million tons.

Based on the 1996 data, FETC (Brown et al., 1998) developed a mercury emission inventory using a similar methodology as that used by EPA (results shown later in Table 15). Coal consumption at each power plant facility was obtained from the Utility Data Institute's Power Plant Statistics database. The quality of the coal and the state of origin were used as proxies to estimate the average state-wide mercury

Table 11. EPA mercury EMFs for particulate control devices.

EMFs for Coal-Fired Power Plants	Mercury EMFs
Particulate Matter Scrubber	0.96
Cold-Side ESP	0.68
FFs	0.56

Table 12. SO₂ control for coal-fired power plants (1996).

SO ₂ Control	Coal Consumption, (million tons)	Net Dependable Summer Capacity (GW)	Number of Boilers
FGD Scrubber	240.2	69.5	159
Spray Dryer	22.6	5.2	16
Other	611.9	224.2	860
Total	874.7	299.0	1035

Table 13. EPA Mercury EMFs - flue gas treatment.

Flue Gas Treatment Device	Mercury EMF
FGD Scrubber	0.66
Spray Dryer Absorber/FF	0.7

Table 14. Mercury removal in scrubbers.

Plant Name	Coal Type	Year of Sampling	Mercury Removal, %
Plant A	Bituminous	1998	49.7
Milliken	Bituminous	1996	65.0
Plant B	Bituminous	1994	37.8
Phase I-1	Bituminous	1996	48.0
Phase I-2	Bituminous	1996	58.0
Phase II-3	Bituminous	1998	45.9
Phase II-4	Bituminous	1998	57.0
Milton R. Young (Unit 2)	Lignite	1998	<.5
Coal Creek (Unit 2)	Lignite	1998	3.5

concentration in the coal. As discussed previously, the impact of coal cleaning is significant and has been reviewed in Appendix D of EPA's Utility Report to Congress and a recent article on mercury concentration in coal (Toole-O'Neil et al., 1999).

As described earlier, mercury emissions from coal fired power plants remain a subject of some uncertainty because only limited measurements of mercury are available for each unit process or subsystem that can affect release of mercury to the atmosphere. Using the approach described in the Utility Report to Congress, the following expression describes power plant mercury emissions:

$$M_{hg} = M_{coal} \times \frac{C_{hg}}{10^6} \times ccf \times \prod EMF_i \quad (1)$$

where M_{coal} is the coal consumption (tons/yr), C_{hg} is the mercury content in the coal [parts per million by weight (ppmw)], ccf is the coal cleaning factor, $\prod EMF_i$ is the product of the applicable EMFs on a boiler-level basis, and M_{hg} is the mercury emissions (tons/yr).

To obtain a national inventory of mercury emissions, the concentration of mercury in the coal feed to U.S. power plants is estimated by using the average statewide mercury concentration in coal as detailed in the USGS COALQUAL Data Base. Shortcomings of this approach have been described earlier. Coal consumption at each power plant facility can be obtained from the Utility Data Institute's Power Plant Statistics database. The consumption of coal at the

boiler level is assigned by capacity distribution within the facility. The impact of coal cleaning is estimated with a coal cleaning factor. Power plant characteristics, such as firing configuration, particulate control, and flue gas treatment, are identified on a boiler-level basis, and the subsequent EMFs are assigned based on measurements at representative coal-fired power plants.

A summary of the estimated annual emissions of mercury as a function of firing configuration and points within the mercury capture pathway is provided in Table 15 (Brown et al., 1998).

It can be seen that the largest amount of mercury released to the atmosphere from coal-fired power plants in the United States is from tangentially fired boilers. This is a direct result of the amount of coal consumption for this firing configuration relative to the total coal consumption. Stack emissions are reduced by about half (53%) of the uncontrolled emissions as a result of mercury reductions throughout the coal utilization process. The greatest reduction occurs in the particulate control area of the power plant and represents 20% of the uncontrolled emission reduction. This reduction is strongly influenced by the widespread use of cold-side ESPs. Coal cleaning and scrubbers provide an additional reduction of about 17%, and the coal combustion boiler island provides an additional 15% reduction over the uncontrolled emissions. At this time, this mercury inventory should be considered preliminary.

Based on the new information and analysis performed after the EPA Utility Report to Congress, the following uncertainties are considered to have the largest impact on establishing a more reliable mercury emission inventory:

- Coal cleaning factor—The impact of coal cleaning on the mercury content of coal is substantial and the factor for coal cleaning used in the Utility Report to Congress appears to be high, thus overestimating the average mercury concentration in coal feed to U.S. power plants. Greater mercury removal in coal cleaning is expected from

existing coal cleaning operations.

- The COALQUAL database indicates high variability for state-wide, average mercury content in coal for Maryland, Oklahoma, Pennsylvania, and Washington.

- SO₂ flue gas scrubbing for bituminous coal is expected to yield a higher reduction in mercury than was estimated in the Utility Report to Congress. The EMF is expected to be closer to 0.5. Because most scrubbing is done with high-sulfur bituminous coal, this EMF is expected to be more suitable than the estimate provided in the Utility Report to Congress. Separate emission factors for bituminous and nonbituminous coals are the preferred approach.

- Combustion EMF—The EMF for this section of the power plant should be relatively high as a result of high temperatures. The opposed-fired boiler configuration is of special concern with an estimated emission factor of 0.41 without NO_x control and an emission factor of 0.81 with NO_x control. Mercury testing performed on the coal-fired power plant without NO_x control had a measured flue gas concentration at the ESP inlet of 1.9 µg/Nm³ using EPA Method 29, whereas the concentration based on carbon-trap measurements was 10.9 µg/Nm³. The latter value is more consistent with the average mercury concentration in coal of 0.13 ppmw. Furthermore, the material balance for mercury around the plant was about 32%, suggesting either a high bias in the input coal stream mercury content or a low bias in the mercury content of the ash and flue gas.

- New initiatives by the EPA (U.S. EPA Fact Sheet, 1998) will add to the database for mercury emissions inventory. On April 8, 1998, the Emission Standards Division of the EPA issued the Information Collection Request, or ICR, pertaining to mercury measurements at coal-fired power plants. Section 114 letters require the owner/operator of each coal-fired electric utility steam generating unit with a capacity greater than 25 MWe to perform coal sampling and analysis for mercury content of coal over a period of one year. Section 114 letters require the owner/operator of each of a number of selected coal-fired electric utility steam generating unit to perform stack testing and coal sampling and analysis protocol.

Relative to the methodology developed by the EPA for the Utility Report to Congress, the mercury emission inventory for coal-fired power plants is expected to undergo refinements as indicated in discussions provided by this critical review. The EPA, DOE, and EPRI continue to seek improved understanding of mercury emission behavior, especially as it

Table 15. Summary of mercury emission inventory from coal-fired power plants.*

Firing Configuration	Mercury Emissions (1996), tons/yr				
	Uncontrolled	After Coal Cleaning	After Combustion	After Particulate Control	Stack Emission
Front	10.5	8.9	8.7	6.1	5.9
Tangential	48.5	43.5	38.1	27.7	24.6
Opposed	39.7	34.3	24.1	18.1	15.7
Vertical	1.2	1.0	0.9	0.6	0.6
Cyclone	7.2	6.7	6.1	4.3	3.9
Other	1.5	1.3	1.3	0.8	0.8
Total	108.6	95.7	79.1	57.6	51.46

*Compiled by the FETC using EPA EMFs and EPA methodology.

applies to the partitioning of mercury vapor throughout the power plant's flue gas control equipment. Insights in these areas will likely allow for efficient and cost-effective control approaches to be developed in the event that the mercury emissions need to be lowered.

Preface to Mercury Measurement and Mercury Control Technology Development

The EPA's Mercury Study Report was completed on December 18, 1997 and was submitted to the U.S. Office of Management and Budget (OMB) on the scheduled date of December 12, 1997. The report was subsequently sent to the United States Congress for review and/or use. In Volume VIII, Chapter 2, of the report, recommendations to assess/evaluate potential reductions for mercury emissions from various industries, including utility boilers were made.

A small team from the DOE's FETC and Office of Policy and International Affairs reviewed the EPA's mercury report and provided substantial input, which aided the EPA in determining its findings. The FETC rewrote Section 2.3: Flue Gas Treatment for Utility Boilers in Chapter 2 of Volume VIII, "An Evaluation of Mercury Control Technologies and Costs." The original version of Section 2.3 was updated to include the technology investigations and developments made since 1995 including many of the DOE/FETC \$15 million program efforts on air toxics and mercury measurement and control. In addition, the DOE/FETC costs for controlling mercury utilizing activated carbon (AC) were compared to the EPA's numbers in Appendix B: Model Plant Cost Evaluations of Volume VIII, with the EPA indicating that the DOE "higher end costs are favored as to the potential cost of control." The DOE cost analyses were based on the results from many projects investigating AC conducted from September 1995 through December 1997.

The report was also updated to convey the work completed by other institutions conducting mercury control research and development in this country and internationally. The team also expanded other chapters dealing with research needs, fundamental research, and other mercury-related issues for utility boilers. The perspective of the DOE's Policy Office and the FETC on mercury-related issues concerning utility boilers was clearly indicated in the report.

With this said, the "EPA Mercury Study Report" containing Volume VIII, "An Evaluation of Mercury Control Technologies and Costs" with Section 2.3, and Appendix B can be reviewed or downloaded from the EPA web site, www.epa.gov/airlinks. In addition, the DOE-written Section 2.3 is contained in the EPA "Study of Hazardous Air Pollutants from Electric Steam Generating Units - Final Report to Congress" as Appendix I, which is also on the same EPA web site. This paper written for the Air & Waste Management Association's Critical Review Committee

gives a synopsis for portions of Section 2.3 and Appendix B, and utilizes this as the starting point of the measurement and control section of this paper. The following information will also detail the research and development conducted from December 1997 to the present.

Mercury Measurement and Mercury Control Technology Development: The Technical Challenge

Developing effective mercury control technologies in coal-fired utility applications is extremely difficult if researchers cannot determine the amount of mercury and, most important, the distribution between vapor-phase speciation (elemental vs oxidized mercury), and particulate-bound mercury. Figure 2 provides a simple example of the complexity of not only controlling the mercury, but measuring it.

The mercury contained in the pipeline is representative of the annual 51.6 tons of mercury the EPA has indicated as being emitted from coal combustion in the U.S. electric utility industry. The 51.6 tons of mercury in the pipeline is in proportion to the amount of flue gas emitted annually by coal-fired power plants.

Mercury and Its Speciation

Total mercury (Hg) concentrations in coal, based on data collected since 1993, are relatively constant across the U.S. (20-120 parts per billion on a weight basis, or ppbw) with more than 75% of the coals having concentrations below 100 ppbw. There are a few exceptions with some concentrations being between 200 and 300 ppbw. However, when the different ranks of coal are fired in the utility boilers, there is substantial variation in the concentrations of elemental mercury (Hg^0) versus oxidized mercury (Hg^{2+} as measured at the inlet to the particulate control device). The percentage of Hg^0 varies from 10 to >90% indicating that speciation is very dependent on coal type. The chemical species of Hg formed during the combustion process and postcombustion conditions vary significantly from one plant to another. While combustion conditions vary, the subsequent fly ash, carbon in the ash, and vapor-phase constituents can also play a major role in determining the percentage of the Hg chemical species formed. Understanding the rate-controlling mechanisms (i.e., transport, equilibrium, and kinetics) will not only aid in predicting the Hg species formed, but, eventually, will aid in optimizing existing APCDs for Hg removal. Kinetics may play more of a role on the form of Hg than anticipated. Effective removal is dependent on the species of Hg present in the flue gas. For example, Hg^{2+} is water soluble and is less volatile compared to Hg^0 . Reducing the temperature of the flue gas and utilizing wet scrubbing could result in increased Hg^{2+} removal.

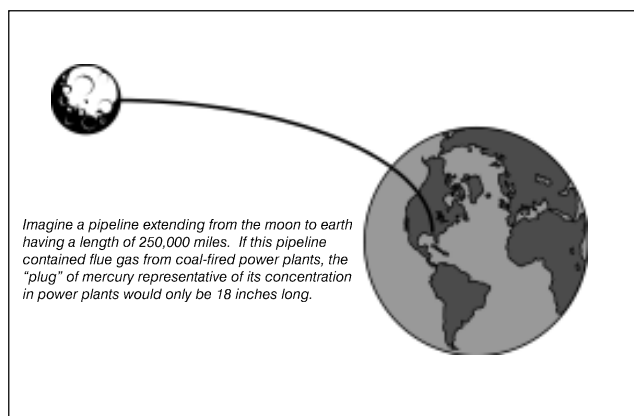


Figure 2. Paradigm for mercury concentration in flue gas (Smith and Brown 1998).

More recent studies indicate that the distribution of Hg species in coal-fired flue gas is also strongly dependent on the type of coal (e.g., bituminous, subbituminous, or lignite) (see e.g., Carey et al., June 1996, July 1996; DeVito and Rosenhoover, 1997; Huggins et al., 1999; Laudal et al., November 1996, December 1997; Redinger, 1996; Redinger et al., 1997; Senior et al., 1997, 1998).

Research at the fundamental level continues in order to determine the mechanisms involved with both gas-phase Hg transformations and the gas-solid interactions. Attempts have been made to use thermochemical equilibrium calculations to predict the Hg species in coal combustion flue gas (e.g., Galbreath and Zygarlicke, 1996). Recent calculations by Physical Sciences, Inc. (PSI), from 500 to 1100 K for a bituminous coal (Pittsburgh) are shown in Figure 3 (Senior et al., 1999).

The results of equilibrium calculations for Hg speciation in flue gas as a function of temperature are summarized below:

- (1) Above about 975 K (700 °C), 99% of the Hg is predicted to exist as gaseous Hg, and the remaining 1% is predicted to be gaseous mercuric oxide (HgO).
- (2) Below 725 K (450 °C), all Hg is predicted to exist as mercuric chloride (HgCl₂).
- (3) Between 725 and 975 K, the split between HgCl₂ and Hg⁰ is determined by the chlorine content of the coal, via the hydrogen chloride (HCl) content of the flue gas.

The HCl concentration in flue gas from U.S. coals is typically in the range of 1-130 parts per million by volume (ppmv). Even at the lowest concentrations, the reaction between Hg and HCl dominates the equilibrium chemistry. At temperatures representative of the inlet to the APCD, therefore, all the Hg should exist in the gas phase as HgCl₂, if equilibrium is attained in the flue gas.

However, this is not the case and there are strong arguments against the existence of chemical equilibrium in the flue gas of a coal-fired power plant. The flue gas cools

rapidly as heat is transferred to water and steam; typical cooling rates are on the order of 500 K/sec. Minor species in the flue gas, such as carbon monoxide (CO) and sulfur dioxide (SO₂), do not have time to equilibrate as the gas cools. For example, the oxidation of SO₂ to sulfur trioxide (SO₃) in coal combustion flue gas does not proceed at a fast rate below about 1500 K (Flagan and Seinfeld, 1988) and thus, the SO₃ concentration is effectively quenched below this temperature. Equilibrium calculations predict that all sulfur contained in the coal exists as SO₃ at low flue gas temperatures. Flue gas measurements from coal combustion indicate only on the order of 1% and as high as 3% of the sulfur is actually converted to SO₃.

Similarly for other trace species, present in ppmv or ppbv amounts, equilibrium may not be attained as the flue gas cools. Kinetic calculations also indicate that the conversion of another trace species, HCl to Cl₂, is quenched as the flue gas cools (Senior et al., 1997). PSI is continuing its studies to determine the mechanisms involved with Hg speciation during combustion and the rapid transition to postcombustion conditions while firing different ranks of coal. Studies are also continuing to determine the mechanisms involved with Hg speciation during postcombustion conditions.

Evidence from studies conducted on pilot- and full-scale combustion systems is not consistent with the assumption of equilibrium for Hg species in flue gas at the temperatures (nominal 300 °F, 149 °C), corresponding to the location of the APCDs. At the inlet to the first APCD, measurements taken using the Ontario Hydro Mercury Speciation Method (Ontario Hydro Method) in both pilot- and full-scale combustion systems indicate a wide range of Hg²⁺ percentages while firing coals of various ranks:

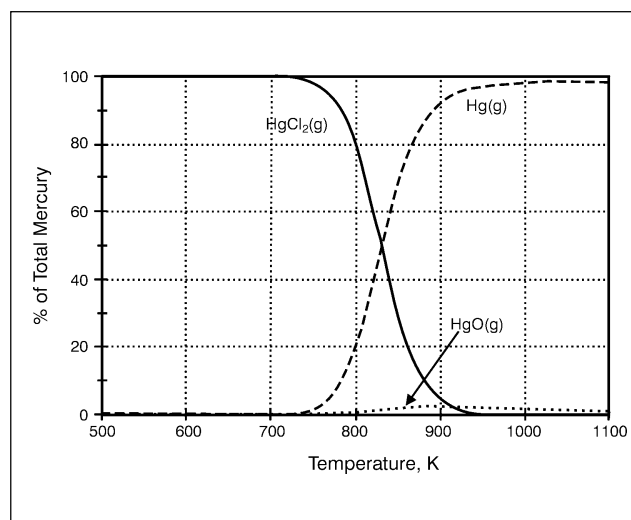


Figure 3. Predicted distribution of mercury species at equilibrium, as a function of temperature for a starting composition corresponding to combustion of a bituminous coal (Pittsburgh) in air at stoichiometric ratio of 1.2 (Senior et al, FPT, 1999).

- (1) Bituminous coal: Hg^{2+} values from 70 to 88%, (DeVito and Rosenhoover, 1999; Janati et al., 1998; Laudal et al., July 1997, December 1997, December 1998, June 1999);
- (2) Powder River Basin (PRB)/subbituminous coal: Hg^{2+} values from 15 to 50% (Blythe et al., 1999; Haythornthwaite et al., 1999; Laudal et al., 1996, December 1997); and
- (3) Lignite coals: highly variable Hg^{2+} values from 10 to 30%, but as high as 50%. (Blythe et al., 1999; Laudal and Kurz, January 1999; Kurz and Laudal, April 1999).

Bituminous coals have the highest chlorine concentrations in the range of 500-1300 ppmw, with 50-130 ppmv of HCl measured in the flue gas. As seen, the Hg^{2+} percentages are the highest in the flue gas from these coals. Lignite has some of the lowest chlorine concentrations from nondetected to 60 ppmw, with corresponding HCl measured concentration in the flue gas ranging from nondetected to 2 ppmv. Flue gas from the combustion of Lignite coal contains a corresponding low Hg^{2+} percentage. PRB/subbituminous coals also yield low concentrations of Hg^{2+} in the flue gas while also having low chlorine concentration from nondetected to 60 ppmw. This corresponds to HCl concentrations measured in the flue gas from nondetected to <5 ppmv.

Even at the lowest level of chlorine in the coal, chlorine is in excess compared to the Hg in the coal (20-120 ppbw) for the oxidation of Hg as predicted by equilibrium calculations. Figure 4 illustrates the speciation of Hg in flue gas at equilibrium corresponding to a typical PRB coal containing 26-ppmw chlorine. Even for this low chlorine level, 100% of the Hg is predicted to exist as HgCl_2 at APCD inlet temperatures. In contrast to the bituminous coal (Figure 3), equilibrium for a PRB coal shows oxidation of Hg^0 occurs at a lower temperature and the formation of more mercuric oxide (HgO) between 700 and 900 K.

There is some evidence from laboratory and pilot data that the kinetics of Hg oxidation are slow at low temperatures. Based on pilot data, the addition of HCl at temperatures below 450 K (180 °C) did not increase the amount of HgCl_2 in coal combustion flue gas, indicating no reaction at those temperatures (Galbreath and Zygarlicke, 1996).

*Equilibrium calculations and results in the two figures were determined by using SOLGASMIX (Ericksson and Rosen, 1973). Thermochemical data on the species of interest were provided from the thermochemical database in the HSC package. (HSC Chemistry for Windows, Version 3.0) The species considered in the equilibrium calculation were:

Gas: CO , CO_2 , Cl_2 , H_2 , HCl , H_2O , Hg , HgCl_2 , HgO , N_2 , NO , NO_2 , O_2 , SO_2

Condensed: C , Hg , HgO , and HgSO_4

The assumption of gas-phase equilibrium for mercury-containing species in coal-fired power plant exhaust is not valid. Preliminary evidence suggests that the oxidation of Hg^0 to Hg^{2+} in the flue gas is quenched when the gas cools below 750-900 K. Again, kinetic calculations on the formation of Cl_2 , which is highly reactive with Hg^0 , indicate that the conversion of HCl to Cl_2 does not attain equilibrium given the time-temperature history of flue gas in a power plant. The calculated results lend support to the conclusion of quenched equilibrium for Hg oxidation.

As indicated above, mercury in a flame is completely converted to volatile Hg^0 while its transformation compounds can presumably occur in the gas phase or in condensed phase. The previous equilibrium calculations indicate that Hg may condense as HgO , HgCl_2 , or HgSO_4 , but nitrates and other forms may also occur as intermediates. Equilibrium predicts a complete conversion of Hg^0 to Hg^{2+} at air preheater outlet temperatures, but measurements of boiler emissions indicate only 10 to <90% as Hg^{2+} , suggesting that kinetic limitations are the controlling mechanisms. Recent research has speculated that the major kinetic pathway for the formation of HgCl_2 involves the reaction of atomic chlorine with Hg^0 (Sarofim et al., 1998). Kinetic simulations predict that the concentration of atomic chlorine in a cooling combustion gas is rapidly reduced by interconversion with HCl and Cl_2 , and possibly Cl and Cl_2 , as indicated in the following elementary reactions where M is a third body inert:

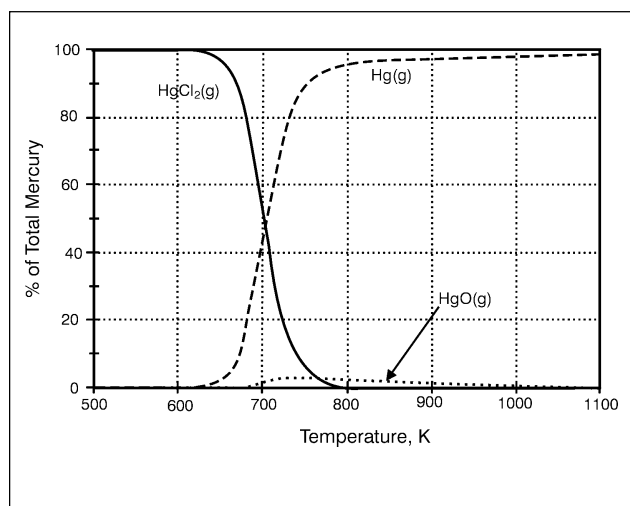
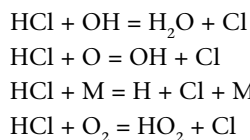
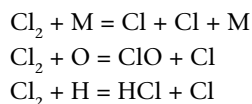


Figure 4. Predicted distribution of mercury species at equilibrium, as a function of temperature for a starting composition corresponding to combustion of a typical PRB coal containing 26 ppmw in air at stoichiometric ratio of 1.2 (PSI et al., 1997).

Interconversion Reactions
of Cl and HClInterconversion Reactions
of Cl and Cl₂

The lower concentration of atomic chlorine and the decrease in the rate coefficient for reaction with Hg⁰ at lower temperature may result in "quenched" Hg²⁺ concentrations corresponding to equilibrium values around 530 °C. Additional research on this kinetic system should provide a better understanding in predicting the formation of HgCl₂ (Sarofim et al., 1998).

Understanding gas-phase speciation of Hg in coal-fired power plant flue gas is not sufficient to describe the transformations of Hg in the combustion system. To understand the capture of Hg in APCDs and the effectiveness of sorbents for Hg capture, a better understanding of the gas-to-particle conversion is needed, particularly the relationship(s) between fly ash properties and oxidation and adsorption of Hg.

Low-, medium-, and high-sulfur bituminous coals, and PRB/subbituminous coals with low-sulfur content are very different with regards to the Hg distribution between the Hg⁰ and Hg²⁺ forms in the flue gas. The fly ash characteristics of these coals are extremely different and some of the PRB/subbituminous coals produce fly ashes that appear to be highly reactive with a corresponding increase in equilibrium sorption capacity. In contrast, fly ashes from bituminous coals appear to oxidize the gaseous Hg⁰ at higher rates with much lower equilibrium sorption capacities. The conversion of Hg⁰ to Hg²⁺ and adsorption of either Hg⁰ or Hg²⁺ by the various fly ashes are not only impacted by temperature, but also, in a significant manner, by the interactions of the composition of the fly ash with the vapor-phase compounds. (Carey et al., June 1996, July 1996; DeVito et al., 1993; DeVito and Rosenhoover, 1997, 1998; EPRI, 1994; Hargrove, Jr., et al., 1997; Huggins et al., 1999; Laudal et al., 1996, November 1997, December 1997, 1998; Miller et al., 1994, 1995; Pavlish and Benson, 1997; Prestbo and Bloom, 1995; PSI et al., 1997; Senior et al., June 1997, November 1997, 1998; U.S. DOE Report, 1996). This is discussed in more detail in the Factors Influencing Mercury Speciation and Adsorption section.

Mercury Speciation and Its Measurement

In the early 1990s, the EPRI and DOE/FETC initiated very extensive air toxics characterization programs designed for the utility industry. As part of these programs, measurements of mercury speciation in the flue gas were under-

taken at each plant. Because no validated Hg speciation sampling method was available, the following methods were utilized: EPA Method 29 and the Mercury Speciation Adsorption (MESA) Method, often referred to as "Brooks Rand" or "Bloom Method." For more detailed descriptions of these methods, see Laudal et al. (June 1996, July 1997, December 1997). The results from these characterizations indicated that EPA Method 29 does not properly speciate Hg under certain coal combustion conditions, but is fully capable of measuring total Hg concentrations. In addition, there were questions about the ability of the MESA Method to speciate Hg in flue gas from coal combustion.

The most obvious inconsistency between the Hg⁰ and Hg²⁺ distributions in the methods was demonstrated during the inlet and outlet sampling across WFGD systems designed for SO₂ removal. The oxidized form of Hg at the time was considered to be HgCl₂, which is highly soluble in calcium-based scrubber solutions utilized for SO₂ capture. Results from both the DOE and EPRI characterization studies indicated that when utilizing EPA's Draft Method 29 and the MESA Method, the Hg⁰ at the outlet of the scrubber was 10-40% higher than that measured at the inlet. After careful analysis of the data, two questions were raised: "Were the current speciation methods capable of accurately measuring the oxidized form of Hg?" and "Was the oxidized form of Hg being captured in the WFGD scrubber solutions being released as an 'alternate form or non-Hg²⁺' not capable of being collected in the appropriate impinger solutions?" Others were conducting research to determine whether either (or both) questions was/were correct and what are the possible answers (Hargrove, Jr., et al., 1995; Holmes et al., 1998; Laudal et al., 1995; Redinger et al., 1997).

Dr. Keith Curtis of Ontario Hydro Industries, Toronto, Canada, had been investigating other impinger solutions to replace the acidified peroxide solutions of the Method 29 train. He speculated that the acidified peroxide solutions may be oxidizing Hg⁰ while providing a high bias measurement of the oxidized mercury present in the flue gas. Field studies were performed with potassium chloride (KCl) as a replacement for the acidified peroxide solutions. After several investigations, it was apparent that the high value of the HgCl₂ measured at the inlet of the WFGD systems was reduced by utilizing the new method and was apparently consistent with the value measured at the outlet of the scrubber systems.

The Southern Research Institute (SRI), funded by the DOE/FETC, conducted a comprehensive toxic emissions study of a utility equipped with a WFGD system. The study was designed to investigate the impact of scrubber operating parameters on Hg removal, and to compare EPA Method 29 with Dr. Curtis' Ontario Hydro Method (Bush et al., 1997). Shown in Figure 5, comparison of the two

methods revealed an apparent high bias of Method 29 towards the oxidized form of Hg. As seen, Method 29 indicated an increase in Hg⁰ at the outlet of the WFGD system of 4.4 µg/Nm³ (Ontario Hydro at 6.13 µg/Nm³) as compared to the inlet Hg⁰ of 2.6 µg/Nm³ (Ontario Hydro at 5.86 µg/Nm³). This represents an increase of 69% for Hg⁰ at the WFGD outlet as reported by Method 29, as compared to an increase in Hg⁰ of only 5% as reported by the Ontario Hydro Method. Method 29 overestimated the Hg²⁺ at the inlet of the WFGD system by 36% compared to the Ontario Hydro Method.

Concurrently with the SRI field study, Radian International was also conducting innovative pilot-scale studies at the EPRI's Environmental Control Technology Center (ECTC) to address the two previously stated questions. Extensive flue gas and intra-train mercury spiking tests were conducted to investigate the acidified peroxide solutions of Method 29 (solutions for collecting the oxidized form of Hg). The first series of tests had Hg⁰ and HgCl₂ injected separately into the flue gas stream at the inlet of the WFGD. Results indicated 96% of the HgCl₂ (naturally occurring and spiked) was collected across the WFGD and the increase in Hg⁰ across the WFGD was from 0.66 to 0.96 µg/m³. The results for the Hg⁰ spiking indicated 37% of spike was measured in the acidified peroxide solutions and the total Hg removal was only 29%. These results indicated the injected HgCl₂ was being effectively collected in the scrubber solutions and not being reduced and subsequently re-emitted as Hg⁰. In addition, Method 29 appeared to be ineffective in speciating the Hg at the inlet of this WFGD system when Hg⁰ was spiked.

The intra-train spiking of either form of Hg into the flue gas further indicated the inability of Method 29 to accurately measure the distribution of the Hg²⁺ and Hg⁰ in the flue gas at typical conditions upstream of a WFGD. Radian conducted these initial tests in 1994 and repeated

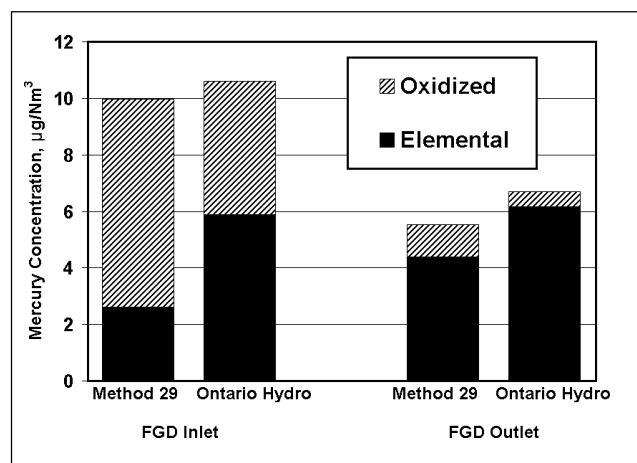
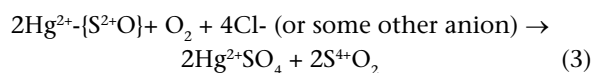
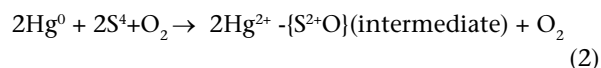


Figure 5. Comparison between EPA Method 29 and Ontario Hydro Method at the inlet and outlet of a wet FGD system at a coal-fired power plant firing bituminous coal (Bush et al., 1997).

them in 1995 (Hargrove, Jr., et al., 1995).

In both the pilot-scale work conducted at the EPRI's ECTC by Radian and that conducted by the University of North Dakota Energy & Environmental Research Center (EERC) for both the EPRI and DOE, it was apparent that EPA Method 29 does not properly speciate Hg under certain flue gas conditions. Further Method 29 studies at the EERC indicated that high SO₂ concentrations yield an overestimation of the Hg²⁺ up to 50%. Bench-scale studies with simulated flue gas constituents (SO₂, NO, NO_x, HCl, HF, etc.) conducted under a replicated full-factorial experimental design provided some insights as to the Hg²⁺ overestimation of the method. Results indicated the overestimation was occurring in the acidified peroxide impinger solutions of the method at SO₂ concentrations >500 ppmv. It was also observed that this conversion of the Hg²⁺ was not occurring as a gas-phase reaction. Earlier studies conducted by Meij (1994) indicated the possibility that trace metals, including Hg⁰, could react with SO₂ to oxidize the metal. Two reactions were proposed by Meij and are indicated below:



While Method 29 did indicate an overestimation of Hg²⁺ in the bench- and pilot-scale investigations, the method needed to be tested under EPA Method 301 validation criteria (briefly discussed below; method description and use can be found in U.S. EPA, Method 301 (July 1993). In addition, tests were initiated to evaluate for subsequent selection one or more of the other promising sampling methods for possible validation because of the aforementioned concerns regarding the ability of Method 29 to report speciation accurately. Some of the promising Hg speciation sampling methods considered for further testing included the following:

- EPA Method 29
- Mercury Speciation Adsorption Method (MESA Method, also Bloom Method, Brooks Rand, and Frontier Geosciences)
- Ontario Hydro Method (Ontario Hydro Industries)
- Tris-Buffer Method (Radian International)
- EPA Draft Method 101B (Research Triangle Institute)

For details on these methods, see Laudal et al. (November and June 1996, July 1997, December 1997).

Validation of Method 29 under Method 301 criteria was not achieved for the speciation of mercury (Laudal et al., July 1997). Bench- and pilot-scale studies showed that

the MESA Method did not speciate Hg correctly. These results confirm that the MESA Method provided poor speciation when tested under certain flue gas conditions from coal-fired utility boilers. The method is greatly affected by an interaction between SO₂ and NO_x in the flue gas. When SO₂ is present in concentrations from 500 to >1500 ppmv and NO_x >250 ppmv, the MESA Method overestimates the Hg²⁺ fraction by 20-75% (Laudal et al., November 1996). Based on the exploratory research conducted by Dr. Curtis and the research and development conducted at the EERC pilot-scale facilities, the Ontario Hydro Method was selected to be formally validated using the sampling protocol and statistical analysis established in EPA Method 301.

EPA Method 301 only provides the precision and bias associated with six quadrain replicate samples. (As stated in the method, "A sampling system capable of obtaining four replicate samples that were collected as closely as possible in sampling time and sampling location.") This rigorous requirement is needed to statistically determine the internal consistency of the method being tested. The statistical calculations require, for the method to be validated, that the relative standard deviations (RSDs) are less than 50%, and the correction factor (CF), if significant, is between 0.7 and 1.3. Only analyte spiking (Hg spiking in the method impinger solutions) is conducted for the method being validated. In addition, there is no standard or reference method to compare to EPA Method 301 for determining the accuracy of the method being validated. To obtain the apparent accuracy of the speciated Hg measurement methods, it was necessary to do dynamic spiking of Hg in the flue gas stream.

The Ontario Hydro Method did not indicate the conversion of Hg⁰ when spiked into the flue gas at the outlet of the extremely high efficiency FF (99.95% for particulate) compared to EPA Method 29. This testing was done to provide information on the fate of the spiked Hg⁰ into the flue gas with and without particulate matter present. As previously stated, particulate matter has a dramatic impact on converting Hg⁰ to Hg²⁺ in the flue gas from the combustion of eastern bituminous coals. Performing the spiking tests at this location indicated that EPA Method 29 did report higher Hg²⁺. The method consistently reported (each quadrain run at the outlet location) a nominal 35% conversion of a 8-μg/Nm³ Hg⁰ spike in the flue gas from the combustion of an eastern bituminous coal (Blacksville) with a nominal 1400 ppmv of SO₂ in the flue gas. In contrast, the Ontario Hydro Method showed no significant conversion under the exact same conditions. Subsequently, the dynamic spiking during the validation of the Ontario Hydro Method was first done with Hg⁰ and then with HgCl₂.

Validating a "speciation method" is a real challenge when conducting the validation in a flue gas that

contained acid gases, fly ash, and several different mercury species. In addition, the coal selected for the validation at the EERC pilot-scale facility was a blend of Ohio No. 5 and No. 6 bituminous coals, which provides the most challenging flue gas constituents. The coal had both high sulfur (4.35%, flue gas SO₂ as high as 3100 ppmv) and chlorine (1250 ppmw, flue gas HCl at approximately 100 ppmv). The nominal Hg coal concentration was 300 ppbw, with a corresponding nominal 20-25 mg/Nm³ of total Hg in the flue gas. These and other coal and flue gas Hg concentrations were approximately twice those previously tested (Blacksville coal) while sampling with the Ontario Hydro Method.

Results showed that the Ontario Hydro Method clearly passed EPA Method 301 criteria with RSDs being lower than 50% while dynamic Hg spiking was conducted (both Hg⁰ and Hg²⁺). During the Hg⁰ spiking, the RSDs were

- (1) 8.94% for the KCl impinger solutions (Hg²⁺ capturing solution),
- (2) 6.97% for the peroxide and permanganate impinger solutions (Hg⁰ capturing solution(s)-the peroxide impinger is located after the last KCl impinger),
- (3) 5.13% for total vapor-phase Hg, and
- (4) there was no significant bias correction factor.

The method was able to report not only the total Hg, but also the apparently accurate distribution between the Hg²⁺ and Hg⁰, in the flue gas with the dynamic Hg spiking. Testing was conducted at higher levels of SO₂ (as high as 3100 ppmv) in the flue gas as compared to the previous studies (a nominal 1400 ppmv) that attempted to validate EPA Method 29. The Ontario Hydro Method did indicate a 10% conversion of the spiked Hg⁰ at the outlet of the FF and this may have resulted from the highly elevated levels of SO₂ and HCl. The particulate removal efficiency (99.95%) of the FF for the fly ash from this coal was similar to the fly ash removal efficiency for the Blacksville coal (99.94%).

After the pilot-scale validation tests, the Ontario Hydro Method was recommended as the best method to measure the distribution between Hg⁰ and Hg²⁺ in coal-fired combustion systems. The method proved to provide good precision, no significant bias, and accurate recovery of spikes of mercury. In addition, this method is relatively easy to use, compared to some other methods tested. The method has been submitted to the American Society for Testing and Materials (ASTM D22.03) for review, evaluation, and for acceptance as a standard reference method under the ASTM protocol (Laudal et al., December 1997). In addition, the EPA has recommended the Ontario Hydro Method as the method of choice for its ICR for mercury speciation data from approximately 70 coal-fired utilities. The protocol as submitted to the ASTM is posted on the EPA's web site at <www.epa.gov/ttn/emc/prelim.html>.

Researchers at the EERC and Radian recently completed an EPA Method 301 validation of the Ontario Hydro Method at a power plant firing a high-sulfur eastern bituminous coal. The power plant had two ESPs followed by a wet limestone FGD system controlling SO₂ emissions at >90%. Sampling was conducted at both the inlet and outlet of the WFGD system, with the validation of the Ontario Hydro Method taking place at the inlet location. The load was consistent over the five days of sampling, but the SO₂ concentrations were highly variable based on the hourly values, from as low as 2000 ppmv to as high as 2900 ppmv, with an average concentration of 2600 ppmv.

Modifications to EPA Method 301 were made to accommodate sampling at the WFGD inlet. Dynamic spiking could not be done and only five separate quadtrains sampling efforts were completed as compared to the required six quadtrain runs. Five efforts were selected due to time constraints and because there were enough data from all the pilot-scale tests for completing the statistical calculations for validation. In total, there were 20 individual Ontario Hydro Method sampling efforts utilized for the validation. In addition, the analyte-spiking protocol for the impinger solutions was utilized during the sampling efforts. Results showed that the Ontario Hydro Method clearly passed EPA Method 301 criteria with RSDs being lower than 50% while analyte spiking of Hg⁰ was conducted. The statistical results (with mean and standard deviations given in terms of µg of mercury) with and without analyte spiking for precision of the quadtrain data from the testing of the Ontario Hydro Method were as follows:

With Analyte Spiking

- (1) Standard deviation (0.81), RSD (8.83%), and the mean (9.15) for the KCl impinger solutions (for capturing Hg²⁺);
- (2) Standard deviation (0.82), RSD (21.81%), and the mean (3.78) for the peroxide and permanganate impinger solutions (Hg⁰ capturing solution(s)-the peroxide impinger is located after the last KCl impinger); and
- (3) Standard deviation (0.19), RSD (1.49%), and the mean (12.93) for total vapor-phase Hg.

Without Analyte Spiking

- (1) Standard deviation (0.61), RSD (7.40%), and the mean (8.29) for the KCl impinger solutions (Hg²⁺ capturing solution);
- (2) Standard deviation (0.62), RSD (19.77%), and the mean (3.13) for the peroxide and permanganate impinger solutions (Hg⁰ capturing solution(s)-the peroxide impinger is located after the last KCl impinger); and

- (3) Standard deviation (1.21), RSD (10.55%), and the mean (11.42) for total vapor-phase Hg.

The statistical results for bias (all values are in µg/Nm³) were as follows:

- (1) Bias (0.86), pooled standard deviation (1.01), t-value (0.850), and t-statistic (2.57) for the KCl impinger solutions (Hg²⁺ capturing solution);
- (2) Bias (0.65), pooled standard deviation (1.03), t-value (0.635), and t-statistic (2.57) for the peroxide and permanganate impinger solutions (Hg⁰ capturing solution(s)-the peroxide impinger is located after the last KCl impinger); and
- (3) Bias (1.51), pooled standard deviation (1.22), t-value (1.237), and t-statistic (2.57) for total vapor-phase Hg.

The method was able to report not only the total Hg, but the distribution between the Hg²⁺ and Hg⁰, in the flue gas with analyte spiking of Hg⁰ (within ±10% as indicated by calculation). No dynamic spiking was conducted, but the Hg²⁺ measured by the method was being effectively (93%) captured in the upstream WFGD. The validation was conducted at high and variable SO₂ concentrations (average of 2600 ppmv) in the flue gas as compared to the previous studies (a nominal 1400 ppmv) when an attempt was made to validate EPA Method 29. Mercury speciation in the flue gas stream was highly variable from day to day, as were the SO₂ concentrations. Even with the variability of these constituents in the flue gas concentrations, the RSD range was only 1.5-22%, which was still below the required 50% criteria of EPA Method 301. Calculations also indicated that there was no statistical bias (i.e., the pooled standard deviation is less than the t-statistic). The Hg distribution in the flue gas was fairly constant over the five-day sampling effort at 70% for Hg²⁺ and 30% for Hg⁰. The distribution remained constant while there were large variations in both the concentrations of Hg (each form) and SO₂ concentrations. (See reference EPRI and U.S. DOE, 1999, for details on the field validation of the Ontario Hydro Method.)

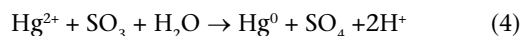
It must be stated that the protocol has to be strictly followed, as detailed by the ASTM Subcommittee and described on the EPA web site. For example, there are specific procedures that must be followed during the recovery of the KCl impinger solutions to eliminate the possible loss of Hg from these solutions.

Under Step 13.2.8.3 of the proposed ASTM protocol, "Add a 5% w/v KmnO₄ solution to each impinger until a purple color remains." In addition, Step 13.2.8.5 indicates combining all three of the KCl impingers in a container designated as No. 3, and "...If the solution in Container 3 becomes clear, add a small amount of the 5% w/v KmnO₄ solution until a pink or slightly purple color is obtained. Check again after 90 min to ensure the purple

color remains." If not done or done incorrectly, a considerable loss of the Hg from the KCl impinger solutions will occur, resulting in a lower Hg²⁺ concentration and, subsequently, lower total Hg values.

Tests comparing EPA Method 101A (total Hg only), the Tris Buffer (described below), and the Ontario Hydro mercury speciation methods were conducted at the EERC during the firing of an Eastern bituminous coal (Blacksville) and sampling at the outlet of their pilot-scale baghouse. Lower concentrations of Hg²⁺ are clearly demonstrated in Figure 6 for the Ontario Hydro Method, which also indicated lower total Hg during both the baseline test (No. 27) and during the Hg²⁺ spiking test (No. 35), in this case a 10 µg/Nm³ of HgCl₂. It should be noted that the Hg⁰ values were consistent with the other methods. These results were consistent during the initial pilot-scale mercury speciation method comparison tests utilizing the Ontario Hydro Method.

An apparent loss of the Hg²⁺ was occurring in the Ontario Hydro Method, and it was speculated the loss was occurring in the KCl impingers during the recovery and preparation of the solutions for analysis. It was postulated that SO₂ from the flue gas was accumulating in the KCl impingers, reducing the pH of the solution, resulting in the Hg²⁺ being lost when opened to the air. The reduction was thought to be occurring via the following chemical reaction:



To investigate this possibility, a KMnO₄ solution was added to the KCl impingers during the recovery step of the impinger solutions. The KMnO₄, being a strong oxidizing agent, neutralized the SO₂ and preserved the Hg in the KCl impinger solution. After this procedure was followed during all new sampling efforts, the Hg²⁺ values and subsequent total numbers were consistent with the other respective methods, as shown in Figure 7. This resulted in the addition of Steps 13.2.8.3 through 13.2.8.5 under the ASTM protocol for the Ontario Hydro Method.

Previous work conducted by Radian indicated the need for this step, the addition of KMnO₄ to reduce the loss of Hg in the Tris [Tris(hydroxymethyl) aminomethane buffer solution] impinger solutions, because all the SO₂ in the sampling of flue gas is captured within the solution. Tris has been demonstrated to form trigonal complexes with Hg²⁺ in alkaline and neutral media (Myshkin and Konyaev, 1994). An ethylenediaminetetraacetic acid (EDTA) chelating agent was also needed when using the Tris solution as the agent to capture the SO₂, and thus to protect the permanganate impingers required to collect Hg⁰.

The Tris-Buffer Method developed by Radian was not considered for further testing and validation. The

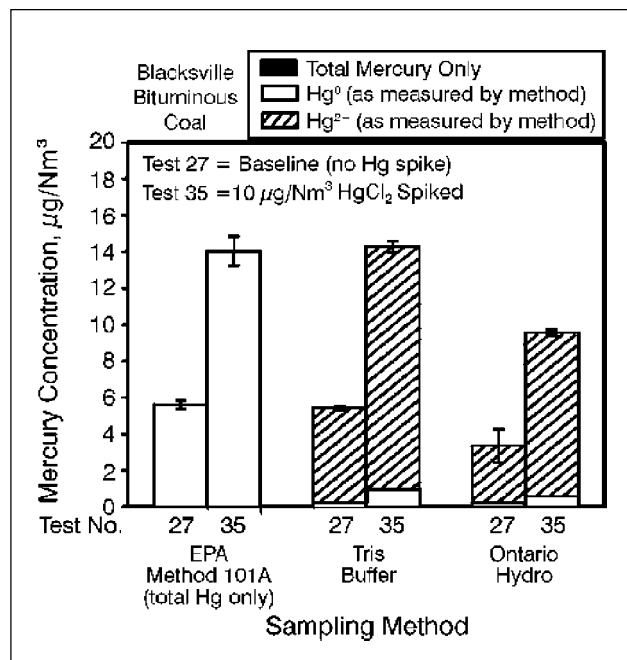


Figure 6. Comparison of mercury speciation sampling methods while spiking Hg⁰ and sampling at the baghouse outlet (Laudal et al, November 1996 and December 1997).

method did perform as well and at times better than the Ontario Hydro Method for total and speciated Hg while sampling during dynamic spiking. However, since high SO₂ (>1500 ppmv) concentrations causes the pH of the Tris solution to drop after the buffering capacity of the solution is reached, the method has sampling times limited to 45 to 60 minutes. The sampling time would be even shorter at utilities with SO₂ concentrations from 1500 to 3000 ppmv.

Sampling time is critical for collecting a valid sample above the detection limit(s) in gas streams with low Hg concentrations. In addition, the preparation procedure for the impinger solutions is complicated. The work initiated by Radian and funded by the EPRI provided valuable insight on the operation of WFGD systems for Hg removal, and most importantly, information on the conversion of Hg⁰ and loss associated with SO₂, and impinger solutions.

DOE and EPRI have funded many field studies and characterizations on mercury speciation utilizing the Ontario Hydro Method as indicated in the section on Emissions Inventory. Figure 8 indicates Hg⁰ and Hg²⁺ measurements at the inlet and outlet of five WFGD systems at different plants firing a variety of medium- to high-sulfur bituminous coals.

The five plants were each equipped with a WFGD system. Triplicate FGD measurements at the inlet and outlet at each site indicated a larger proportion of Hg²⁺ compared to Hg⁰, with a range of Hg²⁺ removal in the FGD system between 85 and 95%. The total mercury removal of the ESP and WFGD systems at each plant ranged

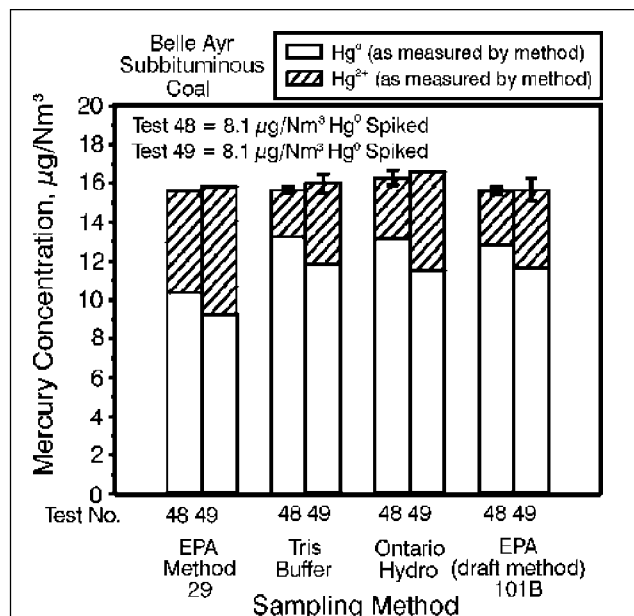


Figure 7. Comparison of mercury speciation sampling methods while spiking Hg^0 and sampling at the baghouse outlet (Laudal et al., November 1996 and December 1997).

between 60 and 66%, with a corresponding removal of SO_2 between 82 and 96% across the WFGD system. Sulfur dioxide concentrations for the five plants were between 2400 and 2900 ppmv (average of 2600 ± 100 ppmv) at the inlet, and between 100 and 500 ppmv (average of 330 ± 10 ppmv) at the outlet. Further details of these five sampling efforts can be found in the referenced paper prepared by CONSOL, Inc. (DeVito and Rosenhoover, 1999).

The recent pilot-scale speciation measurement studies and these field results with the Ontario Hydro Method indicate less of an increase in the apparent re-emission of the captured Hg^{2+} as compared to other sampling efforts with Method 29. However, under certain conditions, there is an apparent increase at the outlet of non- Hg^{2+} species compared to the inlet of the WFGD system. The possible re-emission of a non- Hg^{2+} form or possible overestimation of Hg^{2+} at the inlet of WFGD systems as reported by Ontario Hydro for the five plants are as follows:

- Plant 1, a 38.5% increase;
- Plant 2, a 23.1% increase;
- Plant 3, an 18.6% increase;
- Plant 4, a 16.7% increase; and
- Plant 5, a 7.1% increase.

These and other possibilities are being investigated and will be discussed in the section on control technology investigations and development for coal-fired utility applications.

Validation of the Ontario Hydro Method has provided researchers with a valuable tool to measure, within $\pm 10\%$, the distribution between Hg^0 and Hg^{2+} , along with total Hg in flue gas from coal combustion. This method has aided in the understanding of the

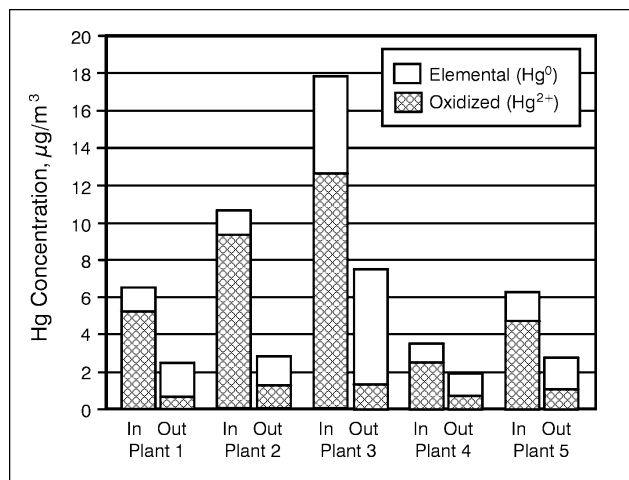


Figure 8. Elemental and oxidized mercury in coal-fired power plants firing bituminous coals and equipped with WFGD (DeVito and Rosenhoover November 1997 and June 1999).

different forms of Hg and which form is captured or emitted. Many researchers have modified this method and have been using it in a semicontinuous mode for their respective bench- and laboratory-scale Hg sorbent evaluation and development projects. While there has been some success in the semicontinuous mode, more development and evaluation with subsequent validation of Hg continuous emissions monitors (CEMs) at coal-fired utilities need to be completed. The Ontario Hydro Method can now be utilized as a standard for the testing and possible validation of the promising CEMs.

While the Ontario Hydro Method has been validated, it is a labor-intensive wet chemistry method requiring long sampling times, with the results being provided often weeks after the sampling event. Real-time data on total and speciated Hg are needed to fully evaluate the control technologies under development. Correlating APCD operating parameters, sorbent and additive injection rates, temperature effects, etc., with real-time monitoring is critical to the development of low-cost Hg control technologies. The DOE has been funding researchers to develop a Hg CEM as a research tool to aid in the evaluation of the promising control technologies for Hg control in coal-fired utilities.

On-line mercury analyzers were evaluated during the EPRI- and DOE-funded Hg speciation methods program by the EERC at its coal-fired pilot-scale facility. Total Hg measurements of commercial Hg CEMs have shown that they generally can provide data that are within $\pm 25\%$ of wet chemistry methods. Although these instruments can provide some useable data, further development work is needed before they can be used extensively by power plants.

Work has been ongoing to develop and evaluate CEMs for total Hg, and either individually or by difference, the

distribution of Hg^0 and Hg^{2+} . Possible candidates* that have been tested at the pilot scale in the United States include ADA Technologies, Perkin-Elmer MERCEM, PS Analytical Sir Galahad, and Semtech Hg 2000. (Details on these analyzers can be found in the following references: Laudal et al., November 1996; Laudal et al., December 1997; Heidt et al., 1998; Laudal and Kurz, January 1999; Kurz and Laudal, April 1999.)

The ADA instrument is designed to speciate Hg by measuring total and elemental, and then determining the oxidized form by difference (Sjostrom et al., 1997). A prototype unit is currently being evaluated at two different facilities. ADA has successfully utilized its instrument to indicate trends in the development of its novel Hg removal system when varying sorbent injection and while spiking either Hg^0 or Hg^{2+} .

The Perkin-Elmer instrument is currently being used at incineration facilities in Europe. The PS Analytical instrument has been used almost exclusively for measuring mercury in ambient air and in natural gas lines. This instrument has the capability to measure very low levels of mercury in gas streams. The Semtech mercury analyzer was originally designed to measure only Hg^0 . A conversion cell was added with the intent of measuring total mercury, and by using a bypass valve Hg^0 can then be measured, giving mercury speciation by difference. In previous bench-, pilot-, and full-scale studies conducted by EERC (Laudal and Kurz, January 1999; Kurz and Laudal, April 1999) and in studies on simulated flue gas conducted at the University of Göteborg, Sweden (Wang et al., 1995), the Semtech mercury analyzer indicated reliable and relatively accurate measurements of actual and spiked Hg^0 . (Details on these analyzers can be found in the following references: Laudal et al., November 1996; Laudal et al., December 1997; Laudal and Kurz, January 1999; Kurz and Laudal, April 1999.)

During the initial pilot-scale tests conducted in late 1997 and early 1998 evaluating Hg CEMS, the ADA and Semtech instruments did not operate properly. However, relatively good results were obtained for the Perkin-Elmer MERCEM and PS Analytical Sir Galahad CEMs. Evaluations were conducted for two different coals (one bituminous-Blacksville-and one subbituminous-Absoloka) at baseline conditions (no Hg spiking) and with Hg^0 spiking, and then with $HgCl_2$ spiking. Figures 9, 10, and 11 show comparisons of the CEMs to the manual speciation methods for the bituminous coal at the three conditions, while Figures 12, 13, and 14 show the comparisons for subbituminous coal at the three respective conditions. All measurements were taken at the outlet of the EERC's highly efficient baghouse where virtually no particulate was present in the exiting flue gas. This was done to provide a more direct comparison of the manual methods

and CEMs. In addition, the Ontario Hydro Method consistently indicated lower total mercury values because the addition of $KMnO_4$ (as previously stated, to preserve the Hg in the KCl impingers) was not yet part of the protocol for the method. As seen from the figures, the CEM values for each instrument were $\pm 20\%$ of the manual methods for the baseline and spiking of Hg into the flue gas stream. All the CEMs showed variability, which is not considered unusual owing to the variable coal Hg concentrations. Some of the individual spikes of Hg as indicated by the CEMs are still being investigated.

Although the total Hg values for the CEMs were within only $\pm 20\%$ of the manual methods, the monitors are potentially valuable tools for real-time monitoring of Hg capture. The very innovative evaluations conducted by the researchers at the EERC indicated the detection concepts for Hg CEMs did work, as indicated by the ability to detect spikes of either form of Hg. These detection concepts included: cold-vapor atomic absorption spectroscopy (CVAAS), cold-vapor atomic fluorescence spectroscopy (CVAFS), and atomic emission spectroscopy (AES). The major finding of this work was the need to condition the flue gas to provide a representative Hg sample to the detectors and to eliminate potential interfering gases (e.g., HCl, SO_2 , SO_3 , and other acid gases).

The EERC has been testing a CEM sample conditioning and Hg conversion systems at the pilot scale and at the full scale, while comparing the CEM Hg values with the validated Ontario Hydro Method. The sample conditioning system contained calcined sodium bicarbonate to collect the acid gases and yet allow all the Hg to go through unaffected, while the Hg^{2+} to Hg^0 conversion system contained stannous chloride (Sn_2Cl).

The conditioning and conversion systems were installed at the front end of the Semtech monitor with valves being incorporated to bypass either system. Bypassing the conversion system allowed the monitor to measure only Hg^0 , which can be compared with the manual method. This not only provided a comparison of the Hg^0 values, but an evaluation of the ability of the sodium bicarbonate to allow all the Hg to pass through to the detector. Figure 15 indicates, at the pilot scale, the comparison between the Semtech Hg 2000 CEM, incorporating the sample conditioning and conversion systems developed by the EERC, and the Ontario Hydro manual method.

The relative residual values of the Semtech as compared to the Ontario Hydro Method are within 0 and 10.0% for both the total Hg and Hg^0 while the flue gas was flowing through and bypassing the conversion system, respectively. Spiking of $15 \mu g/Nm^3$ of Hg^0 was done with both methods indicating the same values. Many bench- and pilot-scale investigations with the conditioning and conversion systems were conducted

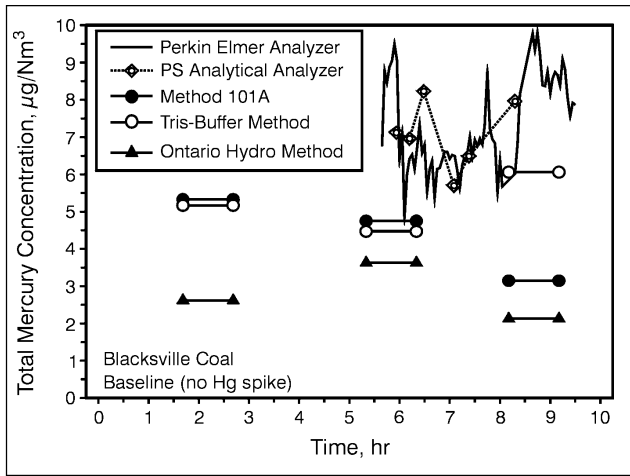


Figure 9. Comparison of CEMs to impinger-based mercury sampling methods (Laudal et al, November 1996 and July 1997).

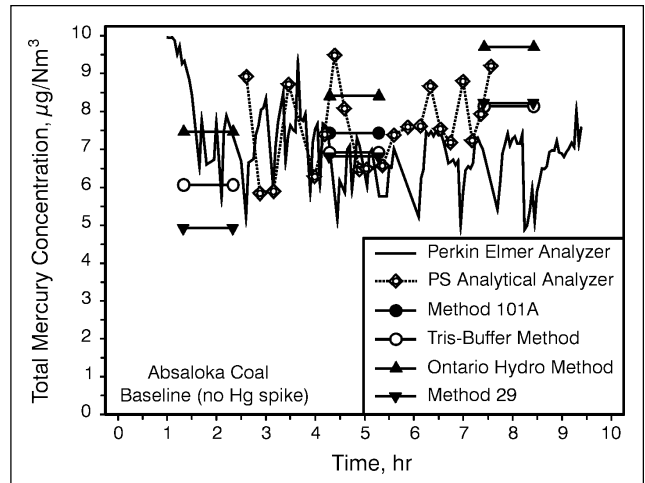


Figure 12. Comparison of CEMs to impinger-based mercury sampling methods (Laudal et al, November 1996 and July 1997).

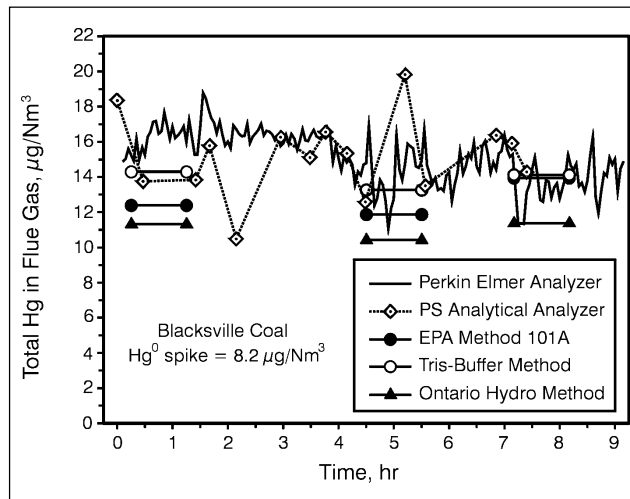


Figure 10. Comparison of CEMs to impinger-based sampling methods (Laudal et al, November 1996 and July 1997).

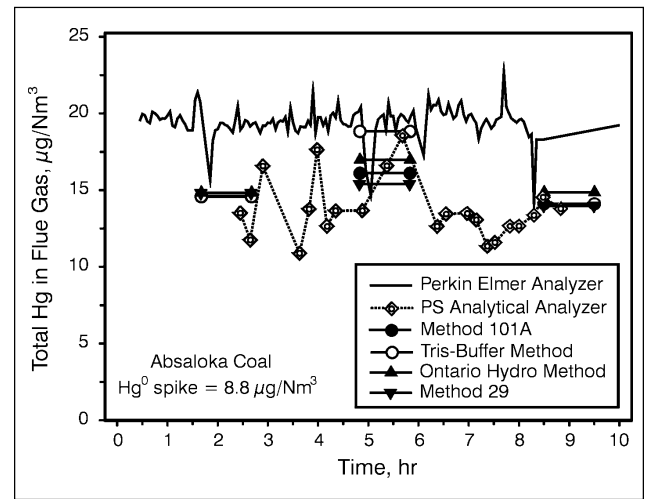


Figure 13. Comparison of CEMs to impinger-based sampling methods (Laudal et al, November 1996 and July 1997).

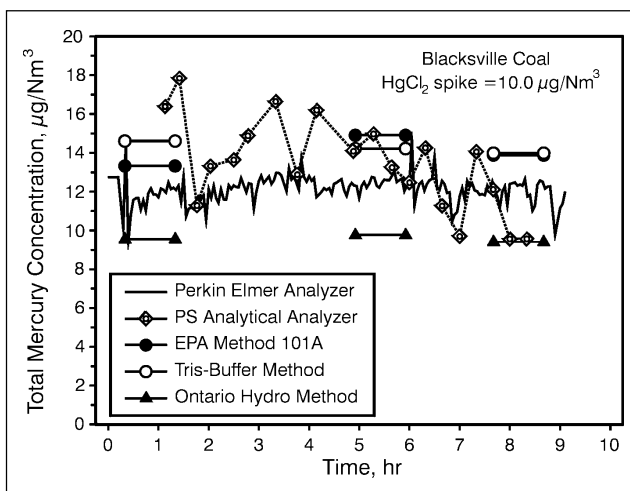


Figure 11. Comparison of CEMs to impinger-based mercury sampling methods (Laudal et al, November 1996 and July 1997).

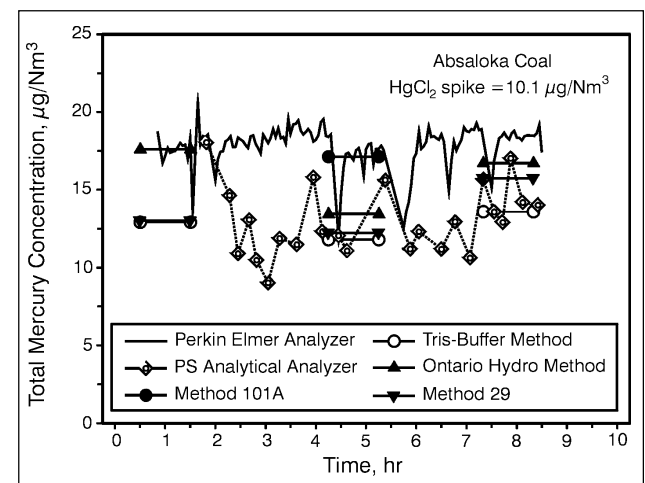


Figure 14. Comparison of CEMs to impinger-based mercury sampling methods (Laudal et al, November 1996 and July 1997).

before reliable measurements could be obtained. Evaluation typically lasted 5-10 hr and fairly comparable data relative to the Ontario Hydro Method were collected. The EERC has conducted comparison studies between the Semtech Hg 2000 CEM and the Ontario Hydro Method at three utilities. Figures 16-19 show mercury measurements at the inlet of the WFGD system over four days of testing for one of the utility sites.

The Semtech Hg 2000 monitor was compared with the Ontario Hydro Method at the same utility site where the validation of the Ontario Hydro Method was performed. The SO₂ values at the location of the CEM were high and variable from 2000 to 2900 ppmv, (average of 2600 ppmv) as were the total Hg values. Again, the relative residual values of the Semtech instrument as compared to the Ontario Hydro Method were within 0 and 10.0% for both the total Hg and Hg⁰, while the flue gas was flowing through and bypassing the conversion system, respectively. The conditioning system for removing acid gases (gases interfering with Hg⁰ measurements of the Semtech monitor) was utilized throughout the four days of testing, with the exception of the end of the fourth day. As seen in Figure 19, when the conditioning system was bypassed, no conversion of Hg²⁺ to Hg⁰ was indicated, and only Hg⁰ in the flue gas stream was measured. The high SO₂ concentration in the flue gas inhibited the Sn₂Cl conversion system from converting the Hg²⁺ to Hg⁰ for measurement by the Semtech 2000 Hg monitor.

These results indicate a need for both a conditioning and Hg conversion system to provide accurate total Hg values and, by difference, Hg²⁺ values. While these systems provide excellent results, their use as truly continuous Hg monitors is far from realization. These systems have not been tested over long periods of time and may not represent the actual systems to be used for long-term

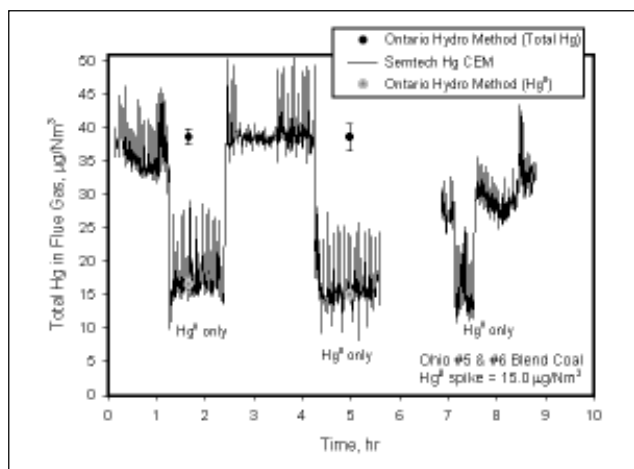


Figure 15. Comparison between Semtech CEM and the Ontario Hydro Method at EERC pilot-scale facility (Laudal et al., December 1997).

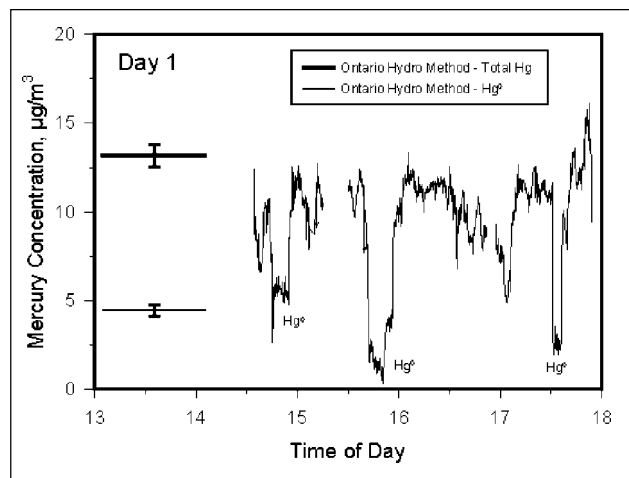


Figure 16. Comparison between Semtech CEM and the Ontario Hydro Method at Site E-29 (EPRI and U.S. DOE, April 1999 and Laudal et al, June 1999).

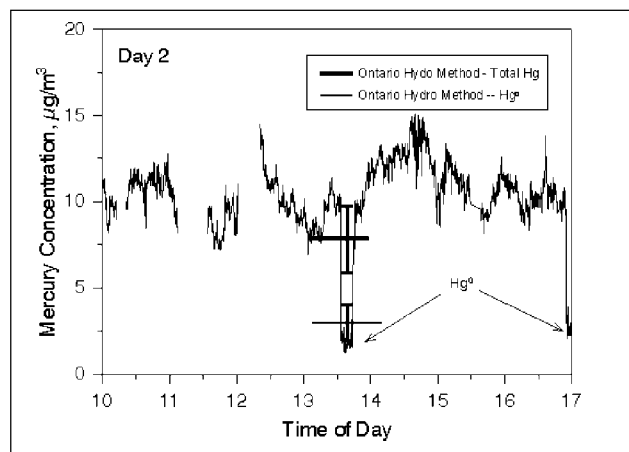


Figure 17. Comparison between Semtech CEM and the Ontario Hydro Method at Site E-29 (EPRI and U.S. DOE, April 1999 and Laudal et al, June 1999).

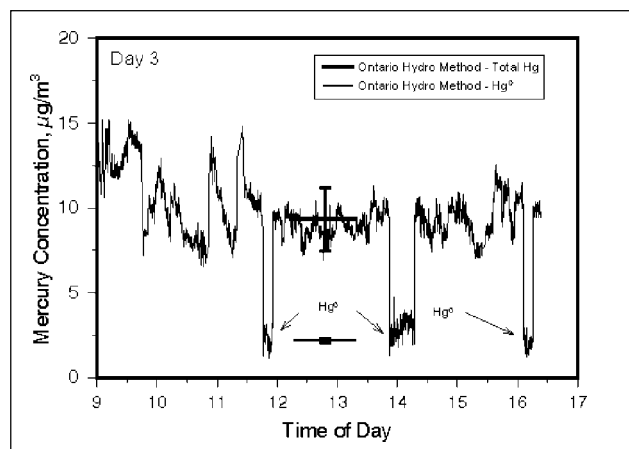


Figure 18. Comparison between Semtech CEM and the Ontario Hydro Method at Site E-29 (EPRI and U.S. DOE, April 1999 and Laudal et al, June 1999).

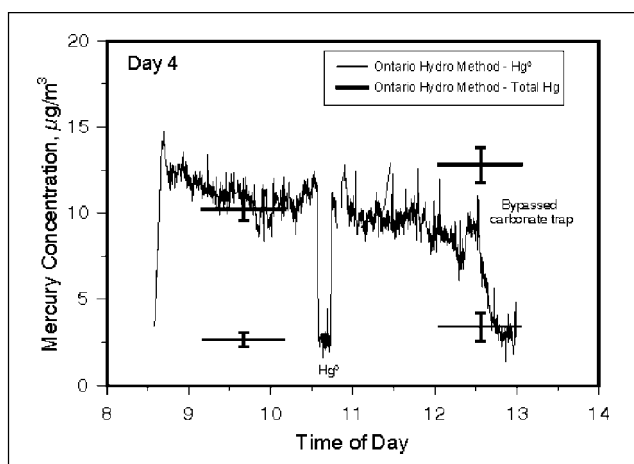


Figure 19. Comparison between Semtech CEM and the Ontario Hydro Method at Site E-29 (EPRI and U.S. DOE, April 1999 and Laudal et al, June 1999).

monitoring. These tests indicate that they may be utilized during testing of promising Hg control technologies. The front-end systems for Hg CEMs will allow real-time Hg monitoring under varying operating conditions and/or with injection of Hg capturing media of the promising control technologies. Optimization could be determined and new data could be collected on the formation of Hg^{2+} or the conversion of Hg_0 to Hg^{2+} at temperatures at the inlet of the first APCD.

These front-end systems for Hg CEMs work well in flue gas free of particulate or with extremely low particulate loadings, but they need to be tested at the higher particulate loadings found at the inlet of utility particulate control devices (ESPs and baghouses). Particulate matter converts Hg_0 to Hg^{2+} and adsorbs Hg, allowing for false indications relative to the vapor-phase and particulate-bound Hg and distribution. Conditioning systems for Hg CEMs are also needed to eliminate the buildup of particulate, which produces false indications of the Hg species. In addition, Hg standards for monitor calibration are needed for both Hg_0 and Hg^{2+} . Informal communications with vendors have indicated that they are able to provide Hg_0 standards at <3 ppbv (e.g., Spectra Gases), and are working on standards for lower concentrations and for other forms (e.g., Hg^{2+}).

The DOE has been reviewing proposals under its Small Business Innovative Research (SBIR) Program to address conditioning systems for Hg CEMs. All of the above-mentioned aspects for accurate Hg measurement and Hg distributions were addressed in the solicitation issued in early 1999. Novel concepts were sought to provide total utilization of Hg CEMs in any flue gas stream resulting from coal combustion. A lot of innovative work is needed before Hg CEMs are available for use in the utility industry as reliable, accurate, and low-maintenance monitors. The

DOE will utilize the conditioning and conversion systems to monitor, in real-time, the development of Hg control technologies for the utility industry, provided they are needed. The findings and development of these two systems will be adapted by all of the DOE contractors involved with Hg control development.

The validated Hg speciation method (Ontario Hydro Method) can now be utilized to measure mercury concentrations at any location in coal-fired utility boiler systems. As a result of the breakthroughs made by the EERC for conditioning and conversion systems, CEMs have the potential to be a valuable research tool for real-time gas-phase mercury measurements. The measurements can be in conjunction with sorbent injection and/or gas or liquid-phase additive injection to indicate mercury removal as the injection rates are varied. Many questions still need to be answered, as previously discussed in this section, to have reliable and low-cost control options for utilities, if Hg regulations are indeed promulgated. These monitoring methods will enable researchers to gain a better understanding about Hg transformations and its subsequent control.

As previously stated, equilibrium does not provide a complete explanation for the speciation of Hg in coal-fired utility boilers. There are still some questions regarding the presence of Cl_2 at typical APCD temperatures and its gas-phase reaction with Hg_0 to form Hg^{2+} . There is some evidence of interactions with vapor-phase constituents and fly ash (catalysis) in the flue gas streams to convert Hg_0 to Hg^{2+} .

Two key questions are now postulated: first, "What are the processes/mechanisms by which fly ashes (and certain other solids) seem to catalyze the transformation of gaseous Hg_0 to 'oxidized forms'?" and second, "What Hg species are adsorbed on fly ash?" Answering these questions will require a detailed look at the constituents of the fly ash and how they interact with Hg at temperatures characteristic of the flue gas (400-600 K) as it enters the first APCD. Figure 20 indicates some of the possible mechanisms impacting both Hg speciation and adsorption in coal-fired utility flue gas. Studies designed to answer these questions will be addressed in the next section.

Factors Influencing Mercury Speciation and Adsorption

In the process of developing methods for measurement of total mercury, vapor-solid distribution, and mercury speciation, a great deal of data was obtained over a variety of experimental conditions. Both the vapor-solid distribution and speciation varied widely in the results from the early testing, and it was not clear whether the variability was real or caused by artifacts in the sampling methods. Once the sampling method problems were addressed, the variability seemed to be dependent on the

coal type, and more specifically, on flue gas and fly ash composition. Compared to other coals, bituminous coals generally produce higher levels of Hg^{2+} in the vapor phase and lower levels of solid-phase mercury. Subbituminous coals produce higher levels of Hg^0 in the vapor phase and can have high levels of solid-phase mercury. To understand the factors affecting mercury speciation and adsorption, a number of studies have been conducted. These studies have focused on understanding the mechanisms for mercury chemistry, including both oxidation/reduction and adsorption. Investigations at both bench and laboratory scales with simulated flue gas have indicated certain bituminous coal fly ash and vapor-phase constituents play a role in the oxidation of Hg^0 . PRB/subbituminous coal fly ashes have shown high adsorption capacities as compared to the bituminous coal fly ashes, but indicate, in most cases, very little oxidation. Generally, the adsorption rate increases as the temperature in the flue gas decreases. Work is continuing to investigate these observations and determine the mechanisms responsible for both oxidation and adsorption of Hg by the various fly ashes. This section will summarize the results of these studies with a discussion of the research on subbituminous coals first, then the work on bituminous coals, and, finally, a discussion of some research on identifying the actual mercury compounds as they exist in or on fly ash, char, and other sorbents.

It has been speculated that the oxidized form of Hg in flue gas from coal combustion is mercuric chloride (HgCl_2). The existence of molecular chlorine (Cl_2) at temperatures measured near the first APCD of coal-fired power plants has been postulated. Kinetic calculations also showed that the chlorine atoms combine to form primarily HCl with minor amounts of Cl_2 (Sarofim et al., 1998). If small concentrations of Cl_2 are present in the flue gas streams exiting the air preheater, then reactions could be occurring with the Hg^0 to subsequently form HgCl_2 . Consideration of the elementary reaction of mercury in flue gas has led

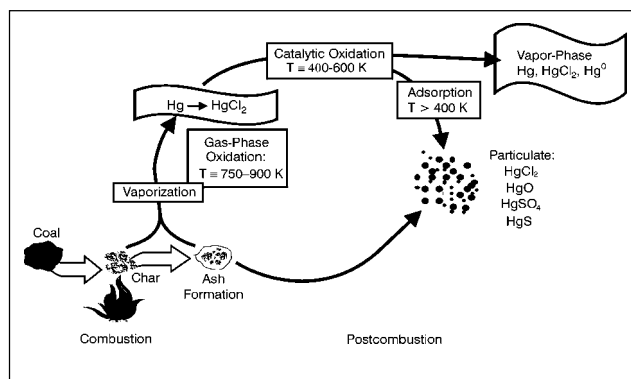


Figure 20. Proposed Hg transformations in coal-fired power plant flue gas from Senior et al, 1997, Sarofim et al, 1998; and Galbreath, et al, June 1998.

several groups (Sliger et al., 1998; Sarofim et al., 1998) to conclude that the reaction of Hg^0 and atomic chlorine (Cl) in the flue gas initiates the conversion to HgCl_2 . Since molecular chlorine is formed by the reaction of atomic chloride, the presence of Cl_2 or molecular chloride in the flue gas is a possible indication of the presence of atomic chloride. Alternatively, mercury could react with other vapor-phase compounds and/or fly ash constituents to form other oxidized mercury compounds.

To investigate possible mercury-chlorine-fly ash interactions, pilot-scale studies were recently conducted by researchers at the EERC (Galbreath et al., June 1998; Galbreath and Zygarlicke, December 1998). Tests were conducted in a gas mixture of oxygen (O_2) and nitrogen (N_2) at 2282 °F (1250 °C), and in flue gas from the combustion of a PRB/subbituminous coal (Absaloka-0.052-ppmw Hg and 50-ppmw chlorine) in a small-scale furnace. Spiking of 10 $\mu\text{g}/\text{Nm}^3$ of Hg^0 with and without 100 ppmv of HCl was conducted during the O_2/N_2 gas mixture tests, while 50 and 100-ppmv HCl were injected into the furnace at 2426 °F (1330 °C). The oxygen concentration for all tests was about 8.5%.

Figure 21 shows duplicate mercury speciation results for the O_2/N_2 gas mixture tests with a 10- $\mu\text{g}/\text{Nm}^3$ Hg^0 spike with and without the 100-ppmv HCl spike. About 50% of the injected Hg^0 was converted to an oxidized form as the gas cooled from 1250 to 200 °F (667-93 °C) in approximately 2.5 sec when no HCl was injected. The EERC considered the possibility that the Hg^0 was converted to HgO through a gas-phase reaction with O_2 , but decided that the conversion would be kinetically inhibited owing to the relatively short residence time in the test furnace. (Hall et al., 1990; Hall et al. WA&SP, 1991; Wu et al., 1997). EERC researchers then speculated the reaction is catalyzed by components of the refractory-lined furnace. Analysis of the refractory material indicated the presence of rutile and corundum, which are catalysts known to enhance the above reaction. Calcium sulfate was also detected on the refractory walls from deposition during combustion of previous coals.

The reported Hg speciation values when a 100-ppmv spike of HCl was injected in the gas stream require some interpretation. The EERC speculated that the low recoveries of the spiked Hg^0 were the result of the formation of HgCl_2 [melting point of 529 °F (276 °C), and boiling point of 576 °F (302 °C)] and subsequent deposition on the furnace walls. They suggested that corundum in the furnace could provide sites to catalyze Cl_2 formation from the injected HCl, which would then react with the elemental mercury. Further investigations are needed to determine what refractory components could catalyze a number of reactions, promoting heterogeneous conversion of Hg^0 to an Hg^{2+} form.

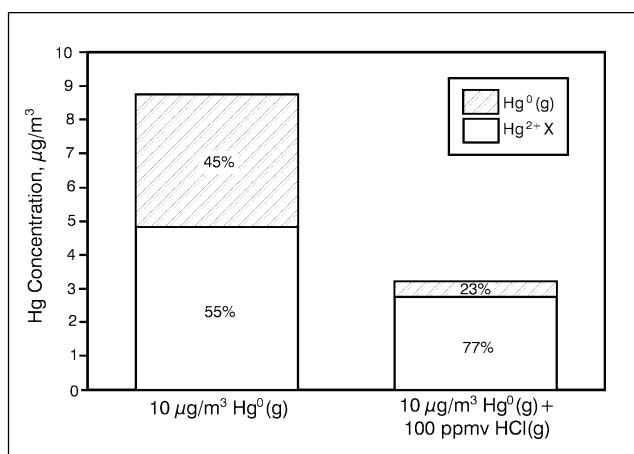


Figure 21. Mercury speciation results for Hg⁰ spike and Hg⁰ + HCl spike tests (Galbreath et al., June 1998).

Mercury speciation results, with and without HCl spiking in the furnace, during the combustion of Absaloka PRB/subbituminous coal are shown in Figure 22. Speciation results indicated approximately 41% of the Hg was associated with the fly ash, while 40% is reported as Hg⁰ and the remaining 19% as Hg²⁺. This distribution and particle-bound Hg was consistent with numerous tests conducted while firing this coal (Dunham et al., September 1995, September 1998; Laudal et al., November 1996 and December 1997; Miller et al., 1995). Spiking of 100-ppmv HCl did inhibit the adsorption characteristics of the fly ash for Hg, even as the particles adsorbed Cl. Analysis of the fly ash indicated that Cl was present, but its presence did not apparently promote active sites for Hg chemisorption. In addition, the carbon content of the fly ash was 8 times higher during the baseline tests for this coal. The presence of chlorine and the higher carbon values did not promote Hg adsorption when the 100 ppmv of HCl was injected.

Fly ashes from the combustion of this and other PRB coals contain a large portion of CaO that is converted to CaSO₄ during combustion. Previous tests showed CaO and portlandite (Ca(OH)₂) are effective sorbents for both Hg⁰ and HgCl₂. Researchers from the EPA and Acurex provided evidence of inhibited adsorption of HgCl₂ for a Ca(OH)₂ sorbent while HCl was present. They speculated that the inhibited HgCl₂ sorption was the result of competition with HCl for the alkaline sites (Ghorishi and Gullet, 1997). The results of the work conducted by the EERC indicates an inverse relationship between particle-bound Hg and Cl, which is consistent with the work by Ghorishi et al.

To test the hypothesis that CaO is an important mercury sorption component of fly ash, the EERC added calcium acetate monohydrate to the Absaloka coal to increase the CaO concentration in the fly ash. Although the CaO concentration increased significantly from 25.0 to 37.6% by weight, the relative proportion of the particle-bound mercury decreased from 41 to only 2% (see Figure 23;

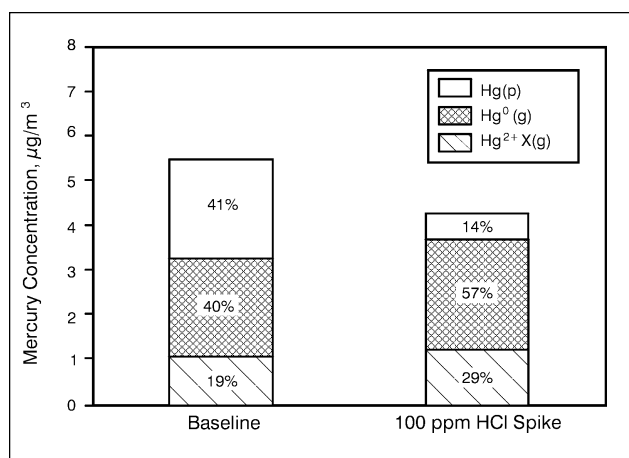


Figure 22. Average mercury speciation results for the Absaloka baseline and HCl spike tests (Galbreath et al., June 1998).

mercury speciation with Calcium Acetate Spiking). The increase in CaO apparently inhibited Hg adsorption. The EERC theorized that the addition of CaO changed the mineralogy of the fly ash by formation of merwinite at the expense of ferrite spinel, which has been shown to be the predominant host for a variety of trace metals. This suggests that the ferrite spinel may be the mercury host in Absaloka fly ash and is more important than the concentration of CaO, but additional research is needed.

Other researchers have also conducted studies with PRB coals. In the past 14 months, researchers at Radian have conducted sorption and oxidation investigations on a PRB fly ash having a high loss-on-ignition (LOI) of 70%. Tests were conducted in a fixed bed with 200 milligrams (mg) of fly ash dispersed in 10 grams (g) of sand. This material was then exposed to a simulated flue gas containing 50 µg/Nm³ of elemental mercury. Mercury speciation measurements were made with the Tris-Buffer Method. The test conditions were designed to determine temperature and HCl effects on adsorption capacity and oxidation of the fly ash. The results are shown in Table 16.

The baseline condition showed a moderate adsorption capacity, probably as a result of the high carbon content of the ash. The high temperature test condition showed no adsorption capacity and minimal oxidation. This is consistent with other tests using AC, indicating that the high LOI ash behaved similar to carbon rather than fly ash. The test condition with the HCl spike showed the highest adsorption and oxidation. These results appear to contradict the findings of Galbreath and Zygarlicke regarding decreased mercury sorption for PRB ashes with increases in HCl. However, the different findings may be a result of differences in fly ash composition (high calcium vs. high carbon).

Additional studies of PRB coals were conducted under another DOE-funded Mega PRDA project using actual flue

gas. The results showed measurable Hg⁰ removals for the following pilot-scale particulate control devices and conditions:

- (1) Removals across a pilot-scale pulse-jet FF (air-to-cloth ratio of 4 ft/min) of 10 and 17% at 275 °F (135 °C) and 65% at 250 °F (121 °C).
- (2) Removals across a pilot-scale reverse-gas baghouse were 67% at 200 °F (93 °C), with less than 20% for an average temperature of 289 °F (143 °C).
- (3) Removals were measured upstream of a pilot-scale ESP with an average of 30% at 200-228 °F (93-109 °C).

All tests were conducted with the flue gas and fly ash (nominal <0.5% carbon in ash) from the combustion of PRB Belle Ayre coal (Haythornthwaite, 1997; PSCo/ADA Technologies, Inc. et al., 1997; Sjostrum et al., 1997).

Recent tests at the facility indicate Hg⁰ removals for the following pilot-scale particulate control devices and conditions:

- (1) Removals were measured upstream of the pilot ESP of 53-61% at 230 °F (110 °C), 10-39% at 271-306 °F (133-182 °C), and -2 to 26% at 350 °F (177 °C).
- (2) Removals across the reverse-gas baghouse of 72-79% at 230 °F (110 °C), 34-78% (average 66%) at 280 °F (138 °C), and below 30% at 330-350 °F (166-177 °C).

The pulse-jet filter results showed a less clear trend, with a decrease in Hg removal at the intermediate temperature

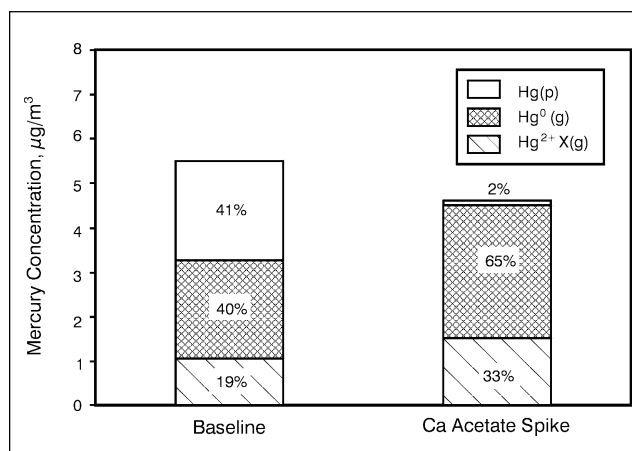


Figure 23. Average mercury speciation results for the baseline and Ca Acetate-spiked coal combustion flue gases (Galbreath et al., December 1998).

Table 16. Adsorption capacities and percent oxidation of Hg⁰ associated with high LOI ash.

Test Conditions	Temperature (°F)	Sorption Capacity (µg/g)	Hg ⁰ Oxidation (%)
Baseline	300	68	4
High Temperature	700	0	8
1-ppm HCl Spike	300	165	70

of 310 °F (154 °C) and an increase with temperature at 350 °F (177 °C). The pulse-jet filter Hg removal of about 50% at 350 °F (177 °C) is higher than measured in either the ESP or reverse-gas baghouse configurations (Haythornthwaite et al., 1998).

The conclusions of this study were that mercury removal with the fly ash is strongly dependent on the temperature of the flue gas, but is also dependent on the type of particulate collection configuration. The range of Hg removal by the ash alone has been demonstrated at the pilot-scale test facility located in the Comanche Station to be very temperature dependent. Removal of mercury associated with an ESP is upstream of the ESP or in-flight, and not across the ESP. Higher Hg removals are indicative of the baghouse configurations because the flue gas filtering through the fly ash collected on the bags increases the contact of the Hg in the flue gas with the captured fly ash. Most of the tests conducted at temperatures between 330 and 350 °F (166-177 °C) yielded Hg removals below 30%, with the exception of a few pulse-jet filter tests that showed higher Hg removal results. The pulse-jet filter data are being further investigated to determine the apparent increase in mercury removal at the higher temperatures.

As stated earlier, in the interest of understanding the sorption of Hg by a certain fly ashes, laboratory tests are being conducted under this and other projects to examine the capacity and reactivity of the ash. This ash has a low carbon content (<0.5%), so carbon does not fully explain the ash's affinity for Hg adsorption.

In addition to the bench- and pilot-scale studies described above, there have been a number of full-scale studies. One such study involved a Riley Stoker front-fired utility boiler firing a PRB coal from the Montana area. The only APCD present was a reverse-gas baghouse for particulate control. Mercury measurements utilizing Method 29 and the MESA were taken simultaneously at the inlet and outlet of the baghouse with two different methods. Inlet total Hg measurements were reported at the 6.4 and 6.5-µg/Nm³ levels, respectively, with approximately 60% of the total being measured as Hg⁰ for each method. The Hg⁰ was essentially removed across the baghouse by the native fly ash (carbon contents of the fly ash for the three test periods were 3.5, 2.9, and 2.9% with an average of 3.1%). Outlet Hg concentrations were 2.6 and 3.1 µg/Nm³ of Hg²⁺ as measured by the respective methods. Removals indicated by the two methods were 60 and 52% of the total, respectively, at average temperatures at the air heater outlet of 372 °F (189 °C); baghouse inlet at 346 °F (174 °C); and baghouse outlet of 330 °F (166 °C).

Approximately 40% of the total Hg was found on the filter catch of the EPA Method 29 train [filter at 250 °F ± 15 °F (121 °C ± 8°C)] located at the baghouse outlet. Mercury

was removed as it passed through fly ash captured on the fabric of the baghouse. The hopper ash samples indicated a comparable level of Hg to those indicated by both Hg measurement methods. The Hg capture during this testing was indicative of removals across the baghouse and not in-flight capture upstream of the baghouse (Jackson et al., 1994).

More recent full-scale data were obtained in a sampling effort conducted by CONSOL for the Public Service Company of Colorado (PSCO) at its Comanche Station. Testing was conducted utilizing the validated Ontario Hydro Method (O/HM-1) in late 1998 at the Comanche Station to (1) obtain scalable data between the pilot-scale unit(s) being tested there, (2) speciate the Hg at both the pilot-scale inlet location and the station's air preheater outlet, and (3) perform special sampling tests to possibly determine the adsorption of Hg on the ash-laden filter of the Hg speciation method in order to obtain a more representative particle-bound Hg measurement in the flue gas. A modified Ontario Hydro Method (O/HM-2) was designed with an oversized nozzle directed away from the flue gas flow to minimize the amount of particulate entering the sampling probe and subsequently collected on the filter of the train. These tests were conducted to provide a more representative measurement of the vapor-phase Hg (including speciation) and, hopefully, the particulate-bound Hg prior to collection of the fly ash in the station's baghouse. In-flight capture is important to ascertain, because pilot-scale and field data have indicated that the fly ashes from the combustion of PRB/subbituminous coals have the capacity to adsorb more Hg than bituminous coal fly ashes (Haythornthwaite et al., August 1997, December 1998, June 1999; Laudal et al., November 1996, December 1997). In addition, the in-flight capture is important because many utilities fire different PRB subbituminous coals in boiler systems utilizing an ESP as the only control device.

Six O/HM-1 tests were conducted at a location near the outlet of the station's air preheater and prior to the inlet of the station's reverse-gas baghouse. Some variability in the results were indicated, but in general, the tests were repeatable in terms of total Hg and Hg speciation. The total Hg averaged $11.3 \mu\text{g}/\text{Nm}^3$ (range $9.7\text{-}14.6 \mu\text{g}/\text{Nm}^3$) and the distribution of Hg at this location was: particulate Hg ($\text{Hg}_{(p)}$) averaged 30% (range 16-52%) of total Hg, vapor-phase oxidized Hg ($\text{Hg}^{2+}_{(g)}$) averaged 19% (range 12-34%) of total Hg, and vapor-phase Hg^0 ($\text{Hg}^0_{(g)}$) averaged 50% (range 36-59%) of total Hg. The tests were designed to conduct three O/HM-2 sampling efforts simultaneous with and at the same location as three of the six O/HM-1 sampling efforts. A comparison of the measurements from the two methods during the three simultaneous sampling efforts is indicated in Figure 24.

The objective of these sampling efforts was to possibly determine the adsorption of Hg on the ash-laden filter of the Hg speciation method to obtain a more representative particle-bound Hg measurement in the flue gas. The average particulate mass or grain loading on the filter of the standard O/HM-1 was 2.31 grains/dry standard cubic feet (gr/dscf), with a range of 2.1 to 2.6 gr/dscf as compared to the range of 0.23-0.26 gr/dscf for the O/HM-2. While the difference in particulate mass for the two methods was a factor of 10, Hg capture on the particulate of O/HM-2 was lower only by a factor of 1.1-2.4 as compared to O/HM-1. A plausible explanation could be that the ash fines captured on the O/HM-2 filter have a high efficiency for Hg capture in comparison with the bulk, larger particulate, which is representative of the station's flue gas stream, collected by the O/HM-1 filter. Another possibility is that the Hg present on the fines is already there prior to sampling. It is interesting to note that the percentage of carbon in this fly ash is consistently less than 0.5%.

Another interesting result of this sampling effort was that the 10-fold difference in the particulate mass of the two methods did not affect either the measure total Hg or the $\text{Hg}^{2+}_{(g)}$ concentration. The $\text{Hg}^0_{(g)}$ value was greater for the O/HM-2 sampling train as compared to the O/HM-1 sampling train. A reasonable conclusion is that during sampling with the O/HM-1 method, which collected a high mass of particulate, the $\text{Hg}^0_{(g)}$ was adsorbed or reacted with the ash. Figure 24 shows the range of results for each parameter; note that the difference in elemental concentration over the range is small but consistent.

Simultaneous sampling in conjunction with the O/HM-1 at the inlet and outlet of the station's reverse-gas baghouse provided data to determine Hg removal associated with this fly ash and possible Hg speciation. Baghouses or FFs provide very efficient particulate collection (>99.95%), and provide a dust cake on the filter for the flue gas to pass through. This enables the Hg in the

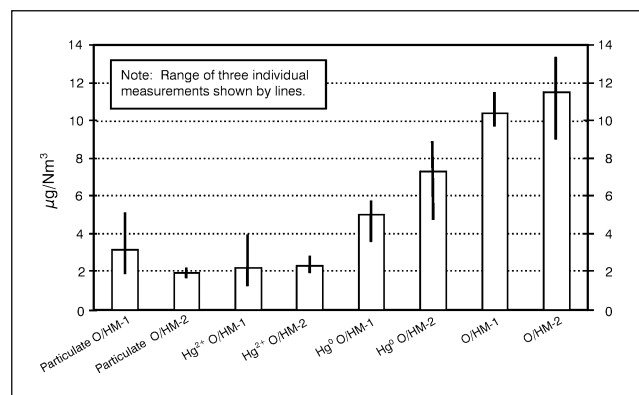


Figure 24. Comparison of the validated and a modified Ontario Hydro Methods (Haythornthwaite et al., December 1998).

flue gas to be in contact with the fly ash for possible increased adsorption and/or reaction. The Hg at the outlet ranged from 3.6 to 4.7 $\mu\text{g}/\text{Nm}^3$, with $\text{Hg}^{2+}_{(g)}$ being the predominate form averaging 3.5 $\mu\text{g}/\text{Nm}^3$ compared to the inlet $\text{Hg}^{2+}_{(g)}$ which averaged 2.2 $\mu\text{g}/\text{Nm}^3$. The average quantity of Hg removed across the baghouse was 62% of the total Hg and was higher than the particulate Hg quantity measured from the filter catch of the O/HM-1. The $\text{Hg}_{(p)}$ percentage of the total Hg for the particulate captured on the O/HM-1 filter averaged 30%. This is an indication that there is further adsorption of $\text{Hg}_{(g)}$ or more specifically $\text{Hg}^0_{(g)}$ across the station's baghouse. The temperature at the two sampling locations averaged 300 °F (149 °C) during the sampling efforts.

Two possibilities exist for the apparent increased $\text{Hg}^{2+}_{(g)}$ at the outlet of the baghouse: (1) oxidation occurred across the particulate collected in the baghouse, or (2) the inlet $\text{Hg}^{2+}_{(g)}$ values were low as a result of the presence of fly ash in the flue gas stream and on the filters in the mercury speciation sampling trains. This may be further supported by the comparable $\text{Hg}^{2+}_{(g)}$ values for both the O/HM-1 and O/HM-2 methods as indicated in Figure 24. The data do strongly indicate that $\text{Hg}^0_{(g)}$ is effectively removed by fly ash across the station's reverse-gas baghouse.

The most recent data on mercury removals across particulate collection devices at three full-scale utilities firing PRB coal were obtained by ADA and the PSCO. One unit was a 45-MWe unit with an ESP; the other two units (110 and 350 MWe) had reverse-gas baghouses for particulate removal. The mercury data were obtained using a modified MESA Method. Triplicate measurements at the inlet and outlet of the particulate control device were made for each test series. Although vapor-particulate distributions and some mercury speciation measurements were made, these results were somewhat questionable. However, the total mercury measurements were believed to be reliable, and these were used in calculating removal efficiencies and mercury mass balances. Figure 25 shows the removal efficiency results. Also shown in this figure are removal efficiencies from a 150-MWe unit firing a bituminous Colorado coal.

The removal efficiency for the 45-MWe unit with an ESP for one test series in the summer was too inconsistent to be reliable. The calculated removals ranged from -40 to almost +60%. The removal efficiency for the winter test series was more consistent and averaged 28%. Much higher removals were seen in the two units with baghouses. For the 110-MWe unit, removals averaged 82% for the summer test series and 63% for the winter test series. The average removal efficiency for the one test series at the 350-MWe unit was 62%. These results show the adsorption capability of PRB ash. The higher removals seen with the baghouses are the result of the

contact between the flue gas and the fly ash provided by the filter cake. The material balances for these tests were very good, generally $\pm 20\%$, giving confidence to the removal efficiency results.

For the test with the Colorado bituminous coal, the removal efficiency of the baghouse averaged 98% in one test series and 99% in another. These suggest that this fly ash may be an even more effective sorbent than PRB fly ash. However, the mercury mass balances for these tests were biased high (>150% closure), with more mercury measured in the ash than entering the unit in the coal. Nevertheless, the extremely low concentrations of mercury measured in the stack (<0.1 $\mu\text{g}/\text{Nm}^3$) indicate that further research with this ash is warranted.

These results demonstrate the influence of the fly ash in capturing mercury in flight (upstream of an ESP) and across the baghouse from the combustion of these Western PRB and bituminous coals (Haythornthwaite et al., December 1998 and June 1999). Many bench- and laboratory-scale investigations are being performed to determine the mechanisms involved with this fly ash and vapor-phase constituents to provide high levels of $\text{Hg}^0_{(g)}$ capture. Tests are also being conducted with fly ashes from other PRB/subbituminous coals shipped from the Absaloka mine, Wyodak seam, Big Sky mine, and of course, Belle Ayre mine (Blythe et al., 1999; Brown, et al., 1997; Galbreath et al., 1998; Huggins et al., 1999; Laudal et al., November 1996, December 1997; Senior et al., June 1997).

The underlying conclusion from all of these studies is that fly ash from the combustion of the Western PRB/subbituminous and certain bituminous coals tested can effectively adsorb mercury compounds from flue gas. Research is being conducted to identify the mechanisms involved with the high adsorption capacities for Hg associated with PRB fly ash, and the possible mechanisms inhibiting Hg sorption. Bench-scale studies under controlled conditions, combined with identification of the mercury compounds sorbed onto the ash from these experiments may help to understand the chemistry involved.

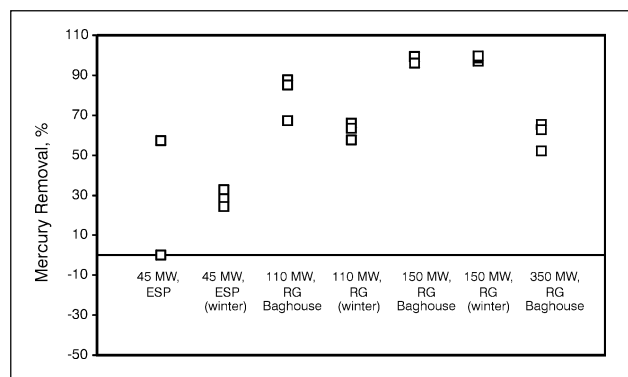


Figure 25. Mercury removal across full-scale particulate collectors (Haythornthwaite et al., June 1999).

Mercury speciation and sorption mechanisms for eastern bituminous coals appear to be much different than those for many western PRB/subbituminous and bituminous coals. The data on eastern bituminous coals suggest that the vapor-phase mercury is predominantly in the oxidized form and that there is generally less natural adsorption than for subbituminous coals. The fly ash, therefore, appears to catalyze the vapor-phase oxidation. Sorption seems to be related to the carbon content rather than to the mineralogy of the ash. The following discussion emphasizes the studies on eastern bituminous coals.

Typical Hg removal for fly ash from the combustion of low- and medium-to-high sulfur bituminous coals is approximately 15% or less, and the measured value can be influenced by the sampling method. The fly ash is captured on a filter of the sampling train at 250 °F (121 °C, which is lower than the flue gas temperature) before the chilled impinger solutions used to collect the vapor-phase Hg. Passing of the flue gas through the captured fly ash on the filter can provide false indications of in-flight capture of Hg. As indicated, the assumed removals of Hg by fly ash in-flight can be inflated based on the sampling method, but in most cases are below 15% (DeVito et al., 1997, 1999; EPRI, 1994; Hargis, Jr., et al., 1996; Holmes et al., 1997; Laudal et al., November 1996, November, 1997, December 1997; Miller et al., 1994, 1995; Redinger et al., 1997; Waugh et al., 1997; U.S. DOE Report, 1996).

Full-scale mercury speciation characterizations were conducted by CONSOL at five utilities firing medium-to-high sulfur bituminous coals during the past two years. Mercury measurements were made on samples collected from the bottom ash of the boilers and, where applicable, the economizer ash. Most importantly, ESP hopper ash was collected during the flue gas sampling at the inlet and outlet of each ESP, with all being analyzed for mercury. In addition, flue gas sampling was done at the inlet and outlet of each WFGD system, along with the other effluent streams, to characterize the Hg removal (DeVito and Rosenhoover, 1999). The WFGD Hg removals were previously indicated in Figure 8.

The sampling efforts at the various ash collection locations indicated Hg removals between 7 and 35% of the total Hg in the coal. No significant level of Hg (Plants 3 and 5 indicated approximately 2%) was measured in the bottom ash samples of the pulverized coal-fired (PC-fired) plants, but the stoker-fired unit (Plant 4) indicated 13% of the total Hg was associated with this ash. In general, the economizer ash samples for the applicable units (PC-fired; Plants 1, 2, 3, and 5) indicated insignificant amounts of Hg. On the other hand, ESP ash samples indicated the majority of the Hg removed compared to the other fly ash samples. Mercury removal ranged from 7 to 13% and averaged 9.3%. In contrast, the stoker-fired unit (Plant

4) indicated the highest Hg removal with an average of 35% for the ESP ash. Plant 4 ESP ash also had the highest amount of carbon at approximately 45%, which could account for the high Hg removal.

Table 17 provides a comparison of the percentage of total Hg associated with the five ESP hopper ash samples and the percentage of carbon in each ash sample. While the higher percentage of Hg is in the ESP ash from the stoker-fired unit (Plant 4) and is associated with the highest percentage of carbon of all the fly ashes, the other four plants do not show this association. Plants 1, 3, and 5 show relatively the same percentage of Hg associated with the ash, while the percentage of carbon in the ESP ash ranged from 0.01 to 5%. Plant 2 has a relatively small percentage of Hg while the percentage of carbon is 35-350 times higher than Plants 1, 3, and 5, with a range of 32-38%.

Analyses of the Hg data from the most recent and previous pilot-scale and field studies indicate coal composition, and the resulting vapor and particulate-phase constituents may influence not only Hg speciation in the flue gas, but may have a greater impact on the Hg adsorption characteristics of the fly ash (Schmidt and Brown, 1994; PSI et al., 1997; Laudal et al., December 1997 and December 1999). During the five field sampling efforts, daily coal samples were collected and comprehensive coal analyses were done; little variability in Hg and chlorine concentrations were observed in these samples. The five plants were firing high-sulfur bituminous coal with a nominal sulfur content of 3.7%. Illinois Basin bituminous coal(s) were fired at Plants 1, 2, 4, and 5 with nominal Hg concentration of 0.09 ppmw, and a blend of southern Ohio coals was fired at Plant 3 with a Hg concentration of 0.19 ppmw. The Hg concentrations were fairly consistent and representative of most U.S. coals, with the exception of Plant 3, which has twice the Hg concentration in the coal. Chlorine concentrations in the coals ranged from 1100 to 2300 ppmv, which is consistent with eastern bituminous coals.

The percentage of Hg²⁺ of the total vapor-phase Hg in the flue gas entering the five WFGD systems at the plants ranged between 55 and 85%, with removal of the Hg²⁺ ranging from 86 to ~95%. This indicates that the Hg²⁺ at each plant was soluble in the lime-based slurries utilized in WFGD systems for high SO₂ removals, which ranged between 82 and 96%. NO_x concentrations were not measured at the plants and could have been highly variable among the plants, as reflected in the variability in both the carbon content of the fly ashes and the O₂ levels measured at the outlet of each boiler. The section entitled Activated Carbon and Other Sorbent Injection Technologies for Mercury Capture details studies conducted by the EERC on the effects of NO_x, specifically NO₂ on the adsorption and conversion of Hg⁰ associated with activated.

Table 17. ESP ash Hg removal; percent of total Hg input.

% Hg Removed in Ash	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5
Number of Tests	4	3	3	4	3
Hg in ESP Ash	7	13	8	35	9
% Carbon in ESP Ash	0.8-1.2	32-38	0.1	41-44	2-5

Over the past five years, many mercury speciation sampling efforts have been funded by the DOE, EPRI, CONSOL, Ohio Coal Development Office (OCDO), Illinois Clean Coal Institute (ICCI), and others to investigate the removal of mercury and its forms across existing APCDs. Most importantly, they have been designed to aid in identifying and understanding the possible mechanisms involved with the oxidation and adsorption of mercury. This involves the interactions with the fly ash and the role that the vapor-phase constituents have on speciation and adsorption of the Hg. The bench- and laboratory-scale tests conducted under the DOE, EPRI, EPA, and USGS funding have provided valuable quantitative information on Hg modes of occurrence, speciation of mercury, and its potential to be captured with the fly ash and novel sorbents (e.g., AC). This also includes the understanding of the potential capture across existing APCDs (e.g., wet and dry FGD systems) utilized in the utility industry.

Radian has been conducting both laboratory and field studies, under the DOE's Mega PRDA Program, to investigate the possible catalytic oxidation of vapor-phase Hg⁰ in coal-fired utility flue gas streams. The objective of this research is to investigate the catalytic oxidation of vapor-phase Hg⁰ to increase the total Hg²⁺ removal in existing APCDs (e.g., WFGD), and in other developing Hg control technologies (e.g., sorbent injection). Having >90% of the Hg in one form (Hg⁰ or Hg²⁺) is important for maximum Hg capture. Not all technologies being developed capture both forms of Hg effectively. Catalyst materials that were identified and warranted further investigation included several ACs, iron-based materials, a conventional SCR catalyst, and various coal combustion fly ashes.

Testing of the catalysts at the EPRI ECTC facility was difficult owing to the naturally occurring Hg²⁺ in the flue gas from the combustion of the Blacksville coal was already 90%. Samples of the particulate-laden flue gas spiked with Hg⁰ at levels as high as 90 µg/Nm³ still indicated that 80% of the Hg was being converted to Hg²⁺ as reported by the sampling methods, without the catalysts. The data also indicated that the Hg was not only easily oxidized, but most of the Hg (>80%) was subsequently removed across the pilot WFGD system. There was speculation that a possible interaction between the fly ash from the Blacksville coal and the vapor-phase constituents was

playing a role in converting the spiked Hg⁰ to Hg²⁺.

Radian conducted fixed-bed laboratory tests with this fly ash as well as other fly ashes from different ranks of coal (all dispersed in sand) showed oxidation of Hg⁰, with many of the fly ashes having different Hg adsorption capacities. In addition, both the oxidation and adsorption of Hg

decreased as the temperature was increased from 300 to 700 °F (149-371 °C). Preliminary tests showed that variations in SO₂ and HCl concentrations had little or no impact either on the degree of oxidation or on the adsorption capacity of the fly ash samples. As the fly ash samples were saturated with Hg (reached the equilibrium sorption capacity), the resulting Hg at the outlet of the fixed bed was measured as Hg²⁺. Radian did identify a carbon-based material, which was tested on a pilot-scale FF continuously for 10 consecutive days. High levels of Hg⁰ spiking was done and the results showed greater than 75% of the inlet vapor-phase Hg⁰ was oxidized to Hg²⁺. Greater than 90% of the Hg²⁺ converted across the carbon-based catalysts from the spiked Hg⁰ was subsequently removed across the pilot WFGD system.

Radian has tested the ability of a variety of fly ashes from the combustion of lignite, bituminous, and PRB coals under simulated conditions without NO_x for both the adsorption of Hg⁰ and Hg²⁺ and the oxidation of Hg⁰ to Hg²⁺ (see Figure 64 and the narrative for the figure under Radian International in the section entitled Enhancing Mercury Capture in Flue Gas from Utility Wet Desulfurization (WFGD)). Figure 26 shows the sorption capacities for one fly ash both Hg⁰ and Hg²⁺ at different LOI. The figure also compares the fly ash results to those for an activated carbon (FGD carbon also designated as LAC, from a lignite coal). As previously indicated, the LOI for this fly ash varied from 0 to 82% with the fly ash being collected from different locations within the power plant (Carey et al., August 1997).

The figure also implies a correlation between an increase in LOI and an increase in mercury (both Hg⁰ and Hg²⁺) adsorption. The full-scale data collected by CONSOL do not show a correlation between the carbon content of the ash (carbon content of fly ash is essentially the same as LOI) and an increase in mercury sorption. The laboratory- and full-scale data both indicate that a larger increase in fly ash carbon content does not necessarily result in a higher mercury sorption capacity compared to fly ashes with lower LOI or carbon concentrations.

As previously discussed, ADA Technologies data for a PRB fly ash with a carbon content of >0.5% showed effective in-flight mercury removal and effective mercury

removal across both a pilot- and full-scale fabric filter. All of the data suggest that factors other than just carbon content may be important in determining the adsorption capacity and rate of adsorption of Hg. The formation of the carbon during the combustion processes, the associated elements and compounds of these elements with the carbon, and the vapor-phase constituents may play more of a major role than anticipated. Work is being conducted to ascertain what factors are important in mercury adsorption and oxidation.

While the sorption capacities of the fly ash are much lower than that of the FGD carbon, model predictions by Radian indicate that the measured capacities are sufficient to effect measurable mercury capture in utility flue gas streams.

Similar results were obtained at a full-scale facility by measuring oxidation of carbon on the filter of a Hg speciation sampling method. These results confirmed the ability of the carbon-based material to oxidize Hg⁰ under different flue gas conditions (with and without HCl and various levels of NO_x). Several other catalyst materials that were identified and the recent results of their testing are presented in the section entitled Mercury Control Technology Investigations and Development for Coal-Fired Utility Applications (Carey et al., June 1996, July 1996, August 1997; Radian International et al., 1997).

Earlier studies indicated gas-phase Hg²⁺ is readily captured by AC, while Hg⁰ has a much lower affinity for carbon. Researchers postulated that the surface of the carbon is crucial for adsorbing both Hg²⁺ and most importantly Hg⁰; adding sulfur or iodine can dramatically increase the capacity of AC for elemental mercury (Dunham and Miller, 1996; Krishnan et al., 1994; Vidic and McLaughlin, 1996). Residual carbon from coal combustion is not the same as AC. The pore structure, surface properties, and inorganic content may be strikingly different. Nonetheless, coal char does have some capacity for adsorbing mercury. Based on

recent experimental work (Senior et al., 1997), it can be concluded that the mechanisms for adsorption of Hg⁰ and Hg²⁺ on coal char are very different. Properties of the coal char (surface area, sulfur content, and forms of sulfur) have been shown to determine the amount of mercury adsorption. While there is evidence for the adsorption of mercury on coal fly ash (Carey et al., June 1996, July 1996), the specific species that are adsorbed are not known.

Recent laboratory- and pilot-scale evidence suggests that solids such as AC and fly ash can not only adsorb Hg²⁺, but can adsorb Hg⁰ with the solids, acting as catalysts to oxidize elemental mercury. Kinetic experiments in a continuous flow reactor showed that the oxidation of Hg⁰ by oxygen only occurred in the presence of AC (Hall et al., 1991). In a series of bench-scale experiments Radian International explored the catalytic effect of solids, including traditional metal catalysts, AC, and coal fly ash, on the oxidation of Hg⁰ in simulated flue gas fixed-bed reactor. Fly ash from five different coals was tested at temperatures of 300 and 700 °F (149 and 371 °C) (Carey et al., June 1996). The results showed that some coal fly ashes converted gaseous Hg⁰ to Hg²⁺ while adsorbing the Hg⁰. At 300 °F (149 °C), 20-50% of the Hg⁰ was converted to a gaseous oxidized form, probably HgCl₂ based on equilibrium considerations, while 0-80% was adsorbed from the solids. It is unknown what the adsorbed species may be, but it is speculated that they could be HgCl₂, HgO, or HgSO₄. There was a wide variation in the amount of adsorbed mercury depending on coal type. At 700 °F (371 °C), less Hg⁰ was observed to be adsorbed and converted.

Until recently, the mechanisms for adsorption of mercury could only be inferred from flue gas speciation measurements and total mercury analysis of solid material. The speciation measurements only differentiate between elemental and oxidized forms, and this differentiation may not be exact as a result of the sampling train influences. Direct evidence of the compounds of mercury formed on the solids is needed to elucidate the mechanisms. Research by Huggins, Huffman, and Senior using a powerful new tool, X-ray absorption fine structure spectroscopy, or XAFS, may be able to provide this direct evidence. Measurements can identify various compounds, such as HgO, HgS, and HgCl₂. Information on the reactions of mercury species with fly ash can now be obtained by identifying specific mercury species on the surface of char or carbon and then inferring the reaction pathway. A preliminary analysis of the forms of mercury on four carbon-based sorbents (as described in PSI et al., 1997) was recently completed (Huggins et al., 1997). These samples were treated with a simulated flue gas containing N₂, O₂, CO₂, SO₂, H₂O, HCl, and Hg⁰.

To better understand the forms of adsorbed mercury,

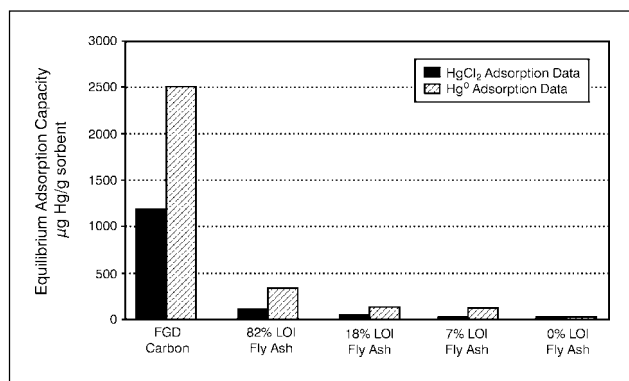


Figure 26. Sorption capacities and oxidation capabilities of one fly ash for both Hg⁰ and Hg²⁺ at different LOI compared with an activated carbon (Carey et al., August 1997).

XAFS spectra were collected at the mercury LIII edge at approximately 12,284 eV at the Stanford Synchrotron Radiation Laboratory. By combining the XAFS spectra with additional X-ray absorption near-edge structure (XANES) spectra, one could speculate that the type of Hg bonding in the three different mercury sorbents is different. In the iodine-impregnated activated carbon (IAC), the mercury bonding appears consistent with Hg-I. In the sulfur-impregnated carbon (SAC) and LAC, the bonding is more consistent with Hg-Cl or Hg-S. Further study, particularly of the Cl-edge XAFS spectra in the SAC and LAC samples, is required.

Thus, particulate matter can promote oxidation of Hg⁰ and collect a significant amount of mercury in flue gas. The amount retained in the particulate matter seems to depend on carbon content, properties of the carbon surface, inorganic constituents in carbon particles, fly ash composition, mercury speciation in the flue gas, and vapor phase constituents (SO₂, NO_x, HCl, etc.).

Recent studies (Huggins et al., 1999) looked at the chars from two bituminous coals (Pittsburgh and Illinois) and one subbituminous coal (Wyodak) after exposure to mercury. Both Hg⁰ and HgCl₂ were introduced to a laboratory fixed-bed reactor containing the chars at 158-320 °F (70-160°C). A simple gas mixture of oxygen, nitrogen, and moisture was used. After exposure, the chars were analyzed by XAFS. When the chars were exposed to HgCl₂, the adsorbed species appeared to be a mercury-chlorine compound; whereas Hg⁰ exposure, the chars contained a mixture of Hg⁰ and HgCl₂, depending on the amount of chlorine in the coal. The researchers concluded that "there are likely to be a number of competing mechanisms for low-temperature mercury sorption by a given material in a real flue gas." Future studies will identify mercury compounds adsorbed on solids from realistic flue gases.

These chars and fly ashes with varying carbon contents are being investigated and analyzed with very novel and sophisticated diagnostic techniques to aid in determining the constituents of the solid matter responsible for Hg sorption. In addition, these techniques are being utilized to determine the form of Hg associated with the particulate matter by several research organizations.

Tests conducted by the EERC and Radian have indicated, in their respective fixed-bed facilities under simulated flue gas conditions, vapor-phase constituents (SO₂, NO_x, and HCl) have some, but generally little or no, effect on the adsorption and oxidation of Hg with the fly ash collected at full scale. Studies on fly ash samples with high LOI (high carbon) on the other hand do tend to act like AC. The impact of these gases are generally more noticeable and investigations are being conducted to search for possible mechanisms. Tests conducted under actual coal combustion conditions and while injecting certain vapor-phase constituents do indicate an impact

on both the adsorption and oxidation of Hg in flue gas. It is also a totally different story, with very dramatic effects, when these vapor-phase constituents are varied when injecting promising carbon-based sorbents for Hg capture in coal-fired produced or simulated flue gas.

The previous discussion of the factors affecting mercury speciation and sorption mainly dealt with reactions that occur naturally in the flue gas that, combined with conventional APCDs, can reduce emissions of mercury to the atmosphere. A thorough understanding of the mechanisms involved in these reactions is important in the application of engineering principles to develop control technologies specifically designed for the capture and removal of mercury. As mentioned briefly above, techniques to convert elemental vapor-phase mercury to oxidized mercury could be combined with wet scrubbing to control mercury emissions. Also, an understanding of natural mercury sorption by fly ashes would aid in the development of efficient and cost-effective sorbents for mercury control technology. The next section discusses the research efforts aimed at the development of control technology and the costs associated with such control as applied to electric utilities.

Control Technology Investigations and Development for Coal-Fired Utility Applications

Considerable effort has gone into developing efficient, low-cost technologies for mercury emission reductions from utility plants. The goal for the DOE Mercury Measurement and Control Program has been established at one-quarter to one-half of current cost estimates. DOE performed a detailed cost analysis of AC injection under four different control scenarios for the EPA for Volume VIII, Appendix B of its "Mercury Study Report" presented to Congress in December 1997. DOE's costs ranged from \$2.5 to \$6 billion annually to the U.S. utility industry to control mercury at the 90% removal level indicated by the EPA in the mercury report. Details of DOE's assumptions (including the EPA's), along with the cost estimates, can be found in a paper prepared by the FETC Mercury Team (Brown et al., July 1998). In addition, most of the cost estimates and information will be presented in this section.

There are critical factors that impact these cost analyses and estimates for the control of mercury and specifically, the 90% level indicated by the EPA. One factor or assumption utilized in the EPA cost model, and utilized by DOE for comparison in its cost estimates, was 10 µg/Nm³, of mercury in the flue gas, a level typical of 90% removal, with all the mercury being in the oxidized form. As stated earlier, coal mercury concentrations and the distribution between elemental (Hg⁰) and oxidized mercury (Hg²⁺) vary considerably while firing the different ranks of coal. Nearly 90% of all coals, regardless of rank, have

less than 100 ppbw of mercury and subsequently have less than 10 $\mu\text{g}/\text{Nm}^3$ of vapor-phase mercury with varying levels of Hg^{2+} resulting in the flue gas. Hg^{2+} is in the range of <10% to as high as 70% of the total mercury. The actual mercury control or removal level will vary from plant to plant, with one scenario indicating over 90% of the plants requiring capture efficiency well below 90%. One very important mercury control sensitivity that must be considered before any regulation(s) are determined is presented below.

Mercury Control Sensitivity

Existing coal-fired power plants have diverse coal consumption patterns that are associated with numerous power plant designs as well as the postcombustion flue gas treatment. The coal-feed system may rely on pulverization of as-received coal to very fine particles that are principally less than 200 μm , or the feed system requirements may be relaxed, such that only crushed particles are passed into the combustion chamber. This difference in burner particle size requirement creates a difference in combustion design parameters, such as heat release rates and furnace temperature profiles. The time-temperature history of the combustion products is significantly affected by these design considerations. Whether the mineral in the coal is converted to fly ash that passes through the furnace into the flue gas treatment system or is recovered from the bottom of the furnace as a slag or ash is a result of the coal-feed and boiler design specifications. The exhaust flue gas from the boiler island is dependent on these and many other factors that have been shown to be important in properly considering mercury control strategies and opportunities.

A characterization of the mercury feed to power plants, and subsequent emissions into the atmosphere as a consequence of coal-fired power generation, has been described in the emission inventory section. Existing coal preparation, combustion, and flue gas emission controls are capable of reducing the potential amount of mercury released to the atmosphere by more than 50%. These controls, however, vary considerably on a plant-by-plant and boiler-by-boiler basis and can range from essentially no control to as high as 85%.

Figure 27 shows the cumulative mercury emissions as a function of cumulative coal consumption. There are several interesting features of this plot. First, the estimated mercury emissions were sorted by ascending order of mercury emissions per ton of coal consumed. If all of the power plants emitted mercury at the same emission rate, a straight line would result. However, as can be seen in the figure, estimated mercury emission rates are quite low for the first 10% of cumulative coal consumption and increase steadily beyond this point. At the point for which

two-thirds of the coal consumption has been accounted, only about one-half of the total mercury emissions are realized. Therefore, the remaining one-third of the national coal consumption accounts for half of the U.S. mercury emissions. This portion of the boiler population tends to use either bituminous coal or lignite and are generally not equipped with FGD systems.

A sensitivity analysis for mercury emission control has been performed to examine how control options may impact the diverse power plant population. The first option, shown in Figure 27, considers setting a cap on emissions of 0.03 tons of mercury emitted per million tons of coal consumed. At this level of control, about 10% of the power plants that have low mercury emissions come under the cap with little or no additional controls needed. For about half of the total coal consumption, less than 40% additional control would be required. On about 10% of the total coal consumption, fairly significant control would be required, ranging from two-thirds to 85% reduction from the existing emissions level. The overall reduction in mercury emissions from the national mercury emissions inventory estimate for the reference year 1996 is about 50%.

In the second option, a 90% reduction of mercury contained in the mined coal is considered. This scenario credits mercury removal from coal preparation and existing power plant controls toward the overall goal of a 90% reduction. Approximately 60% of the coal consumed would require controlled reduction between 80 and 90%. Nearly 98% of the coal consumed would require reductions of at least 50%. The overall reduction in mercury emissions from the national mercury emissions inventory estimate for the reference year 1996 is about 80%.

This sensitivity analysis demonstrates that mercury control options are highly dependent on the existing power plant's operating characteristics and design. As stricter control options are considered, the flexibility to achieve these reductions begins to diminish.

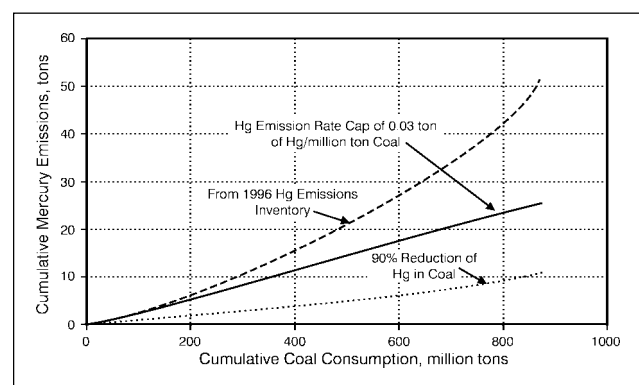


Figure 27. 1996 mercury emissions and control scenarios (Smith, D.N. 1999).

Sponsors of Mercury Control Research and Development for Coal-Fired Utility Applications

Much of the mercury research in the United States is being sponsored by four organizations: the U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC), the Electric Power Research Institute (EPRI), the U.S. Environmental Protection Agency (EPA), and the United States Geological Survey (USGS). This section describes ongoing mercury control research conducted under DOE/FETC funding, along with the collaborative efforts with the other three organizations. The results to date are summarized.

Tables 18-21 list the areas of research currently being sponsored by the four organizations regarding control of mercury emissions from coal-fired utility boilers.

DOE's Initiated and Collaborative Air Toxics Emissions Measurement and Control Programs

The FETC (formerly, PETC) of DOE's Office of Fossil Energy (FE) issued a Request for Proposals (RFP) in late 1992 to perform comprehensive assessments of HAPs from at least 14 coal-fired power plants. A total of five contractors were selected to perform a total of eight assessments in Phase I of the program and potentially eight more in a Phase II effort. The introduction of this document indicated some of the results of these efforts, with other assessments being addressed throughout the document.

One of the goals of these assessments was to acquire data as input to the EPA's "Study of Hazardous Air Pollutant Emissions from Electric Steam Generating Units" and the "Mercury Study Report" that were mandated under Title III of the CAAA. The FETC's \$12 million HAPs Characterization Program, along with EPA funding of \$250,000 for the quality assurance and quality control (QA/QC) aspects, conducted eight utility assessments prior to January 1, 1994. These assessments were coordinated and in collaboration with the EPRI, the Utility Air Regulatory Group, and the EPA. In addition, the FETC characterized an additional three plants since 1994, with one being an advanced coal gasification unit. One of these units was equipped with an on-site coal preparation plant and the other was equipped with an ESP and WFGD system. The FETC plans to characterize two more plants during 1999 and 2000 in coordination with transport and deposition studies in the Lake Superior Basin.

Work under this program also involved the characterization of trace metal removal capabilities of the various conventional and advanced pollution control devices enabling utilities to predict the distributions and releases of these analytes. With both the DOE and EPRI data, Ralph Roberson of RMB Consulting developed an important algorithm, correlating trace element concentrations in the coal with particulate removal device efficiencies of ESPs and FFs. This algorithm is being utilized by coal-fired utili-

ties to estimate trace element releases as required under the EPA's TRI reporting. This has provided a substantial cost savings to the utility industry by eliminating extensive sampling efforts to determine the trace element releases. Assessing of trace element source, distribution, and fate, indicated mercury was the key analyte selected for further research and control development.

Results of these assessments can be obtained from a variety of documents including: the DOE Report prepared by the UNDEERC entitled "A Comprehensive Assessment of Toxic Emissions for Coal-Fired Power Plants: Phase I Results from The U.S. Department of Energy Study," September 1996; EPRI's "Electric Utility Trace Substances Synthesis Report - Volumes 1-4," Report No. TR-104614-V3, Project 3081,3297, November 1994; and the EPA Mercury Study Report issued December 1997, and the Study of Hazardous Air Pollutant Emissions from Electric Steam Generating Units Report issued February 1998.

FETC also issued a two-phase Program Research and Development Announcement (PRDA) in early 1995 for innovative concepts to control all possible air pollutants from the combustion of coal. The PRDA solicited proposals to address precombustion, combustion, and postcombustion understanding and control of the possible pollutants, including trace metals associated with fine particulate, and highly volatile mercury and its associated forms. The PRDA was appropriately titled "Advanced Emissions Control Technology (or Mega PRDA) Program," with nine different topic areas. Topic 7 of the PRDA dealt with the trace element and mercury understanding and subsequent control technology development of these potential hazardous pollutants. A requirement under the RFP was a 20% or more cost share from the proposers to support the project during both phases of the research and development. In addition, there was a down selection after Phase I to select the most promising projects for funding under Phase II.

Eleven Phase I mercury control projects were selected with DOE funding of \$14 million and a cost share totaling \$3 million. EPRI, the contractors, and several utilities provided the >20% cost share for both phases of the program. The Phase I efforts began in October 1995 and encompassed two years of laboratory- and bench-scale testing and evaluation of several approaches for controlling the emission of mercury from coal-fired utility boilers. The approaches included those listed in Table 18. In September 1997, DOE selected six Phase II proposals (2-3-year efforts) to further investigate and develop fine particulate and mercury control technologies and concepts. Details of the research efforts will be provided in other sections below. The six Phase II projects required a DOE funding level of \$7.2 million while EPRI, the contractors, and the utility industry provided nearly \$2 million in cost sharing.

Table 18. Current U.S. DOE/FETC funded mercury control research for utility boilers.

Contractor	Research Area
Radian [†] , Physical Sciences, Inc., (PSI) [†] , Univ. of Pittsburgh (UPitt), Univ. of Washington, UNDEERC ² , CONSOL ³ , Univ. of Iowa & AMES Labs.	Fundamental and bench-scale investigation of adsorption and conversion of mercury by fly ash
Radian, PSI [†] , CONSOL, UNDEERC, Univ. of Washington, Univ. of Kentucky (UKen), Univ. of Iowa & AMES Labs., UPITT, Univ. of Cincinnati	Fundamental & characterization studies; model development/predict Hg speciation, partitioning, and fate - advanced measurement methods
UPitt, PSI [†] , DOE/FETC In-House R&D (DOE/FETC), Radian [†] , UNDEERC, ADA Technologies, (ADA), UKen, TDA Research Inc. (TDA), University of Cincinnati	Fundamental and bench-scale studies on enhanced sorbents for mercury adsorption - advanced diagnostic instrumentation
Public Service Comp. of Colorado (PSCO) [†] , ADA [†] , PSI, UNDEERC [†] , TDA, DOE/FETC, Environmental Elements Corp.	Pilot-scale field studies on sorbent injection for conventional APCDs and waste characterization
Radian [†] , Argonne National Laboratory, McDermott Technology, Inc., UNDEERC	Enhanced removal of oxidized and elemental mercury in wet FGD systems
ADA [†] , Radian [†] , DOE/FETC, UNDEERC, Environmental Elements Corp.	Capture of total mercury with regenerable sorbents; Conversion of Hg ⁰ to Hg ²⁺
PSCO [†] , ADA [†] , CONSOL, UNDEERC, DOE/FETC, PSI [†] ,	Characterization and stabilization mercury in fly ashes and sorbents
DOE/FETC, EXPOR Tech; Previous Work: CQ Inc. [†] , ICF KAISER, VPI&SU ^{4†} , Little Bear Industries [*] , Entech Global, CONSOL	Coal cleaning (physical, dry magnetic separation, biological, mild chemical)
UNDEERC, ADA, DOE/FETC, Advanced Technology Systems, Radian	Development, evaluation & validation, of manual Hg measurement methods and continuous emission monitors (CEMs)

¹ Radian International

² UNDEERC - University of North Dakota Energy & Environmental Research Center

³ CONSOL INC, major bituminous coal producer in the United States

⁴ Virginia Polytechnical Institute & State University

* MegaPrda - Phase I Projects, † Phase I and Phase II, only five, but multiple R&D efforts

The DOE/FETC Mega PRDA Program and associated projects represent the largest mercury control development program for the coal-fired utility industry in the United States and in the world. The following six Phase II research and development projects are 2-3-year efforts to further investigate and develop fine particulate and mercury control technologies and concepts.

- (1) ABB Power Plant Laboratories, Combustion Engineering, Inc., Windsor, CT: "Ultra High Efficiency Electrostatic Precipitator (ESP) Development for Air Toxics Control." Approximately \$1.3 million for 30 months, including approximately \$300,000 cost sharing by ABB Power Plant Laboratories.

ABB Power Plant and ADA are investigating novel improvements to ESPs for more efficient collection of particles less than 2.5 mm in size and the trace toxic metals associated with these particles. Phase I tested flue gas cooling using moisture or heat exchangers. The investigators were able to cut fine particle levels below the current required standards for par-

ticulate matter of 0.03 lb/million Btu down to a value below 0.01 lb/million Btu. In addition, one of the mercury control technology options for utilities is to inject fine carbon particles, along with moisture, to reduce the flue gas temperature resulting in high mercury capture. This option captured more than 90% of the mercury found upstream of the ESP. Phase II will test carbon particle injection, with the added moisture, in a pilot-scale facility drawing flue gas from a full-sized utility burning a variety of coals.

- (2) ADA Technologies, Inc. (ADA), Englewood, CO: "A Novel Process for Removal and Recovery of Vapor-Phase Mercury." Approximately \$1.1 million for 24 months, including approximately \$200,000 cost sharing by ADA.

ADA, and its participants, CONSOL, Public Service Gas & Electric, and Burns and McDonnell, are developing a process with highly efficient mercury removal and recovery, and sorbent regeneration and reuse, which has

Table 19. Current Electric Power Research Institute funded Hg control research for utility boilers.

Sponsor	Research Area
Electric Power Research Institute	Bench-scale: adsorption of Hg onto fly ash, activated Carbon, & other novel sorbents; Sorbent regeneration, & recycle; Stability of adsorbed Hg
	Fundamental studies & model development to predict mercury speciation, partitioning, and fate in coal-based power systems
	Field scale: pilot tests (two sites) of sorbent injection with ESP's and fabric filters Model development to predict sorbent injection effectiveness and cost
	Wet scrubber controls for mercury, oxidation of Hg ⁰ to soluble forms
	Multi-pollutant (NO _x , SO _x , Hg, particulate) control process development
	Field and laboratory assessment of novel Hg control processes

Table 20. Current U.S. Environmental Protection Agency funded Hg control research for stationary sources.

Sponsor	Research Area
U.S. Environmental Protection Agency	Bench-scale research and modeling of Hg speciation in combustion systems (coal-fired boilers and incinerators)
	Development and evaluation of multi-pollutant sorbents
	Engineering and economic studies of Hg emission control technologies and pollution control options
	Evaluation of coal mercury data and coal-fired power plant data being collected by the utility industry
	Experiments to evaluate the stability of Hg in air pollution control device residues
	Pilot-scale tests to evaluate carbon based Hg sorbents and lime-based multi-pollutant sorbents in a fluidized-bed dry scrubber and a pulse jet baghouse
	Evaluation of manual Hg measurement methods and continuous emission monitors

been termed "Mercur-RE." This process uses gold, or other precious metals, as the sorbent to capture mercury in its various chemical forms at ordinary flue gas temperatures and to desorb the Hg from the gold in order to recover the mercury as a useful byproduct. Neither the Mercur-RE process nor the captured mercury will have an impact on waste disposal or byproduct recovery of other materials produced as a result of coal combustion. Phase I investigations were conducted at the laboratory and bench scale to assess the effective use of gold-when used in a kind of open metal honeycomb structure to allow coal-fired utility flue gas to move freely through it-to cap-

ture and recover mercury. Phase II will conduct long-term testing of the gold-coated metal honeycomb structure for mercury capture and recovery. This work will provide important information on the durability of the gold after many cycles of capturing and recovering mercury from the flue gas. The investigators will also explore increasing the scale of the process for commercial utility use.

(3) Physical Sciences, Inc. (PSI), Andover, MA: "Toxic Substances from Coal Combustion - A Comprehensive Assessment." Approximately \$3.4 million for 36 months, including approximately \$700,000 cost sharing by PSI.

PSI is conducting a fundamental investigation to predict the distribution and fate of mercury, arsenic, chromium, and their various chemical forms from a variety of combustion conditions. Knowing the form, or forms, is important in understanding the potential risks-because chemicals can be more toxic in some forms than in others-and to develop strategies to capture specific trace elements. Both research phases of this project are studying what happens to these chemicals during combustion and postcombustion operations in

order to understand how the chemicals change and to set up strategies to capture them. This information is useful to the eventual development of highly effective low-cost mercury control. Both experimental and modeling activities will be conducted with a variety of coals under different combustion conditions to develop an engineering model to predict the distribution and subsequent fate of the metal species. PSI is teamed with the following participants: the Massachusetts Institute of Technology, University of Kentucky, University of Arizona, University of Connecticut, Princeton University, University of Utah, and UNDEERC. The USGS, EPRI, and

Table 21. Current U.S. Geological Survey funded mercury research for coal utilization.

Sponsor	Research Area
U.S. Geological Survey	Development of updated coal quality inventory for U.S. coals
	Development of reliable coal quality inventory of foreign coals
	Generating quantitative information on Hg modes of occurrence
	Collaboration with CQ, Inc., on developing model(s) for Hg behavior during coal cleaning

VTT/ATG (Finland) are also cooperating; and a Technical Advisory Board, consisting of the EPA, CONSOL, ABB Combustion Engineering, DB Riley, and New England Power, has been formed.

- (4) Public Service Company of Colorado (PSCO), Denver, CO: "Investigation and Demonstration of Dry Carbon-Based Sorbent Injection for Mercury Control." Approximately \$1.5 million for 36 months, including approximately \$300,000 cost sharing by PSCO.

PSCO and its team members, ADA and EPRI, are demonstrating mercury removal with a pilot-scale technology to inject carbon, or other solid chemical capturing materials, as part of a coal-fired utility APCD, such as an ESP or FF. The investigators are conducting engineering and economic studies to look at the technology's fit in different utility configurations. Phase II will take the most promising technologies to increasing size scales from the small pilot-scale to near full-scale designs, with the goal of demonstrating them commercially.

- (5) Radian International LLC, Austin, TX: "Enhanced Control of Mercury and Other Hazardous Air Pollutants (HAPs) by Innovative to Wet Flue Gas Desulfurization Processes." Approximately \$895,000 for 12 months, including approximately \$200,000 cost sharing by EPRI and Radian.

Radian and its team members, Electric Power Research Institute and Meserole Consulting, are investigating the conversion of elemental mercury to a more soluble form to remove more than 95% of it with WFGD systems. On average only 50% of the mercury is captured in WFGD systems because elemental mercury is not soluble. This process has the potential to decrease mercury emissions as much as 10 tons/year from the estimated U.S. total emission of 52 tons/year. In Phase I, the project tested the actual rate to convert elemental mercury to a soluble form using several iron-based catalysts and carbon, under simulated and actual flue gas conditions, with the subsequent removal across the WFGD system. Phase II will evaluate the most promising catalysts at the pilot scale and under

more realistic conditions at three coal-fired utilities.

- (6) University of North Dakota, Energy and Environmental Research Center (UNDEERC), Grand Forks, ND: "Advanced Hybrid Particulate Collector." Approximately \$840,000 for 24 months, including approximately \$170,000 cost sharing by the UNDEERC.

The UNDEERC is investigating a highly reliable advanced hybrid particulate collector that can provide more than a 99.99% collection efficiency rate for all particle sizes and will be applicable for use with all U.S. coals and cost-competitive with exist-

ing technologies. The UNDEERC is teamed with W.L. Gore and Associates, Inc. and Allied Environmental Technologies Company. The concept is based on integrating ESP principals and FF technology to create particulate control devices that will be as much as 75% smaller than similar conventional devices. In Phase I, a working model was designed, constructed, and installed for testing at a 200-actual cubic feet per minute slipstream from a pilot-scale coal-fired combustor. Testing indicated both particulate and toxic trace element removals greater than 99.99%. Phase II will consist of long-term testing on a slipstream (9000 acfm) from a full-scale coal-fired utility site. The larger scale testing will provide both technical and economic data for commercial utility applications.

Other Important Collaborative Efforts

The FETC Mercury Team was part of a federal interagency review of the EPA Mercury Study and Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units Reports submitted to Congress. The FETC and EPRI's contributions on recent research and development (1995-1997) on mercury measurement and control were incorporated with 40 additional pages added to Chapter 2 of Volume VIII of the Mercury Study Report. FETC and EPA costs for control were compared throughout the report. The Mercury Team aided in expanding the research and development requirements/needs before regulatory determinations are considered.

The FETC team and EPA addressed the uncertainties and the need for more research and development regarding emissions and potential health effects of mercury, arsenic, dioxin and furan compounds, HCl and HF, and nickel subsulfide of the Utility HAPs Report. The EPA and DOE are collaborating on an investigation/sampling effort of dioxin and furan compound formation at a utility equipped with a hot-side ESP. The sampling event will be conducted in July 1999, with the findings of this study potentially having a significant impact on coal-fired utilities for the reporting of these potential hazardous pollutant emissions

under EPA TRI requirements.

The FETC met with the EPA representatives in March 1998 at their Research Triangle Park, NC offices to discuss the DOE/FETC Mercury Control Technology Research and Development Program and the maturity level of the FETC's mercury control technologies developments for coal-fired utilities. Discussions also addressed mutual and future collaborative research and development efforts. The EPA representatives were from the Office of Air Quality Planning and Standards (OAQPS): Emissions Standards Division; Air Pollution Technology Division; Air and Energy Engineering Research Laboratory; Risk and Exposure Group; and the Great Waters Program Office.

The EPA in collaboration with the DOE/FETC, EPRI, and USGS organized and coordinated a workshop on "Control of Mercury Emissions from Combustion Sources." The workshop was held on October 27 and 28, 1998, at the EPA offices in Research Triangle Park. At the time, EPA was in the process of expanding its program on the control of air pollution emission of mercury from combustion sources. A primary goal of its effort is the development and evaluation of technologies for the control of mercury emissions from coal-fired utility boilers and waste combustion systems. A short planning meeting was held after the workshop to discuss EPA's expanded research program and to discuss the best means of designing the EPA program to feature the past and ongoing work of the DOE/FETC, EPRI, and USGS. Collaborative efforts were the main topic of discussion. The four organizations are developing a plan for assessing mercury control strategies, larger-scale demonstrations of the promising technologies, and the level of control that would be required. A draft plan will be completed during the fall of 1999.

The FETC Mercury Team also collaborated with CONSOL, the UNDEERC, EPRI, and EPA by providing technical information on the sampling of coal for determining mercury concentrations, and the flue gas mercury speciation method selection for the EPA's ICR. The FETC also provided reports on the sampling efforts that it funded or collaborated on for mercury, including speciated mercury. The reports also included plans for other sites to be tested under DOE funding during the ICR request period. The FETC is collaborating with the EPRI to conduct the sampling efforts for mercury speciation measurements of the approximately 70 utility boiler systems selected by the EPA. DOE will collaborate with the utility industry and UNDEERC under the JSRP between DOE, EERC, and industry. In addition, efforts are being planned to collaborate with CONSOL on other field sampling efforts designed under the EPA ICR. DOE will also be funding the QA/QC auditing of sampling contractors performing the mercury speciation measurements under the ICR.

The EPRI and FETC collaborated and funded a \$3 mil-

lion program under the DOE/UNDEERC JSRP to evaluate, develop, and validate a mercury speciation method for coal-fired produced flue gas. There was a 60/40% split of the funding, as required under the JSRP for this two-year effort. The work conducted by the EERC indicated the Ontario Hydro Method as the best mercury speciation method. The EERC has validated the method at the pilot and full-scale (Radian aided in the full-scale validation), with a written protocol of the method being finalized through the ASTM.

The protocol was written by the EERC and was reviewed and finalized under the ASTM Committee D-22 on Sampling and Analysis of Atmospheres. Under Subcommittee D22.03 on Ambient Atmospheres and Source Emissions, a working group was formed for "Manual Method for Both Speciated and Elemental Mercury Determinations." This working group has representatives from Land Instruments International, FETC, EPRI, EERC, EPA, RMB Consulting, CONSOL, Consultant Barry Jackson, ADA, U.S. Department of Commerce/National Institute of Standards and Technology (NIST), PS Analytical, McDermott Technology, Inc., and Dr. Keith Curtis of Ontario Hydro, who originally developed the method.

The Ontario Hydro Method is specified under the EPA's ICR as the method to be used for mercury speciation measurements at the selected utility sites. The development of this method by Dr. Curtis and further development and validation by the EERC, CONSOL, Radian, and Advanced Technology Systems, Inc., are one of the major accomplishments in mercury research and development. This valuable tool has dramatically aided in our understanding of mercury in the flue gas from the combustion of coal. The significant accomplishments made in mercury research the past four years could not be fully realized if not for the perseverance of the research teams at Ontario Hydro and EERC, and the other contributing research organizations.

DOE/FETC has representatives on the Research Advisory Committee of the EPA's Center of Excellence at North Dakota's EERC. In addition, a FETC staff member is the Chairman of the Committee. Over the past six years, the Center for Air Toxic Metals (CATM) has funded researchers to perform fundamental and applied research and development on trace metal understanding and control, with a focus on mercury.

A Proposed Collaborative Effort: "Fate of Mercury in the Lake Superior Basin"

FETC, EPRI, EPA, Wisconsin Department of Natural Resources (DNR), Minnesota Pollution Control Agency (MPCA), Michigan Department of Environmental Quality, and U.S. and Canadian utilities, and Environment Canada are part of a proposed collaborative effort and

proposal titled "Fate of Mercury in the Lake Superior Basin". The proposal was prepared by the EERC, with them providing coordination through Project Management. The objectives are to increase the understanding of mercury loadings (local and regional transport and deposition) to the lake from coal-fired power plants (Hg^{2+} and Hg^0) along with ongoing research in mercury methylation and bioaccumulative effects. The tasks of the proposal include the following:

Task 1: Mercury speciation measurement for coal-fired power plants. Work will include mercury speciation measurements at four coal-fired power plants, two in Canada (Environment Canada and Ontario Hydro funding at approximately \$300,000) and two in the United States (DOE/FETC funding at \$525,000). The sampling will be conducted by Roy F. Weston, with the analysis being completed by the EERC. Several investigations will be made to determine if surrogate tracers act as fly ash to obtain representative samples from the power plant being monitored during the deposition studies [EPA Great Lakes National Program Office (GLNPO) funding at approximately \$250,000]. Plume mercury transformations will be investigated with promising techniques (DOE/FETC at \$50,000 and utility funding at approximately \$50,000) with Frontier Geosciences and EERC conducting the work.

Tasks 2 & 3: Transport, deposition, and air-surface exchange of mercury associated with emissions from a coal-fired power plant; and modeling mercury transport, chemistry, and deposition to Lake Superior. Task 2 involves the continued characterization of the chemical and meteorological conditions across north-central Minnesota while determining the three-dimensional meteorological [Mesoscale Meteorological Model 5 (MM5)] fields during the power plant stack and tracer sampling. Establishing source-receptor relationships between emissions from a given source, and site-specific chemical conditions through the collection and subsequent analysis at specific distances, are critical to this study. Combining these data with modeled meteorological data will provide input to both the mesoscale transport and deposition model and the EERC source emissions model.

Work under Task 3 will expand upon the heterogeneous chemical model developed by Sillman et al. (1993) for mercury and mercury compounds while developing a potential description of gas-particle dynamics. These data will also serve as input to the MM5 or the Regional Atmospheric Modeling System (RAMS). Testing and evaluation will also be conducted with the new synthesized model and compared to the Michigan Atmospheric Toxics Modeling System (MATOMS) using data collected by University of Michigan Air Quality Laboratory. Funding for these critical tasks is pending from the EPA at a level of

\$1,101,500. The work under these two tasks is critical to determine the local contribution of mercury flux or deposition from the stationary sources within the Lake Superior Basin. The University of Michigan Air Quality Laboratory will perform this critical work.

Tasks 4 & 5: Methylmercury production within Lake Superior and its watershed; and fate of methylmercury produced in the Lake Superior basin. The work under these tasks would expand upon other research in the Lake Superior region to understand the methylation rates of mercury from monitored and nonmonitored tributaries. In addition, investigations will be conducted to assess methylmercury production rates in sediments and wetlands while assessing seasonal distributions of total and methylmercury in lower trophic levels (phytoplankton and zooplankton) in near shore (close to riverine influences) and open lake regions of Lake Superior. The proposed efforts under these two tasks would be performed by the Academy of Natural Sciences and the University of Wisconsin Water Chemistry Program at a proposed funding level of \$627,500.

Task 6: Modeling of mercury cycling in Lake Superior. The focus under this task will be directed at assessing the importance of the various mercury sources, including coal-fired electric generation on methylmercury accumulation in fish. This effort will also be directed at identifying the characteristics of the Lake Superior ecosystems contributing to mercury accumulation in fish, while identifying the factors leading to the variability in mercury concentrations of the fish in the lake. Funding is being provided by EPRI at a level of \$345,500, with Tetra Tech, Inc., performing this modeling.

Task 7: Project management and reporting. All parties would share the compiled data collected through the efforts of the first six tasks. The fate of anthropogenic mercury in the Lake Superior region will be modeled based on the data collected. These models will be used to predict the effects of mercury reduction strategies on the bioaccumulation of methylmercury in fish. The verified models would be utilized to determine the rate and mechanisms of mercury transport in the atmosphere, and potentially, the fate of mercury in other ecosystems.

After the EPA's ICR for mercury data collection, the verified models under this effort would be utilized to determine the fate of mercury in other regions of the United States and Canada. This work would further provide information on not only local and regional effects of mercury, but could provide insight to the global cycling of mercury.

This is an extremely important research effort and would constitute one of the most comprehensive efforts of its kind. The results are critical in providing data to the EPA when it considers regulatory rule making for mer-

cury emissions from the coal-fired steam generating utility industry. These results, along with the health studies, and mercury control technology availability, should also be considered before regulatory decisions are proposed and promulgated.

The DOE/FETC Mercury Measurement and Control Program is further augmented by projects from the Department's University Research Coal Program (UCR), SBIR, and the UNDERC's JSRP. The JSRP is funded by industry with DOE providing 40-50% of the funding for each proposed research effort.

Recent Research and Development and Emerging Mercury Control Technologies for Coal-Fired Utility Boiler Systems

Given the relative maturity level of these technologies, commercial deployment is at least several years away and will be strongly dependent on the results of the DOE/FETC Phase II efforts. Research continues on developing potential technologies for mercury emission reduction from utility plants. The research is designed to augment existing pre- and postcombustion technologies, with investigations studying different combustion conditions for possible mercury removal or mercury speciation modifications. The postcombustion research and development focuses on the addition of some type of sorbent technology (including gas-phase additives) to adsorb the mercury, or using new technology for mercury control. Before any of the technologies are fully realized for utility application, the fundamental mechanisms of the flue gas and mercury chemistries during the combustion and postcombustion conditions, along with the various interactions with the different types of fly ash, must be understood (Brown, T.D., 1997).

Coal Preparation or Coal Cleaning

Coal cleaning is an option for removing mercury from the fuel prior to combustion. Approximately 77% of the bituminous coal produced in the eastern and midwestern regions is cleaned to meet customer specifications for heating value, ash, and sulfur contents (Akers and Dospoy, 1993; EPA, December 1997). Virtually none of the subbituminous or lignite coals produced in the western states are cleaned.

The fundamental methodology for separating coal from the unwanted mineral matter (essentially, the ash-forming material, such as shale, slate, sandstone, and clays, and pyritic sulfur that are embedded with the coal or recovered along with the coal as out-of-seam dilution during the mining process) is based on differences in the physical characteristics of the various components. Although coal and many of its associated impurities vary in a number of physical characteristics including hardness (friability and grindability) and electrical and magnetic properties, the

primary methods used to separate the various components are based either on the relative density or the surface characteristics of the individual particles. Coal has a relative density of 1.23-1.70 making it substantially less dense than its associated impurities (shale, clay, and sandstone at 2.4-2.6 and pyrite at 5.0). Fresh coal tends to be very hydrophobic in nature compared to the hydrophilic surfaces found on most mineral components.

A vast majority of the coal cleaned commercially is separated by processes that rely on the density differential of the various components. Technologies that make separations on this basis are particularly effective for treating the coarse to intermediate sizes of coal (i.e., particle sizes ranging from greater than 10 cm to about 0.1-0.5 mm) with efficiency decreasing as particle size decreases. With very few exceptions, all coal cleaning is done using aqueous media.

The processing options are great as there are numerous types of density-based cleaning devices and processes available, each designed to treat a specific size range of coal. Some of these processes use only water as the separating medium while others use pseudo heavy liquids, made up of finely ground magnetite suspended in water, to make the separation. These density-based processes are particularly effective in removing pyrite from coal. The water-only devices operate on the principles of stratification, hindered settling, and differential acceleration. The application of centrifugal force to increase the separating force on the particles often is applied to improve the separations particularly for the finer particles. Examples of water-only cleaning devices include jigs, concentrating tables, hydrocyclones, and spirals.

Density-based separations are also achieved using a dense medium instead of a water-only medium. Dense-medium systems are more expensive to install and operate than water-only systems but their superior performance make them particularly well suited for cleaning difficult to clean coals. Separations using dense mediums are effected by creating a pseudo heavy liquid having an intermediate density between the coal and mineral matter by adding very finely ground magnetite to water. Particle separation is then made based on the upward buoyancy of the coal particles causing them to float and the downward buoyancy of the mineral matter components causing them to sink. Static bath-type vessels and cyclones which use centrifugal forces are commonly used to treat all but the finest particles.

Although particles less than 0.1 mm in size can be treated using density-based separation processes, coal cleaning in this size range is usually based on differences in surface chemistry of the particles. The hydrophobic nature of coal permits its separation from the hydrophilic

mineral matter by either injecting air bubbles into a coal slurry or by adding an agglomerate, such as fuel oil, to coalesce and remove the carbon-bearing materials while leaving the mineral particles suspended in the water phase. These surface-based processes are particularly effective in removing clays and other mineral matter from coal, but are not very effective in removing pyrite, which has surface characteristics similar to coal. Numerous processes that exploit the differences in particle surface chemistry have been commercialized, including froth flotation, column flotation, and selective agglomeration.

The precombustion removal of mercury and other trace elements from coal has been a fortunate consequence of the application of coal cleaning as it was not the designed aim of any coal cleaning operation. This unintentional removal of mercury occurs because a significant portion of the mercury in coal is associated with the pyritic and ash-forming mineral components. Hence, conventional coal cleaning to remove the pyrite and mineral components results in a reduction in a coal's mercury content. Processes that make separations according to the density differential of particles have generally proven to be more effective in removing mercury than surface-based processes. This is because the primary mode of occurrence of mercury in coal is with pyrite, which if liberated, is easily removed by density-based processes, but not by the surface-based processes where similar surface characteristics of pyrite and organic matter make separation of the two components difficult.

Various studies have indicated that the application of conventional coal cleaning processes has resulted in mercury removal of up to 64%, with overall average reductions between 21 and 37%. The degree of mercury reduction varies widely from coal to coal and is often quite variable for coal from different locations within the same seam. This variation may be explained by several factors, including different cleaning techniques, different mercury concentrations in the raw coal, mode of occurrence, and different mercury analytical techniques.

Additionally, washability studies, which provide theoretical maximum separations, indicate that at high energy recoveries, mercury removals of between 30 and 50% can easily be achieved. This is supported using data from the USGS where, based on comparisons of run-of-mine coal to clean coal samples from the same coal seams, it has been estimated that the application of conventional coal cleaning techniques has resulted in an average mercury reduction of about 37% (Toole-O'Neil et al., 1999).

It is expected that, in most cases, significantly higher mercury reductions can be achieved over those realized via conventional coal cleaning technologies by the application of advanced, emerging coal preparation processes. These processes are all aimed at improved cleaning of fine

size particles and may include a first step of particle size reduction to increase liberation of the impurities. Many of these advanced fine coal cleaning technologies are surface-property driven but several are density-based.

Reduction in mercury content through any of the coal cleaning techniques results in a decrease in mercury emissions and possible alteration in the distribution of the mercury form(s) from utility boilers firing cleaned coals. The mercury removed by cleaning processes is transferred to coal-cleaning wastes, which can be utilized or transferred to settling ponds. While there are data supporting mercury reductions from coal cleaning, no data are currently available to assess the release of mercury from the coal-cleaning slurries and settling ponds. In addition, there are no data on coal cleaning altering the distribution of the mercury form in the flue gas.

Advanced Coal Cleaning: From the EPA's Mercury Study Report and Work Conducted under DOE Funding

Advanced coal cleaning methods, such as selective agglomeration and column froth flotation, have the potential to increase the amount of mercury removed by conventional cleaning alone. In one bench-scale study, five types of raw coal were washed by conventional cleaning methods followed by column froth flotation or selective agglomeration. Conventional cleaning and column froth flotation reduced mercury concentrations from the raw coals by 40 to greater than 57%, with an average of 55%. Column froth flotation reduced mercury concentrations remaining in the washed coals by 1 to greater than 51%, with an average of 26%. Conventional cleaning and selective agglomeration reduced mercury concentrations from the raw coals by greater than 63-82%, with an average of 68%. Selective agglomeration reduced mercury concentrations remaining in the washed coals by greater than 8-38%, with an average of 16% (all reported results from Smit et al., 1996).

In a second bench-scale study, three types of coals were cleaned by a heavy-media cyclone (a conventional cleaning method) followed by a water-only cyclone and a column froth flotation system. The heavy-media cyclone reduced mercury concentrations in the raw coal by 42-45%. The water-only cyclone and column froth flotation system reduced the concentrations of mercury remaining in the cleaned coals by 21-23%. The combined reduction in mercury concentrations from the coals ranged from 63 to 65% (all reported results from Ferris et al., 1992).

DOE is currently funding a project to investigate dry coal cleaning using magnetic separation for removing mercury. This technology, known as the Mag Mill process, is aimed at the removal of pyrite, and hence, the associated mercury, by processing the internal recycle stream from the pulverizers at pulverized-coal power stations. The

added liberation of the pyrite created by the particle size reduction in the pulverizer is expected to significantly aid in mercury removal at a very low cost.

Bench-scale testing has also been conducted by DOE to investigate the use of naturally occurring microbes and mild chemical treatments to reduce the mercury content in coal. While the chemical coal cleaning process showed some promise, they were viewed as being a potentially high-cost control technology and DOE is no longer funding any effort in this area.

Commercialization of Coal Cleaning Technologies

Most coal is cleaned by conventional methods that have been slowly improved over the years. Few truly new beneficiation technologies have made any significant inroads into the commercial industry in the past 10-20 years. One of the most promising technologies that has more than just a few commercial applications is column flotation. Column flotation differs from conventional flotation in that columns have a much greater height-to-width ratio and do not require mechanical agitation to induce particle-bubble attachment. Columns are claimed to be more effective than conventional cells for beneficiating the finer particles owing to better control of bubble size (smaller is better), improved particle-bubble interaction, and their froth washing capabilities. There are a number of column processes that are somewhat similar in nature, with each possessing one or more unique technological advances. The most significant of these processes include Microcel, Kenflote, Flotaire, and the packed column. The Jameson Cell differs from these columns in that particle-bubble contact is not achieved in the slurry column itself but rather in a downcomer tube where air and feed mixing is achieved in a venturi-type arrangement. The Microcel technology has been applied commercially for the recovery of fines from both freshly mined coal and refuse ponds and also has realized significant applications in the minerals industry.

Additionally, improved separation performance of fine particles has resulted from recent advances in the design of several new water-only devices including various concentrating spirals, the Kelsey Jig, the Multi-Gravity Separator, the Falcon Concentrator, and the Knelson Concentrator. The development of advanced ultra-fine dense-medium systems, such as Carefree Coal and MicroMag, also offers the potential of the improved cleaning of coal fines. However, none of these has yet achieved any significant degree of commercialization.

While advanced cleaning technologies can reduce mercury from the coal (30 to greater than 60%), the potential impact on postcombustion from and control of the remaining mercury has not been thoroughly inves-

tigated. Mercury mass transfer limitations are encountered in emissions control systems on furnaces firing raw or conventionally cleaned coals. Advanced coal cleaning may exacerbate this problem. In addition, chemical cleaning techniques being considered may provide a coal that yields a different form of mercury under combustion and postcombustion conditions. This could adversely impact the natural mercury capture of the fly ash and across wet/dry FGD systems. There is a need to conduct additional laboratory-, bench-, and pilot-scale combustion and subsequent postcombustion studies to evaluate these potential impacts. In addition, the added costs for advanced coal cleaning separately and in combination with postcombustion controls for mercury have not been fully developed.

Modes of Occurrence

Of the 25 or so most significant trace elements found in coal, mercury typically has the lowest concentrations. A study of over 7000 coal samples collected from all of the major U.S. coal seams by the USGS indicates an average assumed mercury content of U.S. coals of about 0.20 $\mu\text{g/g}$ with a range of about 0.003-3.0 $\mu\text{g/g}$ (Toole-O'Neil et al., 1999). These extremely low concentrations of mercury are compounded by the fact that analysis of mercury by methods requiring heating is not possible because it is volatile at fairly low temperature, making it difficult to determine the modes of occurrence of mercury in coal. As a result, very little direct information on the modes of occurrence of mercury is available. Much data of the available data has been derived by correlating the removal of mercury to those of the ash-forming and pyrite components.

It has commonly been found that most trace elements have multiple modes of occurrence in coal with several of the elements even having various degrees of association with both the inorganic and organic components. Mercury falls into this latter grouping. Mercury has been reported to occur as mercury sulfide, metallic mercury, and organometallic compounds (Toole-O'Neil et al., 1999). Others have suggested the presence of elemental mercury in coal (Porritt and Swaine, 1976). Most of the available data indicate that mercury has a strong association with sulfide minerals. This has been reported by some researchers who have found strong correlations between pyrite and mercury removal. Yet, others have found a primary relationship between mercury and ash-bearing mineral matter removals and little mercury-pyrite association. However, despite the divergence of some of the data, the majority of the evidence points toward a predominate mercury-pyrite association in coal with some evidence suggesting that this relationship is responsible for up to 65-70% of the mercury in some coals. It is not unusual for up to 25-35% of the mercury in coal to

be associated with the organic fraction.

The precombustion removal of mercury from coal has typically been accomplished in an indirect way by exploiting its association with the pyritic and ash-forming mineral components found in coal. Coal cleaning involves the use of techniques that separate the organic fraction of the raw coal from the mineral components according to the differences in either the density-based or surface-based characteristics of each component. Because the primary mode of occurrence of mercury in coal is with pyrite, which is very dense compared to the other components found in coal, density-based separation processes have typically proven to be more effective in removing mercury than surfaced-based processes where the similar surface characteristics of pyrite and the organic matter make separation of the two components difficult. Washability studies, which provide theoretical maximum separations, indicate that at high energy recoveries, mercury removals of between 30 and 50% can easily be achieved (Akers and Raleigh, Jr., 1998). This is supported using data from the USGS where, based on comparisons of run-of-mine coal to clean coal samples from the same coal seams, it has been estimated that the application of conventional coal cleaning techniques has resulted in an average mercury reduction of about 37% (Toole-O'Neil et al., 1999).

AC and Other Sorbent Injection Technologies for Mercury Capture

Considerable research and development has been conducted to understand mercury capture with AC and other novel adsorbents in the varying flue gas conditions from the combustion of coal. The amount of carbon injected is dependent on the mass carbon-to-mercury ratio for each system, which can have a profound impact on the cost of controlling mercury. To date, there have been many fundamental, laboratory-, bench-, and pilot-scale studies investigating the flue gas constituents that either enhance or impede mercury capture associated with AC. In some cases, the bench- and laboratory-scale studies have indicated either excellent or poor adsorption of mercury, while some of the same sorbents have shown opposite results in actual flue gases. Understanding the factors enhancing mercury capture with AC and novel adsorbents will allow for potential low-cost technologies for mercury control, if required, for the utility industry.

No individual mercury technology being investigated can be universally realized for the utility industry. AC in parallel with the capture of mercury with native fly ashes, and with enhancements for particle collection, has potential application in a majority of the utility boiler systems. Nearly 65% of the utility industry firing coal as a fuel has an ESP as the only control device. Approximately

10% of the industry has a FF, or baghouse, as the only control device, which is primarily utilized in boiler systems firing low-sulfur PRB/subbituminous coals. The remaining utilities utilize dry or wet FGD systems with either an ESP or FF. Sorbent injection has been investigated for application as a control option for the approximately 75% of the industry utilizing a particulate control device as the only APCD.

AC injection is successfully utilized in the municipal waste combustor industry and is capable of removing >90% of the mercury at very modest carbon-to-mercury ratios. A fraction of a pound increase in carbon injection rate can mean as much as 30% more removal of the flue gas mercury. AC technology is not directly applied, or can have only limited application, to the coal-fired steam generating utility industry for several reasons. First, the low concentrations of mercury present in the relatively high volumes of flue gas (1 ppbv of Hg with two different forms in flue gas volumes ranging from 500,000 to 5,000,000 acfm) cause this limitation. Second, there are higher concentrations of competing species that will occupy the active sites of the carbon. In addition, the flue gas residence time upstream of an ESP is in a nominal range <0.5 to 1.5 seconds with flue gas velocities in the range of 50-60 ft/sec at 300 °F (149 °C) (U.S. DOE, 1988 and 1993). Compounding these factors are mass transfer limitations of the injected sorbents and the decrease in carbon reactivity and equilibrium sorption capacity at this nominal but high temperature. Particle size of the AC can also impact the mass transfer of the mercury.

Darco FGD AC provided by Norit Americas, Inc., from a lignite coal, has been extensively utilized more than any other commercial AC for the DOE- and EPRI- funded mercury control studies investigating sorbent injection. The measured parameters of the FGD carbon include a mass mean diameter of 15 mm, a BET surface area of 600 m²/g, and a nominal equilibrium adsorption capacity for Hg₀ of 500-μg Hg/g C (microgram of mercury per gram of carbon). These parameter values have been measured by many research institutions and are in agreement with Norits' specifications (Miller et al., 1994 and 1995; Chen et al., 1996; Hunt, 1996; ABB et al., 1997; Carey et al., July, 1996 and June, 1997; Radian International, et al., 1997; Sjostrum, et al., 1997; Haythornthwaite et al., 1997, December 1998, and 1999; PSCo/ADA, et al., 1997; Rostam-Abadi et al., 1997; and Waugh et al., August and December, 1997).

The equilibrium adsorption capacity of the AC may be important for the FF systems, but for flue gas residence times of less than 1 sec upstream of an ESP, higher equilibrium adsorption capacity may not be a critical parameter. Reactivity may need to dominate, but is typically suppressed at the nominal temperature of 300 °F (149 °C)

upstream of utility ESPs.

Chemically impregnated carbons may increase the reactivity and subsequent capture of mercury, but very few studies have indicated the effectiveness of chemically impregnated carbons for in-flight capture of mercury (especially at 1 sec or less residence time). These carbons may be cost prohibitive if injected upstream of an ESP because they were designed for higher sorption capacities reflective of longer residence or contact times (carbon beds or FFs, etc.). An extensive study of chemically impregnated carbons and virgin ACs in a pilot-scale combustion and FF facility has been reported by the EERC. The studies, which were funded by the EPRI and DOE, were completed in September 1998 (Dunham et al., September 1998 and Miller et al., December 1998).

AC injection with reduced flue gas temperatures (i.e., spray cooling or use of heat exchangers) promotes higher mercury capture efficiencies. This is an appropriate application with low-sulfur PRB and other subbituminous coals, but not necessarily for the facilities utilizing bituminous coals because sulfuric acid mist may form as a result of sulfur trioxide (SO₃) condensing at or below the acid dew point(s) of the flue gas. The SO₃ may be either a direct result of combustion or injected separately or in combination with ammonia for enhancing fine particle collection. In addition, pilot-scale tests have indicated that certain carbons convert SO₂ to SO₃ while the carbon is captured on the filter of the baghouse. This conversion could dramatically reduce the bag life of the baghouse system.

Figure 28 illustrates the different sorbent injection options being investigated at the pilot-scale. The options are:

- Option A: Only sorbent or carbon injection upstream of the existing ESP;
- Option B: Sorbent or carbon injection downstream of the existing ESP associated with a downstream FF, with and without flue gas cooling; and
- Option C: Sorbent or carbon injection upstream of the existing ESP, with flue gas cooling.

Low-sulfur bituminous coals, PRB/subbituminous coals, and lignite coals are very different regarding the mercury distribution between the elemental and oxidized forms in the flue gas. Their fly ash characteristics are extremely different and some subbituminous coals produce fly ashes that are more reactive and adsorb mercury at higher rates than fly ashes from the bituminous coals. In addition, bituminous coal fly ashes tend to convert the elemental mercury at higher rates and levels compared to fly ashes from subbituminous coals.

Recent studies indicate that high levels of sulfur dioxide up to and >1600 ppmv, with 50- ppmv HCl, have a profound negative impact on the equilibrium adsorption capacity of certain virgin ACs for both Hg⁰ and Hg²⁺. Fur-

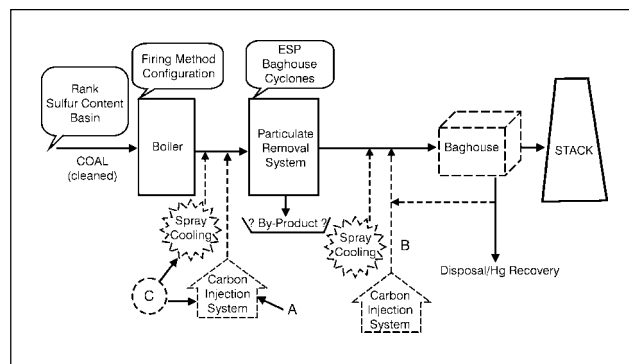


Figure 28. Different sorbent-based injection options being investigated for mercury control in coal-fired power plants (Brown et al., 1998).

thermore, the removal of HCl does not impact the Hg²⁺ equilibrium adsorption capacity, but it does prevent the carbon from adsorbing Hg⁰. NO_x can also negatively impact the reactivity and equilibrium sorption capacity of AC 1998 (Dunham et al., September 1998 and Miller et al., December 1998).

Recent studies further support mass transfer limitations because the removal of mercury above the 50-90% level for in-flight capture and above the 75%-90% level for extended contact times (>one-half hr across a FF) is dependent on near exponential increases in the carbon injection or carbon-to-mercury ratios. The PSCo/ADA studies indicate a nominal 5000:1 carbon-to-mercury mass ratio (carbon is Norit or Darco FGD) at 222 °F (106 °C) upstream of a pilot-scale ESP and a residence time ranging between 0.75 and 1.5 sec to remove the mercury at a level of 48%. This 48% includes 30% of the mercury being removed by the fly ash. Studies have indicated the fly ash from this PRB coal (Comanche or Belle Arye coal from Wyoming) has a high equilibrium adsorption capacity for mercury even at <0.5% carbon levels in the fly ash (Miller et al., 1994 and 1995; Laudal et al., November 1996 and December 1997; PSCo/ADA et al., 1997; and Haythornthwaite et al., June, July, December 1998, and 1999). The overall mercury adsorption is higher than for bituminous coals with the same amount of carbon in the fly ash. The adsorption capacity or reactivity for both ranks of coal increases with a decrease in temperature, but not at the same rate or level.

Mass carbon-to-mercury ratios of >100,000:1 may be required at 1 sec or less residence times upstream of an ESP at 300 °F (149 °C) to achieve 90% mercury removal. As indicated in Figure 27, a 90% removal would not be required if a cap on mercury emissions was imposed by regulatory action. If not, these high ratios could put the carbon content of the fly ash over the required limit for the sale of the fly ash. This would be of further concern to utilities installing LNB systems, which often increase the LOI (unburned carbon) of the

fly ash.

Some of the plants equipped with only ESPs may require downstream FFs to comply with potentially stricter control requirements for primary particulate matter less than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$). The pulse-jet filter has the advantage of a small footprint and is ideally suited for retrofit situations. The downstream FF could also provide for multipollutant control of fine particulate escaping an under-performing ESP while potentially controlling SO_3 and other acid gases associated with calcium-based sorbent injection technology.

A pulse-jet FF is an option to be utilized at the outlet of an ESP for mercury capture, while serving as an effective fine particulate polishing device. If the older ESP is 98.5-99 % efficient (greater than the 0.03 lb/MMBtu NSPS limit), then a considerable amount of particulate (less than $5 \mu\text{m}$) will accumulate or be collected with the injected AC. This is a benefit, but it could have an adverse impact on pressure drop and cleaning frequency of the pulse-jet filter. These conditions could limit the utilization of the carbon for mercury capture and the pressure drop would require additional fan power. If the size of the pulse-jet filter requires higher air-to-cloth ratios between 6 and 8 ft/min, the pressure drop would increase in a shorter period of time requiring more frequent cleaning and consequently, the mercury capture would decrease per unit mass of carbon injected as a result of less contact time.

Problems have been encountered using pulse-jet filters as polishing devices while cleaning on-line for fine particulate (reentrainment of the fine fly ash) because an adequate dust cake is not formed. Humidification may help, but it has not been fully tested under this type of application. Taking the filter off line would demand additional costs for operation. A design could be provided to recirculate the underutilized carbon and fly ash mixture, which would require an additional cost for handling and re-injection of the solids. If there is no recirculation of the carbon collected in the hoppers, more carbon would be needed. It would be less than the requirement of a reverse-gas FF downstream of an ESP because of the amount of carbon needed to cover the overall area of the fabric in this larger type of baghouse/FF

DOE/FETC analyzed the amount of carbon needed for 90% mercury removal in a reverse-gas baghouse. These calculations which are included in the EPA Mercury Report to Congress and Brown et al., 1998 are for EPA Model 3b in Appendix B of their report. The model unit is a 100-MWe low-sulfur coal-fired boiler system equipped with an ESP. Mercury concentrations are set at 10 mg/dscm and a reverse-gas baghouse is the downstream collecting device with respect to the ESP. The mercury control system also utilizes water spray flue gas cooling for maintaining the flue gas temperature upstream of the

baghouse at 200 °F (93 °C). Based on the set parameters in the EPA model and the factors below, the following calculations were made by DOE/FETC:

- The minimum thickness for the AC on the fabric was assumed to be 1/128 in. (1/32-1/16 in. is considered normal for a dust cake thickness for carbon in a reverse air baghouse, based on pilot-scale data). $1/128 \text{ in.} \times (1\text{ft}/12 \text{ in.}) = 6.51 \times 10^{-4}\text{ft}$
- The net cloth area of the baghouse in this model was calculated to be equal to 139,966 ft². The amount of carbon needed was based on one compartment (5% of baghouse area) being pulsed in 1 hr, therefore: $(139,966 \text{ ft}^2)(6.51 \times 10^{-4}\text{ft})(0.05/\text{hr})(25 \text{ lb}/\text{ft}^3) = 113.9 \text{ lb}/\text{hr}$ of carbon needed (where 25 lb/ft³ is the bulk density of the carbon).
- The total Hg (all Hg^{2+}) in the flue gas over a 1-hr period of time was calculated to be = 411,000 dscm/hr $(10 \times 10^{-6} \text{ g Hg}/\text{dscm})(\text{lb}/453.6 \text{ g}) = 9.06 \times 10^{-3} \text{ lb Hg}/\text{hr}$. Therefore, the carbon injection rate = $(113.9 \text{ lb}/\text{hr AC}) \div (9.06 \times 10^{-3} \text{ lb Hg}/\text{hr}) = 12572 \text{ lb C}/\text{lb Hg}$.

This is indicative of the carbon needed to cover the area of the fabric within one compartment of the baghouse. In addition, recycling of the ash and carbon mixture was not a parameter in the EPA model. Details of the DOE/FETC cost of control are indicated in the section on Cost of Mercury Control.

With this prelude, below are data from several research organizations conducting research and development on sorbent injection for possible mercury control in the coal-fired steam generating utility industry.

University of Pittsburgh: Development of Novel AC-Based Adsorbents for the Control of Mercury Emissions from Coal-Fired Power Plants

Under funding from the EPA, researchers at the University of South Carolina and the University of Pittsburgh conducted a study to theoretically examine the removal of Hg^0 under conditions experienced at coal-fired power plants. This study involved assessing the impacts on Hg^0 removal by correlating removal with equilibrium adsorption capacity, carbon particle size and dose, and carbon and flue gas contact time. Both laboratory-batch and modeling studies were conducted under two different temperatures of 77 °F (25 °C) and 284 °F (140 °C) at a Hg^0 level of 20 $\mu\text{g}/\text{Nm}^3$. A commercially available AC, BPL from Calgon Carbon Corporation (Pittsburgh, PA), was utilized during the laboratory-batch testing. Details of the batch system and analytical methods can be found in the paper by Vidic et al. (1997).

Investigations at this fundamental level are important to provide viable control options to effectively remove the relatively low mercury concentrations in the

high flue gas volumes typical of any utility power plant. Experiments have been performed to obtain isotherm parameters and a surface diffusion coefficient of Hg within the carbon. In addition, work has focused on developing a mathematical model using a homogeneous surface diffusion model (HSDM) in conjunction with a model for a batch system (Flora et al., August 1998). The HSDM was developed to describe the kinetics of adsorption of various compounds from the surface of the carbon into the particle. Descriptions of the HSDM can be obtained from papers by Hand et al. (1983) and Traegner and Suidian (1989a, 1989b). The information provided below is from the paper by Flora et al. (August 1998), which synthesizes the results of the modeling and batch studies.

The initial part of this study involved obtaining the Langmuir isotherm constants (q_{\max} and b), the film mass transfer coefficient (k_f), and the surface diffusion coefficient (D_s) from normalized bulk concentration data collected from batch studies at 284 °F (140 °C) [see Figure 29; data were also collected at 77 °F (25 °C), but are not shown here; see Vidic et al., 1997]. Symbol (c_o) in Figure 29 represents the initial bulk concentration expressed in $\mu\text{g}/\text{Nm}^3$. The following parameters were obtained during the batch studies:

q_{\max} = maximum mass of adsorbate per mass of adsorbent ($\mu\text{g}/\text{g}$) = 27.5 $\mu\text{g}/\text{g}$,

b = Langmuir isotherm coefficient ($\text{m}^3/\mu\text{g}$), $2.06 \times 10^2 \text{ m}^3/\mu\text{g}$,

k_f = film mass transfer coefficient (cm/sec) = 19.4 cm/sec , and

D_s = surface diffusion coefficient of Hg in air (cm^2/sec) = $1.21 \times 10^{-6} \text{ cm}^2/\text{sec}$.

Figure 29 shows the model fit and experimental data at 140 °C. The following constants were used in obtaining the best fit of the model to experimental data:

m_c = total mass of adsorbent in the batch system (g) = 0.1 g ,

r_p = particle radius (cm) = $3.72 \times 10^{-2} \text{ cm}$,

V = volume of batch system (m^3) = 0.0125 m^3 , and

ρ_p = density of adsorbent (g/cm^3) = 0.50 g/cm^3 .

An increase in temperature results in a lower capacity of the carbon for Hg, which is characteristic of an exothermic adsorption process and is consistent with other studies (Krishnan et al., 1994; Livengood et al., 1994; Vidic and McLaughlin, 1996). The Langmuir coefficient, b , increased with temperature. This coefficient can be conceptualized as the ratio of the kinetic coefficient for adsorption to the kinetic coefficient for desorption. If the effect of temperature on both kinetic coefficients can be described using an Arrhenius relationship, then b should not change with temperature. It is possible that with an increase in temperature, the kinetic coefficient for adsorption increased but the kinetic coefficient for desorption did not increase with the same magnitude. A shift in the adsorption mechanism from physical to chemical at a higher temperature could result in a proportionately lower increase in the desorption kinetic coefficient (Krishnan et al., 1994).

The film mass transfer coefficient, k_f , increased with an increase in temperature, which is expected based on correlations used to estimate k_f for various flow configurations. For example, because the thickness of the carbon bed was about the diameter of the carbon particles, the carbon bed could potentially be modeled assuming forced convection over individual spheres (eq 1). Using a measured recirculation flow rate of 75 L/min and a bed diameter of 19 mm (0.75 in.), the velocity used in the correlation was 439 cm/sec and the ratio of k_f at 284 °F (140 °C) to k_f at 77 °F (25 °C) was calculated to be 1.46 (28.8 $\text{cm}/\text{sec} \times 19.7 \text{ cm}/\text{sec}$). The surface diffusion coefficient (D_s) of Hg increased with temperature as a result of increased molecular motion at higher temperatures. Overall, an increase in temperature results in a faster approach towards equilibrium between the gas phase and the carbon phase.

$$2k_f r_p = 2.0 + 0.6 \left(\frac{2r_p v_o}{v} \right)^{1/2} \left(\frac{v}{D_g} \right)^{1/3} \quad (5)$$

where D_g = diffusion coefficient of Hg in air (cm^2/sec) and v = kinematic viscosity of air (cm^2/sec).

Because this research focused on Hg removal under conditions that may be encountered in the flue gases of

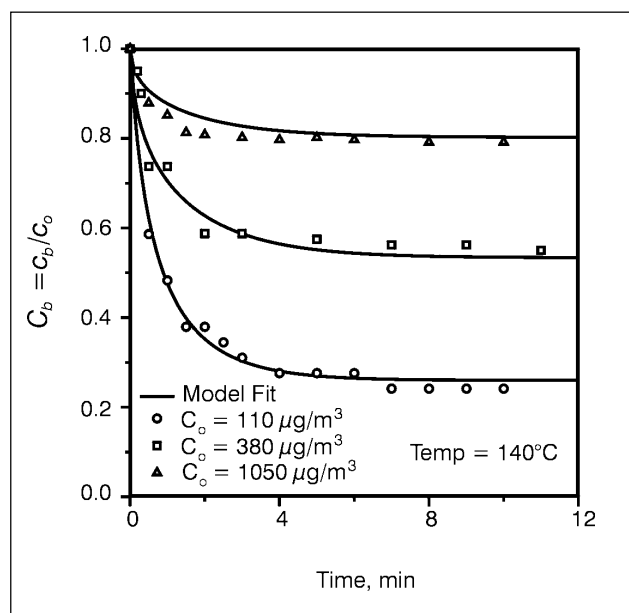


Figure 29. Model fit and normalized bulk concentration data as a function of time for various initial bulk concentrations at 284°F (140°C) (Flora et al., 1998).

coal-fired power plants, the isotherm parameters and D_s obtained from the batch experiments at 284 °F (140 °C) were used for the simulations. Furthermore, ρ_p was assumed to be 0.50 g/cm³ based on the carbon manufacturer's literature and, because the process configuration for the laboratory tests were different from what would be encountered in a flue gas stream, k_f was estimated using an empirical correlation for forced convection around a solid sphere (eq 1 in Figure 30). Figure 30 shows the value for k_f at 284 °F (140 °C) calculated for different carbon particle radii. The value of k_f decreases as the particle radius increases from 10⁻⁴ to 0.02 cm. However, k_f increases for particles greater than 0.02 cm because, from the second term of the right-hand side of eq 1, the increase in relative velocity is more significant with larger radii. Previous researchers neglected the relative velocity of Hg and assumed that k_f is inversely proportional to the particle radius (see dashed line in Figure 30) (Chen et al., 1996). For the conditions in this study, this assumption would underestimate k_f by 2% for an rp of 10⁻³ cm, and by 10% for an rp of 3 × 10⁻³ cm. Although the calculated k_f is actually lower, using this simple relationship for design purposes would be conservative for cases when the system is mass-transfer-limited.

The model developed for a batch system can be used for steady-state, plug-flow conditions in a flue gas stream. An important parameter when modeling steady-state, plug-flow conditions has been referred to in the literature as the carbon-to-mercury ratio (C/Hg ratio), or the mass of carbon applied per influent mass of mercury (Chang and Offen, 1995; Chen, Rostam-Abadi, and Chang, 1996). In using the model, the residence time of AC is assumed to be the same as the hydraulic residence time in the flue gas stack. Because the carbon particles are assumed to settle in the flue gas stream (and, hence, the carbon particle will have a velocity relative to the flue gas stream), the AC residence time will be slightly greater than the hydraulic residence time. Neglecting this difference for the systems that are mass transfer limited would lead to conservative estimates of AC dosage required to accomplish a given Hg removal.

Figure 31 shows the impact of particle radius on the fractional removal of Hg from the influent of flue gases as a function of retention time in the flue gas stack for a C/Hg ratio of 10⁶. An initial mercury concentration of 20 µg/m³ was used in all calculations as representative of the uncontrolled mercury emissions from coal-fired power plants. The fractional removal of Hg increases with longer retention times, with the fractional removal asymptotically reaching a maximum value. At this maximum value, the carbon particles are at equilibrium with the bulk Hg concentration, and further Hg removal cannot be realized. Particles with larger radii require longer residence time to reach equilibrium because Hg has to diffuse a longer distance into the carbon. The average residence

time of AC injected into the flue gas is 3 sec. For this residence time, equilibrium is reached for particles with radius below 30 µm, with larger particles having lower mercury removal.

Figure 32 shows the carbon-to-mercury ratio required to remove various percentages of Hg from flue gases for an influent Hg concentration of 20 µg/m³, a 3-sec retention time, and for different particle radii. The required C/Hg ratio increases with an increase in the required percent removal. For a fixed percent removal requirement, the C/Hg ratio needed is constant for a range of small particle radii. For example, for 90% removal, the C/Hg ratio is constant when the carbon particle radii ranges from 10⁻⁴ to 3 × 10⁻³ cm (1-30 µm). For this size range of carbon particles, the particles reach equilibrium with the bulk Hg concentration in less than 3 sec. When the particles reach equilibrium, the mass of Hg that can be removed depends on the mass of carbon applied. For carbon particles with larger radii, equilibrium may not be attained within 3 sec because of mass transfer limitations. Thus, the mass of carbon required to remove the same amount of Hg increases with an increase in particle radius.

One strategy to increase mercury removal from flue gas is to use carbon particles with a higher adsorptive capacity. To analyze the impact of carbon capacity, simulations were performed with varying q_{max} for various particle radii, while keeping other parameters constant. Figure 33 shows the required C/Hg ratio to achieve 90% removal of Hg for various carbon capacities. Because equilibrium is achieved for small particle radii, the required C/Hg ratio decreases linearly with an increase in capacity. This linear relationship holds for a fixed removal efficiency if all other parameters (e.g., b , D_s , r_p , etc.)

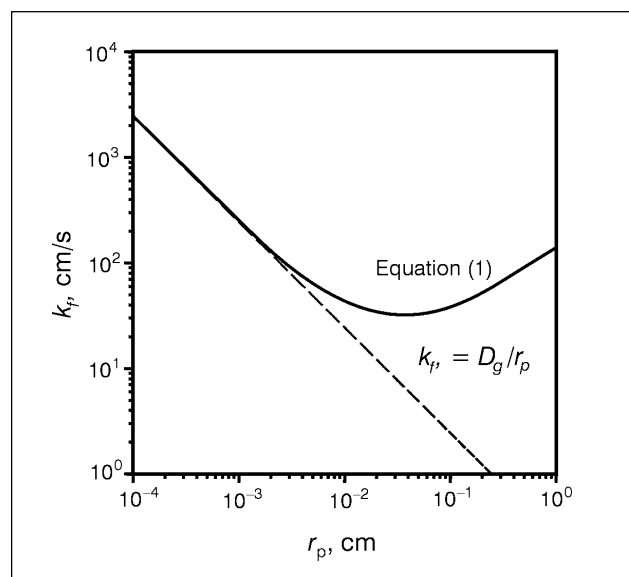


Figure 30. Variation of mass transfer coefficient (k_f) with particle radius at 284°F (140°C) (Flora et al., 1998).

remain constant. For large particle radii, the required C/Hg ratio is less sensitive to the carbon capacity because the system is mass transfer limited. This is particularly evident for particles with a radius greater than 3×10^{-3} cm (30 μm) and for q_{max} greater than 200 $\mu\text{g/g}$. Under these circumstances, Hg removal is primarily dependent on the amount of Hg that can diffuse from the bulk into the carbon particle. Using a smaller particle size would provide more efficient use of the carbon for Hg removal.

Simulations for Figures 29-33 show values of the C/Hg ratio ranging from 104 to 107, while typical values used in flue gas range from 3×10^3 to 4×10^4 . This discrepancy could be the result of a somewhat lower adsorptive capacity of the virgin carbon used in this study. However, if simulations were performed using a higher capacity carbon, the analysis of the impact of particle size, adsorptive capacity, carbon dose, and retention time on the removal of Hg from flue gas would still be the same.

As seen in Figure 29, good model fits to the data sets were achieved with the parameters obtained showing that adsorption capacity was lower at 284 °F (140 °C), but indicating faster adsorption kinetics. Attaining adsorption equilibrium within the system is the key condition that determines the parameters influencing the removal of Hg. If sufficient retention time in the flue gas allows attainment of adsorption equilibrium, then the sorption capacity solely determines the carbon injection rate required to remove a certain percentage of Hg. The system is mass transfer limited if equilibrium is not attained, and numerous factors, such as particle size, retention time, and adsorption capacity, can be manipulated for improved Hg removal. Strategies that are being adopted in other stud-

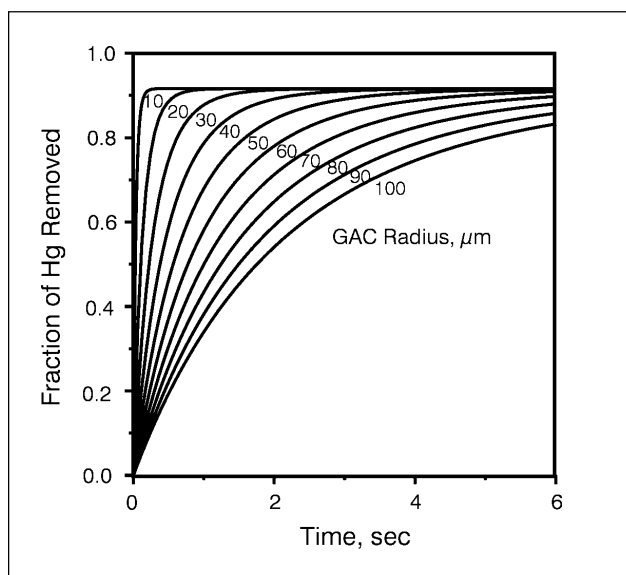


Figure 31. Fractional removal of mercury for different particle radii and retention time for a carbon-to-mercury ratio of 10^6 at an inlet Hg^0 of 20 mg/Nm^3 (Flora et al., 1998).

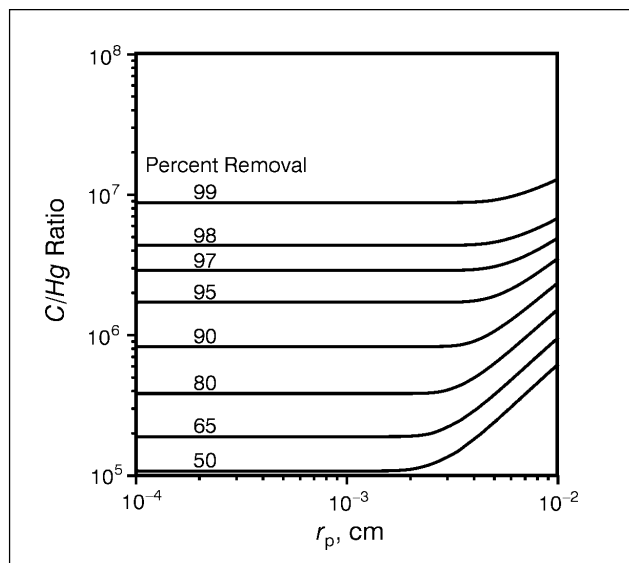


Figure 32. Required carbon-to-mercury ratio for Hg removal for different particle radii, 3 second retention time, and a Hg^0 concentration of 20 mg/Nm^3 (Flora et al., 1998).

ies include reducing the particle size, increasing retention time (also referred to as contact time) and using carbon with a higher sorption capacity. The latter is important if the retention time is much higher than the nominal 1-sec retention or residence time upstream of utility ESPs.

The batch investigations transported Hg in a carrier gas of nitrogen to the AC. No other flue gas constituents were utilized during these tests. The University of Pittsburgh facility now has the capability of generating simulated coal-fired flue gas. Oxidized mercury will also be injected into the flue gas stream to determine sorption capabilities of the virgin and novel SIC that the University is developing.

Work has also been conducted at the University of Pittsburgh to investigate novel ways to promote sulfur impregnation of AC(s). Enhanced mercury sorption can be potentially achieved by impregnating the carbon(s) with sulfur at elevated temperatures of 752-1112 °F (400-600 °C). This method promotes a more uniform distribution of short linear chains of sulfur allotropes (S_2 and S_6) on the carbon surface as opposed to the predominate S_8 rings condensed in the macropore region in commercially available SICs. In addition, the SICs prepared at elevated temperatures have exhibited significantly better thermal stability because no sulfur loss was observed even after exposure at 752 °F (400 °C). The SICs exhibited high Hg^0 uptake efficiency at 284 °F (140 °C) compared to commercially available ACs. The dynamic adsorption capacity of these carbons was measured as high as 4000 mg Hg/g C , which is almost 3 orders of magnitude greater than the capacity of virgin AC and an order of magnitude greater than the capacity of commercially available, impregnated AC (Flora et al., 1998; Korpiel and Vidic, 1997; Liu et al., 1997, 1998, December 1998, March 1999; Vidic and McLaughlin, 1996).

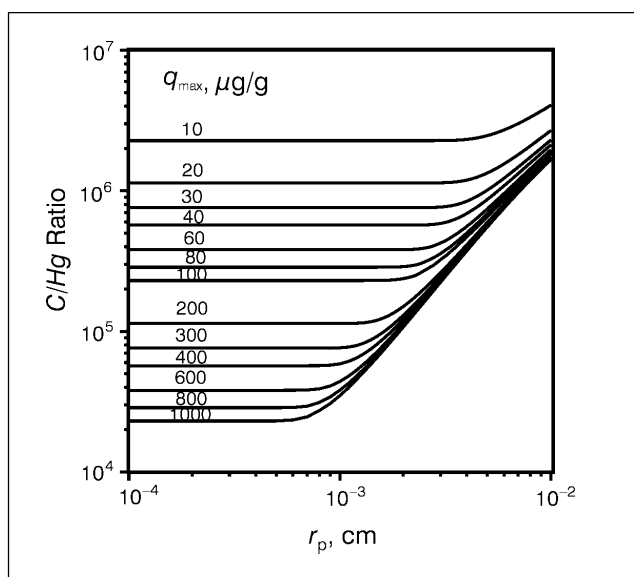


Figure 33. Required carbon-to-mercury ratio for 90% Hg^0 removal for different particle radii, 3 second retention time, a Hg^0 concentration of 20 mg/Nm^3 , and for different adsorption capacities (Flora et al., 1998).

Studies have been conducted with other flue gas constituents added to the Hg^0 and N_2 carrier gas in the University's laboratory facility (Liu et al., March 1999). Figure 34* shows the impact of carrier gas moisture content on Hg^0 uptake by BPL-S-4/1-600 carbon, which is the Calgon Carbon Corporation BPL virgin AC impregnated with sulfur at 1112 °F (600 °C) with a sulfur-to-carbon ratio of 4:1. The total Hg^0 uptake capacity did not change when 5% moisture was introduced in the carrier gas. However, the carbon adsorptive capacity decreased as much as 25% when the moisture content was increased to 10%. Because the adsorptive capacity of carbon did not change at low moisture content, it can be concluded that moisture does not affect the reaction between sulfur and mercury. Therefore, it is postulated that the effect of moisture is related to the adsorption of water by the carbon surface. The carbon surface can bind water molecules to form hydrogen bonds with other molecules (Duninin, 1980). Higher vapor pressure will increase the amount of adsorbed water. For the 5% moisture test, the capillary condensation may be the dominant process. As the water vapor pressure increased to 10%, water molecules were able to fill the micropores and isolated water zones merged and formed a thin layer on the carbon surface, thereby creating an apparent increase in mass transfer resistance for the adsorption of the Hg^0 .

Another factor affecting the carbon performance is hydrogen formation via dissociation of water by carbon. It was reported that hydrogen and CO can be formed if enough water vapor pressure is present at elevated temperatures. Furthermore, hydrogen is preferentially retained by carbon (Walker, 1970) because the molecular diameter of hydrogen is extremely small, which makes it is very

easy for hydrogen molecules to deploy in carbon pores and form a strong hydrogen-carbon complex. As a result, the available meso-pore area is decreased, and Hg^0 is unable to react with sulfur in those pores.

Sulfur dioxide (SO_2) is one of the trace components in flue gas with concentrations varying from several hundred to a few thousand ppmv. The SO_2 may be further oxidized to SO_3 in the presence of O_2 . The co-existence of SO_x , NO_x , and moisture will form various acids in the flue gas, for example, H_2SO_3 , H_2SO_4 , and HNO_3 . Licata et al. (1996) proposed that Hg^0 could react with H_2SO_4 and form mercurous sulfate (Hg_2SO_4). Hall et al., (1991) observed that HgO was formed when vapor-phase Hg^0 was mixed with NO_2 gas at 340 °C. These results strongly suggest that SO_2 and NO_x could have an impact on mercury adsorption. Therefore, it was considered crucial to investigate how these gases will affect the adsorptive capacity of BPL-S-4/1-600 under these specific conditions.

It is known that SO_2 can interfere with atomic absorption spectroscopy (AAS). Therefore, a "gas-washing" system (0.1 M NaOH solution) followed by a Nafion Dryer was used before the gas was analyzed. The impact of SO_2 on both virgin BPL and BPL-S-4/1-400 was studied using a SO_2 concentration of 300 ppmv. To create 300-ppmv SO_2 , pure nitrogen at 0.4 L/min passed the mercury permeation cell, and 500-ppmv SO_2/N_2 mixture (Praxair Inc., Bethlehem, PA) joined this gas at 0.6 L/min. After passing the "gas-washing" solution and the Nafion Dryer, the mercury concentration was verified at 40 mg/m^3 by AAS.

Figure 35 compares the Hg^0 uptake by virgin BPL in pure N_2 with 300-ppmv SO_2 in the carrier gas. The mercury uptake capacities for virgin BPL were essentially the same for both cases.

Figure 36, which shows the column tests with BPL-S-4/1-600, suggests that the capacity of sulfur-impregnated AC was also unaffected by the presence of 300 ppmv of SO_2 in the gas. The mercury uptake capacities for virgin BPL were essentially the same for both cases. Mercury throughput in the figures represent the amount of mercury supplied to the adsorber with time, and is a function of mercury concentration and carrier gas flow rate. Use of mercury throughput instead of time on horizontal axes allows for a direct comparison of breakthrough curves from adsorber tests conducted using different flow rates or different influent mercury concentrations.

It is well known that SO_2 can interact with carbon via physisorption or chemisorption at relatively high temperatures 932 °F (>500 °C) and high concentrations (Puri and Hazra, 1971; Stacy et al., 1968; Teng et al., 1992). The possible reactions are

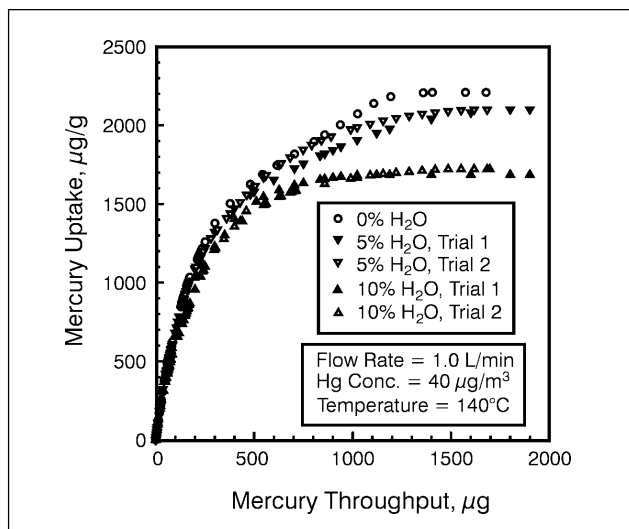
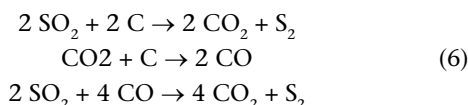
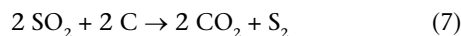


Figure 34. Impact of Hg^0 and N_2 carrier gas moisture content on Hg^0 uptake by BPL-S-4/1-600 carbon (Liu et al., March 1999).



The overall reaction is



Low SO_2 concentration and low reaction temperatures retarded the possible reaction. Low SO_2 concentration did not provide sufficient concentration gradient through the carbon- SO_2 interface and, consequently, the mass transfer resistance was high. In addition, low reaction temperatures further slowed the kinetics of the reaction.

In early 1998, the University was awarded a contract to study the mechanisms and kinetics of vapor-phase sorption of mercury by carbonaceous materials. The research program focuses on the fundamental chemistry and physics involved in the adsorption of mercury onto ACs. Graphite will be used as a model substrate for the investigation. Experiments will include both linear and nonlinear optical techniques that will measure the effects of mercury adsorbed on graphite on the amplitude and polarization of light. Based on the experimental results, modeling of the process on a molecular level will be conducted to elucidate the mechanisms of the sorption process.

**University of North Dakota Energy & Environmental Research Center (EERC):
Investigation of Sorbent Injection for Mercury Control in Coal-Fired Boilers**

The EERC has been investigating virgin and chemically impregnated ACs since 1994 and continues to be one of

the research organizations on the leading edge of associated research and development in this area. Research conducted by Felsvang et al. (1993) with chemically impregnated AC indicated that mercury reacts with the chemical that is bound to the carbon, and the carbon is removed by the downstream ESP. It is postulated, that mercuric sulfide ($\text{HgS}_{(p)}$) is formed when Hg^0 reacts with the sulfur on or in the pores of the carbon. Pilot-scale studies by Felsvang et al. (1993) indicated that mercury removal for SICs and iodide-impregnated carbons were 25-45% greater than achieved with an equivalent amount of virgin AC. Other studies however, have shown that the effectiveness of different carbons is dependent on the mercury species, and in some cases, AC had better mercury removal than iodated-impregnated carbons (Krishnan et al., 1994; Miller et al., 1995). Miller and Dunham have been conducting numerous studies on the capability of ACs at both the bench and pilot scales, under simulated and actual flue gas conditions, respectively (Dunham et al., September 1995, February 1996, June 1996, June 1997; Dunham and Miller, July 1996, September 1998; Miller et al., June 1994, August 1995, August 1997, June 1998, December 1998).

Initial laboratory-scale tests at the EERC also indicated, under certain conditions, iodine-impregnated carbon is much more effective than LAC in removing Hg^0 (Miller et al., 1994). Pilot-scale tests indicated, at flue gas temperatures ranging from 257 to 392 °F (125-200 °C), iodine-impregnated carbon had a high removal efficiency of Hg^0 (>95%) for one subbituminous coal. However, for a second subbituminous coal, the iodine-impregnated carbon appeared to convert the Hg^0 to Hg^{2+} with little net total mercury removal. A reason for the difference was not obvious, but may be the result of differing concentrations

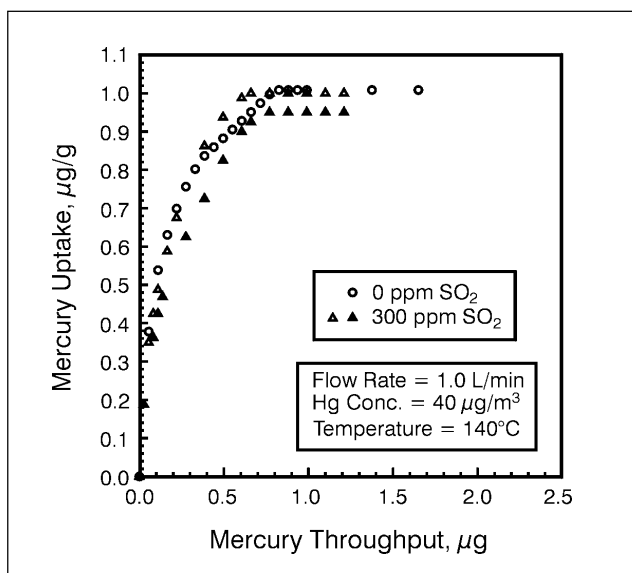


Figure 35. Comparison of Hg^0 uptake by virgin BPL in pure N_2 to the addition of 300 ppmv SO_2 (Liu et al., March 1999).

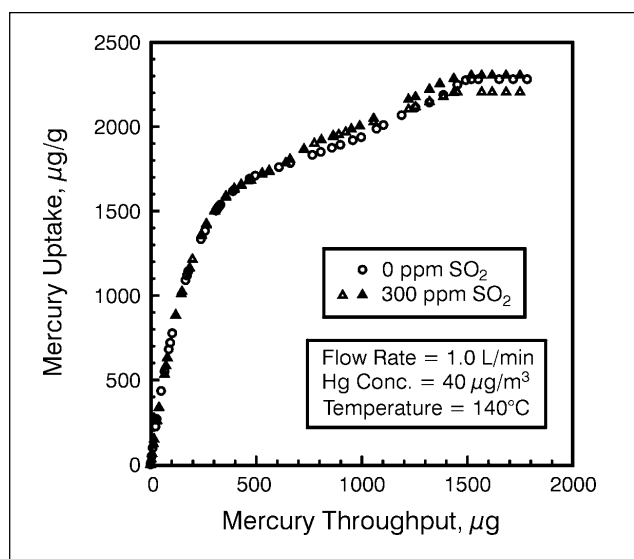


Figure 36. Comparison of Hg^0 uptake by BPL-S-4/1-600 in pure N_2 to the addition of 300 ppmv SO_2 (Liu et al., March 1999).

of SO_2 , HCl , NO_x , HF , and possibly CO in the flue gas. LAC removed approximately 50% of Hg^0 at 266 °F (130 °C), however, the Hg^0 removal efficiency dropped dramatically as the temperature increased. For both carbons, the removal efficiency of Hg^{2+} was highly temperature dependent. At 257 °F (125 °C), the iodine-impregnated carbon was somewhat effective at removing Hg^{2+} , while it removed no Hg^{2+} at 347 °F (175 °C). The lignite AC showed a similar trend (Miller et al., 1994, 1995).

Bench-scale tests conducted over the years by other research organizations indicate that sorbent capacity is highly dependent on temperature, mercury species, mercury concentration, and other flue gas constituents (Carey et al., 1997; Dunham et al., February 1996, June 1997; Dunham and Miller, September 1998; Ghorishi et al., 1997; Haythornthwaite et al., 1998; Miller et al., August 1995, June 1998, December 1998; Roberts et al., 1997; Waugh et al., 1997). The sorbent reactivity to mercury is also likely to be highly dependent on these variables, but may not be directly predictable from the capacity data. Recent studies at the EERC have focused on the interactions of the vapor-phase and particulate phase flue gas constituents, with virgin and chemically impregnated ACs related to the impacts on mercury removal.

Studies initiated on sorbent development were designed with experiments under less complex flue gas conditions (e.g., Hg^0 in N_2) to provide insight as to the sorbent-mercury chemistry. This was appropriate because many of the past investigations conducted tests for determining sorbent capacity with higher mercury concentrations than flue gas from coal combustion and over very long exposure times. In addition, many of these studies did not include the reactive gases present in flue gas, with

possible results not reflecting the performance under real process conditions. The EERC further designed its sorbent investigations under realistic conditions that include all of the reactive gases known to be present in coal combustion flue gas.

EERC constructed a bench-scale test system where independent control over parameters such as temperature, sorbent type, flue gas species, mercury species, and mercury concentration could be achieved. Construction of this system, which was completed with funding from the EPRI and DOE, is described in references by Dunham et al. (June 1997); Dunham and Miller (September 1998); and Miller et al. (June 1998). Initial results are also documented in these references.

Sorbent breakthrough tests were first conducted by preloading a quartz filter with carbon-based sorbent and then exposing the sorbent to a simulated flue gas. A Semtech Hg 2000 analyzer was used to continuously measure the Hg^0 and Hg^{2+} . The Semtech Hg 2000 mercury analyzer was briefly described with the Hg^{2+} to Hg^0 conversion system (SnCl_2) developed by the EERC, in the section Mercury Speciation and Its Measurement.

Tests were conducted to interpret Hg breakthrough to establish that the sorbents are not mass transfer limited. This is reflected either by an initial period of 100% capture for a given test or by 100% capture demonstrated with a more reactive sorbent, but with the same particle size and mass. Because the results shown in Figure 37 with an IAC were repeatable and clearly demonstrated a time of 100% capture, it can be concluded that for sorbent masses of 10 mg or greater with a similar particle size distribution, the capture is not mass transfer limited. Thus, any breakthrough observed then is the result of a reactivity or capacity limit that allows a relative comparison to be made for differing sorbents or gas composition. The comparative tests presented in this paper, using a LAC is Norit Americas, Inc., Darco FGD, labeled LAC in all the figures), were performed with a sorbent mass of 100-150 mg, which is well beyond the range where mass transfer might be a concern.

Earlier studies conducted at high Hg concentrations and longer exposure times indicated a much higher adsorption capacity, which may not be indicative of the lower Hg concentrations in utility flue gas. The EERC designed the tests to interpret capacity data at mercury concentrations where the sorbents are targeted. Recent bench scale indicate that the initial breakthrough capacity increases linearly with respect to mercury concentration (Dunham and Miller, September 1998). All of the simulated flue gas tests with the LAC were with a fairly low mercury concentration of approximately $15 \mu\text{g}/\text{Nm}^3$, which is within the range observed for coal-fired boilers.

Other studies indicated significant effects of NO_2 and other flue gases on mercury sorption and oxidation (Dunham et al., June 1997; Dunham and Miller, September 1998; Miller et al., June 1998). Therefore, EERC conducted its studies under a full-factorial design with experiments being focused on the effects of SO_2 , HCl , NO , and NO_2 , individually and in combination on the capture of Hg^0 and conversion to Hg^{2+} after breakthrough, associated with the LAC commercially available AC.

The fixed-bed tests are not intended to simulate the conditions where a sorbent is injected continuously upstream of a particulate control device, but they provide a good indication of sorbent effectiveness, providing the exposure conditions are similar. For the test flow rate of $0.9 \text{ m}^3/\text{hr}$ and a Hg^0 concentration of $15 \text{ } \mu\text{g}/\text{nm}^3$, 150 mg of sorbent would correspond to a sorbent-to-mercury ratio of 3700:1 at the end of 3 hr. This carbon-to-mercury ratio would be reasonable to use in a large boiler, although the goal would be to achieve effective mercury control with less carbon, in the range of 1000:1. If the mercury capture at the end of 3 hr is at least 80%, it is an indication that the sorbent would provide good mercury capture at a reasonable carbon-to-mercury ratio. However, if significant breakthrough is seen before 3 hr, the implication is that the sorbent would not provide good mercury capture at reasonable carbon-to-mercury ratios. The baseline flue gas constituents were 6% O_2 , 12% CO_2 , 8% H_2O , and a balance of N_2 .

All but one of the tests were with a sorbent mass of 150 mg and most were run for a period of at least 3 hr. In all of the tests, the Semtech was set up to analyze total mercury so all of the breakthrough graphs represent the total mercury passing through the sorbent bed. For most tests, a determination was also made of the Hg^0 at the outlet for a short time by bypassing the converter system. These intervals are shown on the breakthrough graphs. If a significant fraction of the mercury is oxidized across the bed, this is indicated by a marked decrease in the Hg^0 concentration compared to the total mercury concentration. In cases where little or no difference was observed between the total and Hg^0 , the indication is that the breakthrough mercury species was unchanged from the inlet. A brief check of the inlet Hg concentration is shown in a number of tests. Table 22 shows the full-factorial design associated with the four gases (SO_2 , HCl , NO , and NO_2).

Figure 38 depicts the breakthrough curve for Run 767 at baseline flue gas conditions, without acid gases. Because only 10% initial capture was seen, the test run was for less than 1 hr. No conversion of Hg^0 was observed during this baseline test. The results indicate that the LAC is ineffective at capturing Hg^0 in a gas matrix of O_2 , CO_2 , H_2O , and N_2 at $225 \text{ }^\circ\text{F}$ ($107 \text{ }^\circ\text{C}$).

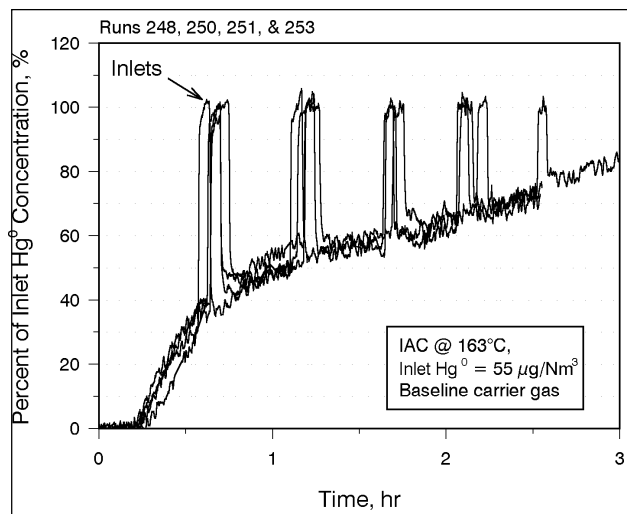


Figure 37. Hg^0 breakthrough for an iodine-impregnated activated carbon (IAC) at baseline conditions (Miller et al, December 1998).

Figures 39-42 indicate breakthrough while testing individually each of the four acid gases. While it is unlikely that flue gas mixes from a real process would contain only one each of SO_2 , HCl , NO , or NO_2 gas, tests were conducted to determine possible mechanisms. Figure 39 depicts Run 745, with 1600-ppmv SO_2 alone; Figure 40 depicts Run 744, with 50-ppmv HCl alone; Figure 41 depicts Run 713, with 300-ppmv NO alone; while Figure 42 depicts Run 735, with 20-ppmv NO_2 alone, but with the baseline gases. The results are as follows:

- (1) Run 745 had an initial capture of 50%, which decreased to only 10% capture after 1 hr, and no conversion of Hg^0 was seen. SO_2 alone has a small benefit on Hg^0 capture. The LAC sorbent is considered ineffective at these conditions. A conversion of Hg^0 to Hg^{2+} was noted.
- (2) Run 744 showed nearly 100% capture at the 50-ppmv HCl level. HCl alone has a significant benefit. Mercury at the outlet of the fixed bed was measured as oxidized Hg.
- (3) Run 713 had an initial capture of 85-95%, increasing to 100% after 2.5 hr at the 300-ppmv level of NO . Similar to the results with HCl alone, other than the apparent improvement in capture with time. A very positive effect on Hg^0 capture compared to the baseline gases.
- (4) Run 735 indicated 90-100% Hg^0 capture for a period of 8 hr at a level of 20 ppmv of NO_2 . An apparent zero-drift occurred that was corrected with the auto zero function of the Semtech instrument.

The results indicate a high reactivity of Hg^0 with NO_2 on the carbon sorbent that is consistent with earlier studies of Pierce and Noyes, Jr. on glass surfaces (1928). It is speculated that different mercury species are formed on the carbon surface, because both HCl and NO_x

alone indicated high sorption of the inlet Hg^0 .

The next series of tests were conducted at six combinations of two each of the four study gases. The combinations are depicted in Table 22 as Tests 6-10. The results of the breakthrough curves are depicted in Figures 43-50 with the following results:

- (1) Run 689, with SO_2 and HCl, but only 102 mg of LAC (all other tests with 150 mg) had nearly 100% capture at the start that slowly decreased to 80% capture by 3.5 hr. HCl and SO_2 give slightly poorer performance than HCl alone, but much better than SO_2 alone. There is a slow increase in mercury breakthrough for the combination compared to a fairly flat breakthrough curve with HCl alone. No conversion of Hg^0 was observed with both SO_2 and HCl.
- (2) Run 743, with NO and SO_2 , showed an initial capture of 40% but increased to 85% after 3 hr. Similar to NO alone, but initial and final breakthrough is greater with both NO and SO_2 . The 15% breakthrough appeared to be Hg^{2+} . The addition of SO_2 to NO showed a small decrease in the level of Hg^0 capture with possible oxidation of the Hg^0 that is not captured.
- (3) Run 740, with SO_2 and NO_2 , show significantly different results compared to NO_2 alone. A 90% capture was initially observed for the first half-hour, with rapid breakthrough above the 100% mark. The breakthrough Hg appeared to be all Hg^{2+} .

The following observations were made while an additional test was conducted. Because with NO_2 alone, nearly 100% capture was observed for a period of 8 hr

Table 22. Test matrix of a full-factorial design with four different gases.

Test No.	SO_2 , ppm	HCl, ppm	NO, ppm	NO_2 , ppm	Run No.
1	1600	50	300	0	712
2	1600	50	300	20	721
3	1600	50	0	0	689
4	1600	50	0	20	714
5	1600	0	300	0	743
6	1600	0	300	20	763
7	1600	0	0	0	745
8	1600	0	0	20	740
9	0	50	300	20	761
10	0	50	300	0	742
11	0	50	0	20	741
12	0	50	0	0	744
13	0	0	0	0	767
14	0	0	300	0	713
15	0	0	0	20	735
16	0	0	300	20	762

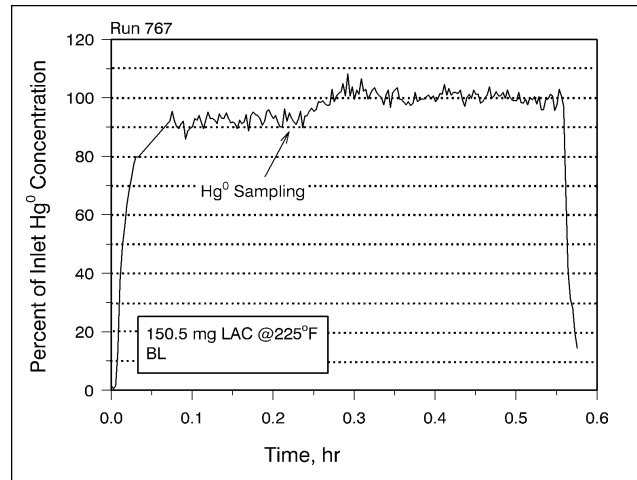


Figure 38. Hg^0 breakthrough for a Lignite coal activated carbon (LAC) at baseline flue gas conditions (Miller et al, December 1998).

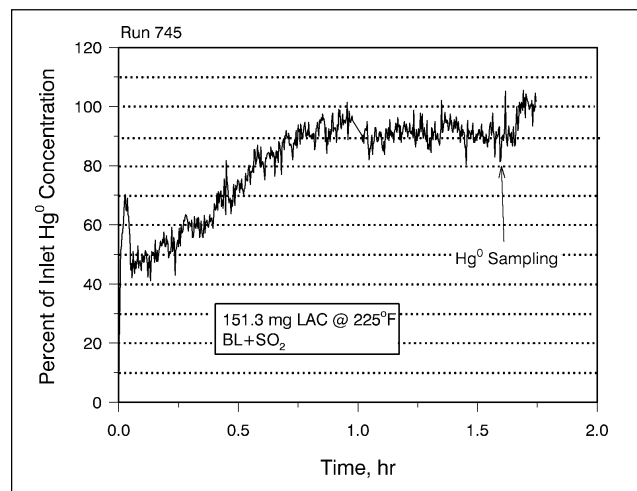


Figure 39. Hg^0 breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO_2 (Miller et al, December 1998).

(Run 740, Figure 45), these results indicated a significant interaction between the SO_2 and NO_2 . To confirm this effect, a repeat test was conducted in which only NO_2 was added for the first 2.5 hr, after which SO_2 was also added (see Figure 46, Run 769). For the first 2.5 hr, the capture was again nearly 100% with one minor and one major zero-drift correction. However, immediately after SO_2 injection was started, the mercury breakthrough increased rapidly and reached a level twice the inlet mercury concentration. This indicated that not only did the SO_2 cause the sorbent to lose its ability to capture mercury, but it also caused the sorbent to desorb the mercury that was captured in the first 2.5 hr. As the test continued for a total of 8 hr, the outlet mercury concentration slowly approached the inlet level. In addition, Hg^0 measurements at 3.5 and 8 hr indicated that almost all of the breakthrough Hg was Hg^{2+} . Analysis of the sorbent after the test showed that the sorbent

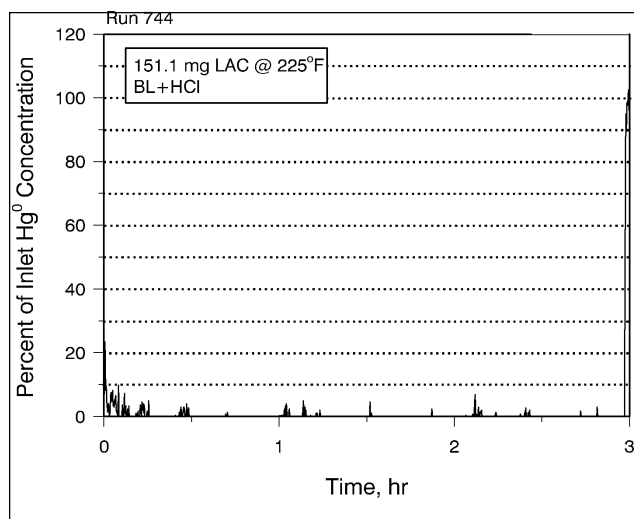


Figure 40. Hg^0 breakthrough for the LAC at baseline flue gas conditions with 50 ppmv HCl (Miller et al, December 1998).

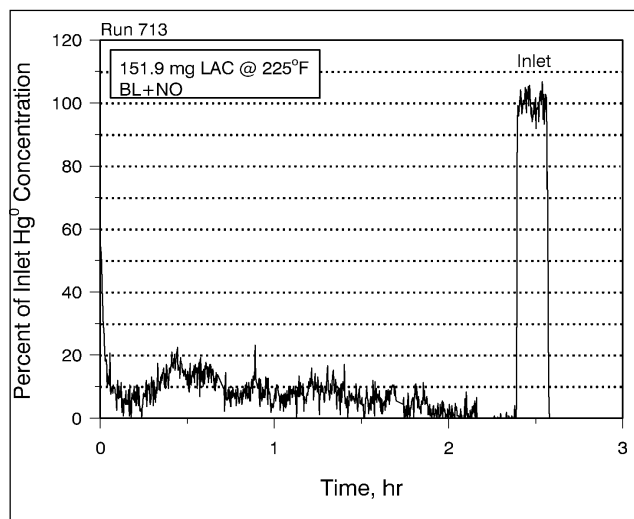


Figure 41. Hg^0 breakthrough for the LAC at baseline flue gas conditions with 300 ppmv NO (Miller et al, December 1998).

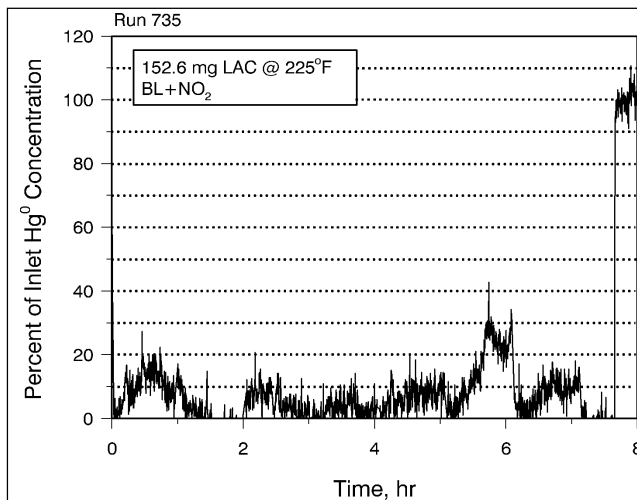


Figure 42. Hg^0 breakthrough for the LAC at baseline flue gas conditions with 20 ppmv NO_2 (Miller et al, December 1998).

retained only 8.7 mg of mercury compared to 106.1 mg injected, confirming that most of the initially captured mercury was desorbed after starting SO_2 . These results provide very strong evidence of a major interaction between these gases and mercury, but the exact mechanisms by which this occurs remain unclear. Because a volatile oxidized form of mercury is produced under conditions without HCl, there is a question as to the exact mercury species that is desorbed. The possibility exists that traces of chlorine compounds are in the sorbent that could serve as a source of chlorine for the production of $HgCl_2$. However, that the oxidized mercury desorption is observed only when NO_2 is present suggests that possibly a mercury- NO_2 -sorbent complex is the initially captured form of mercury, which is then possibly converted to mercuric oxide (HgO) when SO_2 is present. Mercuric oxide would be expected to be stable

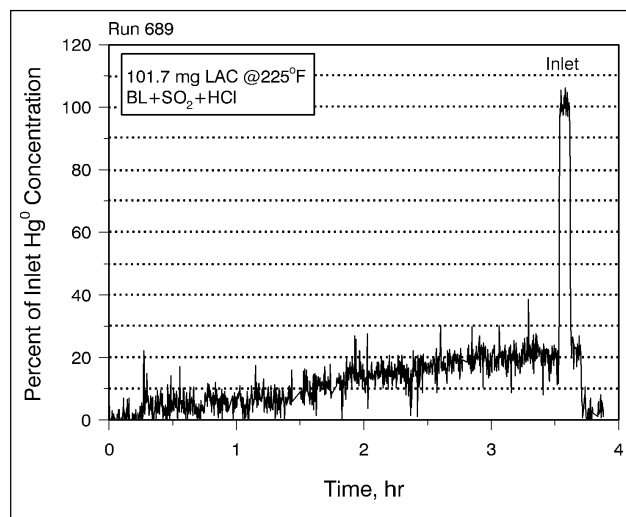


Figure 43. Hg^0 breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO_2 and 50 ppmv HCl (Miller et al, December 1998).

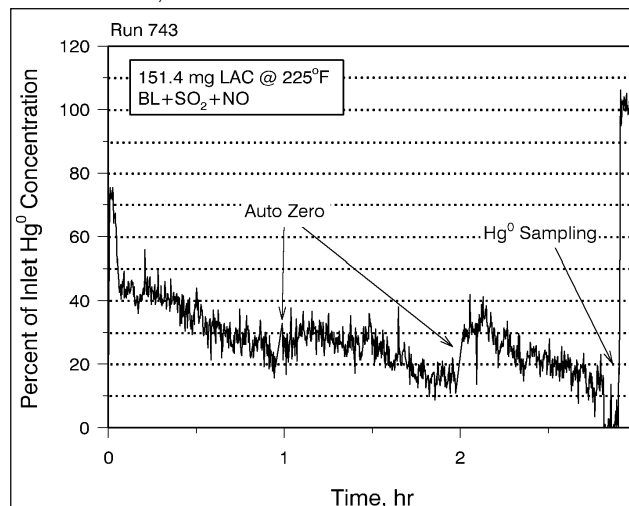


Figure 44. Hg^0 breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO_2 and 300 ppmv NO (Miller et al, December 1998).

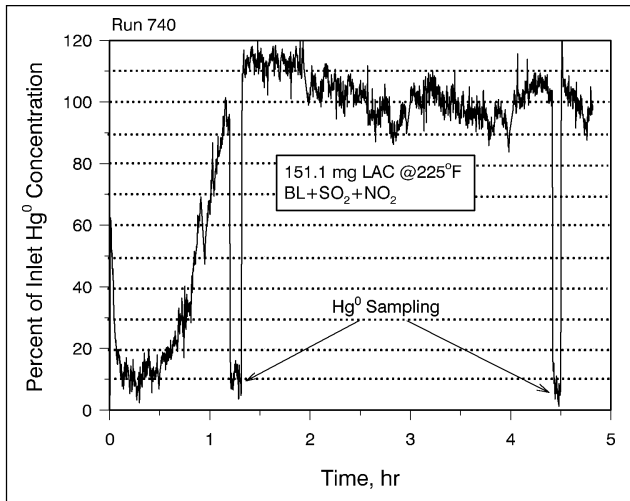


Figure 45. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO₂ and 20 ppmv NO₂ (Miller et al, December 1998).

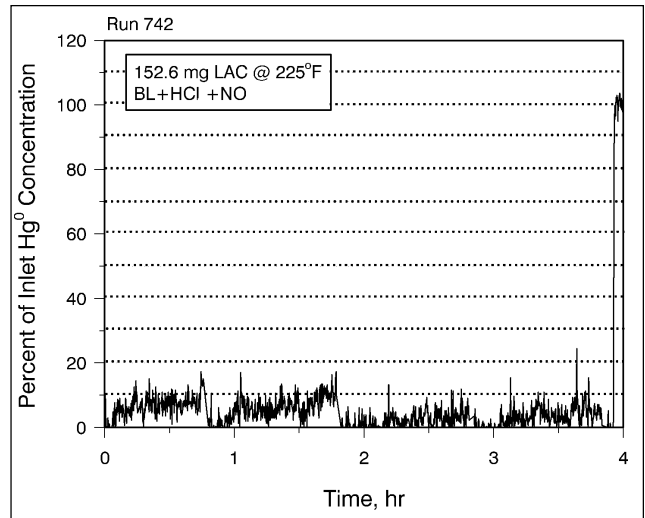


Figure 48. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 300 ppmv NO and 50 ppmv HCl (Miller et al, December 1998).

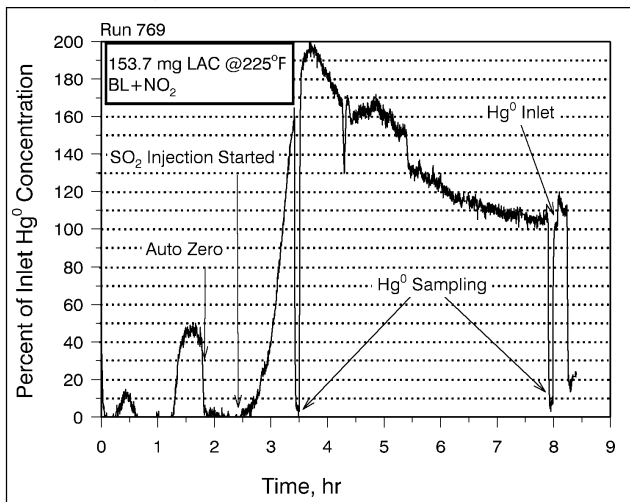


Figure 46. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 20 ppmv NO₂ alone and then with 1600 ppmv SO₂ started after 2.5 hours (Miller et al, December 1998).

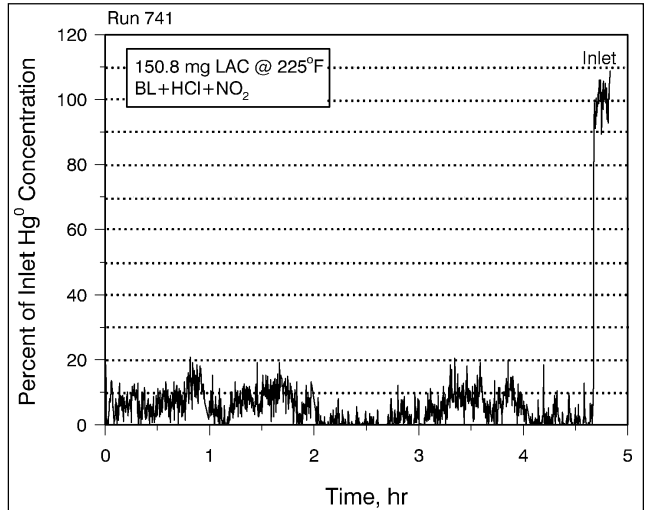


Figure 49. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 50 ppmv HCl and 20 ppmv NO₂ (Miller et al, December 1998).

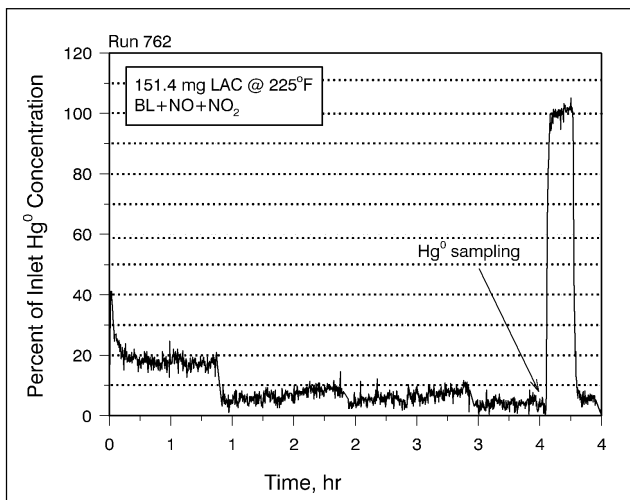


Figure 47. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 300 ppmv NO and 20 ppmv NO₂ (Miller et al, December 1998).

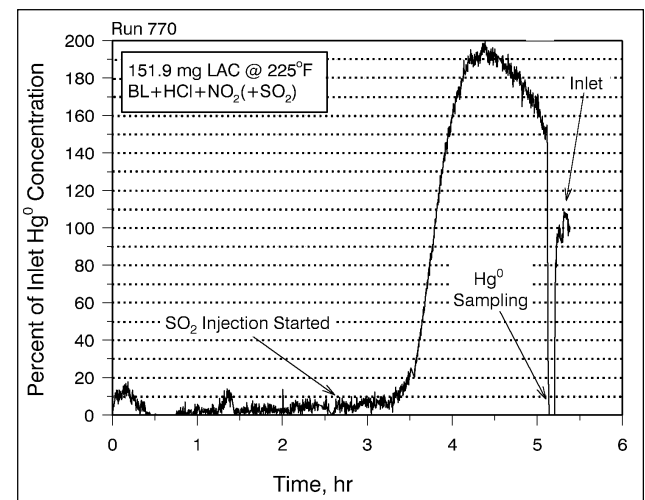


Figure 50. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 50 ppmv HCl and 20 ppmv NO₂, and then with 1600 ppmv SO₂ started after 2.5 hours (Miller et al, December 1998).

at 225 °F (107 °C) and have sufficient vapor pressure to occur in the gas phase under these conditions. However, the mechanism responsible for the release of the HgO (or other Hg²⁺ species) is not known. The identification of this significant interaction that is strong enough to completely dominate the effectiveness of a sorbent is a major finding, but much more work is needed to understand the mechanism.

The mercury species formed under these conditions was converted to Hg⁰ after passing through the SnCl₂ conversion system developed for the semtech analyzer. Future testing should include measurements with the Ontario Hydro Method to see where the converted or non-Hg⁰ form is collected (KCl impingers for Hg²⁺ capture or passing through as a non-Hg²⁺ form in the permanganate impingers).

- (4) Run 762, with NO and NO₂, initially indicated a capture of 80%, but improved to 95% by 3.5 hr. This is similar to the tests for NO alone due to capture improving with time, but is also similar to NO₂ alone in that excellent capture was observed. Based on this one test, results for the combination of NO and NO₂ are not significantly different from those of either NO or NO₂ alone.
- (5) Run 742, with HCl and NO, indicated 95% capture after 4 hr. These results are similar to HCl alone in that capture was constant over the entire test period, while for the test with NO alone, capture improved somewhat with time. NO and HCl together are similar to NO or HCl alone, under these conditions
- (6) Run 741, with HCl and NO₂, indicated nearly 100% capture after 3 hr. Similar results as HCl or NO₂ alone. In all three cases, close to 100% capture was observed.

Additional tests with HCl and NO₂ provided some interesting results. A change in experimental conditions such as a reduced sorbent mass possibly could reveal differences, but these tests did not. For Run 770 (Figure 50), SO₂ was added after 2.75 hr of testing with HCl and NO₂. After a period of about 40 min, there was rapid breakthrough up to 200% of the inlet mercury concentration, and the breakthrough mercury was all oxidized. This is similar to the result in which SO₂ was added after starting a test with NO₂ alone (Run 769, Figure 46), with one difference. In Run 769, the breakthrough occurred almost immediately after starting the SO₂, while in Run 770 (Figure 50) there was a distinct delay in the time before breakthrough. This suggests that the combination of SO₂ and NO₂ is dominating the mercury capture, desorption, and oxidation, but that HCl also is playing a role in what is happening on the sorbent surface.

The next series of tests included four possible combinations of the gases taken three at a time. Figures 51-54

show the breakthrough curves under the four different conditions as follows: results are indicated below:

- (1) Run 712, with SO₂, HCl, and NO, initially indicated a 10-25% breakthrough reaching at least 95% after 2 hr. This result is similar to a number of tests with NO (exception, combination of SO₂ and NO₂). Comparing the results from Run 712 with those of Run 742, which included only NO and HCl, suggests that the addition of SO₂ may make the initial breakthrough higher, but after several hours this difference disappears. The net result is that the combination of SO₂, HCl, and NO still provided good sorbent performance for the given test conditions.
- (2) Run 761, with HCl, NO, and NO₂, initially indicated a 10-20% breakthrough with capture improving with time and some zero-drift problems were encountered. Analysis of the sorbent after the run suggests 100% capture, so the data taken together indicate capture in the range of 90-100%.
- (3) Run 714, with HCl, SO₂, and NO₂, indicated close to 100% capture at 1-1.5 hr, with rapid breakthrough above the 100% level. Similar results were indicated with other tests with SO₂ and NO₂. The interaction between SO₂ and NO₂ has a profound negative effect on sorbent performance under these conditions.
- (4) Run 763, with SO₂, NO, and NO₂, indicated an initial good capture followed by rapid breakthrough. There does appear to be more rapid breakthrough than for the combination of HCl, SO₂, and NO₂. This suggests that HCl is also playing a role in the breakthrough phenomenon, possibly delaying the onset. Again, the breakthrough mercury appears to be all oxidized without any HCl present, suggesting a volatile mercury species other than HgCl₂.

The last test included the combination of all four gases (SO₂, HCl, NO, and NO₂) and was designated as Run 721 with the breakthrough curve presented in Figure 55. This combination is the most representative of the possible gas concentrations that are known to be present in real flue gas from a medium-sulfur, medium-chlorine bituminous coal. The results are as follows:

- Run 721, with SO₂, HCl, NO, and NO₂, indicated an initial period of good mercury capture for 1 hr with rapid breakthrough up to 100% of the inlet level. The breakthrough did not appear to exceed the inlet level, which occurred in the tests with the combination of SO₂ and NO₂.

The condition with all four gases was also evaluated at 325 °F (163 °C) in duplicate tests. At the higher temperature, the initial capture was somewhat lower, but the same

trend occurred, showing significant breakthrough after 1 hr and approaching the inlet concentration by 3 hr. Essentially all of the breakthrough mercury was measured as oxidized mercury.

These results have significant implications because they show that the interaction between SO₂ and NO₂ has the potential to dominate Hg⁰ capture with the LAC. Because some SO₂ and NO₂ are always present in coal combustion flue gas, this effect is likely to have an impact on sorbent performance for a variety of coals. In addition, because the effect occurred at both ends of the wide temperature range from 225 to 325 °F (107-163 °C), it cannot be easily avoided by a small change in temperature. The results also imply that previous bench-scale studies of mercury sorbent capacity and reactivity that did not include both SO₂ and NO₂ may provide misleading results (Dunham and Miller, September 1998; Miller et al., December 1998).

Conclusions

- (1) Without acid gases present, upon exposure to a baseline gas mixture of O₂, CO₂, N₂, and H₂O, the LAC sorbent provided only about 10-20% mercury capture of Hg⁰ at 225 °F (107 °C). Under these conditions, the LAC sorbent was completely ineffective at capturing elemental mercury.
- (2) When the sorbent was exposed to SO₂ in addition to the baseline gases, LAC sorbent capture improved slightly, but the LAC sorbent was still ineffective at capturing elemental mercury.
- (3) Upon exposure of the sorbent to HCl, NO, or NO₂ added one at a time to the baseline gases, the mercury capture improved to 90-100% at 225 °F (107 °C). Under these conditions, the LAC is a highly effective sorbent for capturing elemental mercury.

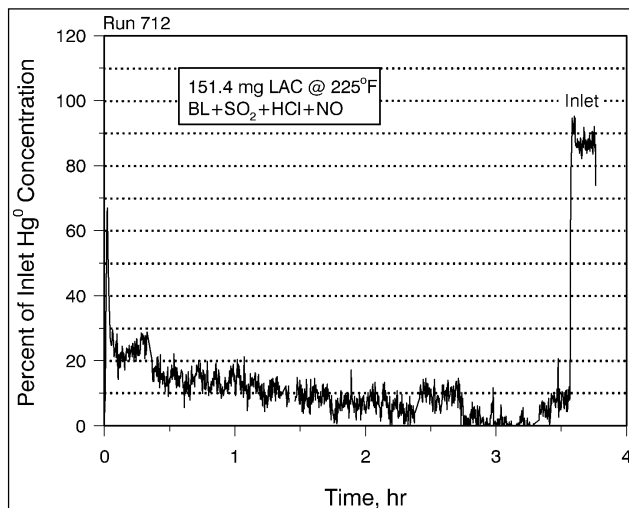


Figure 51. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO₂, 300 ppmv NO, and 50 ppmv HCl (Miller et al, December 1998).

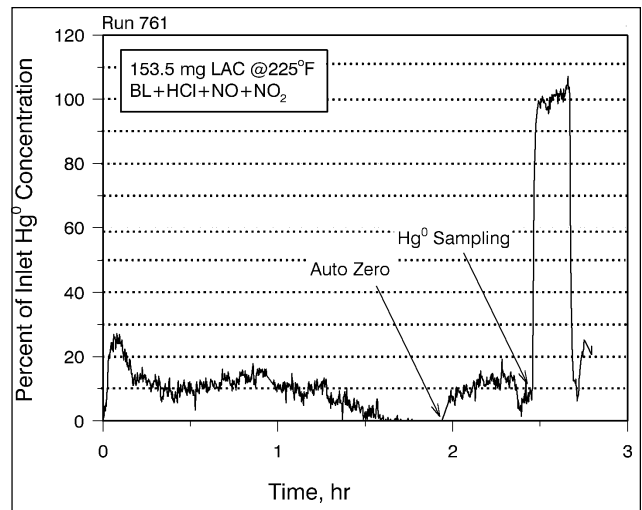


Figure 52. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 300 ppmv NO, 20 ppmv NO₂, and 50 ppmv HCl (Miller et al, December 1998).

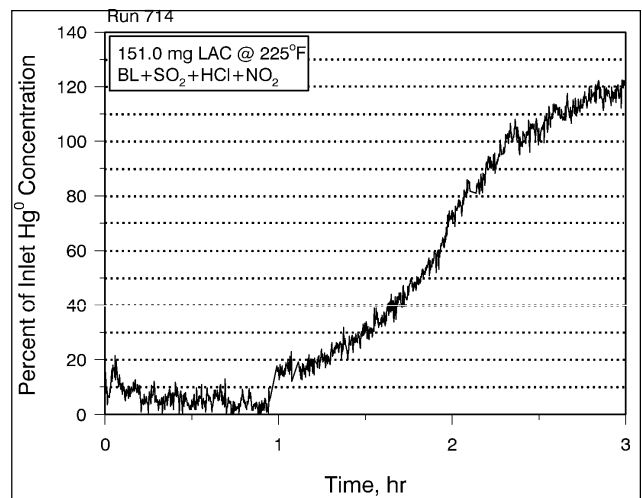


Figure 53. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO₂, 20 ppmv NO₂, and 50 ppmv HCl (Miller et al, December 1998).

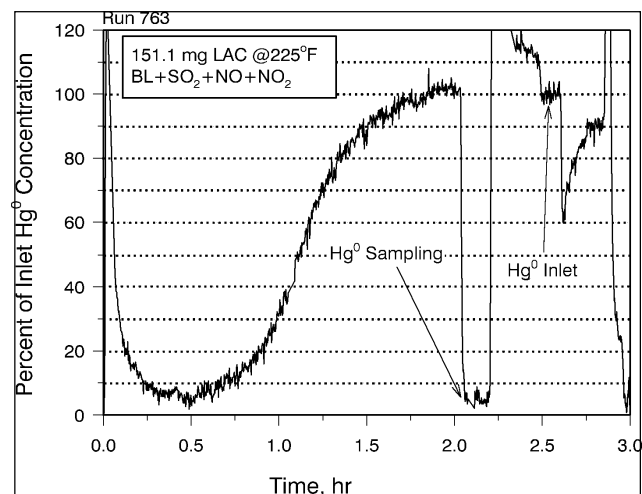


Figure 54. Hg⁰ breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO₂, 20 ppmv NO₂, and 300 ppmv NO (Miller et al, December 1998).

- (4) An apparently significant interaction between SO_2 and NO_2 gases and the sorbent caused a rapid breakthrough of mercury as well as conversion of the mercury to a volatile oxidized form. This effect occurred at both 225 and 325 °F (107 and 163 °C) and with or without the presence of HCl and NO.
- (5) In the presence of all four acid gases (SO_2 , HCl, NO, and NO_2), rapid breakthrough and oxidation of the mercury occurred at both 225 and 325 °F (107 and 163 °C). This suggests that the interactions between NO_2 and SO_2 gases and the sorbent produced poor sorbent performance, which may be a major effect. This may be likely to occur over a variety of conditions typical of coal-fired boilers, and represents a hurdle that must be overcome in order to achieve effective mercury control by this control method.

The EERC continues to investigate these and other interactions with not only the flue gas vapor-phase constituents and ACs, but with fly ash and the AC. Data are being compiled on the LAC at various pilot-scale facilities located at different power plants firing either bituminous or subbituminous coals. In addition, other type of sorbents are being developed and investigated under similar, simulated flue gas conditions as the EERC studies, but not under a full-factorial design. There are other possible vapor-phase constituents impacting mercury capture or enhancing it, but more testing is needed to determine the mechanisms being involved with enhanced mercury capture. A better understanding is needed before any regulatory decisions are made. AC injection is a promising technology, but further research is needed to provide the best sorbent providing effective capture at a low cost (less

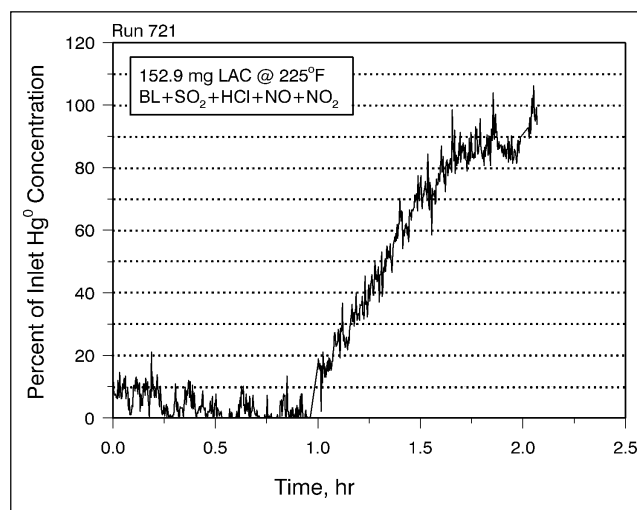


Figure 55. Hg^0 breakthrough for the LAC at baseline flue gas conditions with 1600 ppmv SO_2 , 20 ppmv NO_2 , 300 ppmv NO, 50 ppmv HCl (Miller et al, December 1998).

than \$0.25/lb). Equilibrium sorption capacity may not be the driving force for better sorbent performance, while the reactivity with the basic forms of mercury (Hg^0 and Hg^{2+} forms) may be the critical factor.

University of Kentucky: Development and Utilization of XAFS for the Characterization of Mercury Sorption

The synchrotron-based technique of XAFS spectroscopy is proving to be a valuable direct, nondestructive probe of the sorption by various materials of gaseous mercury species present in combustion flue gases. Using both the XANES and EXAFS regions of the mercury LIII XAFS spectra, new insights have been obtained on how mercury is bound to various carbon-based and other sorbents and how such bonding can be affected by external conditions, particularly the gas-phase chemistry of the flue gas and species (e.g., sulfur and iodine) added as activating agents to carbon-based sorbents.

All XANES spectra of mercury captured on a sorbent material are more or less similar to that shown in Figure 56a. However, a specific common mercury compound has not been found that gives rise to a Hg XANES spectrum that matches well with any of such spectra, indicating that the sorption of mercury does not involve formation of well-defined crystalline mercury species. As shown in Figure 56b, each mercury absorption edge has two prominent inflection points that appear as a pair of well-defined peaks in the first derivative spectrum. It has been demonstrated that the separation of these two peaks, referred to as the inflection point difference (IPD), is a reflection of the chemical bonding of mercury in a wide range of chemical compounds (Table 23). The determination of the IPD from the Hg XANES spectrum of a carbon-based sorbent is indicated by the two arrows showing the measurement positions in the second derivative spectrum (see Figure 56c). Basically, the smaller and more polarizing the anion to which the mercury is bound, the larger the value of the IPD parameter. Hence, large IPD values are found for oxygen anions and small values are found for iodide anions. This parameter has been used to interpret the bonding of mercury captured on various sorbent materials.

For sulfur- and iodine-activated carbons, the XANES IPD spectral parameter indicates that the interaction with the mercury is principally via the formation of Hg-S and Hg-I complexes, respectively, apparently regardless of whether the mercury is present in the flue gas as elemental Hg or HgCl_2 . Furthermore, detailed analysis of the EXAFS region of the spectra of the iodine-activated carbons indicates the Hg is bound to the carbon via a very long bond, that is only consistent with the formation of an Hg-I complex (Figure 57). A third AC prepared from a

lignite, but without the addition of an activating element, exhibited more variable behavior that appeared to depend on the chemistry of the flue gas, specifically the mercury speciation (whether Hg or HgCl₂), and the presence of HCl. Complementary XAFS studies of sulfur and chlorine on this carbon indicated the acidic species (H₂SO₄ and HCl) were readily adsorbed onto this carbon. But the Hg XAFS data were only compatible with complexation with chloride, not with sulfate.

In addition, various coal-based chars have been prepared for use as mercury sorbents and these too have been examined by Hg XAFS spectroscopy. In such cases, small but significant differences in the mercury IPD parameter were noted between two bituminous coals and a subbituminous coal. The IPD values for mercury in chars from the bituminous coals were close to those observed for mercury chlorides, whereas those for the subbituminous coal were significantly smaller. This difference is thought to reflect the much lower chlorine content of the subbituminous coal relative to the bituminous coals. Again, this suggests that chlorine is important in mercury sorption, but also that it is not the only factor. Researchers at the University of Kentucky are developing sorption models for various trends in the XANES parameters in terms of mixtures of sulfur- or chlorine-activated sites and sites that are active without an activating element. Our current interpretation of the data trends is that the chlorine promotes the formation of an activated (chemisorption) site, but that in the absence of such chlorine-activated sites, there are other (physisorption) sites for Hg⁰.

In addition, zeolite sorbents for flue gas mercury have also been examined by XAFS spectroscopy. The values for the IPD parameter for Hg in these materials were determined to be significantly higher than those for mercury in carbonaceous sorbents. As mercury sorption by zeolites must involve Hg-O bonding, this result is consistent with the data shown in Table 23.

Currently, there is much interest in how mercury sorption on carbonaceous materials varies with gas-phase chemistry, especially the acidic species, H₂SO₄ and HCl, and more recently, nitrogen oxides. The IPD parameter is also being used to follow this behavior. Other ongoing Hg characterization involves two fly ash samples, one from the Cherokee power plant, and the Comanche power plant (Colorado) provided by personnel at ADA. These particular fly ashes are very efficient at sorbing mercury. The researchers are in the process of separating it into carbon- and glass-rich fractions for more detailed study of the partitioning of the mercury between the carbon and aluminosilicate fractions.

The development and utilization of these techniques at the University of Kentucky have provided and will

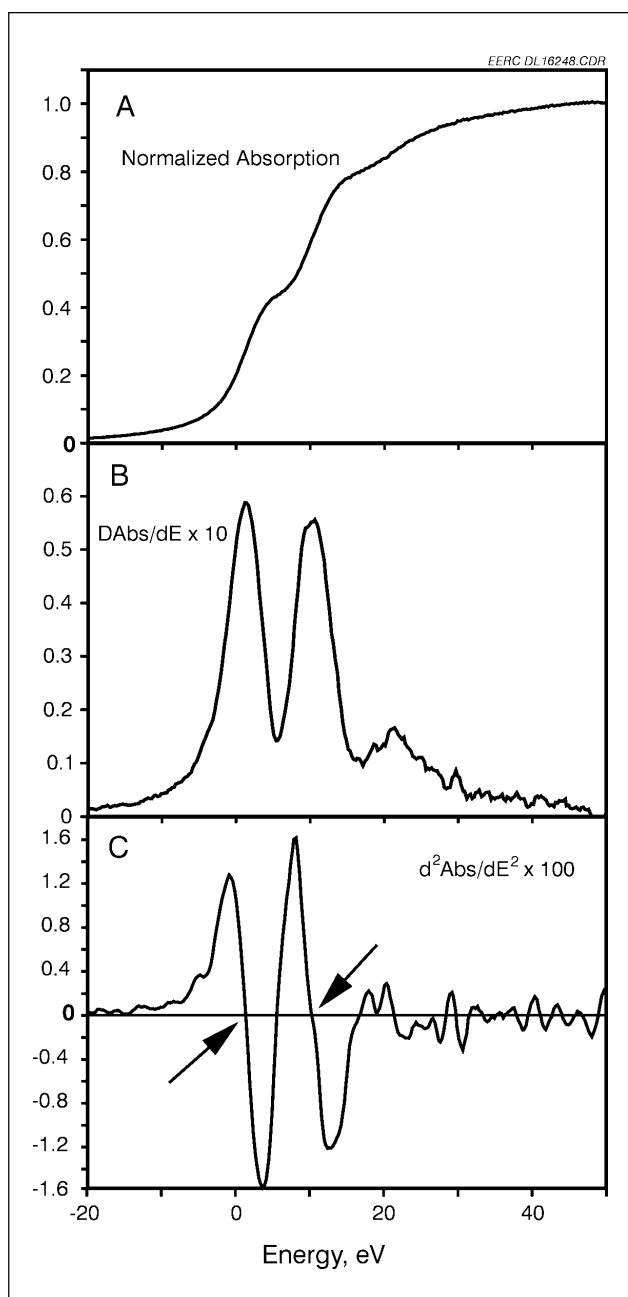


Figure 56. Determination of inflection point difference (IPD) from Hg XANES spectrum of a carbon-based sorbent. Arrows show measurement positions.

continue to provide invaluable information on the chemical form(s) of Hg associated with the various virgin and chemically impregnated ACs, and certain fly ashes. The use of these techniques is critical in the understanding of Hg capture, optimization of Hg capture, and knowing the stability regarding the Hg form(s) on or in the ACs. These techniques have the capability of providing information that supports or disputes the theories regarding the Hg chemistry associated with the various sorbents being investigated for use in the utility industry to effectively capture Hg and

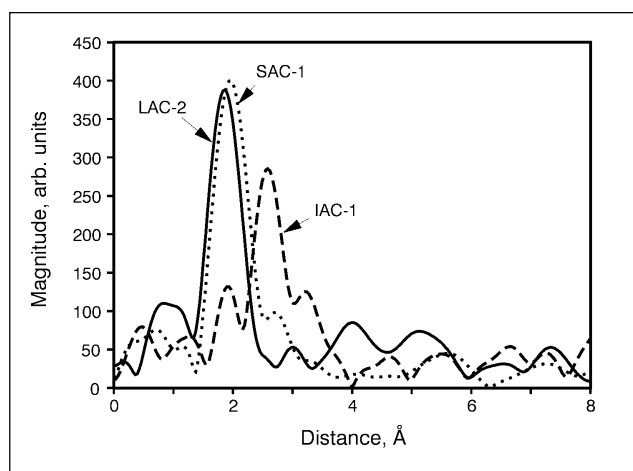


Figure 57. EXAFS/RSFs for three activated carbon samples. Note the peak at about 2.7 Å for the iodine-activated carbon (IAC-1) Bolded information for figures only.

subsequently provide for safe sequestration.

The DOE/FETC In-House Research Program: Laboratory- and Pilot-Scale Investigations of Commercial and Novel Adsorbents for Mercury Capture in Flue Gas from the Combustion of Coal

The in-house research program at FETC includes a laboratory-scale packed-bed reactor system and a pilot-scale coal combustion unit that mimics a utility boiler and includes a furnace, air preheater, ductwork, and ancillary flue gas clean-up equipment. The laboratory-scale system is used to screen sorbents for their capability to remove elemental mercury from various carrier gases (Granite et al., 1998). The coal combustion unit (nominal 500 lb/hr) has been characterized in the past in terms of the distribution and fate of HAPs including mercury (Hargis, Jr. and Pennline, 1996). Most recently, a series of tests have been conducted on this unit to initiate operation of a sorbent injection system and obtain preliminary results on mercury removal with dry sorbent injection (Hargis, Jr., et al., 1999). Significant interaction between these two experimental units is planned for the future, with promising sorbents identified in the laboratory-scale system being evaluated in the pilot unit. The following discussion describes recent results from both of these units.

A unique feature of the laboratory-scale packed-bed reactor system is that an on-line atomic fluorescence spectrophotometer (AFS) is used in a continuous mode to monitor the elemental mercury concentration in the inlet and outlet streams of the packed-bed reactor. Several commercially

available ACs, as well as novel sorbents, have been characterized in terms of their capacity to adsorb elemental mercury from an argon carrier gas and the time until mercury breakthrough occurred. Mechanisms of mercury removal by the sorbents can be inferred by combining the results of the packed-bed testing with various analytical results.

A description of the assembly used for measuring sorbent capacities is given in the reference and is summarized here. The unit consists of an elemental mercury permeation tube, a packed-bed reactor, an on-line AFS, and a data acquisition system. A controlled flow of argon over the permeation tube provides a constant flow rate of elemental mercury to the reactor. The overall length of the vertically positioned quartz reactor tube is 20 in. with an inner diameter of 1/6 in. Inert materials (either Teflon or quartz) were used to minimize the possibility of surface effects with mercury. The depth of the packed bed in the reactor tube is only a few millimeters, with the typical amount of sorbent being about 10 mg. A clamshell furnace around the tube maintains the temperature such that the difference in temperature between the top and bottom of the bed is within 1.8 °F. Reactor effluent gases pass through a Brooks Rand CVAFS-2 cold-vapor atomic fluorescence spectrophotometer that has a detection limit below 0.1 ppbv for elemental mercury in argon.

A gas feed of 4800 mg/Nm³ elemental mercury in argon was used. Even though this is orders of magnitude higher than that typically measured in a flue gas from a coal-fired utility, the fundamental results of capacity are still a relative indication of sorbent activity. In addition, argon was used as a carrier gas to maximize the sensitivity of the AFS for elemental mercury. However, it is recognized that the capacity of the sorbents in argon may be quite different from the capacity in flue gas, and this will be the subject of future investigations. The temperatures at which sorbent capacities were determined were 140, 280, and 350 °F (60, 138, and 177 °C). These temperatures were chosen as representative of those that may be experienced at the particulate control device of a coal-fired utility or after a wet scrubber.

Table 23. Hg XAFS systematics for compounds.

Mercury Compounds	IPD, eV	RSF, A	Mercury Compounds	IPD, eV	RSF, A
HgO (yellow)	13.3		HgS (metacinnabar)	7.7	2.12
HgO (red)	13.3	1.68	HgS (cinnabar)	7.3	2.05
Hg acetate	10.6	1.72	HgCH ₃ I	6.9	2.49
Hg ₂ SO ₄	9.6		Hg diphenyl	6.8	
HgSO ₄	9.5		Hgl ₂	6.5	
Hg ₂ Cl ₂	8.4		K ₂ Hgl _a	4.6	2.52
HgCl ₂	8.4	2.02	Hg (liquid)	0.0	

The capacity and breakpoint are used to characterize the behavior of the sorbent toward elemental mercury removal. Capacity is defined as the amount of elemental mercury removed by the sorbent after 350 min on stream, and breakpoint is the time when the outlet concentration of mercury from the reactor bed is 10% of the inlet mercury concentration. Some of the sorbents examined to date are listed in Table 24. A description of the preparation methods and the various analytical techniques used to characterize the fresh and spent sorbents is provided by Granite et al. (1999).

The reproducibility of the experimental technique was very good (capacity ± 0.2 mg/g and the breakpoint time $\pm 25\%$). Experiments were conducted to show that the mass transfer resistance due to the diffusion of mercury into the sorbent at the sizes used in the testing was negligible and that bulk mass transfer effects, heat transfer effects, channeling, and pressure drop would not be significant.

Although the 350-min capacities and the 10% breakpoint times for the sorbents are listed in the reference of Granite et al. (1999), a brief summary of the results follows. The iodine-promoted AC showed the highest capacity and longest breakpoint time. The chemically promoted ACs had higher capacities for mercury than unpromoted carbons. The capacities of the ACs increased with decreasing temperature, as expected. The metal oxides showed some promise as alternatives to AC sorbents, with MnO_2 having a moderate capacity for mercury removal. Future work will concentrate on using an oxygen-containing carrier gas and then a simulated flue gas, and the addition of mercuric chloride to these gases. Selected promising sorbents identified at the laboratory scale will be further evaluated in the 500-lb/hr combustion unit.

Previous testing on this pilot unit has been conducted to evaluate mercury sampling and speciation methods (Hargis, Jr. and Pennline, 1997; McManus et al., 1997). Most recently, a series of tests have been conducted to

initiate operation of a sorbent injection system and obtain preliminary results on mercury removal with dry sorbent injection (Hargis, Jr., et al., 1999). One test was with natural gas firing, sorbent injection, and spiking of the flue gas with elemental mercury. Other tests were conducted under coal-firing conditions, with and without sorbent injection. The coal was a blend of Ohio #5 and Ohio #6 coals that have been used in previous mercury investigations by other researchers. The sorbent was a commercially available AC. A total mercury measurement method (EPA Method 101A) was used for these tests.

In the natural gas-firing test, mercury was spiked at a level of about 50 mg/m^3 and the AC was injected to give a mass ratio of sorbent to mercury of about 6000:1. Mercury removal across the ductwork and baghouse was about 65%. For the coal-firing tests, mercury levels in the flue gas were about 20 mg/m^3 and sorbent was injected to give a mass ratio of sorbent to mercury of about 20,000 to 1. Mercury removals with sorbent injection were about 90%, compared to negligible removals without sorbent injection. These tests show that high mercury removals may be possible with a commercially available AC.

Testing is now under way with a low-sulfur, eastern bituminous coal. This coal was selected because this type of coal would be burned at utilities that do not have

Table 24. Sorbents used in packed-bed testing.

Sample	Composition	Description
I-AC	3.5% I	Iodine promoted activated carbon, containing both elemental iodine and potassium iodide
S-AC	7.6% S	Sulfur promoted activated carbon
AC-1	0.9% S	Unpromoted carbon from Calgon
AC-2	0.4% S	Unpromoted carbon from CarboChem used commercially for decolorizing corn syrup
Cl-AC-1	6.0% Cl	HCl treated activated carbon
Cl-BPL-AC	6.7% Cl	Chlorine treated activated carbon
HNO_3 -AC-1	—	Treated activated carbon prepared by boiling AC-1 in 70% nitric acid
S-BPL-AC	5.9% S	Sulfur promoted activated carbon prepared by U. of Pittsburgh
V_2O_5 -Celkate-1	8% V_2O_5	Vanadium pentoxide dispersed on celkate
V_2O_5 -Celkate-2	50% V_2O_5	Vanadium pentoxide dispersed on celkate
Celkate	MgSiO_3	Synthetic magnesium silicate
Cl-Celkate	15% Cl	HCl treated celkate
KO_2 - V_2O_5	3.4% K, 1.4% V	Potassium superoxide promoted vanadium pentoxide sorbent supported on celkate
MoO_3 /Celkate	46% MoO_3	Molybdenum oxide supported on MgSiO_3
Alumina	Al_2O_3	High surface area alumina
MnO_2 / Al_2O_3	7% MnO_2	Alumina supported MnO_2
CaCl_2 / Al_2O_3	10% CaCl_2	Supported halide salt
TS-7	3.5% S	Thiol promoted aluminosilicate sorbent provided by Pacific Northwest National Laboratory
MoS_2	87% MoS_2	Hydrodesulfurization catalyst prepared in-house at FETC
CFA	64% C	Unburned carbon separated from fly ash from combustion of Black Creek coal
CERF-FA-#2	59.3% C	Fly ash from a Pittsburgh #8 coal
CERF-FA-#4	37% C	Fly ash from a Pittsburgh #8 coal

desulfurization systems, and units burning these coals are the most likely market for sorbent injection systems to remove mercury. Mercury measurements are being made with the Ontario Hydro Mercury Speciation Method. Future testing will determine the impact of temperatures, duct residence times, baghouse cleaning cycles, and flue gas humidity on the removal of mercury species with various sorbents.

Public Service Company of Colorado (PSCO) and ADA Technologies, Inc. (ADA): Investigation and Demonstration of Dry Carbon-Based Sorbent Injection for Mercury Control

Under the DOE/FETC Mega PRDA Program, DOE, (PSCO), and EPRI are funding both phases of work being conducted at the pilot and full scales to evaluate carbon injection as a mercury control technology. ADA performs the fabrication, pilot operation, and reporting.

The pilot evaluations are being conducted on a pilot-scale particulate control module (PCM) drawing a 600-acfm slipstream of flue gas from the 350-MWe Comanche Station, Unit 2 of PSCO. The station has an opposed-fired furnace firing a PRB coal from the Belle Ayr mine. Figure 58 shows a schematic of the pilot-scale unit. Flue gas can be either drawn from the inlet (high particulate loading) or the outlet (essentially particle-free) of the station's reverse-gas baghouse. In addition, the PCM can be configured as an ESP, a reverse-gas baghouse or pulse-jet FF, and EPRI's TOXICON.

There are duct locations for mercury spiking; sorbent injection at various locations to investigate in-flight residence times (0.5-3 sec) upstream of the PCM; sorbent injection for acid gases (primarily SO₂); and there is an in-duct heater and water spraying to investigate the effects of mercury sorption at different temperatures. The flexibility of the PCM is needed for the evaluations that would be encountered in the utility industry if mercury control technology was required. The flexibility of the PCM is also needed owing to the native fly ash in the flue gas at this station. As detailed in the section Factors Influencing Mercury Speciation and Adsorption, the fly ash has an affinity to capture mercury in-flight and across a FF and increases as the temperature decreases. The possible interactions of the flue gas and fly ash present challenges in terms of measuring mercury emissions using conventional sampling procedures, but the PCM is designed to investigate these interactions and also test with minimal impact from the interactions.

The objectives of this two-phase project include the following:

- (1) Determine mercury removal rates as a function of temperature and of carbon injection rate.
- (2) Examine the impacts on operation of particulate control configurations, as well as fly ash impacts from the injection of carbon. Establish accurate

"baseline" performance data, such as particulate control efficiency, electrical characteristics for an ESP, and pressure drop/cleaning characteristics for a baghouse.

- (3) Evaluate the impacts on mercury removal during continuous injection of carbon and intermediate injection for the FF configurations.
- (4) Quantify mercury removal by Comanche's ash separately from an injected sorbent.
- (5) Quantify the temperature range or other operating conditions for maximum adsorption of mercury capture of the Comanche/Belle Ayr coal fly ash. In addition, investigate reasons for the sorptive capacity of this ash.
- (6) Evaluate synergistic effects of multipollutant control, mercury via carbon injection, and SO₂ via sodium sesquicarbonate.

The Phase I work conducted from September 1995 through July 1997 has been detailed in many papers presented at national conferences and in a DOE/FETC-required Phase I Final Report (Haythornthwaite et al., June 1996, August 1997, September 1997; Sjostrom et al., June 1997). The discussion will be mainly on the recent Phase II efforts, but will contain information found in Phase I.

Figure 59 illustrates the capture of mercury with the fly ash alone (on the y-axis) and with the AC. The AC is Norit's Darco FGD activated from a lignite coal. Another AC that will be shown later and designated as AC-1 was developed under funding from EPRI through the activation of an eastern bituminous coal. As previously discussed, the fly ash shows a trend of increased mercury capture with decreasing temperature 230 °F (110 °C) with spray cooling of the native flue gas. Likewise, the Norit carbon shows the same trend with the lowest capture at the 350 °F (177 °C) at the lower injection rate of 1 lb/MMac [carbon-to-mercury (C:Hg) ratio of 2,100:1], but

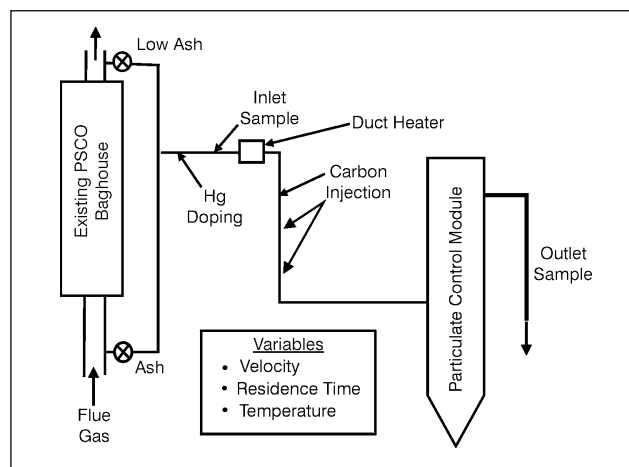


Figure 58. PSCO 600 acfm PCM pilot-scale unit at the Comanche Power Plant (Hunt et al., 1996 and Haythornthwaite et al., August 1997).

no increase in mercury capture, even when the injection rate is increased to 4 lb/MMacf (C:Hg of 10,500:1). The same trend occurs at the 270-310 °F (132-154 °C) temperature range with the mercury only being captured in flight upstream of the ESP configuration of the PCM. These are Phase II results, but they are similar to those of Phase I at the same temperatures and residence times of 0.5-1.0 sec. The inlet Hg concentrations varied from 4 to 13 µg/Nm³ over the two-month testing.

The data in the figures show mercury removal efficiency as a function of carbon concentration in the flue gas. This expression of carbon injection rate (lb/MMacf) does not vary with inlet mercury concentration, which ranged from 4 to 13 µg/Nm³ @ 3% O₂. Under mass-transfer-limited conditions, the vapor-phase mercury removal efficiency is dependent on the carbon concentration and not the mercury concentration. Mass-transfer-limited conditions normally apply when the carbon has sufficient capacity and reactivity. The carbon capacity and reactivity are dependent on temperature and mercury concentration. When the temperature is too high or the mercury concentrations are too low, mass transfer limitations may not apply and vapor-phase mercury removal efficiencies will be lower than predicted by mass transfer. In the case of Comanche flue gas, the flue gas vapor-phase mercury concentrations are very low and this may affect mercury removal efficiency achievable by carbon injection. In some cases, very little additional vapor-phase mercury removal will be observed with carbon injection (Haythornthwaite et al., 1999).

Other results or conclusions from testing with AC injection upstream of the ESP configuration include the following:

- (1) Greater than 50% mercury capture was achieved for all temperatures at the injection rate of 3.5 lb/MMacf (C:Hg of ~10,000:1), but on average the fly ash accounted for ~one-half of the total mercury captured.
- (2) Mercury removal leveled off with increased carbon concentrations, which is typical for AC injection at other test facilities (Waugh et al., August 1997; Waugh, December 1997). This demonstrates diminishing returns with the addition of more AC as also demonstrated by Flora (1997) in his modeling studies.
- (3) Spray cooling to 230 °F (110 °C) has the same mercury removal as that obtained for carbon injection at a rate of 1 lb/MMacf carbon (C:Hg of ~2,000:1) at a temperature of 300 °F (149 °C).
- (4) Residence time variation (0.5-1.0 sec) did not produce a noticeable change in mercury capture. The flue gas residence time in ducts upstream of an ESP is typical in this range (U.S. DOE, 1988 and 1993).
- (5) The increase in mercury concentrations at high

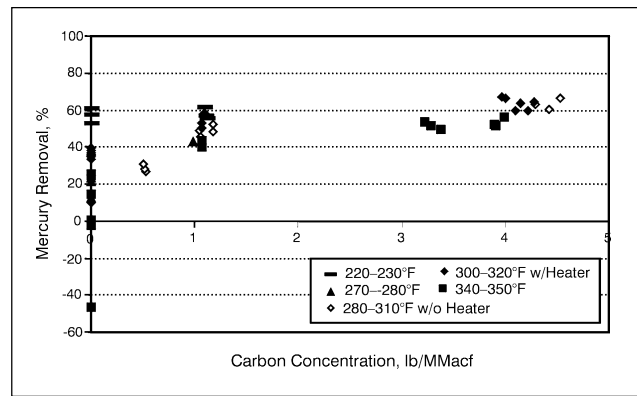


Figure 59. Comanche reverse-gas pilot-scale unit mercury removal with fly ash alone and at various carbon concentrations, and at different temperatures (Haythornthwaite et al, December 1998).

temperatures, 350 °F (177 °C) (Figure 59) is unexpected and requires further investigation before any conclusive explanation can be given.

Figure 60 depicts the mercury removed across the pilot pulse-jet FF configuration with and without carbon injected and at various temperatures. The following observations are made:

- (1) The fly ash and AC also show the trend of increased mercury capture with decreasing temperature, but at a higher level as compared to the ESP configuration.
- (2) Higher mercury removals are indicated for the lower temperatures, 250-275 °F (121-135 °C) at a lower level of injected carbon [2-3 lb/MMacf (C:Hg of 7,000:1 and 10:000:1, respectively) as compared to 4.0 lb/MMacf (C:Hg of 11,000:1) for the ESP]. Higher removals are also indicated at this injection rate at the 300 °F (149 °C) temperature.
- (3) Even at an air-to-cloth ratio of 3.8 ft/min, the mercury removal is higher than the ESP configuration. The collected fly ash and AC (dust cake) on the fabric of the pulse-jet filter provide better contact with the flue gas and sorbent media.

The reverse-gas baghouse configuration also indicated higher mercury removals with and without carbon injection as the temperature decreased. The temperatures tested were the same for the other configurations tested. Mercury removal measurements were made using carbon concentrations from 0.6 to 4.3 lb/MMacf (C:Hg of 3,500:1 and 11,000:1, respectively). PCM inlet mercury concentration in the slipstream flue gas ranged from 4.6 to 10.6 µg/dNm³. Higher mercury removal efficiency without additional injected carbon as with carbon injection (70-80% removal) at the 230 °F (110 °C) temperature is similar to the ESP testing. The high temperature tests were slightly worse than normal operating temperatures of the flue gas, with 78% versus 91% removal at a carbon concentration

around 4 lb/MMacf (C:Hg of 11,000:1) Even a low-carbon injection rate of 1 lb/MMacf or less (C:Hg of ~3,400:1 to 4,000:1) resulted in fairly high mercury removal efficiencies, from ~74% removal at 334 °F (166 °C) to ~85% at 275 °F (135 °C).

From these data for the FF configurations, for a target mercury removal of 80%, options are to either: inject ~4 lb/MMacf carbon (C:Hg of 10,000:1 to 11,000:1) or cool the flue gas to below 310 °F (154 °C) for the pulse jet; or below 280 °F (138 °C) for the reverse gas and inject ~1 lb/MMacf carbon (C:Hg of ~3,400:1 to 4,000:1). The differences in the amount of carbon injection rates may be attributed to the differences in the air-to-cloth rates of the pulse jet (3.8 ft/min) and the reverse gas (1.6 ft/min) configurations. The lower air-to-cloth ratio provides for more contact with the dust cake of fly ash and carbon. The differences are also attributed to the high Hg removal associated with the fly ash from this PRB coal, with increasing Hg removed with decreasing temperature. The mercury removal at this site has been documented to be from one-half to 90% of the mercury captured, with and without activated carbon present.

Care must be taken in extrapolating this data to other facilities firing different PRB/subbituminous coals, and specifically at facilities firing eastern bituminous coals. As indicated in previous sections, the fly ashes between these two different rank of coals are remarkably different in the ability to adsorb or react with the mercury. Again, the fly ash from the combustion of the Belle Ayr coal and other PRB coals demonstrate an affinity for high Hg capture. The mechanisms for this and other PRB coal fly ash at carbon concentrations in the range of 0.5 to 1.0% are being investigated at the fundamental level and are still not understood. In addition, the majority of the mercury in the flue gas from the combustion of PRB coals is in the

Hg⁰ form (50 to 85%) with lower amounts of Hg²⁺ being captured with the fly ash.

Activated carbon injection tests at a slipstream pilot-scale fabric filter facility firing a low-sulfur eastern bituminous coal indicated much higher C:Hg of 20,000:1 to 50,000:1 to remove 70% to 90% of the mercury in the flue gas at 240 °F (116 °C). The ESP configuration at this site indicated only 35% Hg removed at 272 °F (133 °C) and ~85% at 221°F (105 °C) at the same C:Hg of ~45,000:1 (Vaugh et al., August and December 1997).

Details of the impacts on the operation of the three particulate control configuration can be obtained from Haythornthwaite et al. (September 1997, December 1998, June 1999). The impacts on FF pressure drop, frequency of cleaning, etc., were minimal because the injection rate of the AC was low compared to the native fly ash loadings. There were some cleaning problems encountered during the ESP testing. Removal efficiencies averaged only 92%, which is not typical of utility ESPs. Data collected under the ESP configuration cannot be used to interpret incremental changes in particulate control efficiency that are caused by carbon injection. This question of carbon impacts on ESP performance is being addressed under a separate part of this project.

Sodium injection tests were designed to investigate whether any synergistic removal of mercury, or impairment of SO₂ removal, occurs when carbon and sodium sesquicarbonate are both injected into the flue gas and collected in a FF. Previous testing at Public Service Gas and Electric's Hudson Generating Station in Jersey City, NJ, has suggested that synergistic effects are possible (Vaugh et al., 1997). ADA installed CEM equipment for gas concentration measurements during sodium sesquicarbonate injection testing. The CEM monitored and logged SO₂, NO_x (NO and NO₂), NO_x-NO, CO, and O₂. ADA conducted tests at several carbon injection rates along with several sodium injection rates.

Initially, the normalized stoichiometric ratio (NSR) of sodium to SO₂ was targeted for each test condition based on recommendations by the project team. The target NSRs were 0.8, 1.6, and 2.4, but the NSRs were generally between 1.5 and 4.5. Injection rates in grams per minute (g/min) of sodium sesquicarbonate were based on these targeted NSRs.

At an NSR of approximately 1.6, SO₂ removal varied from 20 to 44% with measurements of 20% at 278 °F (137 °C), 28% at 284 °F (140 °C), and removal of 40-44% at 326 °F (164 °C). In addition, at NSRs ranging from 2.6 to 4.5, corresponding SO₂ removals at a nominal 280 °F (138 °C) ranged from 20 to 59%. There was a trend of increased SO₂ removal with an increase in sodium injection rate. At a nominal NSR of 3.0 and temperature of 325 °F (163 °C), SO₂ removals were higher, ranging from 57 to 64%. There

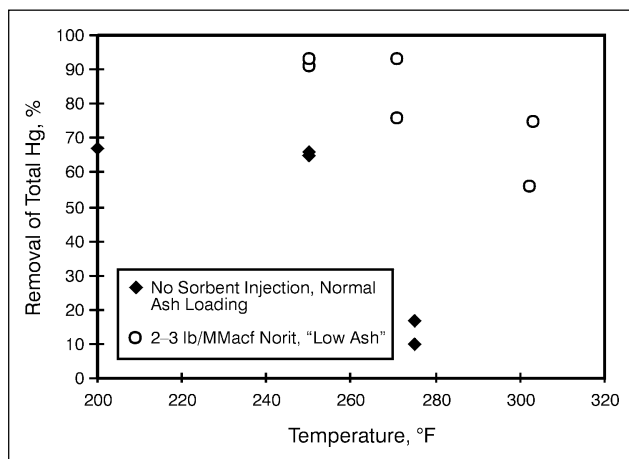


Figure 60. Comanche pulse-jet fabric filter pilot-scale unit mercury removal with fly ash alone and at various carbon concentrations, and at different temperatures (Haythornthwaite et al, December 1998).

was fluctuation at the higher removal levels indicative of the respective ranges. Testing at the higher NSRs of sodium sesquicarbonate is cost prohibitive, but a range for the station's flue gas conditions was investigated strictly for academic interest.

When compared with a range of SO₂ removal results previously observed in baghouses (Sjostrom et al., 1997), these data fall within the lower limits of the range. A noticeable improvement with temperature was observed in the ADA Comanche pilot tests even in the range of 284-326 °F (140-164 °C). Baseline conditions for SO₂ were established and testing for mercury removal was conducted.

The SO₂ removals did not appear to be impeded or improved with the injection of the AC for mercury capture. An apparent impediment on mercury removal was indicated with the injection of the sodium sesquicarbonate with and without the AC injection. This is contrary to the Hudson work in which sodium bicarbonate and hydrated lime were both seen to improve the AC's mercury adsorption capability (Sjostrom et al., 1997).

Based on the limited data, it is speculated that the impediment of mercury capture occurred, either because of inhibition of the sorbent mechanism, or because the addition of sodium increased the mercury in the flue gas. The latter is possible, based on bench-scale tests by the EERC, due to the formation of NO₂ as indicated by Dunham and Miller (September 1998) and Miller et al. (December 1998). In addition, the flue gas at Hudson was from the combustion of a low-sulfur bituminous coal and not a PRB coal. The flue gas conditions of both are very different regarding the criteria pollutant levels and the associated HCl and SO₃ concentrations.

Referring back to the section on AC and Other Sorbent Injection Technologies for Mercury Capture under University of North Dakota Energy & Environmental Research Center (EERC): Investigation of Sorbent Injection for Mercury Control in Coal-Fired Boilers.

The EERC bench-scale data indicate a strong interaction of NO₂ and SO₂ in the baseline simulated flue gas on mercury removal, desorption, and conversion of the injected Hg⁰ associated with the Norit AC. The NO₂ alone and with NO did not indicate negative impacts on these parameters, with the addition of HCl prolonging the rapid breakthrough of the mercury at higher levels at the inlet (desorption). Again, this suggests that HCl is also playing a role in the breakthrough phenomenon, possibly delaying the onset. In addition, the breakthrough mercury appears to be all oxidized without any HCl present, suggesting a volatile mercury species other than HgCl₂.

The apparently significant interaction between SO₂ and NO₂ gases and the sorbent caused a rapid breakthrough of mercury as well as conversion of the mercury

to a volatile oxidized form. This effect occurred at both 225 and 325 °F (107 and 163 °C) and with or without the presence of HCl and NO. In the presence of all four acid gases (SO₂, HCl, NO, and NO₂), rapid breakthrough and oxidation of the mercury occurred at both 225 and 325 °F (107 and 163 °C). This suggests that the interactions between NO₂ and SO₂ gases, and the sorbent produced poor sorbent performance, which may be a major effect. This may likely occur over a variety of conditions typical of coal-fired boilers, and represents a hurdle that must be overcome in order to achieve effective mercury control.

It should be noted, that the testing at the Comanche Station indicates no HCl in the flue gas and chlorine levels in the coal are at or below the detection limits. There is a high concentration of calcium in this station's fly ash, which could capture any HCl or chlorine in the flue gas prior to the location where the mercury removal tests were conducted. If the increase in NO₂ levels during the sodium sesquicarbonate were real, did the NO₂ have a negative impact on mercury removal and subsequent mercury desorption in the flue gas from the combustion of this PRB coal? Work will be designed to possibly answer this and other questions associated with the flue gas and fly ash from the power plant.

The ADA CEMs utilized for criteria pollutants, including NO_x (NO, and NO₂) measurements, indicated increases of NO₂ from 5 to 41 ppmv, with the higher values associated with the higher temperatures tested. Even with the fluctuations in NO₂ (compared to the amount without sodium injection), mercury removal was reported in a range from -104 to -26% (the -104 removal for mercury was associated with a carbon injection rate of 0.5 lb/Mmacf - C:Hg of ~2,000:1), with only two other tests indicating net removals of 2 and 22% when carbon was injected with the sodium sesquicarbonate. Even without carbon injection while sodium sesquicarbonate was injected, the mercury removals, as calculated from the mercury sampling method measurements, were in the negative range. This indicated an increase of mercury from approximately 26% across the particulate control device. When no media was injected, mercury removals ranged from 41 to 76% at the respective temperatures of 323 and 280 °F (167 and 138 °C). One AC injection test, without sodium sesquicarbonate injection, indicated 74% removal at 324 °F (162 °C).

The data from baseline tests (no sodium sesquicarbonate injection, Figures 59 and 60) and in the narrative on the pulse-jet tests regarding mercury removal, are consistent with the tests conducted during this period without sodium sesquicarbonate. The interaction of AC with other injected sorbents for air pollutants other than mercury must proceed with caution. The interactions are not fully understood and the interactions could be further exacerbated, either positively or negatively, when the flue

gas temperature is decreased from the normal operating temperatures during spray cooling. It is also possible that this strong oxidizer (NO_2 produced by the sodium sesquicarbonate) strips mercury from the pilot system's internal surfaces, resulting in higher mercury measured at the outlet than the inlet. If this were the case, the effect would diminish over time as the mercury on the walls of the pilot unit came into equilibrium with the flue gas. No tests were run for a sufficient time to observe this effect, and credible mercury data were not available in real time.

Multipollutant control of other pollutants could provide an enormous benefit in the utility industry if mercury regulations are indeed required. The work conducted under this project has indicated possible negative consequences during the parallel injection of sodium sesquicarbonate for SO_2 and AC for mercury control. The interactions of NO_2 with other flue gas constituents regarding mercury capture need to be fully understood before mercury controls are adopted, but most importantly before multipollutant control involving mercury capture is considered.

The work conducted by ADA for PSCo has formed the bases for many investigations on the ability of mercury capture with ACs and novel sorbents for possible use in the utility industry. Work on understanding the adsorptive and reactive parameters of the fly ash from this station has spurred other investigations on identifying the possible mechanisms involved with in-flight capture of mercury with other fly ashes. There is approximately eight months of testing to be conducted at the station on mercury removal with the tests designed to address many of the questions associated with mercury capture with fly ash and AC.

Enhancing Mercury Capture in Flue Gas from Utility Wet Desulfurization (WFGD) Systems

Several DOE/FETC-funded projects involve research and development to enhance Hg^{2+} and Hg^0 removal in WFGD systems designed primarily for SO_2 removal, while removing other acid gases (e.g., HCl and HF). Integrating retrofit technology options with WFGD systems offers lower system complexity and costs compared to other Hg control technologies. From all of the Hg sampling efforts, the nominal Hg removal for WFGD systems on units firing bituminous coal(s) is approximately $55\% \pm 10\%$ of the total Hg, with an associated removal for Hg^{2+} of between 80 and 95%. In addition, these sampling efforts have indicated no appreciable Hg^0 removal across the WFGD systems owing to the very limited solubility of Hg^0 (Devito and Rosenhoover, November 1997 and June 1999; Kurz and Laudal, April 1999; Laudal and Kurz, January 1999).

It is important to note that the high removal percentages of Hg^{2+} across WFGD systems prevent this form of Hg

from entering the local ecosystems. Deposition of Hg^{2+} is typically in the local vicinity (50-100 km) of the power plant enabling methylation and possible bioaccumulation in the food chain. While the Hg^{2+} is captured, the Hg^0 can be part of the global mercury inventory. Of the approximate 80 GWe of installed WFGD capacity in the United States, 50% is utilized at power plants firing bituminous coals, 41% on units firing subbituminous coals, and only 9% on units firing lignite coals (all on a mass basis).

Many of the sampling efforts have indicated an apparent increase in a non- Hg^{2+} , possibly Hg^0 , at the outlet of WFGD system(s) (DeVito and Rosenhoover, November 1997 and June 1999; Kurz and Laudal, April 1999; Laudal and Kurz, January 1999). Therefore, research is also directed at determining a solution for the possible re-emission of this form of Hg. Projects funded by DOE/FETC are investigating the catalytic conversion of Hg^0 to Hg^{2+} upstream of WFGD inlets, while others are investigating the conversion through novel additives being injected in the upstream flue gas and directly into the WFGD systems. The three projects are discussed below.

Argonne National Laboratory: Development of Advanced Environmental Control Technology

Argonne National Laboratory has been investigating the use of oxidizing agents that could potentially convert Hg^0 into more soluble species that would be absorbed in the scrubber. Current research is focused on a process concept that involves introduction of an oxidizing agent into the flue gas upstream of the scrubber. The oxidizing agent employed is NO_xSORB , a commercial product containing chloric acid and sodium chlorate. When a dilute solution of this agent was introduced into a gas stream containing Hg^0 and other typical flue gas species at 300 °F (149 °C), it was found that nearly 100% of the Hg^0 was removed from the gas phase and recovered in process liquids. A significant added benefit was that approximately 80% of the NO was removed at the same time. Thus, the potential exists for a process that combines removal of SO_2 , NO, Hg^0 , and, perhaps, particulate matter.

Continuing laboratory research efforts are acquiring the data needed to establish a mass balance for the process. In addition, the effects of such process parameters as reagent concentration, SO_2 concentration, NO concentration, and reaction time (residence time) are being studied. For example, SO_2 has been found to slightly decrease the amount of Hg^0 oxidized while appearing to increase the removal of NO from the gas phase. Preliminary economic projections, based on the results to date, indicate that the chemical cost for NO oxidation could be less than \$5,000/ton NO removed; while for Hg^0 oxidation, it would be about \$20,000/lb Hg^0 removed. These results will be refined as additional experimental results are obtained.

McDermott Technology, Inc.: Advanced Emissions Control Program (AECDP)

McDermott (formerly Babcock & Wilcox) has been conducting investigations during three different phases of work on mercury removal at its 10-MWe AECDP facility, and specifically, the WFGD system. Previous WFGD studies indicated that increasing the L/G ratio from 37 to 121 gal/1000 acf increased the removal efficiency of Hg^{2+} from 91 to 98%. The studies also indicated that increasing the L/G ratio did not affect the removal of Hg^0 , which was close to 0% removal (Redinger et al., 1997). Similar studies were conducted prior to these studies, producing similar findings (EPRI, 1994; Hargrove, Jr., et al., 1995, 1997).

Previous Phase II studies were conducted at McDermott utilizing the Ontario Hydro Method to measure mercury upstream and downstream of the scrubber. Results have indicated a possible conversion of the Hg^{2+} species captured in the WFGD media and re-emission of a non- Hg^{2+} (reported as Hg^0) at the scrubber outlet. Pilot-scale studies at McDermott indicated this reported non- Hg^{2+} or Hg^0 conversion across the scrubber can be minimized by control of the dissolved species in the scrubbing system slurry (Redinger et al., 1997).

Testing during Phase III of the AECDP at McDermott indicated that control of mercury across a wet scrubber can be optimized with system enhancements. Phase III testing related to control of Hg in WFGD systems focused on methods for enhancing mercury removal in a scrubber when operated downstream of an ESP. Previous testing in limestone scrubbers with forced oxidation has shown that the elemental mercury levels typically increase across a wet scrubber preceded by an ESP. Three different enhancements were identified as possible methods for minimizing the increase in Hg^0 and increasing the control of both forms of mercury across the WFGD system. These control methods were all developed with the goal of identifying low-cost improvements in mercury control using existing equipment as much as possible (Holmes et al., 1997).

Figure 61 shows the results of testing these three enhancements to improve control of mercury in a WFGD 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 and firing a blend of Ohio 5, 6, and 7 coals. All three enhancements significantly improved mercury control across the wet scrubber and prevented increases in Hg^0 . Mercury removal increased to 80, 71, and 73% for the three enhancements, respectively. The main points of the graph in the figure are that with all three enhancements Hg^0 was relatively constant across the wet scrubber, and corresponding improvements in mercury control were measured.

As the majority of eastern and midwestern bituminous coal shipments to U.S. power plants are already cleaned to

meet customer specifications, wet scrubber technology may provide the best option for further reducing mercury emissions from utility plants using these coals. McDermott is currently planning further evaluation of these enhancements followed by commercial demonstrations.

Radian International: Enhanced Control of Mercury and Other HAPs by Innovative Modifications to WFGD Processes

Radian conducted both laboratory and field studies to investigate catalytic oxidation of vapor-phase Hg^0 in coal-fired utility flue gas streams. Catalytic oxidation of vapor-phase Hg^0 can potentially increase the total mercury removal in the two technologies with the most potential for removing mercury from flue gas: wet scrubbing and sorbent injection. To investigate this process, potential catalyst materials were tested using three different test configurations. These configurations included laboratory fixed-bed tests, pilot-scale FF tests, and sample filter and fixed-bed tests in various simulated flue gases from full-scale plants.

Oxidation of Hg^0 using catalyst materials was successfully demonstrated using each of the test configurations mentioned above. In the laboratory fixed-bed tests, the effects of temperature and flue gas composition were investigated. Generally, oxidation of Hg^0 decreased as the temperature increased. Flue gas composition also appears to be important to oxidation, with HCl and possibly NO_x affecting oxidation. Figure 62 illustrates the adsorption and subsequent oxidation of Hg^0 in a simulated flue gas of one of the iron-based catalysts at 300 °F (149 °C). As breakthrough of Hg occurs from the catalysts and the bed approaches its equilibrium sorption capacity, the inlet Hg^0 is being converted to a Hg^{2+} form. At 100% breakthrough (no more Hg^0 sorbed or catalysts reaches equilibrium sorption capacity), all of the mercury exited the fixed bed as Hg^{2+} . Because all of the Hg^0 is being converted to an oxidized form, another way of stating this is that the Hg^0 is being removed (% Total Hg^0 removal, as indicated in Figure 62).

Fourteen different compositions of catalysts and 11 fly ashes were tested in the bench-scale, fixed-bed configuration to determine the best materials for oxidation of Hg^0 to Hg^{2+} using simulated flue gas conditions. Table 25 indicates the simulated flue gas conditions and the most-active catalysts and fly ashes for the oxidation of Hg^0 .

Figure 63 shows that adsorption and oxidation of Hg^0 is greater at 300 °F (149 °C) than at a higher temperature of 700 °F (371 °C). Iron- and palladium-based materials along with carbon indicated the highest amount of adsorption and oxidation of the mercury. The activity of carbon was considered the highest because a lower mass was utilized during the tests compared to the other materials. Radian has suggested that the Hg^0 is adsorbed first, with an equilibrium sorption being reached, then oxidation of Hg^0 to Hg^{2+} occurs.

Results of the fly ash tests at 300 °F (149 °C) for adsorption and oxidation are presented in Figure 64. Because the results indicated higher adsorption and oxidation at the lower temperature as for the catalysts, and lower results at the higher temperature, only the lower temperature results are presented. The subbituminous and bituminous coal fly ashes generally showed higher oxidation rates than the lignite coal fly ashes. As seen, the #2 bituminous coal fly ash had varying adsorption and oxidation rates depending upon where the fly ash samples were collected. Those collected from hoppers of the first field of the ESP indicated lower oxidation of Hg^0 , but a higher adsorption of Hg compared to the finer fly ash collected in the fifth and final field of the ESP. Although not shown, fly ash captured by a pre-cutter cyclone in the mercury speciation sampling train indicated a higher adsorption but no oxidation of Hg^0 . Fly ash from the fifth field of the ESP indicated the highest rate of oxidation and the lowest size-fractionated particles. This may be associated with the size differences of the fly ash and/or the surface chemistry of the finer fly ash being enriched in trace metals or other condensed or adsorbed compounds from the flue gas during the combustion of bituminous coal (in this case, Blacksville).

Testing at the EPRI ECTC indicated many of the catalysts showed deactivation after a relatively short period of exposure to the flue gas at the pilot facility. Sulfate was suspected as the deactivating compound. Testing at Radian's laboratories with injection of 10-ppmv sulfur trioxide (SO_3) in the simulated flue gas indicated both a decrease in the adsorption and the oxidation of Hg^0 . Figure 65 shows the oxidation decreased from 29 to 4%, while the percentage of Hg^0 passing through the catalysts went from 8 to 96%. Possible deactivation mechanisms are currently being investigated.

Other flue gas vapor-phase constituents were investigated at the bench scale to determine the impact on both

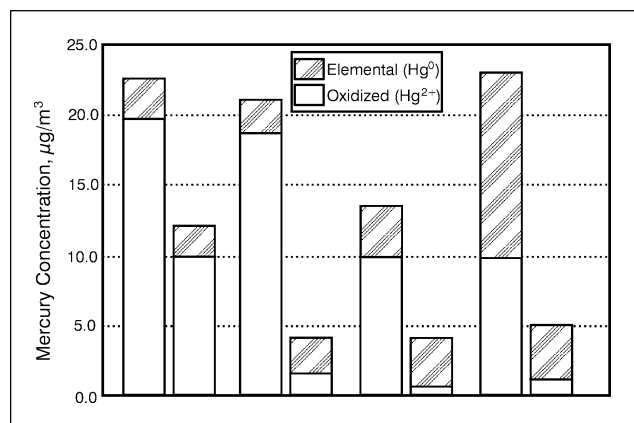


Figure 61. Results of McDermott testing three enhancements for mercury capture in a pilot-scale WFGD system downstream of a pilot ESP (Holmes et al., 1997).

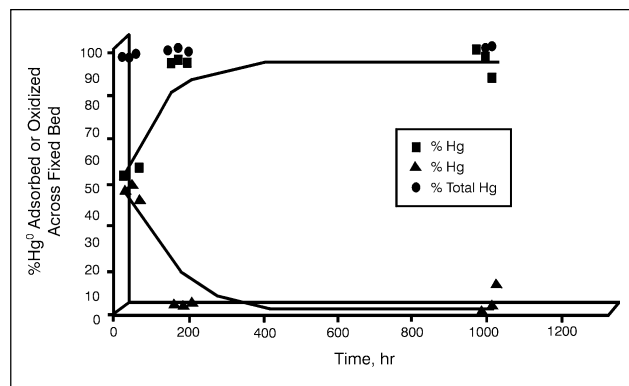


Figure 62. The adsorption and subsequent oxidation of Hg^0 in a simulated flue gas at 300°F (149°C) for an iron-based catalyst (Brown 1997).

adsorption and oxidation of Hg^0 . Results from the simulated flue gas tests with FGD carbon indicated little to no oxidation when the HCl concentrations were below 10 ppmv. Testing of FGD carbon on actual flue gas with 50-ppmv HCl indicated a high oxidation rate after the carbon reached its equilibrium sorption capacity and maintained the oxidation for more than 10 days (Carey et al., November 1997). Tests conducted by both Radian and the EERC have indicated a possible dependence on NO_x related to the inhibited adsorption and oxidation of Hg^0 . A detailed discussion on the impacts of NO_x was presented in the section entitled University of North Dakota Energy & Environmental Research Center (EERC): Investigation of Sorbent Injection for Mercury Control in Coal-Fired Boilers.

Based on laboratory- and pilot-scale tests, the most successful catalyst was a carbon-based material. After injecting about 20 lb of this material into a pilot-scale FF, greater than 75% of the spiked inlet vapor-phase Hg^0 was oxidized across the FF for 10 consecutive days. The oxidation occurred after the carbon reached its equilibrium sorption capacity. Similar results were obtained at a full-scale facility by measuring oxidation across a sample filter. These results confirmed the ability of the carbon-based material to oxidize elemental mercury under different flue gas conditions (with and without HCl and various levels of NO_x). Other catalyst materials that were identified and warrant further investigation included several iron-based materials, a conventional SCR catalyst, and certain fly ash samples (Carey et al., June 1996, July 1996, 1997; Hargrove, Jr., et al., 1997; Radian International et al., 1997).

Testing was conducted in the past year at two other utility sites with different flue gas conditions. Flue gas from the combustion of a Texas lignite and a PRB/subbituminous coal was investigated for catalyst oxidation and longevity of the catalyst activity. Nearly six months of testing was conducted at the plant firing Texas lignite coal. Total mercury concentrations at this site varied from 7 to 35 $\mu\text{g}/\text{Nm}^3$, with the Hg^0 concentrations varying from 4 to 18 $\mu\text{g}/\text{Nm}^3$. The inlet Hg^{2+} also was variable from 30 to

Table 25. Simulated flue gas conditions with the most active catalysts and fly ashes indicated for oxidation of Hg⁰ to Hg²⁺

Parameter	Baseline Conditions	Most-Active Catalysts	Most-Active Fly Ashes
Fixed-Bed Temperature	300°F and 700°F	Fe #1 (1000 mg)	Subbituminous #1
Hg ⁰ Injection	45 to 60 mg/Nm ³	Pd #1 (1000 mg)	Subbituminous #2
Oxygen	7%	Fe #2 (200 mg)	Bituminous #1
Carbon Dioxide	12%	Fe #3 (200 mg)	Bituminous #2-Field 1*
Moisture	7%	NO _x Catalysts (1000 mg)	Bituminous #2-Field 5*
Sulfur Dioxide	1600 ppmv	Fe #4 (1000 mg)	Bituminous #3
HCl	50 ppmv	Pd #2 (1000 mg)	Lignite #1
Gas Flow Rate	1 l/min	Carbon (20 mg)	Oil-Fired #1

* Fly ash collected at the first and fifth field of the ESP at the EPRI ECTC.

The catalysts were exposed to flue gas between 600 and 620 Nm³ over a period of 3480-3490 hr. Other carbon samples (Carbons #1, #4, and #6 for a reference) were inactive at the 100-hr level and were returned to Radian for regeneration testing. Only Carbons #1 and #2 showed activity after the temperature was increased from 220 to 300 °F (104-149 °C). The heater of the test rig holding the

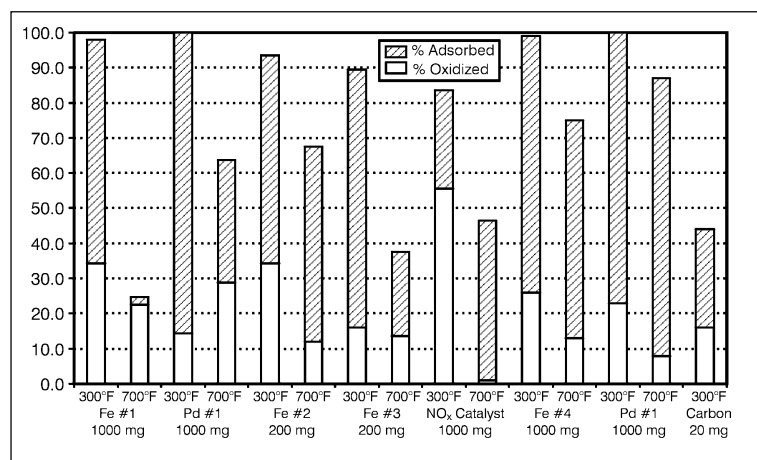


Figure 63. The adsorption and oxidation of Hg⁰ of promising catalysts at 300°F (149°C) and 700°F (371°C) (Carey et al., August 1997).

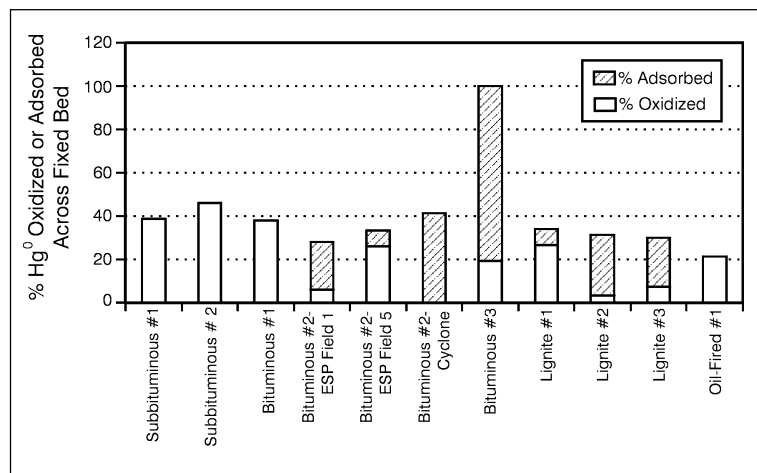


Figure 64. The adsorption and oxidation of Hg⁰ of various fly ashes at 300°F (149°C) (Carey et al., August 1997).

80% of the total, with SO₂ and NO_x varying considerably during the testing period (Blythe et al., 1999).

Testing of the promising catalysts was conducted at the utility firing Texas lignite coal (designated as Site 1).

The catalysts failed during the period between 2400 and 3055 hr. It is interesting to note the fly ash sample (SB #5) was the only material to indicate oxidation at the lower temperature, but indicated no oxidation after the temperature was increased to baseline conditions. Table 26 shows the results over the five-month plus period of testing.

After 2400 hr, Carbon #1 retained about half of its original activity, while the other material maintained greater than 75% of the original activity. At 3055 hr, all materials but SB #5 material lost all activity, as stated above. At this low temperature, a possible explanation of the lost activity is that species in the flue gas condense and react and/or adsorb on the materials' surface. Sulfuric acid and/or selenium (or selenium compounds) could have condensed and/or adsorbed on the catalysts' materials, possibly blocking active sites of the materials. In addition, some of the Hg measurements indicated the same or just slightly lower Hg at each outlet of the catalysts' beds as compared to the inlet Hg concentrations. This indicated the catalysts were not adsorbing or converting the inlet Hg.

The SB #5 fly ash sample showed Hg removal at 1000 hr, indicating that the equilibrium sorption capacity was not reached. The corresponding oxidation rate of activity was only 36%. As indicated in Figure 62, for the iron-based catalysts, the highest oxidation occurred once 100% breakthrough was achieved. Laboratory tests have indicated that SB #5 has a high equilibrium sorption capacity. It could be postulated that once a higher breakthrough occurred between 1000 and

2400 hr, this impacted the oxidation rate while indicating an increase to the 82% versus the previous 36%. Another possibility is that after the temperature was raised to 300 °F (149 °C), the SB #5 fly ash lost its adsorptive

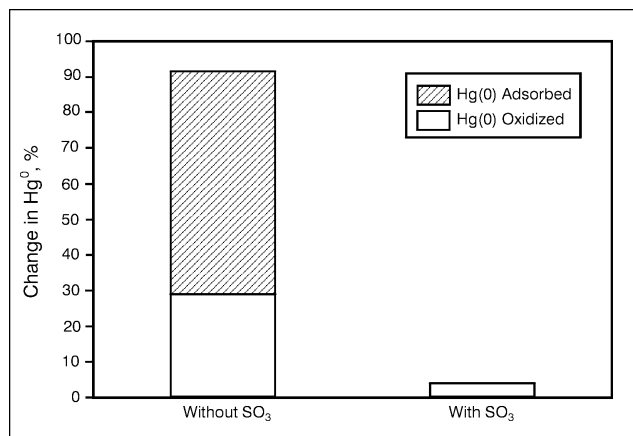


Figure 65. Effect of SO₃ on the adsorption and oxidation of the Hg⁰ for catalyst FE-1 (Carey et al., August 1997).

capacity. This supports previous observations that temperature and adsorptive capacity are inversely related.

Test results of the oxidation of the high LOI (70%) fly ash (SB #5) were previously discussed in the section entitled Factors Influencing Mercury Speciation and Adsorption, and are indicated in Table 16.

The metal-based and some carbon-based catalysts showed deactivation after a short time exposure to the flue gas from Site 1. Sulfur trioxide and selenium (or selenium compounds) are possible flue gas constituents that could rapidly deactivate most of the iron-based and other metal catalysts. Radian has performed studies to regenerate or reactivate the catalysts by exposing them to higher temperatures at various atmospheres.

Bench-scale tests were then carried out to investigate the possibility of regenerating Carbons #1, #4, and #6 catalysts that were deactivated during flue gas treatment at Site 1. Carbons #1 and #4 were unable to oxidize Hg⁰ in the Site 1 simulated flue gas at the Radian bench-scale facilities, but Carbon #6 indicated close to 95% oxidation under these conditions. As previously stated, possible flue gas component(s) adsorbed or reacted on the catalyst surfaces, blocking or modifying active sites needed for Hg reactions. Laboratory tests also indicated that selenium was present at the surface of these catalysts. Regeneration tests involved treating the spent catalysts with either CO₂ (because it is used in the activation process of carbon) or N₂ gas at a given temperature for periods up to several hours. The ability of the treated catalysts to oxidize Hg⁰ in simulated flue gas was then evaluated (Blythe et al., 1999).

The carbons were individually placed in a temperature-controlled column with the regeneration gas flowing across the carbon. Mercury desorbing from the column was measured by the Radian-designed semicontinuous mercury analyzer. Each test ran until no Hg desorbed from the

catalysts; test periods were generally 2-3 hr. At that time, the temperature of each fixed-bed column was adjusted to 275 °F (93 °C).

Mercury adsorption/oxidation tests were then performed by reacting each bed with the Site 1 simulated flue gas conditions. When each catalyst reached adsorption equilibrium, the oxidation across each catalyst bed was then measured.

Results indicated improvements in the oxidation (90%) for Carbons #1 and #4 after regeneration at 700-800 °F (371-427 °C), while Carbon #6 indicated 95 and 98% oxidation at 400 and 700 °F (204 and 371 °C), respectively. Regeneration tests for Carbons #1 and #4 at the lower temperatures of 275 and 400 °F (93 and 204 °C) indicated little improvement in catalytic oxidation.

The extent of adsorption was greater for samples regenerated at higher temperatures and was typically higher than the amount desorbed. This suggests that the regeneration process involves reactions at the surface that change or remove species other than just mercury. Red deposits were observed at some locations in the flow lines or impingers downstream of the column, and it is believed that these deposits were rich in selenium. This indicates a possible role of selenium as an inhibitor to catalytic mercury oxidation.

The regeneration tests results were promising, and indicate that regeneration of the spent catalysts should be possible. It is not known, however, what effect regeneration may have on the catalyst performance over an extended period of operation in flue gas. Additional catalyst regeneration testing is planned and will be conducted on the samples being tested at Site 2. The additional testing will determine the effectiveness of other sources such as flue gas or steam as a regeneration gas, and will determine the minimum amount of exposure time for hot regeneration gas to restore activity.

Long-term catalyst testing at Site 2 was initiated with oxidation measurements being repeated more frequently, to determine any changes in oxidation percentages with time. If a catalyst material stops oxidizing elemental mercury, the catalyst will either be replaced with a larger mass of the same material or with an entirely new catalyst. Any deactivated catalyst will be recovered and investigated in the laboratory to determine what caused the loss of activity and what will be required to restore it.

Another site will be selected from a bituminous coal-fired power plant, since power plants equipped with WFGD systems predominately consume bituminous coal. There are also plans to prepare one or more of the most promising catalysts in a configuration that could be used in future commercial applications (e.g., a honeycomb configuration). Once prepared, these samples will also be tested on flue gas at one or more of the test sites. Results with the commercial catalyst configuration will allow more

Table 26. Field test results of the catalysts during Site 1 flue gas conditions as compared to the laboratory catalysts test results.

Elemental Mercury Oxidation Across Catalysts Bed in %						
Catalysts	Site 1 (24)*	Site 1 (1000)*	Site 1 (2400)*	Site 1 (3055)*	Site 1 (3477)*	Lab Results
Sand Blank	3.3 - 8.1	7	9 - 12	23	0	3
Carbon #1 (1 st Bed)	100	66	45	0	89	100
Carbon #1 (2 nd Bed)	100	81	42 - 59	0	0	100
Pd #1	90	ND	82	0	0	91
Carbon #2	97	ND	76	0	76	96
SB #5	100	36	82	73	0	4/70**
Bed Temp. (°F)	300	300	300	220	300	300
Inlet Hg ⁰ (µg/Nm ³)	3.7 - 16.2	5.4	8.3 - 9.3	17.8	3.7	50
Total Hg (µg/Nm ³)	7.0 - 26.1	9.8	15 - 27	31 - 35	27	50

All catalyst oxidation values corrected for the sand blank oxidation values. * Number of hours passing flue gas through the catalysts materials. Mercury measurements were taken semi-continuously with a monitor developed by Radian, with the monitor description detailed in Reference Blythe et al., 1999. ** Tests were conducted in a simulated Site #1 flue gas with HCl (70% oxidation with 1 ppmv of HCl) and without HCl (4% oxidation).

straightforward scale-up of catalyst space velocity requirements for commercial-scale applications (Blythe et al., 1999).

The oxidation of greater than 90% Hg⁰ will aid in mercury reductions in WFGD systems, as well as other promising control technologies being investigated and developed. Having a high level of Hg in one form provides a better opportunity for total Hg removal. The work being conducted under this and the two other projects should provide for a reduction of total Hg from coal-fired units equipped with WFGD systems. Full-scale testing of these promising technologies should be realized by the fall of 2000. Tests need to be conducted on the stability of the captured Hg in WFGD scrubber waste and any byproduct (e.g., gypsum).

CONSOL, Inc.: Stability Testing of WFGD Solids
CONSOL conducted stability tests on unfixated and fixated WFGD solids from Plant 3, as indicated in previous sections of this report (Mercury Speciation and Its Measurement, and Factors Influencing Mercury Speciation and

Adsorption) and now shown in Figure 66. The solid samples were subjected to the TCLP leaching procedures. [Leachate Tests: The following three extraction tests were conducted on the WFGD waste samples: (1) Toxicity Characterization Leaching Procedure (TCLP, EPA Method 1311)-The extraction was conducted with an acetic acid solution at a pH of 2.8; (2) Toxicity Characterization Leaching Procedure (TCLP, EPA Method 1311)-The extraction was conducted with a sodium hydroxide-buffered acetic acid solution at a pH of 4.9; (3) ASTM leaching procedure, which is identical to EPA Method 1311 TCLP procedure except that the extraction medium was deionized water. All three of these tests are agitated extraction procedures. For each test, 100 g of the sample were agitated with the extraction fluid (2 L) by end-over-end rotation at 30 ± 2 rotations per minute (rpm) for 18 ± 2 hr at 72 °F (22 ± 3 °C). Following extraction, the liquid phase was separated from the solid phase by filtration. The solid-phase sample was followed by air drying, prior to analysis. The Hg concentrations of

the original WFGD wastes, leachates, and extracted solids were determined by acid digestion followed by CVAA.] In addition, the samples were heated to determine whether the captured Hg could be desorbed or re-emitted (volatilized). The Hg concentrations of the unfixated and fixated WFGD samples were 0.70 ± 0.03 and 0.39 ± 0.03 ppmw, respectively. The concentration of Hg found in the leachate samples for all three extraction solutions (acetic acid buffered to 2.8, acetic acid buffered to 4.9, and DI water) was below CONSOL's detection limit of 0.01 mg/L. The Resource Conservation and Recovery Act (RCRA) limit for Hg is 0.20 mg/L and based on these criteria, both WFGD materials would be classified as nonhazardous. Mercury analysis conducted on the unfixated, filtered solids ranged from 0.68 ± 0.03 to 0.73 ± 0.03 ppmw, which is statistically the same as the starting material. The mercury concentration determined on the weighed, fixated, filtered solids was 0.39 ± 0.03 ppmw, which is the same as the starting material. Based on the EPA TCLP method, it was concluded that the Hg contained with the solids is in a nonleachable form (e.g., chemically bound possibly with CaSO₄).

During the volatilization tests, both of the WFGD wastes were exposed to elevated temperatures for 11 weeks with the most stringent case at 140 °F (60 °C). Analyses conducted at the end of the exposure period showed no loss of Hg. It was concluded from these tests that Hg did not re-volatilize when exposed to temperatures up to 140 °F (DeVito and Rosenhoover, 1999). For the volatilization tests, samples of both the unfixated and fixated WFGD solids were placed in four ovens and operated at temperatures of 75, 95, 120, and 140 °F (24, 35, 49, and 60 °C). Each oven is equipped with a continuous Hg-free nitrogen purge to prevent atmospheric Hg contamination of the samples. The samples were then placed in 6 × 3 × 2 in. aluminum pans, and tamped by hand to simulate, as closely as possible, a landfill operation. The samples were held at elevated temperatures for 12-16 weeks. The samples from these pans were obtained at regular time intervals and analyzed for Hg (acid digestion followed by CVAA).

These are encouraging results, but longer term tests need to be conducted under simulated landfill conditions, with further testing of the byproducts from the CaSO₄ (e.g., gypsum). In addition, field testing at WFGD waste landfills needs to be conducted to possibly measure mercury flux. Taking mercury from the flue gas and capturing it in a solid material must render the Hg as a fully sequestered analyte, because it is persistent, bioaccumulative, and potentially toxic at high exposures. If the mercury is not stable in the wastes and byproducts, it will eventually become part of the global mercury cycle.

Conclusions of WFGD Studies

Figure 66, the same as Figure 8 in the section entitled Mercury Speciation and Its Measurement, indicates the removal of Hg⁰ for all the plants tested, including Plant 3. DOE and EPRI have funded many field studies and

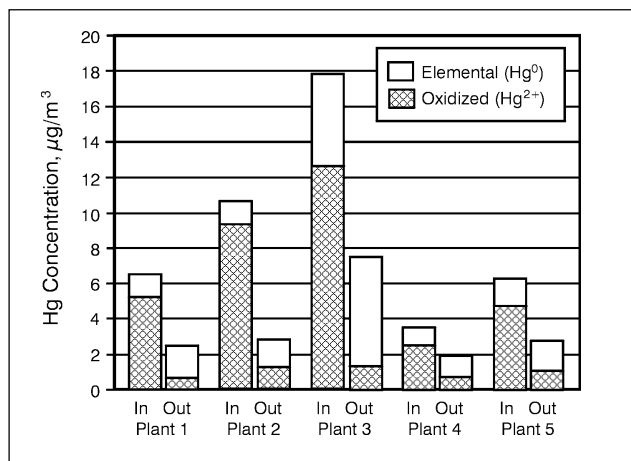


Figure 66. Elemental and oxidized mercury in coal-fired power plants firing bituminous coals and equipped with WFGD (DeVito and Rosenhoover November 1997 and June 1999).

characterizations on mercury speciation utilizing the Ontario Hydro Method, as indicated in the section entitled Emission Inventory. Figure 66 indicates Hg⁰ and Hg²⁺ measurements at the inlet and outlet of five WFGD systems at different plants firing a variety of medium- to high-sulfur bituminous coals. CONSOL cost shared and conducted the measurement with the DOE cost sharing with either the Illinois Clean Coal Institute (ICCI) or the Ohio Coal Development Office (OCDO).

The five plants were each equipped with a WFGD system. Triplicate FGD measurements at the inlet and outlet at each site indicated a larger proportion of Hg²⁺ as compared to Hg⁰, with a range of Hg²⁺ removal between 85 and 95%. The total mercury removal of the ESP and WFGD systems at each plant ranged between 60 and 66% with a corresponding removal of SO₂ between 82 and 96% across the WFGD system. Sulfur dioxide concentrations for the five plants were between 2400 and 2900 ppmv (average of 2600 ± 100 ppmv) at the inlet, and between 100 and 500 ppmv (average of 330 ± 10 ppmv) at the outlet. Further details of these five sampling efforts can be found in DeVito and Rosenhoover, 1999.

As stated, under certain conditions, an apparent increase of non-Hg²⁺ at the outlet is seen compared to the inlet of the WFGD system (possible re-emission of the captured Hg²⁺ at SO₂ levels much greater than the 1500 ppmv from the Blacksville coal) while utilizing the Ontario Hydro Method. The possible re-emission of a non-Hg²⁺ form or possible overestimation of Hg²⁺ at the inlet of WFGD systems (or the ± percentage of Hg⁰ at the outlet relative to the inlet), or the as reported by Ontario Hydro for the five plants are as follows:

- Plant 1, a 38.5% increase,
- Plant 2, a 23.1% increase,
- Plant 3, an 18.6% increase,
- Plant 4, a 16.7% increase, and
- Plant 5, a 7.1% increase.

Pilot-scale studies at McDermott indicated this reported non-Hg²⁺ or Hg⁰ re-emission across the scrubber can be minimized by control of the dissolved species in the scrubbing system slurry. Radian and Argonne have demonstrated potential for removal of Hg⁰ across WFGD systems, and conversion of Hg⁰ to Hg²⁺ for subsequent removal across WFGD systems, respectively. These research efforts have the potential to remove additional mercury in coal-fired boiler systems equipped with WFGD scrubbers at a relatively low cost. The results and findings in the laboratory, pilot, and flue gas slipstreams at various power plants need to be tested at larger scale in the near future. In addition, tests need to be continued on the WFGD wastes and byproducts to make sure the mercury is stable under all conditions of disposal and use.

Other Innovative Approaches for Mercury Control in the Coal-Fired Utility Industry

Research has also been directed at developing other innovative concepts for control of mercury from coal-fired utility boiler systems to augment existing APCDs, and also as new technology. Figure 67 illustrates (dashed lines) some of the strategies being investigated under DOE/FETC funding, including novel sorbent development that would not impact the use of fly ash as a salable byproduct, to a technology capturing both forms of mercury and through a regenerative process, and a possible byproduct of mercury that is not associated with any waste or other byproduct as a result of coal combustion. The various projects are discussed in the following.

ADA Technologies, Inc. (ADA): Novel Process for Removal and Recovery of Vapor-Phase Mercury

A new technology for controlling all forms of mercury from coal-fired electric utility units, funded under the DOE/FETC Mega PRDA Program, has been investigated at the laboratory scale on simulated flue gas and at a 20-cfm scale on actual flue gas from a pilot-scale coal combustion unit. ADA has been developing this technology, the Mercur-RE process, which uses a regenerable noble metal as a sorbent. This allows for the recovery of liquid elemental mercury from the flue gas in the regeneration cycle. Noble metals on either a metal monolith or pellets have provided total mercury capture in both the laboratory and pilot scales, with simulated and actual coal-fired produced flue gas, respectively.

Results from laboratory tests showed that the metal monolith-supported sorbent captured virtually all of the elemental mercury and mercuric chloride injected into a simulated flue gas, Figure 68 shows the inlet and outlet of the monolith from the ADA CEM, with the outlet readings indicating near complete removal of both forms of Hg. Over 55 capture and recovery cycles were performed on the laboratory monolith with no degradation indicated. At the test conditions, the superficial velocity was 0.25 ft/sec, the superficial residence time was 2 sec, and the pressure drop was less than 0.1 in. of water (Roberts et al., 1997; Turchi et al., 1999).

Tests with the 20-cfm unit were conducted on actual flue gas from the combustion of four different coals. An example of the mercury concentration measured at the inlet and outlet of the monolith using a continuous analyzer from the combustion of Blacksville coal is shown in Figure 69. At the test conditions, the superficial velocity was 1 ft/sec, the superficial residence time was 1.5 sec, and the pressure drop was less than 0.2 in. of water (Roberts et al., 1997; Turchi et al., 1999). The major conclusions reached by ADA as a result of this testing were as follows:

- (1) The metal monolith-supported sorbent (noble metal) could remove over 95% of total mercury from the inlet flue gas.
- (2) The regeneration of the sorbent bed gave off mercury in amounts quantitatively close to the expected amount.
- (3) There was no discernible decrease in sorbent performance over 180 hr of sorption and 250 hr of regeneration (Turchi et al., 1999).

After this testing, some modifications were made to improve the regenerator performance and the method of removing mercury from the regenerator off-gas. In addition, a different bed configuration was designed for comparison with the monolith design. During subsequent testing, ADA decided that the results showed no obvious advantage between the two designs. However, ADA has plans to incorporate the best features of both designs in future testing on a slipstream from a full-scale utility. Different noble metal concentrations on the monoliths will be applied and tested to determine the impact on reducing the residence time of the flue gas across the monolith. Testing is planned for the spring of 1999 at Public Service Gas and Electric's Hudson Station.

Environmental Elements Corporation (EEC): A Circulating Fluid Bed Fine Particulate and Mercury Control Concept

Under the DOE SBIR, the EEC has been developing a CFB to promote agglomeration of fine particulate matter, allowing for their capture in an ESP. In addition, a single injection of IAC was added to the fluid bed to adsorb mercury vapor. High residence time, as a result of particle recirculation, allows for effective utilization of the carbon and high collection of the fine particles. Laboratory tests with heated air indicate with a high density of fly ash at a 4-sec residence time within the bed, fine particle emissions are reduced by an order of magnitude (Helfritch et al., 1997).

Results from the laboratory-scale testing indicate spiked elemental mercury was significantly reduced when passed through the fluidized bed of fly ash (50% mercury removed)

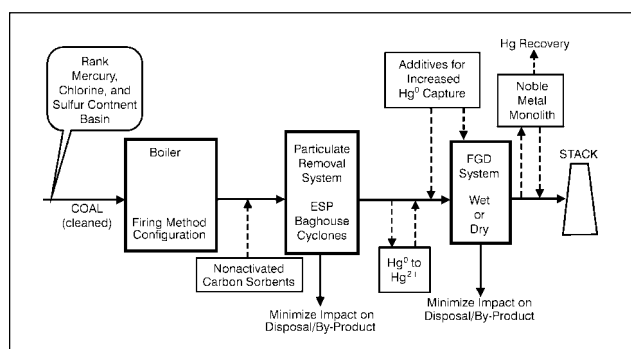


Figure 67. Other mercury control strategies being funded under DOE/FETC (Brown 1997).

with a further reduction to essentially zero, when AC was injected into the bed ($25 \mu\text{g}/\text{Nm}^3$ to zero) at 230°F (110°C). The IAC was fully utilized after >2 hr within the bed. An adsorption capacity was calculated to be $770 \mu\text{g}/\text{g}$ for the carbon and $480 \mu\text{g}/\text{g}$ for the bed of ash. Other field tests were conducted at Public Service Gas and Electric's Mercer Station with similar results (Helfritsch et al., 1997).

Wisconsin Electric Power Company (WEPCO) has retrofitted an EEC particle agglomerator on the Presque Isle Station's Unit 6 coal-fired boiler located in Marquette, MI. Unit 6 is a 90-MWe generating station firing a low-sulfur ($<1\%$) eastern bituminous coal that is equipped with an ESP. The agglomerator was installed as part of the unit's ESP with testing of the mercury concentrations at the inlet of the agglomerator and at the outlet of the ESP.

A series of mercury concentration measurements were performed at each location at three different sampling periods. Mercury content of the coal ranged from 0.52 to 0.1 ppmw with the chlorine at approximately 58 ppmw during the sampling effort. The mercury entering the agglomerator for the three sampling events were 7.0, 4.0,

and 4.0×10^{-3} lb/hr with corresponding outlet concentrations of 2.93, 5.57, and 2.41×10^{-4} lb/hr, respectively. The corresponding mercury removal efficiencies were 96, 85, and 95%. The removals were only associated with the fly ash in the agglomerator's fluidized bed (Michaud, 1999).

A more detailed parametric study of the mercury removal is being planned for June 1999. DOE/FETC and WEPCO are funding this and another mercury sampling effort at another unit at the station, which is equipped with a hot-side ESP. In addition, the EPA and DOE/FETC are collaborating on a sampling effort to measure possible dioxin and furan formation across the unit's hot-side ESP.

The sampling effort for the agglomerator would entail inlet and outlet sampling for mercury (speciation measurements with the Ontario Hydro Method); fly ash loadings and carbon content (including the fly ash density of the fluidized bed, calculated); calculation of residence time(s) within the bed; mercury and chlorine in the coal; ESP hopper ash mercury concentrations and mercury sorption capacity; possibly other trace metals with EPA Method 29; and other acid gases (e.g., HCL, SO_2 , SO_3).

The EEC particle agglomerator has indicated promising results at the laboratory-, pilot-, and now on a full-scale (90 MWe) coal-fired utility boiler system for both mercury and fine particulate removal. This is the first control device to be developed from a concept through the various stages of scale-up, testing, and development to an installation in a utility boiler system for both fine particulate and mercury control. The agglomerator also has the capability of being a truly multipollutant control device for these and other potential pollutants, including HCL, SO_2 , and SO_3 . The residence time of approximately four seconds within the fluidized bed of the agglomerator is extremely important for multipollutant control of the other vapor-phase pollutants. Parametric testing is warranted and hopefully the results of such an effort would provide information on the high-efficiency mercury collection capability associated with other fly ashes and possibly AC.

TDA Research, Inc: An Economic Sorbent for the Removal of Mercury from Coal Combustion Flue Gas

TDA Research, Inc., (TDA) has identified and tested a novel method for producing a carbon-based, sulfur-containing sorbent. This sorbent is produced from a low-cost feedstock and uses a preparation method that should keep the cost of the sorbent well below $\$500/\text{ton}$. It has physical properties that facilitate efficient mercury capture in an injection process. In this SBIR Phase II project, TDA prepared, characterized, and screened sorbents.

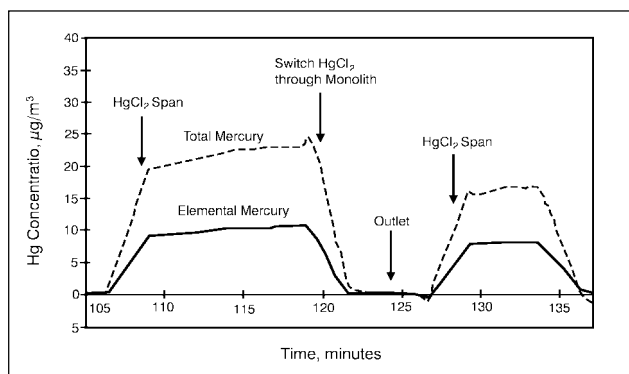


Figure 68. Hg^0 and Hg^{2+} measurements at the inlet and outlet of ADA's Mercu-Re process in a simulated flue gas (Roberts et al., 1997 and Turchi et al., 1999).

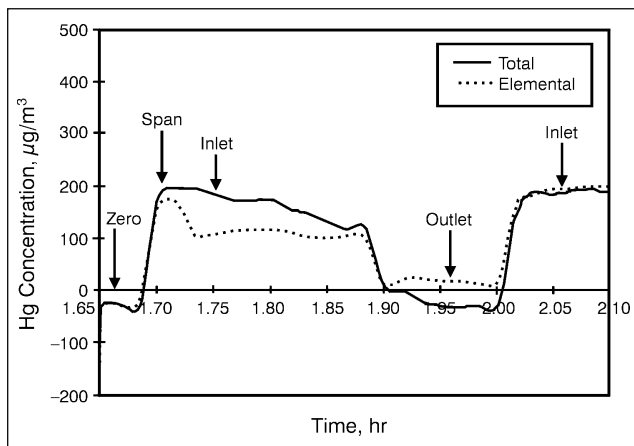


Figure 69. Hg^0 and Hg^{2+} measurements at the inlet and outlet of ADA's Mercu-Re process in flue gas from the combustion of a bituminous coal (Roberts et al., 1997 and Turchi et al., 1999).

The most promising sorbents were prepared in quantities suitable for a field test using dry powder injection. The work was carried out by ADA under subcontract from TDA, at a test facility located at the PSCo Comanche Station facility in Pueblo, CO. Significant control of the operating conditions during sorbent testing is possible at this facility. A full description of the test facility has been published previously by Sjostrom et al. (1997). TDA prepared six sorbents under different preparation conditions that were screened for mercury removal downstream of the existing Comanche PCM. The PCM can be configured as an ESP, pulse-jet FF, reverse-gas FF, or as EPRI's TOXICON FF. The results of the screening compared to other sorbents tested by ADA in this program are shown in Figure 70. The performance of TDA's sorbents compared favorably with the other sorbents tested.

Based on the initial screening results, one of the sorbents was chosen for parametric testing using two different duct temperatures, three different sorbent injection rates, and two different PCMs. The parametric testing was performed in particulate-laden flue gas upstream of the Comanche PCM to ensure more realistic flue gas conditions for evaluating mercury capture with the novel sorbents. Each data point was performed in triplicate and then averaged. Despite a large scatter in the data as a result of varying mercury inlet concentrations, TDA's sorbent showed removal percentages up to 86%. Overall, the results obtained from sorbent injection agreed with expected trends in temperature and PCM configuration. Mercury removals were higher at lower temperature, and higher when using a pulse-jet baghouse as the particulate control device rather than an ESP. A portion of the removal was also attributed to the Comanche fly ash, which has an affinity for mercury capture. Regardless, the TDA sorbent indicated mercury removals at the levels of the ACs tested at this pilot-scale facility. With these levels of removal, and the possible sorbent cost being one-half to one-quarter the cost of commercially available AC, the sorbent developed by TDA are promising is a low-cost effective sorbent. In addition, the sorbent should not have a negative impact on the fly ash being sold as a byproduct. The tests are discussed in full detail in Broderick et al. (1998).

TDA also tested the six sorbents pr-red for the field tests in a packed sorbent bed using a simulated flue gas to challenge the sorbents. The simulated flue gas consists of approximately 12% CO₂, 6% O₂, 1.5% H₂O, 1600 ppmv SO₂, and 50-μg/Nm³ Hg⁰. No NO_x was included in this round of packed-bed tests, but it will be planned in future work. The sorbent was held at a temperature of 212 °F (100 °C) throughout the tests. The results of these tests are shown in Figure 71. In these sorption studies, 5-mg sorbent was mixed with 2-g silica sand to ensure reproducible bed depths. Blank

runs were conducted with 2-g silica sand with no sorbent added.

The effluent mercury concentration was measured at 2-min intervals with an Arizona Instruments (Phoenix, AZ) Jerome 431-X mercury analyzer, which measures elemental mercury. The packed bed tests are consistent with the results of the sorbent injection tests at the Comanche Station. The relative performance of the sorbents in the packed bed allowed for evaluation of the effects of preparation method and feedstock on mercury removal, and to fine-tune the methods to maximize sorbent efficiency.

Physical Sciences, Inc. (PSI): Control of Mercury Emissions from Fossil Fueled-Fired Power Plant Gases

The goal of this program conducted by Physical Sciences, Inc. (PSI) is to advance the development of a zeolite sorbent to the point where it has been fully demonstrated at the pilot-scale level as an efficient means of reducing power plant mercury emissions and is ready to fill the potential market for such a product.

In the initial, Phase I program, several sorbents were tested in a fixed bed mode for their ability to remove mercury from a coal combustion flue gas at 302 °F (150 °C). These sorbents included carbon and non-carbon based materials that had been treated with a proprietary additive to enhance their ability to remove all forms of mercury from the gas stream. All of the sorbents tested in this project exhibited some capture of mercury at 150 °C with the higher surface area sorbents generally exhibiting higher mercury capture per gram of sorbent. It has been shown that the PSI additive improved the ability of a zeolite to remove both oxidized and elemental mercury at both low and high temperatures. The combination of the PSI additive and a zeolite sorbent has demonstrated potential as a mercury sorbent. This sorbent can be used for mercury control without impacting the quality of the fly ash, thus preserving the commercial value of the ash.

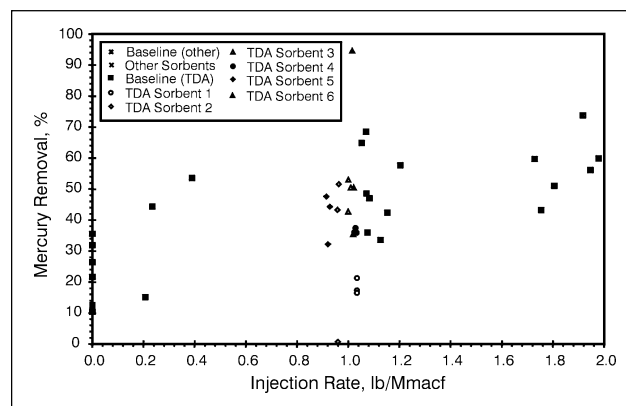


Figure 70. Comparison of TDA's sorbents to other sorbents at the PSCo PCM pilot-scale unit the Comanche station (Broderick et al., 1998).

Leachability tests on this material showed that the sorbent can be safely disposed in a landfill, if sale of the ash is not an option.

PSI has begun a two-year, Phase II program to undertake further development of a zeolite material as a mercury sorbent. The primary goal of this project is to create a product which has been fully tested in both the laboratory and at the pilot-scale level and is ready to fill the potential need for a mercury control technology in the utility market. The key characteristics that this product should possess are: low cost, applicability to a wide range of pollution control scenarios, minimum impact on fly ash quality, and safe disposal in a landfill. To achieve the stated goal, PSI is conducting laboratory tests to optimize sorbent parameters using a selected zeolite material. Following this, pilot-scale testing at Mercer Station of Public Service Electric and Gas (PSE&G) of New Jersey will be conducted, followed by an in-depth process engineering study by Environmental Elements Corporation to determine the costs of integrating the sorbent into various pollution control systems.

University of Cincinnati: In Situ Generated Sorbent Methodology and UV Irradiation for Mercury Capture in Combustion Environments

A novel in situ sorbent precursor injection methodology for capture of heavy metals in combustion environments has been developed by researchers at the University of Cincinnati (US Patent 5,888,926). The process results in the formation of a very high surface area agglomerate with an open structure, that allows the heavy metals to be

chemisorbed prior to their nucleation to form submicrometer sized aerosols (Owens and Biswas, 1996; Biswas and Zachariah, 1997; Biswas and Wu, 1998). Compared to bulk sorbents used for metals capture, the in situ sorbent methodology is effective at comparatively much lower ratios of sorbent to metal; thus requiring the use of trace quantities. Mercury however has a closed outer electronic shell and is not effectively removed by typical sorbents (Owens et al., 1995). However, the use of a titanium dioxide sorbent with uv irradiation has been shown to be very effective in capture of elemental mercury in simulated combustion environments (Wu et al., 1998). Studies currently underway are examining heterogenous pathways of mercury oxidation and the kinetics of titania - mercury reactions under simulated coal flue gas conditions (Biswas and Lee, 1999; Lee and Biswas, 1999).

In the proposed methodology for mercury capture, an organometallic titanium compound is injected into the high temperature combustor, resulting in the formation of an agglomerated titanium dioxide particle. By controlling the injection location and conditions, titanium dioxide particles of sizes in a range that are effectively captured in an ESP can be readily produced. The high surface area allows association of the mercury vapors with the sorbent oxide, however, due to the low reactivity and weak bonds, the mercury is not effectively captured (unlike other heavy metals such as lead which are chemisorbed). However, on irradiation with low intensity uv light, the mercury is oxidized on the surface and complexes with the titanium dioxide sorbent. The process has been shown to be very effective in controlled simulated flue gas environments in laboratory scale tests (Wu et al., 1998; Biswas and Lee, 1999). Detailed kinetic rate measurements have indicated the feasibility of scale up, and the heterogenous first order rate constant, k (sec⁻¹) for the Hg - TiO₂ reaction is

$$k = 1.84 \times 10^{-9} \exp(-1295.2 / T) A_{TiO_2} C_{Hg}^{1.1} I_{uv}^{0.39} \text{ (Reaction control, } T = 280 \text{ to } 360 \text{ K) and,}$$

$$k = 1.24 \times 10^{-9} \exp(3122.3 / T) A_{TiO_2} C_{Hg}^{1.1} I_{uv}^{0.39} \text{ (Adsorption control, } T = 360 \text{ to } 420 \text{ K)}$$

where T is the temperature in K, A_{TiO_2} is the surface area per unit mass (m²/g) of the titania particles, C_{Hg} is the concentration of mercury (µg/m³), and I_{uv} is the intensity of uv irradiation (µW/cm²).

First, it should be noted that the corona in an ESP has sufficient intensity of uv irradiation (Biswas and Wu, 1998) to energize the mercury capture reactions, and thus additional sources of uv irradiation may not be necessary. Secondly, due to the inherent open structure of the titanium dioxide agglomerate particles produced in the sorbent precursor injection methodology, uv light can readily be incident on a sufficiently large surface area of the particles.

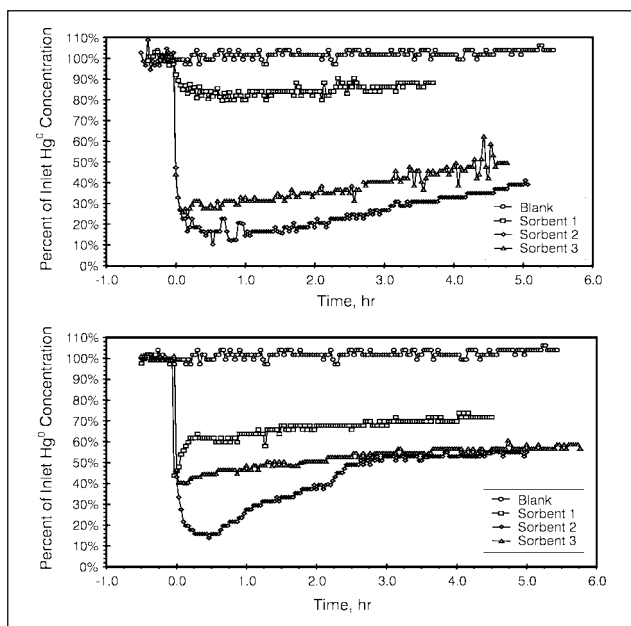


Figure 71. Results of testing TDA's sorbents under simulated flue gas conditions with 50 mg/Nm³ Hg⁰ and at 212°F (100°C) (Broderick et al., 1998).

Third, the rate constant expressions indicate that by injecting sufficient amounts of the titanium precursor (sufficiently high total surface area, A_{TiO_2}), residence times in typical post combustor sections are sufficient for effective capture of the mercury. Fourth, the overall amounts of sorbent material used is very low due to the effectiveness of the process. Clearly, pilot scale testing will help optimize the conditions necessary for use in a full scale system. Finally, it should be noted that titanium dioxide (in various forms) is used as a catalyst for NO_x control, and the in situ sorbent methodology may be effective at polishing off the NO_x concentrations to desired low levels. Also, titanium dioxide is effective at oxidizing several organic species (such as hydrocarbon, PAHs) with *uv* irradiation.

Cost of Mercury Control

While several mercury control technologies appear promising, most of them are in the early stages of development; thus, control costs are uncertain. Estimates of annual mercury control costs at the 90% control level for the entire U.S. electric utility coal-fired power generation system have ranged from \$1 billion to as high as \$15 billion. These costs have been estimated by EPRI, EPA, and DOE, with the most recent DOE and EPA costs being compared in Appendix B of the U.S. EPA Mercury Study Report, December 1997. Because activated carbon has been tested on actual flue gas from coal combustion, control costs have focused on this technology. A comparison of the EPA and DOE/FETC cost analyses is described in this section for three activated control strategies using a similar modeling approach.

Option A: Direct injection of AC ahead of the existing particulate control device;

Option B: Spray cooling of the flue gas after the existing particulate control device (e.g., ESP), followed by AC injection and a FF to collect the mercury-laden carbon;

Option C: Spray cooling of the flue gas after the air preheater, followed by AC injection before the existing particulate control device.

Figure 72 illustrates the three options relative to existing APCDs in coal-fired boiler systems. The control systems are assumed to be retrofitted into an existing power plants with moderate congestion being considered at the control points. The control systems were designed around two coal-fired power plant models using the EPA's methodology presented in Appendix B of Volume VIII of the Mercury Study Report to Congress.

Both plants are assumed to operate with a capacity factor of 65% with a fuel having chloride levels sufficiently high that all the mercury in the flue gas is in the form of $HgCl_2$ (i.e., Hg^{2+}). The inlet mercury level in the flue gas to the control systems associated with each coal-fired

model plant was also set at 10 mg/dscm (4.4 gr/million dscf) at 68 °F (20 °C).

Model Plant 1 is a 975-MW boiler firing low-sulfur coal with a chloride content of 0.1%. The plant generates 4,050,000 dscm/hr of flue gas and is equipped with a cold-side ESP. The temperature ahead of the ESP is 314 °F (157 °C), and the temperature exiting the ESP is 302 °F (150 °C). No mercury control across the ESP is assumed.

Model Plant 2 is similar to Model plant 1, except that it has a capacity of 100 MW. This plant generates 411,000 dscm/hr of flue gas. The gas temperature ahead of the ESP is 295 °F (146 °C), and the ESP outlet temperature is 280 °F (137 °C). Again, no mercury control across the ESP is assumed.

Table 28 summarizes the EPA model utility boilers and mercury controls used in the cost analysis.

The utility model numbering system conforms with that in Appendix B of Volume VIII of the Mercury Study Report to Congress.

- Models 1A and 2A refer to carbon injection upstream of an existing ESP.
- Models 1B and 2B refer to spray cooling of the flue gas after the existing ESP, followed by AC injection and a FF particulate clean-up module.
- Model 1C refers to spray cooling after the air preheater followed by carbon injection upstream of an existing ESP.

As specified in the EPA set parameters, the mercury removal efficiency of each control system was designed to remove 90% of the mercury in the flue gas. It should be noted that spray cooling is an effective method for reducing the temperature of the flue gas stream, which in most cases, reduced the amount of carbon sorbent required for mercury capture.

Incremental costs associated with mercury control in these settings are addressed first. The design criteria and assumptions that specify each of the three control modules are addressed next. Finally, a summary of the control system costs for each case is provided.

Incremental Costs: Capital Cost Adjustment for Retrofit

The retrofit factors for the mercury control systems are used to account for site-specific criteria, such as access and congestion, underground obstructions, ductwork tie-in difficulty, and distance between control system and waste handling system.

EPRI has developed rough guidelines for capital adjustments that consider these factors (EPRI, October 1995). As indicated, for a relative comparison of costs for crude comparisons, suggested retrofit factors are 1.25 for 5-year-old plants, 1.30 for 15-year-old plants and 1.4 for plants 25 years old or over." In the present cost analysis, a

conservative retrofit factor of 1.3 for the model control systems was used in the development of installation costs.

Incremental Costs: Operating Penalties

It is estimated that 90 million tons of solid byproducts are produced each year from coal combustion in the United States (Robl and McCormick, 1997). The American Coal Ash Association (ACAA) data for 1994 indicate that about 61% of the solid byproduct is fly ash. Fly ash used offsite amounts to approximately 10 million tons/year, of which 7.5 million tons are used as high-quality pozzolan cement in concrete applications. "The price of high-quality fly ash pozzolan is beginning to rise in areas where there are shortages and prices of \$25 to \$30/ton are not uncommon" (Robl and McCormick, 1997). The cost for transportation is between \$0.10 and \$0.30/ton/mi.

Based upon the above observations, FETC determined that 18.2% of all fly ash generated in the United States will be rendered unfit for byproduct sales by use of the AC injection process (used in Models 1A and 2A). This cost is reflected in the levelized cost estimate for mercury control for Models 1A and 2A. A conservative estimate of \$3/ton for lost revenue in fly ash sales is assigned to carbon injection systems, because the carbon-to-mercury ratios are high enough to push fly ash carbon content beyond the specification for pozzolan.

Carbon Injection System

The carbon injection system design considered by FETC consists of a carbon storage silo equipped with pneumatic loading capabilities, a feed bin, a gravimetric feeder, a pneumatic conveyer system, and carbon injection ports. The carbon injection system is evaluated for Cases 1A, 2A, and 1C. In Case 1C, the carbon injection system is integrated with a spray cooler.

For the AC storage silo, a Class III (detailed) level estimate was made using the ICARUS Process Evaluator. (ICARUS) The silo was designed for 15 days of storage and compliance with all relevant construction codes. The design considerations included elevation legs of 8 ft for access

criteria, a carbon-steel shell, and a pulse-jet baghouse for loading the AC from a pneumatic truck transfer system.

The remainder of the carbon injection system cost estimate was based on a recent EPA report (U.S. EPA, 1996). This report provides algorithms for carbon injection systems for hazardous waste combustors that have been validated both by quotes, and by an architectural and engineering design team for the Office of Solid Waste and Emergency Response within the EPA. The level for this estimate is considered to be between a Class I (simplified) and Class II (preliminary). The FETC made only one change in the use of this model: a change in the retrofit factor from 1.15 to 1.3, a more suitable and realistic value for the utility industry. The total capital costs were then adjusted from 1989 dollars to January 1, 1996 dollars as detailed in U.S. EPA (1997) and Brown et al. (1998).

Table 29 provides the FETC capital cost breakdown for the carbon injection system applied to 100 and 975-MW power plants, including a listing of the major design criteria and assumptions. Only one carbon silo is used in the 100-MW plant. Two silos, operating in parallel, are used in the 975-MW plant.

Spray Cooling

Spray cooling or humidification, was a set parameter utilized by the EPA in its models to cool the flue gas from coal-fired power plants upstream of the ESP. While flue gas cooling has been demonstrated during DOE and EPRI pilot-scale tests to increase mercury capture of the AC, it may have limited applicability in the utility industry, owing to the short ducts and residence times (typically less than 1.5 sec) upstream of utility ESPs (U.S. DOE, 1988 and 1993). In the EPA models, the mercury control system also utilizes water-spray flue gas cooling to maintain the flue gas temperature upstream of the baghouse at 200 °F (93 °C), which may not be practical in utility installations. In addition, humidification prior to a FF can be of concern because the increase in moisture content of the flue gas can lead to blinding (e.g., condensed sulfuric acid mist) and cake release problems within the FF. These considerations were not included in the cost analyses, but will be part of a revised cost analyses the FETC is currently performing [e.g., calcium-based sorbent injection for sulfur trioxide (SO₃) capture, prior to it condensing to sulfuric acid mist].

The spray cooling system consists of a water supply tank, pump, compressor, water level control system, in-duct temperature sensor array, and a spray bar with an array of nozzles. The spray cooling chamber is nominally designed for a gas residence time of 0.5 sec, but in the present study, the existing ductwork is considered to be able to substitute for the spray cooling chamber and provide sufficient residence time. Water is injected into the flue gas through a spray distribution header equipped with aerated nozzles. Aeration is provided with compressed air. The water feed tank is a conventional vessel with no mixers.

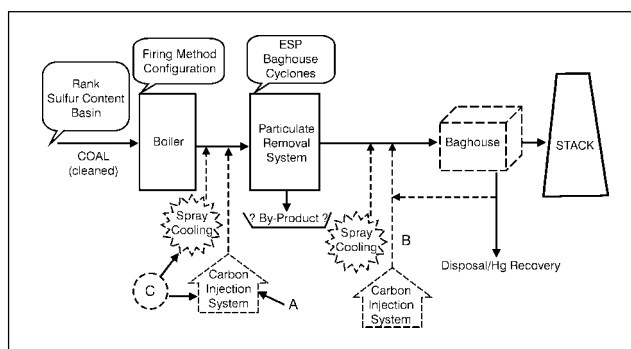


Figure 72. Different sorbents-based injection options being investigated for mercury control in coal-fired power plants (Brown et al., 1998).

Table 28. Description of utility model cases.

Utility Model		1A	1B	1C	2A	2B
Boiler Size	MWe	975	975	975	100	100
Hg Concentration	mg/dscm	10	10	10	10	10
Flue Gas Temperature	°C	157	93	93	146	93
Flue Gas Temperature	°F	315	199	199	295	199
Carbon Usage ^a	g C/g Hg	100,000	9,398	30,000	100,000	12,572
Carbon Injection Rate	Kg C/hr	4,050	381	1,215	411	52
Flue Gas Flow	dscm/hr	4,050,000	4,050,000	4,050,000	411,000	411,000
Spray Cooling		No	Yes	Yes	No	Yes
Carbon Injection		Yes	Yes	Yes	Yes	Yes
Fabric Filter		No	Yes	No	No	Yes
Existing Controls		ESP	ESP	ESP	ESP	ESP
Coal Sulfur Content		low	low	low	low	low
Hg Removal		90%	90%	90%	90%	90%
Capacity Factor		65%	65%	65%	65%	65%

^a FETC derived carbon usage and injection rates from laboratory and pilot-scale mercury sorbent tests. (Miller et al., 1994 and 1995; Chen et al., 1996; Vidic, R.D., and McLaughlin, J.D., 1996; Haythornthwaite et al., 1997, 1998, and 1999; PSCo/ADA Technologies, Inc., 1997; PSI et al., 1997; Rostam-Abadi et al., 1997; Sjostrum et al., 1997; Waugh, E.G., 1997 and December 1997; and Flora et al., 1998) This comprises an enormous database on activated carbon injection tests conducted at the pilot-scale on actual flue gas from the combustion of coal.

The water injection rate is estimated by the following expression derived from an energy balance:

$$W_i = \frac{(T_i - T_o) \times (G_i - M_i) \times C_{pg}}{\lambda_{vap}} \quad (8)$$

where W_i is the water injection rate requirement, and T_i and T_o are the inlet and outlet flue gas temperatures, respectively. The mass flow rate of flue gas into the spray cooler (dry basis) is the quantity $(G_i - M_i)$. The specific heat capacity of the flue gas is expressed by C_{pg} , and the heat of vaporization for the water is expressed as λ_{vap} .

The capital cost estimate for both the spray cooler and FF provided in the Mercury Study Report to Congress were considered reasonable by DOE/FETC and are used in the preliminary assessment. Some areas that require further definition include

- (1) The widespread availability of sufficient duct length between the spray injection point and particulate control device (of concern in Case 1C);
- (2) The ability to control flue gas temperatures sufficiently above the adiabatic saturation temperature so that corrosion problems are avoided;
- (3) The ability to avoid blinding of the FFs (of concern in Cases 1B and 2B); and
- (4) A sufficient straight length of ductwork to avoid wall wetting and ash deposition downstream of the spray injectors.

FF

The FF control system used in the analyses consists of a reverse-gas FF or baghouse (EPA's model, a set parameter), a carbon injection system, and a spray cooler (for Cases 1B and 2B) located after the ESP. The baghouse consists of isolated compartments containing rows of FF bags. Particle-laden flue gas passes along the surface of the bags before exiting radially through the FF. The filter is operated cyclically-alternating between relatively long periods of filtering and short periods of cleaning. During cleaning, dust that has accumulated on the bags is removed from the fabric surface, through the pulsing of either air or flue gas, which is then deposited in a hopper for subsequent disposal.

Most of the energy needed to operate the FF is associated with fan requirements to overcome the pressure drop across the bags and the associated hardware and ducting. The most important design parameter is the air-to-cloth ratio. The largest capital cost associated with Cases 1B and 2B is for a reverse-gas FF. As such, the capital costs for the FF estimated in the Mercury Study Report to Congress were checked by FETC for reasonableness. Other capital components associated with Cases 1B and 2B were also accepted by FETC as reasonable estimates.

A crucial concern for design considerations of the FF control system used in this study is the build-up rate of a dust cake for the filtering of particulate-laden AC that allows for mercury removal. If this rate process is too slow, then a significant amount of mercury will not be exposed to the AC at the FF interface, thereby lowering the utilization

Table 29. Carbon injection system design and costs (1996 dollars).

Reference Power Plant Size	100 MWe	975 MWe
bulk carbon density, lb/ft ³	24	24
carbon injection rate, lb/hr	906	8929
silos volume (15 day storage), ft ³	13,600	134,000
mass of carbon, lb	326,000	3,210,000
	Equipment Item Costs	thousand \$
carbon silo	143	1,722
feed bin	6	24
gravimetric feeder	10	12
pneumatic conveyor	35	96
carbon injection ports	25	36
Total Equipment (1989 basis)	218	1,891
Equipment w/instrument, tax & freight	257	2,231
Escalated Total Equipment (Jan 1, 1996)	291	2,526
Purchased Equipment w/retrofit	379	3,283
Total Capital Cost (Jan 1, 1996)	708	6,139

rate of carbon. Even more importantly, the filtration efficiency of the FF would be jeopardized if the flow rate of particulates was insufficient to establish a filter cake over normal cleaning cycles of the baghouse.

A key design criteria established for the FF system was a minimum cake thickness for AC of 1/128 in., representing a string length of thirteen 15-mm particles. The reverse-gas cleaning cycle was assumed to occur over a 1-hr time period for each compartment in the baghouse. Furthermore, the ESP upstream of the baghouse is assumed to operate at NSPS for particulates. Taking all of these factors into consideration, the requirement for AC exceeds the flow of fly ash by about a factor of 3. The following expression for AC injection rate is used in the development of a preliminary cost estimate:

$$W_{ac} = \frac{A_{cloth} \times T_{cake} \times \rho_{cake}}{t_{cycle}} \quad (9)$$

where w_{ac} is the mass flow rate of AC; A_{cloth} is the net cloth area of a baghouse compartment; T_{cake} and ρ_{cake} are the thickness and the density (prior to cleaning) of the filter cake, respectively; and t_{cycle} is the filtering cycle time period. The flow rates of AC are substantially higher than theoretical requirements proposed by the EPA in its Mercury Study Report to Congress. Potential reductions in the AC requirements could be realized if the configuration of the FF control system were changed (e.g., smaller pulse-jet FF at a higher air-to-cloth ratio, allowing a smaller footprint during installation and less carbon to cover the full area of the fabric).

As previously stated in the section on AC and Other Sorbent Injection Technologies for Mercury Capture, DOE/FETC calculated the carbon needed to cover the FF area for 90% removal of the mercury. The carbon injection rate was calculated to be 12,572 lb C/lb Hg. Again, this is indicative of the carbon needed to cover the area of the fabric within one compartment of the baghouse. In addition, recycle of the fly ash and AC collected in the baghouse dust hoppers was not considered in the EPA models, which might relax the constraint on the carbon injection needed to achieve a reasonable cake thickness and mercury removal.

The OAQPS Control Cost Manual and OAQPS-AIRS software were used to estimate the reasonableness of capital and operating costs provided in the EPA Mercury Study Report to Congress. The results of this analysis for the FF capital cost were compared to EPA's cost estimate. The costs are similar for the 100-MW model and are slightly higher for the 975-MW model. Therefore, for the preliminary assessment of Cases 1B and 2B, the capital costs were taken as those provided in the EPA's cost estimate after including a more practical retrofit factor adjustment for installation.

The following is recommended by DOE/FETC in order to complete a more detailed cost analysis:

- Accounting for auxiliaries such as induced draft (ID) fan and waste conveying system;
- Using a high air-to-cloth ratio pulse-jet filter (e.g., EPRI COHPAC and/or the UNDEERC's Advanced Hybrid Particle Collector) versus a reverse-gas baghouse downstream of the ESP;
- Incorporating manufacturers recommendations for cake thickness and cleaning cycle for dilute particulate streams;
- Examining the impact of recycle on FF performance; and
- Considering control of sulfur trioxide (SO₃) so that lower temperatures can be accommodated.

Summary of Case Studies

Table 30 summarizes the costs for each case. Of the five cases developed in this preliminary assessment, Cases 1A and 2A represent the least complex control configurations. Capital costs are minimized at the expense of higher operating and maintenance costs. The dominant operating cost is for the AC. The next level of complexity is the addition of spray cooling to AC injection (Case 1C). Here, operating costs are reduced significantly and provide a more cost-effective control system than for carbon injection alone. However, uncertainty in the potential adverse impact of spray cooling on downstream equipment and the ability to maintain a close tolerance on the cooling temperature raise concerns on the ability to achieve cost-effective mercury reductions.

The final set of technology control options includes a FF with spray cooling and carbon injection. This option provided the greatest AC utilization rate at the expense of additional capital outlays (Cases 1B and 2B). Although this provides cost-effective removal similar to Case 1C, the reliability of this control option is thought to have similar uncertainties with additional concerns associated with the FF operations, such as the potential for filter blinding.

DOE's position on mercury control system costs under the EPA's parameters is exemplified with the following comparison of DOE and EPA's model boiler cost and performance estimates. DOE's cost analysis became the basis for the system-wide estimate of control costs ultimately used by the EPA in its Mercury Study Report to Congress (Table 31).

Conclusions and Next Steps of Cost Analyses

A preliminary evaluation of costs for mercury control options at coal-fired power plants has been conducted. This evaluation provides insights into the cost tradeoffs associated with controlling the temperature at reduced sorbent utilization versus reduced capital control strategies at higher sorbent injection rates.

A simplified estimate of system-wide control costs can be obtained from the cost-effectiveness and mercury inventory. Using carbon injection control as an example, the annual cost for mercury control is about \$6 billion to reduce mercury emissions by about 46 tons (i.e., 90% of the estimated 51.5 tons currently emitted). The following expression provides a more universal depiction of the factors that impact annual costs.

The cost-effectiveness of mercury control options is strongly related to the following key parameters: AC usage and unit cost; FF installation and parasitic power costs; and contaminated fly ash disposal costs.

The annual mercury emissions inventory for coal-fired power plants contains uncertainty associated with the variable mercury content of coal received at electric utilities, as well as the mercury captured by conventional equipment in flue gas treatment systems (characterized by EMFs).

DOE/FETC and EPRI continue to strive to reduce the uncertainty of the mercury emissions and control options through their respective mercury assessment and control programs. A few examples of current efforts to improve understanding of mercury emissions are

- More detailed evaluation of mercury control technology's cost and performance;
- Assisting EPA on QA/QC aspects of EPA's ICR for both the mercury concentrations in coal and mercury speciation distributions in the flue gas streams at coal-fired power plants;
- Large-scale fate of local and regional mercury studies in the Great Lakes region; and

- Research and development for improved sorbents.

The preliminary findings in the DOE/FETC cost analyses indicate that mercury control measures, if mandated by the regulatory process at the 90% removal, will have a significant impact on coal-fired power plant economics. To place this in perspective, an annual \$6 billion incremental cost for mercury control is about 25% of the total annual cost to deliver coal to U.S. electric utilities. Prudent evaluation of control measures now will provide significant dividends for the electric utility industry and its customers in the future.

Revising the Cost Analysis of Mercury Control Options

These cost analyses were conducted in late 1997 and were developed under the set parameters in the EPA models utilized in its Mercury Study Report. In addition, the EPA models were modified and updated, based on data collected under the DOE/FETC Mercury Measurement and Control Program. There are many factors that will have a direct impact on reducing these costs. The most important factor is the reduction level across the coal-fired utility industry. As indicated through this critical review document, the existing coal-fired power plants have diverse coal consumption patterns that are associated with numerous power plant designs as well various postcombustion flue gas treatment systems.

The coal-feed system may rely on pulverization of as-received coal to very fine particles that are principally less than 200 μm , or the feed system requirements may be relaxed, such that only crushed particles are passed into the combustion chamber. This difference in burner particle size requirement creates a difference in combustion design parameters, such as heat release rates and furnace temperature profiles. The time-temperature history of the combustion products is significantly affected by these design considerations. Whether the mineral in the coal is converted to fly ash that passes through the furnace into the flue gas treatment system or is recovered from the bottom of the furnace as a slag or ash is a result of the coal-feed and boiler design specifications. The exhaust flue gas from the boiler island is dependent on these and many other factors that we have shown to be important in properly considering mercury control strategies and opportunities.

A characterization of the mercury feed to power plants, and subsequent emissions to the atmosphere as a consequence of coal-fired power generation has been described in the section on Emissions Inventory. Existing coal preparation, combustion, and flue gas emission controls are capable of reducing the potential amount of mercury released to the atmosphere by more than 50%. These controls, however, vary considerably on a plant-by-plant and boiler-by-boiler basis and

Table 30. Summary of cost estimation for mercury control (1996 dollars).

Utility Model	1A	1B	1C	2A	2B
Capital Cost	thousand \$				
Purchased Equipment	3,283	16,082	3,529	379	2,182
Installation	984	10,379	1,141	114	1,410
Installed Eq. w/retrofit	4,268	34,399	6,071	492	4,669
Indirect	1,871	7,220	1,685	216	965
Total Capital Cost*	6,139	41,620	7,756	708	5,634
Total Capital Cost, \$/kW	6.3	42.7	8.0	7.1	56.3
Operating & Maintenance	thousand \$/yr				
Operating Labor	104	207	52	39	95
Supervision Labor	16	31	8	6	14
Operating Materials	0	522	220	0	80
Maintenance Labor & Material	114	238	67	38	133
Carbon	27,903	2,622	8,371	2,832	356
Power	14	2,047	959	1	200
Activated Carbon Disposal	761	96	228	77	12
Disposal of Fly Ash	1,012	0	1,012	104	0
Lost Fly Ash Revenue (@ \$3/ton)	101	0	101	10	0
Overhead	140	286	76	50	145
Taxes, Insurance, Admin	246	1,665	310	28	225
Total O&M Cost	30,411	7,714	11,404	3,185	1,260
Annual Cost & Performance					
Capital Recovery, thousand \$/yr	580	3,928	732	67	532
Total Levelized Cost, \$/yr*	30,990	11,642	12,135	3,251	1,793
Total Levelized Cost, mills/kWh*	5.58	2.10	2.19	5.71	3.15
Mercury Reduction, lb/yr	458	458	458	46	46
Cost Effectiveness, \$/lb Hg*	67,730	25,445	26,522	70,018	38,614

* As reported by DOE/FETC in the EPA Mercury Report to Congress and considered as the more representative costs by EPA. (U.S. EPA, 1997)

Table 31. Comparison of DOE and EPA cost analysis (1996 dollars).

Characteristic	Model 1A		Model 1B		Model 1C		Model 2A		Model 2B	
	EPA	DOE	EPA	DOE	EPA	DOE	EPA	DOE	EPA	DOE
Carbon Usage (g carbon/ g Hg)	34,200	100,000	460	9,400	460	30,000	17,200	100,000	460	12,600
Capital Cost (10 ⁶ \$)	1.26	6.14	33.7	41.6	5.52	7.76	0.167	0.708	4.56	5.63
Annual Cost (10 ⁶ \$/yr)	10.1	31.0	7.94	11.6	2.26	12.1	0.66	3.25	1.29	1.79
Cost effectiveness (mills/kWh)	1.82	5.58	1.43	2.10	0.40	2.19	1.16	5.71	2.09	3.15
Cost Effectiveness (\$/lb Hg)	22,100	67,700	17,400	25,400	4,940	26,500	14,200	70,000	27,700	38,600

can range from essentially no control to as high as 85% control.

The utilization of activated carbon injection with reduced flue gas temperatures (i.e., spray cooling or use of heat exchangers) has promoted higher capture efficiencies of mercury. This may be an appropriate application for low-sulfur PRB and other sub-bituminous coals, but not necessarily for facilities utilizing high- or low-sulfur bituminous coals.

DOE conducted a "Boiler Duct Configuration Survey" of targeted electric utility boilers to gather information on the general design basis for existing duct configurations upstream of fine particulate control devices (U.S. DOE, 1988). The survey was conducted to allow for the prediction of optimum operating conditions and component designs needed to determine the applicability of duct injection technologies for SO reductions where WFGD systems can not be utilized.

Approximately 87 GWe of net generating capacity was surveyed to identify the parameter ranges for future R&D efforts, and provide the information to design engineers, if duct injection was commercially available. The information gathered under this survey is directly applicable to the various options for sorbent injection associated with flue gas cooling for mercury capture.

Nearly 87% of the net generating capacity has rectangular ducts in a horizontal alignment, with 59% having two ducts and 34% having one duct, while the remaining capacity had from 3 to 6 ducts. The cross-sectional duct areas fall into two ranges, 21 to 99 sq ft and 100 to 299 sq ft, representing 32% and 44% of the capacity, respectively. Total duct length distribution for 5 to 99 ft was 63%; for 100 to 199 ft 17%; and for an average duct length of 490 ft, the distribution was at 21% of the net generating capacity. The most critical factor is the longest straight run, with the following distribution: 5 to 39 ft at 54% of the net generating

capacity; 40 to 99 ft at 32% and the remaining 14% at an average length of ~200 ft. The average straight run was determined to be 54 ft. Less than two-thirds of the ducts had constant duct dimensions for the longest straight run.

At 100% load through the longest straight runs, velocity of the flue gases representing 72% of the generating capacity, have an nominal velocity of 50 ft/sec. The corresponding nominal flue gas temperature at 100% load in the straight run was 316°F (158°C). The most critical factor for highly efficient capture of mercury with activated carbon is residence time of carbon in the flue gas within the ducts prior to entering the particulate collector (in this case, an ESP). The survey indicated a nominal residence time in the range of <0.5 to 1.5 second.

Residence time is the most critical due to two reasons:

- (1) Amount of time the injected activated carbon has in the flue gas before collection in the ESPs; and
- (2) Amount of time needed to sufficiently reduce the flue gas temperature for optimum mercury capture by the injected activated carbon.

Based on the survey, the configuration of ducts in the utility industry presents many limitations in providing effective reduction of the flue gas temperature from the survey average of 316 °F (158 °C) to a nominal 230 to 250 °F (110 to 121 °C).

Facilities utilizing bituminous coals may not effectively utilize humidification for flue gas cooling for enhanced mercury control as a result of the formation of sub-micron sulfuric acid mist from sulfur trioxide (SO₃) condensing at or below the acid dew point of the flue gas. The SO₃ may be a result of coal combustion or injected separately or in combination with ammonia for enhancing fine particle collection (mainly PRB and other subbituminous coals). In addition, pilot-scale tests have indicated that certain carbons convert SO₂ to SO₃ while the carbon is captured on the filter of the baghouse. This conversion could dramatically reduce the bag life of the baghouse system.

There are limitations in reducing the flue gas temperature in a majority of the utility population in the United States. These limitations would compromise lower activated carbon injection rates at lower temperatures and would require carbon-to-mercury ratios near 100,000:1 upstream of an ESP. Caution must be taken when estimating possible carbon-to-mercury ratios for the 65% of the coal-fired utility industry utilizing an ESP as the only APCD. With multiple ducts, short straight duct lengths, and limited residence times, the cost of control could dramatically increase from DOE costs presented in the EPA Mercury Study Report and previously discussed. The cost increase would be consistent with the 90% level of mercury removal indicated by EPA.

A sensitivity analysis for mercury emission control has been performed to examine how control options may

impact the diverse power plant population. The first option, shown in Figure 73, considers setting a cap on emissions of 0.03 tons of mercury emitted per million tons of coal consumed. At this level of control, about 10% of the power plants have low mercury emissions that are under the cap with little or no additional controls needed. For about half of the total coal consumption, less than 40% additional control would be required. On about 10% of the total coal consumption, fairly significant control would be required, ranging from two-thirds to 85% reduction from the existing emissions level. The remaining 30% of the power plants would require approximately 40 to 67% mercury emissions reduction. The overall reduction in mercury emissions from the reference year 1996 national mercury emissions inventory estimate is about 50%.

In the second option, a 90% reduction of mercury contained in the mined coal is considered. This scenario credits mercury removal from coal preparation and existing power plant controls toward the overall goal of a 90% reduction. Approximately 60% of the coal consumed would require controlled reduction between 80 and 90%. Nearly 98% of the coal consumed would require reductions of at least 50%. The overall reduction in mercury emissions from the reference year 1996 national mercury emissions inventory estimate is about 80%.

This sensitivity analysis demonstrates that mercury control options are highly dependent on the existing power plant's operating characteristics and design. As stricter control options are considered, the flexibility to achieve these reductions begins to diminish.

Appropriate environmental control measures for mercury emissions is undergoing scrutiny from a variety of perspectives. From a health perspective, the Agency for Toxic Substance and Disease Registry (ATSDR) announcement of a recommended mercury reference dose (MRD) or mercury risk level (MRL) of 0.3 µg Hg /kg-bw/day (gram of mercury per kilograms of body weight per day) indicates mercury levels in the United States ecosystems may be able to tolerate higher mercury levels. This recommendation is based upon the Seychelles Island studies compared to EPA's calculated 0.1µg Hg/kg-bw/day based upon acute exposure of eating mercury contaminated seeds in Iraq. If a MRL of 0.3µg Hg /kg-bw/day limit is adopted, it is estimated that 90% to 95% of the state fish advisories would not be required.

As our understanding of mercury behavior in coal-fired power plants improves, refinements to models of mercury emissions and control costs will likely be made. Some consideration for modeling improvements available from this review are recommended in the following:

- (1) Incorporating the mercury speciation and total mercury measurements collected under DOE/

FETC and EPRI measurement programs conducted on coal-fired utilities with the Ontario Hydro Method.

- Over 80% of the total mercury values exiting the boilers (preheater) are below $10 \mu\text{g}/\text{Nm}^3$; and
 - The ratio (speciation) between Hg^0 and Hg^{2+} in the flue gas varies from 90:10, and 10:90, with a nominal ratio of 70:30. There is less oxidized Hg than assumed in previous modeling efforts.
- (2) Both Hg^0 and Hg^{2+} are capable of being captured with the fly ash in flue gas streams from coal-fired power plants.
- 30% in-flight Hg capture associated with PRB coal fly ash, little to no capture in a downstream ESP, while as high as 90% of the Hg associated with fly ash is captured in a FF. A nominal 60% is realized;
 - 10-20% in-flight Hg capture associated with lignite and bituminous coal fly ashes, with little to no Hg capture associated across the ESP;
 - 50-55% vapor-phase Hg capture across WFGD systems, with a range of 85-95% of the Hg^{2+} being removed; and
 - 60-66% total Hg capture in ESP/WFGD systems while scrubbing flue gas from the combustion of medium- to high-sulfur, eastern bituminous coals (>40% of the scrubbed capacity in the United States).

With more than one-third of the utility industry utilizing PRB/subbituminous coals, there will be a considerable amount of mercury captured with the fly ash.

Plants equipped with wet and dry FGD systems do remove Hg at high levels (Hg^{2+}). It should be noted that the high mercury removals are associated with power plants firing bituminous coals. Lower mercury removal levels across WFGD systems at plants firing either PRB/subbituminous or lignite coal. Even though more than 60% of the Hg^{2+} is removed, it only constitutes 10-30%, of the total mercury

The importance of properly accounting for mercury emissions from coal-fired power plants through understanding the complex behavior of mercury speciation and its interaction with flue gas and associated flue gas control equipment is amply described in the above documentation and analysis. Having placed these matters in context of our current understanding of mercury emissions, the U.S. coal-fired power generation industry's contribution to the global inventory can be more seriously debated as well as any considerations put forward to increase control levels beyond those currently realized.

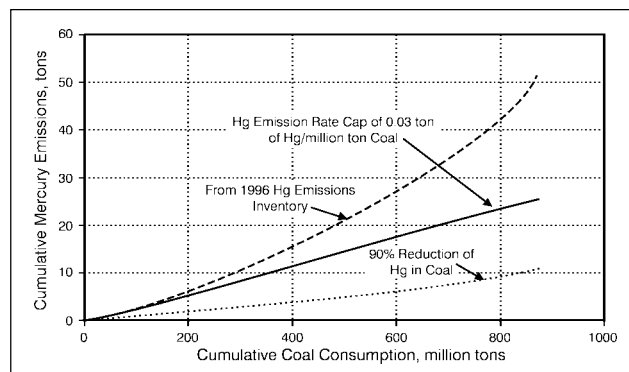


Figure 73. 1996 mercury emissions and control scenarios (Smith, D.N. 1999).

The EPA ICR for mercury concentrations in coal and flue gas streams will augment the previous DOE and EPRI measurements, and the findings on the distribution and fate of Hg^0 and Hg^{2+} in utility boiler systems. DOE/FETC and EPRI support of industry's progress in advancing state-of-the art understanding of mercury measurements and control in the utility industry, is thought to enhance any future regulatory process or requirement by the sound science achieved through these investigations. The ongoing EPA ICR mercury data collection effort and the NAS study will also be important factors in any regulatory decision.

Conclusions and Recommendation on Mercury Measurement and Control

Mercury emission inventory estimates continue to be refined as better information becomes available. EPA's recent Information Collection Request (ICR) for mercury measurements at coal-fired power plants is expected to provide an improved understanding of mercury concentration in "as-received" coal at electric utilities. More reliable relationships between the mercury concentrations in coal "as-mined" and "as-received" can be sought from this new information so that future mercury emissions can be estimated with greater certainty.

Additionally, the ICR will gather information on stack emissions of mercury for a segment of the coal-fired electric utility industry. The new data will add to our understanding of mercury partitioning in flue gas from full-scale operations. This, in turn, will improve the reliability of emission modification factors and the efficacy of mercury emission control options.

Based on recent findings and analysis pertaining to the national mercury emissions inventory, model parameters (such as coal cleaning factor and emission modification factor for FGD scrubbing) require further validation to support the reliability of the inventory estimate.

Research at the fundamental level continues to be conducted to determine the mechanisms involved with

both gas-phase Hg transformations and gas-solid interactions. Attempts have been made to use thermochemical equilibrium calculations to predict the Hg species in coal combustion flue gas. The assumption of gas-phase equilibrium for mercury-containing species in coal-fired power plant exhaust is not valid. Preliminary evidence suggests that the oxidation of Hg^0 to Hg^{2+} in the flue gas is quenched when the gas cools below 750-900 K. Again, kinetic calculations on the formation of Cl_2 , which is highly reactive with Hg^0 , indicate that the conversion of HCl to Cl_2 does not attain equilibrium given the time temperature-history of flue gas in a power plant. The calculated results lend support to the conclusion of quenched equilibrium for Hg oxidation.

Equilibrium calculations indicate that Hg may condense as HgO , HgCl_2 , or HgSO_4 , but nitrates and other forms may also occur as intermediates. Equilibrium predicts a complete conversion of Hg^0 to Hg^{2+} at air preheater outlet temperatures, but measurements of boiler emissions indicate only 10 to <90% as Hg^{2+} , suggesting that kinetic limitations are the controlling mechanisms. Recent research has speculated that the major kinetic pathway for the formation of HgCl_2 involves the reaction of atomic chlorine with Hg^0 . Kinetic simulations predict that the concentration of atomic chlorine in a cooling combustion gas is rapidly reduced by interconversion with HCl and Cl_2 , and possibly Cl and Cl_2 .

Understanding gas-phase speciation of Hg in coal-fired power plant flue gas is not sufficient to describe the transformations of Hg in the combustion system. To understand the capture of Hg in APCDs and the effectiveness of sorbents for Hg capture, a better understanding of the gas-to-particle conversion is needed, particularly the relationship(s) between fly ash properties and oxidation and adsorption of Hg.

Two key questions have been postulated: first, "What are the processes/mechanisms by which fly ashes (and certain other solids) seem to catalyze the transformation of gaseous Hg^0 to "oxidized forms?" and second, "What Hg species are adsorbed on fly ash?" Answering these questions will require a detailed look at the constituents of the fly ash and how they interact with $\text{Hg}_{(g)}$ at temperatures characteristic of the flue gas (400–600 K) as it enters the APCD. Studies conducted under federal and private funding are designed to answer these questions. Again, the EPA ICR could possibly add to the existing databases.

Investigations at both bench and laboratory scales with simulated flue gas have indicated certain bituminous coal fly ash and vapor-phase constituents play a role in the oxidation of Hg^0 . Powder River Basin (PRB) subbituminous coal fly ashes show high adsorption capacities compared to the bituminous coal fly ashes, but indicate, in most cases, very little oxidation. Generally, the adsorption rate

increases as the temperature in the flue gas decreases. Work is continuing to investigate these observations and determine the mechanisms responsible for both oxidation and adsorption of Hg by various fly ashes.

It has been speculated that the oxidized form of Hg in flue gas from coal combustion is mercuric chloride (HgCl_2). The existence of Cl_2 at temperatures measured near the first APCD of coal-fired power plants has been postulated. Kinetic calculations also showed that the chlorine atoms combine to form primarily HCl with minor amounts of molecular chlorine (Cl_2). If small concentrations of Cl_2 are present in the flue gas streams exiting the air preheater, then reactions could be occurring with the Hg^0 to subsequently form HgCl_2 . Alternatively, mercury could react with other vapor-phase compounds and/or fly ash constituents to form other oxidized mercury compounds.

The affinity of fly ash from PRB coals for mercury sorption needs to be better understood. Initial work has identified the effects of HCl, CaO, and carbon on sorption capacity and reactivity. More work is needed to understand the mechanism for the mercury interactions with the fly ash components. Fundamental studies under controlled bench-scale conditions are needed to correlate with full-scale measurements. This should be combined with analysis of the fly ash by XAFS to identify the mercury compounds. Mechanistic models could then be developed and tested. Pilot-scale studies could then build on the fundamental design information to seek optimum conditions for mercury sorption and economic control configurations.

Research is ongoing to identify promising catalysts to promote oxidation of elemental mercury for subsequent capture by flue gas scrubbers. Similar to the studies on PRB coals, these catalysts should be studied under bench-scale conditions and mechanistic models for the reactions should be developed.

One of the most important breakthroughs was realized after the numerous pilot-scale and field studies and subsequent validation at both scales of the Ontario Hydro Mercury Speciation Method. It is recommended as the best method to measure the distribution between Hg^0 and Hg^{2+} in coal-fired combustion systems by EPA, DOE, and EPRI. The method has been proven to provide good precision, low bias, and accurate spiked Hg recoveries.

The method has been submitted to the American Society for Testing and Materials (ASTM) for review, evaluation, and acceptance as a standard reference method. In addition, EPA has recommended the Ontario Hydro Method as the method of choice for their Information Collection Request (ICR) for mercury speciation data from approximately 75 coal-fired utilities.

Validation of the Ontario Hydro Method has provided researchers with a valuable tool to measure, within

$\pm 10\%$, the distribution between Hg^0 and Hg^{2+} , along with total Hg in flue gas from coal combustion. This method has aided in the understanding of the different forms of Hg and which form is captured or emitted. Many researchers have modified this method and have been using it in a semi-continuous mode for their respective bench- and laboratory-scale Hg sorbent evaluation and development projects.

Numerous mercury sampling effort utilizing the Ontario Hydro Method at both pilot- and full-scale combustion systems indicate a wide range of Hg^{2+} percentages while firing coals of various ranks: bituminous coal(s) indicating Hg^{2+} values from 70 to 88%; Powder River Basin (PRB)/subbituminous coal(s) indicating Hg^{2+} values from 15 to 50%; and lignite coal(s) being highly variable indicating Hg^{2+} values from 10 to 30%, but as high as 50%.

A key measurement in all these studies, at least for those at pilot and full scale, is the solid-vapor distribution. Currently, no method ensures that the solid-vapor distribution measured by the sampling train is the same as the distribution as it exists in the flue gas duct, especially upstream from a particulate control device. Similarly, the effect of passing the vapor through the filtered solids on the mercury speciation can not be accurately quantified. The solids are suspected to give bias to the oxidized fraction. A method is needed to separate the solid and vapor fractions without the intimate contact caused by a sample filter.

While there has been some success in using the impinger solutions of the Ontario Hydro Method in a semi-continuous mode, more development and evaluation, with subsequent validation of Hg continuous emissions monitors (CEMs) at coal-fired utilities, needs to be completed. The Ontario Hydro Method can now be utilized as a standard for the testing and possible validation of the promising CEMs.

Real-time data on total and speciated Hg are needed to fully evaluate the developing control technologies being funded. Correlating APCD operating parameters (i.e., sorbent and additive injection rates and temperature effects) with real-time monitoring is critical to the development of low-cost Hg control technologies. DOE has been funding researchers to develop a Hg CEM as a research tool to aid in the evaluation of the promising control technologies for Hg control in coal-fired utilities.

Coal mercury concentrations and the distribution between elemental (Hg^0) and oxidized mercury (Hg^{2+}) vary considerably while firing the different ranks of coal. Nearly 90% of all coals, regardless of rank, have less than 100 ppbw of mercury and subsequently have less than $10 \mu\text{g}/\text{Nm}^3$ of vapor-phase mercury with varying levels of Hg^{2+} resulting in the flue gas. The range of Hg^{2+} varies from

<10% to as high as 90% of the total mercury. The actual mercury control or removal level varies from plant to plant, with one scenario indicating over 90% of the plants requiring capture efficiency well below 90%.

Much of the mercury control research in the United States is being sponsored by four organizations: DOE/FETC, EPRI, EPA, and the U.S. Geological Survey. The research is designed to augment existing pre- and post-combustion technologies, with investigations studying different combustion conditions for possible mercury removal or mercury speciation modifications.

The post-combustion R&D focuses on the addition of some type of sorbent (including gas-phase additives) to adsorb mercury and/or convert the mercury to another form for higher mercury removals; augmenting existing air pollution devices (APCDs) in the utility industry; and using new technology for mercury control.

Given the relative maturity level of these technologies, their commercial deployment is at least several years away. Research continues on developing potential technologies for mercury emission reduction from utility plants. Before any of the technologies can be fully realized for utility application, the fundamental mechanisms of the flue gas and mercury chemistries during the combustion and post-combustion conditions, along with the various interactions with the different types of fly ash, must be understood.

Through many research efforts on modes of occurrence of mercury in coal, the majority of the data supports a predominate mercury-pyrite association in coal with some evidence suggesting that this relationship is responsible for up to 65 to 70% of the mercury in some coals. It is not unusual for up to 25 to 35% of the mercury in coal to be associated with the organic fraction.

Approximately 80% of Eastern and Midwestern U.S. bituminous coals are cleaned prior to combustion to increase their heating value, and reduce their ash, and sulfur content. From comparison of run-of-mine coal to clean coal samples from the same coal seams, it has been estimated that conventional coal cleaning results in an average mercury reduction of about 37%.

Advanced coal cleaning technologies can reduce the mercury concentration of coal (30 to greater than 60%), but the potential impact on post-combustion form and control of the remaining mercury has not been thoroughly investigated. In addition, the added costs for advanced coal cleaning separately, and in combination with post-combustion controls for mercury, have not been fully developed. None of the advanced coal cleaning concepts has yet achieved any significant degree of commercialization.

One existing APCD being investigated to enhance Hg^{2+} and Hg^0 removal is wet flue gas desulfurization

(WFGD) systems designed primarily for SO₂ removal, while removing other acid gases (e.g., HCl and HF). Integrating retrofit technology options with WFGD systems offers lower system complexity and costs compared to other Hg control technologies.

Numerous mercury sampling efforts indicate the nominal Hg removal for WFGD systems on units firing bituminous coal(s) is approximately 55% ±10% of the total Hg, with an associated removal for Hg²⁺ of between 80 to 95%. These sampling efforts have indicated no appreciable Hg⁰ removal across the WFGD systems owing to the very limited solubility of Hg⁰.

It is important to note that the high removal percentages of Hg²⁺ across WFGD systems in plants firing bituminous coals prevent this form of Hg from entering the local ecosystem(s). This represents approximately 50% (on a mass basis) of the 80 GWe of U.S. coal-fired capacity utilizing WFGD systems.

Many of the sampling efforts have indicated an apparent increase in a non-Hg²⁺, possibly Hg⁰, at the outlet of WFGD system(s) from 7 to 40%. Results from testing additives upstream and within a pilot-scale WFGD system indicated no appreciable increase in the Hg⁰ compared without the additives.

Research is being conducted to further investigate the catalytic conversion of Hg⁰ to Hg²⁺ upstream of WFGD inlets, the conversion through novel additives injected in the flue gas upstream of and directly into the WFGD systems, and the reduction in the re-emission of Hg from WFGD systems.

Stability tests were conducted on unfixated and fixated WFGD solids from a full-scale coal-fired power plant. The solid samples were subjected to the EPA Toxicity Characterization Leaching Procedure (TCLP). In addition, the samples were heated to determine whether the captured Hg could be desorbed or re-emitted (volatilized).

Mercury concentrations of the unfixated and fixated WFGD samples were the same after the TCLP tests, with the mercury being below the analytical detection limit of 0.01 mg/L. For comparison, the Resource Conservation and Recovery Act (RCRA) limit for Hg is 0.20 mg/L and based on this criteria, both WFGD materials would be classified as non-hazardous. Based on the EPA TCLP method, it was concluded that Hg contained in the solids is in a non-leachable form (e.g., chemically bound possibly with CaSO₄).

During volatilization tests, both WFGD wastes were exposed to elevated temperatures for 11 weeks with the most stringent case at 140°F (60 °C). Analyses conducted at the end of the exposure period showed no loss of Hg. It was concluded from these tests that Hg did not re-volatilize when exposed to temperatures up to 140 °F.

While the conversion of Hg⁰ to Hg²⁺ has been demonstrated in both laboratory- and small pilot-scale tests and the decrease in the re-emission of Hg from a

pilot-scale WFGD system, there is a need for longer term catalysts tests, and demonstration of additive injection at full scale. This also applies for the stability of the Hg associated with WFGD wastes. Injection rates of the additives for increased Hg⁰ across WFGD systems must be optimized to provide lower cost options.

No individual mercury technology being investigated can be universally realized for the utility industry. Activated carbon injection for mercury capture has been extensively tested at the bench, laboratory, and pilot scales for possible coal-fired utility applications. Investigations involved the potential use of adsorbents for 75% of the utility industry having fine particulate control as the only APCD (65% ESPs and 10% baghouses). Activated carbon in parallel with the capture of mercury with native fly ashes, and with enhancements for particle collection, has potential application for these utility boiler systems.

Activated carbon injection is successfully utilized in the municipal waste combustor industry and is capable of removing >90% of the mercury at very modest carbon-to-mercury ratios. A fraction of a pound increase in carbon injection rate can mean as much as 30% more removal of the flue gas mercury. Activated carbon technology is not directly applicable, or can have only limited application, to the coal-fired steam generating utility industry for several reasons:

- (1) Low concentrations of mercury present in the relatively high volumes of flue gas [(one ppbv of Hg with two different forms in flue gas volumes ranging from 500,000 to 5,000,000 actual cubic feet per minute (acfm)].
- (2) Mercury speciation is highly variable across the boiler population.
- (3) Higher concentrations of competing species occupying the active sites of the carbon.
- (4) Flue gas residence time upstream of an ESP is nominally one second or less with flue gas velocities in the range of 50 to 60 ft/sec at 300 °F (149 °C).
- (5) Compounding these factors are possible mass transfer limitations of the injected sorbents and the decrease in the carbon reactivity and equilibrium sorption capacity at this nominal temperature of 300 °F (149 °C).
- (6) High levels of sulfur dioxide up to and >1600 ppmv, with 50 ppmv HCl, have a profound negative impact on the equilibrium adsorption capacity of certain virgin activated carbons for both Hg⁰ and Hg²⁺.
- (7) Removal of HCl does not impact the Hg²⁺ equilibrium adsorption capacity, but does prevent the carbon from adsorbing Hg⁰.
- (8) Significant interactions between SO₂ and NO₂ gases and activated carbon(s) caused rapid breakthrough of mercury as well as conversion of the

mercury to a volatile oxidized form. This effect occurred at both 225 and 325 °F (107 and 163 °C) and with or without the presence of HCl and NO.

- (9) In the presence of four typical acid gases, SO₂, HCl, NO, and NO₂, in flue gas from coal combustion, rapid breakthrough and oxidation of the mercury occurred at both 225 °F (107 °C) and 325 °F (163 °C).

The interaction of NO₂ and SO₂ with activated carbon produced poor sorbent performance. This is likely to occur over a variety of conditions typical of coal-fired boilers, and represents a hurdle that must be overcome to achieve effective mercury control by this control method. Understanding these factors enhancing or decreasing mercury capture with activated carbon and novel adsorbents will allow for potential low-cost technologies for mercury control, if required, for the utility industry. Particle size of the activated carbon can also impact the mercury capture.

Activated carbon injection is a promising technology, but further research is needed to provide the best sorbent providing effective capture at a low cost. Equilibrium sorption capacity may not be the driving force for better sorbent performance, while the reactivity with the basic forms of mercury (Hg⁰, and Hg²⁺) may be the critical factor.

Different sorbent injection options being investigated at the pilot-scale are as follows:

- Option A: Sorbent or carbon injection upstream of the existing ESP;
- Option B: Sorbent or carbon injection downstream of the existing ESP associated with a downstream fabric filter, with and without flue gas cooling; and
- Option C: Sorbent or carbon injection upstream of the existing ESP, with flue gas cooling.

The utilization of activated carbon injection with reduced flue gas temperatures (i.e., spray cooling or use of heat exchangers) has promoted higher capture efficiencies of mercury. This may be an appropriate application for low-sulfur PRB and other subbituminous coals, but not necessarily for facilities utilizing high- or low-sulfur bituminous coals.

DOE/PETC (now FETC) conducted a "Boiler Duct Configuration Survey" of targeted electric utility boilers to gather information on the general design basis for existing duct configurations upstream of fine particulate control devices. (U.S. DOE, August 1988; and October 1993) The survey was conducted to allow for the prediction of optimum operating conditions and component designs needed to determine the applicability of duct injection technologies for SO₂ reductions where WFGD systems may not be as cost effective.

Approximately 87 GWe of net generating capacity was surveyed in 1986 and 1987, to identify the parameter ranges

for future R&D efforts, and provide the information to design engineers, if duct injection was commercially available. The information gathered under this survey is directly applicable to the various options utilizing sorbent injection, with and without flue gas cooling, for mercury capture. It was determined, based on the survey of current duct parameters, that a lower drying time for the injected sorbent slurries of 1 to 1.5 seconds would be needed, while an increase in sorbent reactivity for optimum SO₂ capture was also needed.

At 100% load through the longest straight runs, velocity of the flue gases representing 72% of the generating capacity, has a nominal velocity of 50 ft/sec. The corresponding nominal flue gas temperature at 100% load in the straight run was 290 °F (143 °C). The most critical factor for highly efficient capture of mercury with activated carbon is residence time of carbon in the flue gas within the ducts at a lower temperature, prior to entering the particulate collector (in this case, an ESP). The survey indicated a nominal residence time at the above conditions to be in the range of <0.5 to 1 second. Even though there is an increase in flue gas residence time with decreasing temperature, effective residence times may not be realized.

As a reference point, optimum conditions for duct injection resulting for SO₂ control is typically achieved with a 20 to 30 °F (11 to 17 °C) approach to the adiabatic saturation temperature [approximately 127 °F (63 °C)]. These conditions were achieved in the Coolside sorbent injection demonstration as part of the Clean Coal Technology demonstration program (U.S. DOE, September 1990). The residence time of the duct injection humidification chamber was about 2 seconds at full load—at the high end of residence time available in straight length ducts at existing power plants.

Residence time is one of the most critical parameters for any sorbent technology including activated carbon injection for mercury capture, owing to (1) the amount of time the injected activated carbon has in the flue gas before collection in the ESPs, since mercury is not captured by activated carbon in the ESP; and (2) the amount of time needed to sufficiently reduce the flue gas temperature for optimum mercury capture by the injected activated carbon.

In addition, facilities utilizing bituminous coals may not effectively utilize humidification for flue gas cooling to enhance mercury control as a result of the formation of sub-micron sulfuric acid mist from sulfur trioxide (SO₃) condensing at or below the acid dew point of the flue gas. The sulfuric acid dew point for high moisture content in the flue gas is nominally in the 230 to 270 °F (110 to 132 °C) temperature range. (U.S. DOE, March 1998) The SO₃ may be a result of coal combustion or injected separately or in combination with ammonia for enhancing fine particle collection (mainly PRB and other subbituminous coals). In addition, pilot-scale tests have indicated that certain

carbons convert SO₂ to SO₃ while the carbon is captured on the filter of the baghouse. This conversion could dramatically reduce the bag life of the baghouse system.

Based on the survey and other flue gas considerations, the configuration of ducts in the utility industry presents many limitations in providing effective reduction of the flue gas temperature from the survey average of 316 °F (158 °C) to temperatures at or below the acid dew point, 230 to 270 °F (110 to 132 °C) for optimum mercury capture with activated carbon. This alone may be the one limiting factor impacting the development of a low cost mercury control for the utility industry through activated carbon injection.

The above limitations in optimizing mercury capture associated with activated carbon impacts a majority of the utility population in the United States. These limitations would compromise lower activated carbon injection rates at lower temperatures, and could require carbon-to-mercury ratios between 50,000:1 to 100,000:1 upstream of an ESP. Caution must be taken when estimating possible carbon-to-mercury ratios for the 65% of the coal-fired utility industry utilizing an ESP as the only APCD. With multiple ducts, short straight duct lengths, and limited residence times, the technical and economic performance criteria of the control technology would be impacted. Future design and system performance modeling activities needs to properly account for these limitations. Possible power plant equipment that may require new or modified components include duct and chimney liners or new fabrications, fan upgrades, and particulate collection system upgrades.

A sensitivity analysis for mercury emission control has been performed to examine how control options may impact the diverse U.S. power plant population (see Figure ES-1). The first option considers setting an emissions cap of 0.03 tons of mercury emitted per million tons of coal consumed. Approximately 10% of the U.S. power plants fall under this cap with little or no need for additional control. Power plants representing about half of the total coal consumption would require less than 40% additional control. Only a few utilities, representing about 10% of the total coal consumption, would require fairly significant control. Even for these utilities, the control would only range from two-thirds to 85% reduction from the existing emissions level. The remaining 30% of power plants would require approximately 40 to 67% mercury emissions reduction. The overall reduction in mercury emissions from the national mercury emissions inventory estimate for the reference year of 1996 is about 50%.

In the second option, 90% reduction of mercury contained in the mined coal is considered. This scenario credits mercury removal from coal preparation and existing power plant controls toward the overall goal. Utilities representing approximately 60% of the coal consumed in the United States would require reduction between 80 and 90%. Nearly all

utilities would require reductions of at least 50%. The overall reduction in mercury emissions from the national mercury emissions inventory estimate for the reference year of 1996 is about 80%.

Mercury control options are highly dependent on the existing power plant's operating characteristics and design. As stricter control options are considered, the flexibility to achieve these reductions begins to diminish.

Appropriate environmental control measures for mercury emissions is undergoing scrutiny from a variety of perspectives. From a health perspective, the Agency for Toxic Substance and Disease Registry (ATSDR) announcement of a recommended mercury reference dose (MRD), or mercury risk level (MRL), of 0.3 µg Hg /kg-bw/day (gram of mercury per kilograms of body weight per day) indicates mercury levels in the United States ecosystems may be able to tolerate current mercury levels. This recommendation is based upon the Seychelles Island studies compared to EPA's calculated 0.1µg Hg/kg-bw/day, which is based upon acute exposure of eating mercury contaminated seeds in Iraq. If a MRL of 0.3µg Hg/kg-bw/day limit is adopted, it is estimated that 90% to 95% of the state fish advisories would not be required.

As our understanding of mercury behavior in coal-fired power plants improves, refinements to models of mercury emissions and control costs will likely be made. Some consideration for modeling improvements available from this review are recommended in the following.

- (1) Incorporating the mercury speciation and total mercury measurements collected under the DOE/FETC and EPRI measurement programs conducted on coal-fired utilities with the Ontario Hydro Method.
 - Over 80% of the total mercury values exiting the boilers (preheater) are below 10 mg/Nm³.
 - The ratio (speciation) between Hg⁰ and Hg²⁺ in the flue gas varies from 90:10, and 10:90, with a nominal ratio of 70:30. There is less oxidized Hg than assumed in previous modeling efforts.
- (2) Both Hg⁰ and Hg²⁺ are capable of being captured with the fly ash in flue gas streams from coal-fired power plants.
 - 30% in-flight Hg capture associated with PRB coal fly ash, little to no capture in an downstream ESP, while as high as 90% of the Hg associated with fly ash is captured in a fabric filter. A nominal 60% is realized.
 - 10 to 20% in-flight Hg capture associated with lignite and bituminous coal fly ashes, with little to no Hg capture associated across the ESP.
 - 50 to 55% vapor-phase Hg capture across wet FGD systems, with a range from 85 to 95% of the Hg²⁺ being removed.
 - 60 to 66% total Hg capture in ESP/wet FGD

systems while scrubbing flue gas from the combustion of medium- to high-sulfur eastern bituminous coals (~50% of the scrubbed capacity in the United States).

- (3) With more than one-third of the utility industry utilizing PRB/subbituminous coals, there will be a considerable amount of mercury captured with the fly ash.
- (4) Plants equipped with wet and dry FGD systems do remove Hg at high levels (Hg^{2+} and in dry FGD cases Hg^0). It should be noted that the high mercury removals are associated with power plants firing bituminous coals. Lower mercury removal levels have been measured across WFGD systems at plants firing either PRB/subbituminous or lignite coal. Even though more than 60% of the Hg^{2+} is removed, it only constitutes 10 to 30% of the total mercury.
- (5) The impacts of low NO_x burners, selective catalytic and non-selective catalytic reduction of NO_x (SCR and SNCR, respectively) are currently being assessed for possible conversion of Hg^0 to Hg^{2+} , and possible mercury reductions.

The importance of properly accounting for mercury emissions from coal-fired power plants through understanding the complex behavior of mercury speciation and its interaction with flue gas and associated flue gas control equipment is amply described in the above documentation and analysis. Having placed these matters in context of our current understanding of mercury emissions, the U.S. coal-fired power generation industry's contribution to the global inventory can be more seriously debated as well as any considerations put forward to increase control levels beyond those currently realized with existing processes and equipment.

The EPA Information Collection Request (ICR) for mercury concentrations in coal and flue gas streams will augment the previous DOE and EPRI measurements, and the findings on the distribution and fate of the Hg^0 and Hg^{2+} in utility boiler systems. DOE/FETC and EPRI support of industry's progress in advancing the state-of-the-art understanding of mercury measurements and control in the utility industry, is thought to enhance any future regulatory process or requirement by the sound science achieved through these investigations. The on-going EPA ICR mercury data collection effort and the National Academy of Sciences (NAS) study will also be important factors in any regulatory decision.

DOE/FETC, in collaboration with EPA, EPRI, and USGS, is developing a program to demonstrate the most promising mercury control technologies at a larger scale or full-scale at different coal-fired utilities. DOE will issue a solicitation before the end of fiscal year 1999 (September 30, 1999). The solicitation, which will ask for proposals to

scale up the promising technologies, will require contractor and industrial cost sharing. These demonstrations need to be completed through many collaborative efforts, before any regulatory decisions can be made based upon sound science. There are many engineering and technical issues that need to be addressed before mercury control is implemented in the utility industry.

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