

# Technologies for Control and Measurement of Mercury Emissions from Coal-Fired Power Plants in the United States: A 2010 Status Report

**Northeast States for Coordinated Air Use Management  
(NESCAUM)**

**July 2010**

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# **TECHNOLOGIES FOR CONTROL AND MEASUREMENT OF MERCURY EMISSIONS FROM COAL-FIRED POWER PLANTS IN THE UNITED STATES: A 2010 STATUS REPORT**

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## **List of Acronyms**

AAS	Atomic absorption spectroscopy
ACI	Activated carbon injection
AEA	Air-entraining agent
AEP	American Electric Power
APCD	Air pollution control device
APH	Air preheater
CAAA	Clean Air Act Amendments
CAMR	Clean Air Mercury Rule
CCR	Coal combustion residue
CEA	Cold-end temperature
CEMS	Continuous emission monitoring system
CMMS	Continuous mercury monitoring system
COE	Cost of electricity
CVAF	Cold-vapor atomic fluorescence
DEP	Department of Environmental Protection
DOE	Department of Energy
EDX	Energy-dispersive X-ray
EIA	Energy Information Administration
EERC	Energy & Environmental Research Center
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic precipitator
FBC	Fluidized bed combustor
FF	Fabric filter
FGC	Flue gas conditioning
FGD	Flue gas desulfurization
GAO	Government Accountability Office
HAP	Hazardous air pollutant
ICP-MS	Inductively coupled plasma mass spectrometry
ICR	Information Collection Request
ICSET	Institute for Combustion Science and Environmental Technology
MRC	Mercury Research Center
MW	Megawatt
ND	North Dakota
NETL	National Energy Technology Laboratory
NO <sub>x</sub>	Oxides of Nitrogen
NIST	National Institute of Standards & Technology

## **List of Acronyms [Cont'd]**

OA	Oxidation additive
PAC	Powdered activated carbon
PCD	Particulate control device
PM	Particulate matter
PRB	Powder River Basin
PSNH	Public Service of New Hampshire
QA	Quality assurance
QC	Quality control
RATA	Relative accuracy test audit
RCRA	Resource Conservation and Recovery Act
RM	Reference method
SCA	Specific collection area
SCR	Selective catalytic reduction
SD	Spray dryer
SEA	Sorbent enhancement additive
SEM	Scanning electron microscope
SNCR	Selective non-catalytic reduction
SO <sub>2</sub>	Sulfur dioxide
ST	Sorbent trap
TX	Texas
WRI	Western Research Institute

## **Executive Summary**

### **ES-1. Objectives**

The current status of mercury control technologies and mercury measurement systems for coal-fired power plants is reviewed in this report, including recent information on performance and costs (capital costs, fixed and variable costs, and operating and maintenance costs). The objective is to summarize the outlook for the next two to three years of various mercury control and measurement options so as to present a realistic picture of mercury emissions reductions that may be achievable in the United States.

Recent experience (2006-2009) with mercury control technologies, including activated carbon injection (ACI) technology, is evaluated, based on projects funded by the U.S. Department of Energy's National Energy Technology Laboratory (NETL), Electric Power Research Institute (EPRI), and others. Key sub-populations of coal-fired boilers (for example, boilers burning different coal types or using different types of control equipment for nitrogen oxides (NO<sub>x</sub>), sulfur oxide (SO<sub>2</sub>), and particulate matter (PM) emissions) have been identified as needing additional technology development to meet stringent mercury emission requirements.

The status of continuous mercury monitoring systems (CMMS), which include mercury continuous emission monitoring systems (CEMS) and sorbent trap (ST) systems, is assessed. Data have been collected and evaluated on measurement technologies including recent experience in the field. For both mercury CEMS and STs, the report provides:

- a brief overview of the technology;
- approximate costs;
- approximate number of units installed and in operation, and where possible, data sorted by state and by CEMS vendor; and
- a brief description of operating issues as well as data on reliability and sensitivity.

The advantages and disadvantages of sorbent trap technology compared to mercury CEMS are also discussed.

#### **ES-1.1. Mercury Control Technologies**

Mercury chemistry in flue gas is complex, because mercury interacts with acid gases (e.g., HCl, SO<sub>x</sub>) and unburned carbon in ash. The compositions of coals that are burned in power plant boilers vary, which results in a range of compositions of flue gas. Thus, there is not a "one size fits all" technology for control of mercury emissions. Instead, solutions must be tailored to a given boiler.

Two general approaches for mercury control have, to date, proven capable of effectively reducing mercury emissions at levels of control of 90% or greater on combinations of coal type and air pollution control devices (APCDs) that represent the majority of coal-fired boilers. These approaches involve use of either existing APCDs or dedicated mercury control technology, primarily powdered activated carbon injection.

There are cases where the existing APCDs alone may be capable of greater than 90% reduction in mercury, but this is not always possible even for similar plant/fuel configurations. In recognition of these considerations, the development of dedicated mercury control technologies over the last 15 years has concentrated on two major areas:

- Development of techniques and technologies to promote oxidation of elemental mercury ( $\text{Hg}^0$ ) to oxidized mercury ( $\text{Hg}^{2+}$ ) in the flue gas for subsequent removal in a wet or dry scrubber; and
- Development of sorbents and associated systems to promote the adsorption of mercury on sorbents.

Increased oxidation of mercury in flue gas can be promoted by two different methods:

- Chemical additives designed to maximize the oxidation of  $\text{Hg}^0$  in the flue gas; and
- Fixed bed oxidation catalysts.

The majority of work involving enhanced oxidation techniques has been focused on plant configurations with wet flue gas desulfurization (FGD) systems, in which the oxidized mercury is captured. The “re-emission” of  $\text{Hg}^0$  after  $\text{Hg}^{2+}$  has been captured and chemically reduced in the scrubber has been observed and can be addressed by the use of additives to the scrubber.

Powdered activated carbon (PAC) is the most widely used mercury sorbent, and in many of these coal-fired power plants, injection of PAC can achieve mercury removal of 90% or greater. Activated carbons are made from coal or biomass and have been chemically treated to enhance mercury removal, using halogens (chlorine, bromine, iodine) or sulfur. While injection of untreated carbon-based sorbents works well for plants burning bituminous coal, this control strategy is not as effective for plants burning subbituminous or lignite coals. Chemically treated sorbents are able to achieve high mercury reductions across all coal types. Other non-carbon based sorbents are also being developed.

Most coal-fired boilers will have options for high levels of mercury control to meet existing state or anticipated federal regulations on mercury emissions. The combination of a wet scrubber and an SCR has demonstrated mercury removal in the range of 70% to 90% on plants burning high-sulfur bituminous coal. Activated carbon has been shown to be cost-effective for high levels of mercury removal (80% to 90%) at boilers with a cold-side ESP or baghouse that burn low-sulfur bituminous coal, subbituminous, or lignite coal, as long as the plant does not use flue gas conditioning with the ESP.

A report by the U.S. Government Accountability Office (GAO) in 2009 identified several power plant configurations for which mercury control by sorbent injection might not achieve 90% removal, including units with high  $\text{SO}_3$  concentrations in the flue gas, units equipped with hot-side electrostatic precipitators (ESPs), and those burning lignite coal. These units might require alternate technologies for mercury control or improvements in existing technologies.

- Lignite is burned at 3% of coal-fired boilers in the U.S. While the overall amount of lignite burned is small, regionally the fuel is important. Lignite from the northern Great Plains is burned in North Dakota and lignite from the Gulf Coast is burned in Texas and Louisiana. Great Plains (GP) lignite is relatively low in sulfur, similar to subbituminous coal, and reasonably good success has been demonstrated in controlling mercury using a combination of boiler additives and

activated carbon. Gulf Coast (GC) lignite can be significantly higher in sulfur, relative to Great Plains lignite. When compared with Powder River Basin subbituminous coals, lower levels of mercury reduction have been observed when firing Gulf Coast lignite.

- Hot-side ESPs are the only particulate control device on about 9% of boilers; these boilers burn both bituminous and subbituminous coals. Activated carbons, even those designed specifically for the high temperatures of a hot-side ESP, have not been able to show 90% removal in hot-side ESPs. Unless sorbents can be found that are effective at temperatures greater than about 700°F, the best control option for hot-side ESPs would be to install a fabric filter (FF) downstream of the ESP for use with sorbent injection.
- High levels of SO<sub>3</sub> are produced in boilers that burn high-sulfur bituminous coal (defined as greater than 1.7 wt% sulfur) or that have a selective catalytic reduction (SCR) unit and burn bituminous coal. The higher the sulfur content in the coal, the higher the resulting concentration of SO<sub>2</sub> in flue gas; SCRs produce additional SO<sub>3</sub> in the flue gas by catalytic oxidation of SO<sub>2</sub>. In both these situations, SO<sub>3</sub> concentrations in the flue gas are high enough to reduce the effectiveness of activated carbon for Hg removal. The combination of an SCR and a wet FGD might achieve 90% Hg removal on these plants. The high-sulfur bituminous plants that have a cold-side ESP without both SCR and FGD make up only 11% of the U.S. boiler population. This percentage is expected to shrink in the next several years as more bituminous-fired plants install advanced NO<sub>x</sub> and SO<sub>2</sub> controls (e.g., SCRs and FGDs). Injection of alkaline sorbents, like trona, can be used to reduce SO<sub>3</sub> in the flue gas and improve the performance of activated carbon. Furthermore, new carbon-based mercury sorbents are being developed that are tolerant of higher levels of SO<sub>3</sub>. The other category of plants that have relatively high levels of SO<sub>3</sub> are plants burning low-sulfur bituminous, subbituminous or lignite coal with cold-side ESPs that require flue gas conditioning to meet limits on stack opacity. Approximately 15% of boilers with cold-side ESPs use flue gas conditioning. SO<sub>3</sub>-tolerant sorbents are being developed to address the difficulty in achieving 90% mercury removal in these systems. Trona injection has been proposed as an alternative to SO<sub>3</sub> as a flue gas conditioning agent and there are other alternative flue gas conditioning agents under development. Another, but more expensive alternative, is to install a TOXECON<sup>TM</sup> fabric filter (an EPRI-patented technology) after the ESP and to inject the sorbent into the fabric filter.

The report contains a summary of the most recently published data available with respect to costs of dedicated or mercury-specific control technologies. Specifically, this includes algorithm-based cost information as well as actual costs on installed systems for mercury control. These recent studies, conducted in 2007-2009, represent a reasonable basis for the current status of estimates of mercury control costs.

The installed capital costs of ACI technology are low (from about \$3.5/kW to about \$9.2/kW). Levelized operating costs of ACI technology are primarily driven by the cost of the sorbent. Hence, quantity and quality of the sorbent are the key factors in the total sorbent cost. In some situations, if ACI would result in a loss of sales of fly ash as a by-product, the operating

costs are higher. Costs for ACI range from about \$6,000/lb Hg removed to \$30,000/lb Hg removed when by-product contamination/sales are not a factor, and between about \$18,000/lb Hg removed and \$50,000/lb Hg removed if revenue from fly ash sales is lost. These estimates correspond to 20-year levelized costs of electricity ranging from about 0.35 mills/kWh to 2 mills/kWh (0.035 to 0.2 cents/kWh) without by-product penalty and about 1 mill/kWh to 3.5 mills/kWh (0.1 to 0.35 cents/kWh) if by-product impacts are present.

If ACI technology is combined with a new fabric filter (TOXECON<sup>TM</sup>), then capital and operating costs will be substantially higher. For example, the TOXECON<sup>TM</sup> system installed at the Presque Isle power plant reported a capital cost of \$128/kW and an overall mercury removal cost of \$67,000/lbHg.

The two types of Hg oxidation technologies (catalysts and additives) have different cost components: catalysts are primarily driven by the initial capital and re-generation costs, while additive technology is not capital-intensive, but as with the ACI technologies, is driven by costs of chemicals. Unlike the estimates above for ACI technologies, the oxidation technology costs were estimated based on pilot-scale results and applied to a nominal 500 MW plant. The capital and operating costs are comparable to those for sorbent injection technologies. Specifically, the incremental cost of electricity was in the range of 1.0 to 1.8 mills/kWh, which is about the same as that for the ACI technologies when by-product impacts are not included.

Cost-effective use of ACI is not necessarily possible on all plants, particularly on plants that sell their fly ash for concrete manufacture. Plants that fire low-rank coal and sell their fly ash represent about 23% of boilers in the U.S., while 21% of plants that fire bituminous coal sell their fly ash. According to the 2008 Production and Use Survey by the American Coal Ash Association ([www.aaa-usa.org](http://www.aaa-usa.org)), of the 30 million tons of fly ash sold for commercial applications, 42% was used to make concrete. Adding enough activated carbon to achieve 90% removal can reduce the economic value of the fly ash, if the fly ash is intended for concrete manufacture. Process variations have been identified that require low activated carbon injection rates to achieve high levels of removal, which might allow for the sale of fly ash. Several sorbent vendors offer activated carbon that is specially treated to allow the fly ash-sorbent mixtures to be made into acceptable concrete. An alternative is to segregate the fly ash collection from the sorbent collection by using add-on technology.

### **ES-1.1.1. Continuous Mercury Monitoring Technologies**

This report examines the technologies for continuous monitoring of mercury emissions from power plant stacks, including continuous analyzers, or mercury CEMS and sorbent trap (ST) methods. Hg CEMS and STs are currently applied on more than 700 coal-fired power plant stacks, with over 600 Hg CEMS and about 100 STs.

The findings of this report for Hg CEMS are summarized below:

- Hg CEMS, at roughly \$500,000 of capital cost per site (with some variation due to site-specific variables), are the more costly of the two approaches to install, but they offer advantages that are discussed below. Although there has been a significant learning curve with Hg CEMS, the technology has advanced rapidly and many of the technical challenges that existed with the technology only a few years ago have been addressed.

- Many issues affecting reliability of Hg CEMS have been addressed, and it is expected that design changes implemented over the past few years as Hg CEMS have been installed will improve future reliability. Although only a small percentage of Hg CEMS have reported annual emissions data to state agencies, they have reported availability of 90% or greater. In other states power plant owners are operating Hg CEMS in anticipation of future state and federal regulatory requirements to report such data; however, official performance statistics are not publicly available from these states. As more state mercury emission rules take effect, more mercury data should become available.
- Measurement accuracy at low mercury levels has improved. Data indicate that Hg CEMS may offer reliable measurements to well below  $1.0 \mu\text{g}/\text{m}^3$ , which is important for situations where Hg emission controls are in place.
- Mercury calibration gas standards (generators) that are traceable to National Institute of Standards and Technology (NIST) measurements are available. Interim calibration protocols have been established.

The findings of this report for sorbent trap methods are summarized below:

- Sorbent traps, at about \$150,000 of capital cost per site (with some variation on this cost due to site specifics), are a lower capital cost alternative to Hg CEMS. However, STs require regular replacement and testing (roughly, every four to seven days) of the sorbent traps, which entails additional labor and cost relative to CEMS.
- Although only three of the more than 100 installed STs have reported annual emissions data to state agencies (Massachusetts), they have a reported availability of about 90% or greater. As more state mercury emission rules take effect, more availability data should become public.
- STs appear to offer reliable measurements to well below  $1.0 \mu\text{g}/\text{m}^3$ , which is important for situations where Hg controls are in place.
- In addition to lower capital cost, STs offer the advantage of requiring less sophisticated technical support compared to that needed for Hg CEMS.

Hg CEMS have some advantages relative to STs. They are:

- Hg CEMS offer results in minutes, while it can take days for ST results to become available.
- Sorbent traps are inherently more labor-intensive than Hg CEMS, and this implies that long-term operating costs for STs may not have as much room for improvement as operating costs for Hg CEMS.
- Hg CEMS offer mercury speciation data, which may be useful for Hg control or for understanding the environmental impact of Hg emissions. STs offering mercury speciation data are available but have not been extensively tested.

Sorbent traps have some advantages relative to CEMS. They are:

- CEMS require significantly higher capital cost: about \$500,000 for CEMS versus about \$150,000 for STs.
- Hg CEMS are more complex than sorbent traps systems and will require more sophisticated technical staff to support.
- Hg CEMS are not able to measure low concentration levels as well as STs. However, Hg CEMS are improving their ability to measure to low levels such that any advantage STs have in this respect may be small.

## **1. Mercury Control Technologies: Strategies and Costs**

### **1.1. Introduction**

#### **1.1.1. Objectives**

The objective of this Chapter is to provide a detailed review of the current status (2006-2009 timeframe) of mercury control technologies for coal-fired power plants in the U.S. The review covers results from actual field applications of control technologies as well as technologies that are under development and getting ready for commercial deployment. The Chapter also provides data on cost performance of the reviewed technologies with focus on the application of most common technology, activated carbon injection (ACI). The report focuses on the near-term outlook for the next two to three years of various mercury control options so as to present a realistic picture of mercury emission reductions that should be achievable in the U.S.

#### **1.1.2. Current and Emerging Regulatory Conditions**

With the U.S. Court of Appeals D.C. Circuit vacatur of the federal Clean Air Mercury Rule (CAMR) in early 2008, about 20 states across the country have moved forward implementing their state-specific approaches and methods to control mercury emissions in the range of 85 to 95%. Some states have percentage reduction requirements (from mercury in coal), others have emission limits (input or output-based standards), and some states have a combination standard, providing the flexibility of meeting the less stringent of the two. A common theme of these state rules is that, unlike CAMR, none of the state rules allow trading of mercury emissions to meet the regulatory requirements. The time frame for compliance with various state requirements is typically from 2007 to 2014, with a few states allowing until 2018.

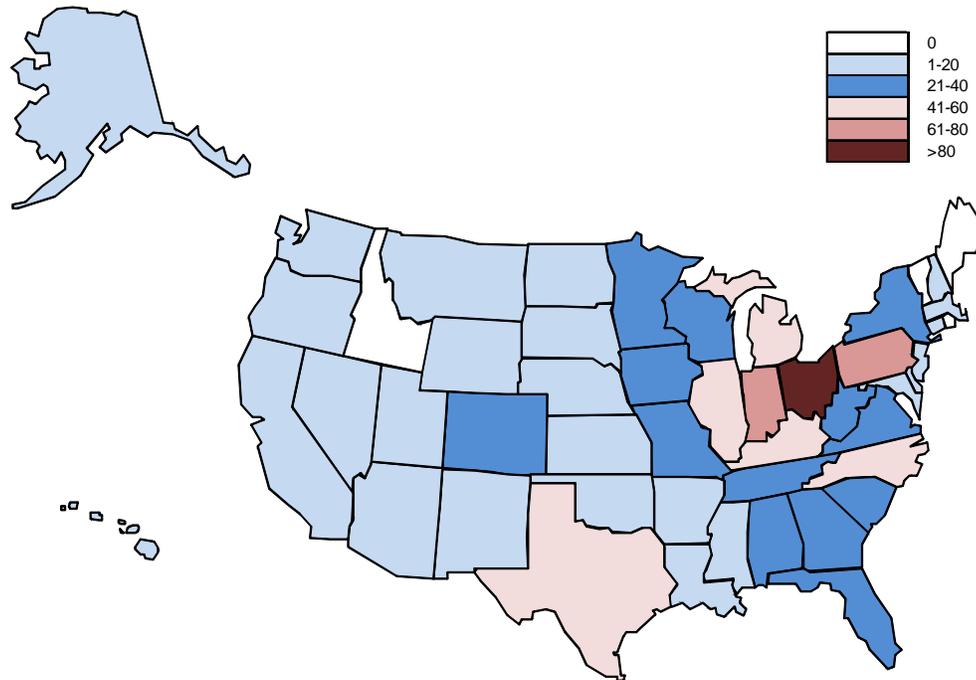
The real-world experience drawn from these ongoing individual state efforts, along with continued industry applications and data collection under real-world conditions, is expected to help steer the design of future federal mercury regulations. Under the current timetable, the U.S. Environmental Protection Agency (EPA) is expected to propose utility MACT regulations no later than March 16, 2011, with finalization of these rules eight months later, by November 16, 2011. The federal utility MACT rules will cover not only mercury, but also other trace metals, acid gases, and other compounds listed under section 112 of the 1990 Clean Air Act Amendments (CAAA).

#### **1.1.3. Boiler and Air Pollution Control Device (APCD) Populations**

Mercury emission rates and capture of mercury from coal-fired power plants depend on the chemical composition of the coal burned and on the design and operation of APCDs on the plant. These relationships will be discussed in detail in Section 1.2. This section introduces the range of coal types and APCDs on coal-fired boilers in the U.S.

A survey of the types of APCDs on coal-fired power plant boilers in the U.S. was carried out using the National Energy Technology Laboratory (NETL) 2007 Coal Power Plant Database,<sup>1</sup> which includes data from the U.S. Energy Information Administration (EIA) 767 database, and a U.S. EPA New Source Review database, which was updated in August 2009.<sup>2</sup> The information on APCDs was updated by using other public information on devices installed

since 2005. There are approximately 1,130 coal-fired boilers greater than 25 MW at more than 500 facilities in the U.S. The locations of these boilers are shown in Figure 1-1. Coal-fired power plants are concentrated in the eastern half of the U.S., with the highest concentrations generally found along the Ohio River (Pennsylvania, Ohio, Kentucky, Indiana, Illinois).



**Figure 1-1. Number of coal-fired boilers > 25 MW per state**

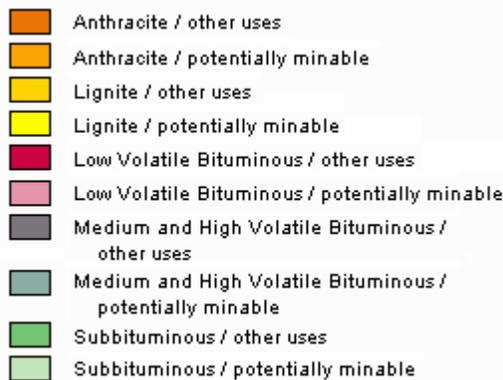
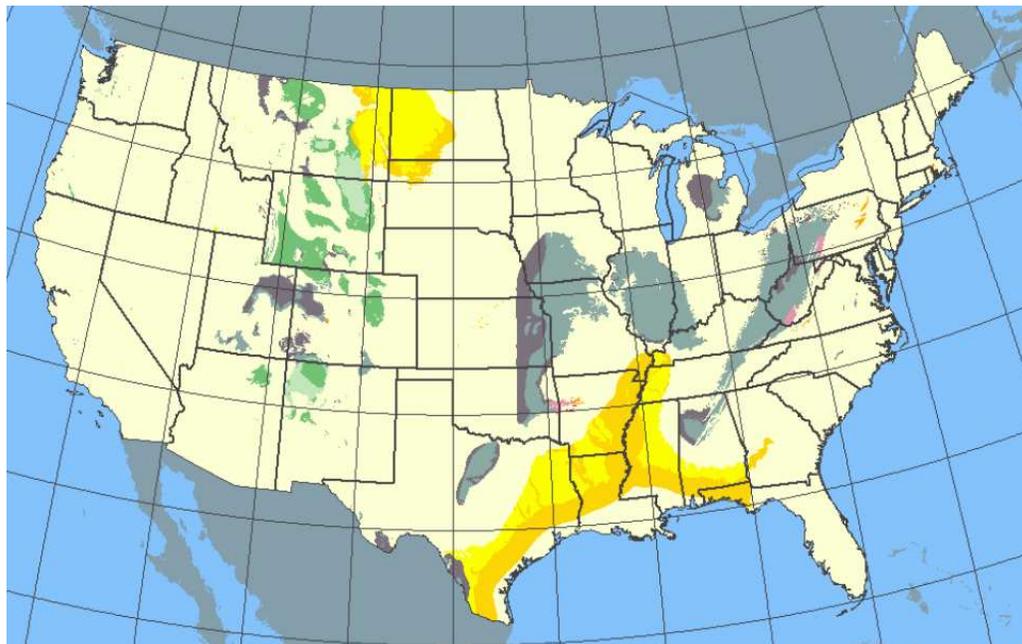
Coal burned in the U.S. may be categorized by rank as either bituminous, subbituminous, or lignite. Often subbituminous and lignite coals are lumped together and called low-rank coals. A small number of plants burn waste coal refuse, which typically consists of high-ash rejects that come from historic mining or coal washing operations. Some plants in the U.S. co-fire petroleum coke (also called petcoke) with coal. The properties of different coal ranks relative to mercury emissions control are discussed in more detail in Section 1.2.

A map of the coal fields in the U.S. is shown in Figure 1-2. Eastern bituminous coals are mined primarily in Illinois, Indiana, Ohio, Kentucky, Pennsylvania, West Virginia, Virginia, and Alabama. Western bituminous coals are mined in Utah and Colorado. Subbituminous coals are mined primarily in Wyoming and Montana, although there are locally used subbituminous sources in Colorado, New Mexico, and Arizona. Gulf Coast (GC) lignite is mined primarily in Texas, while Great Plains (GP) lignite is mined primarily in North Dakota.

A breakdown of coal-fired units by coal rank is shown in Table 1-1 for plants greater than 25 MW, based on data collated from References 1 and 2. Plants that burn blends have been grouped with the rank of the largest share of coal. The majority of the coal-fired units burn bituminous (54% on a MW basis) or subbituminous (42% on a MW basis) coal.

**Table 1-1. Coal-fired units greater than 25 MW in the U.S. by coal rank**

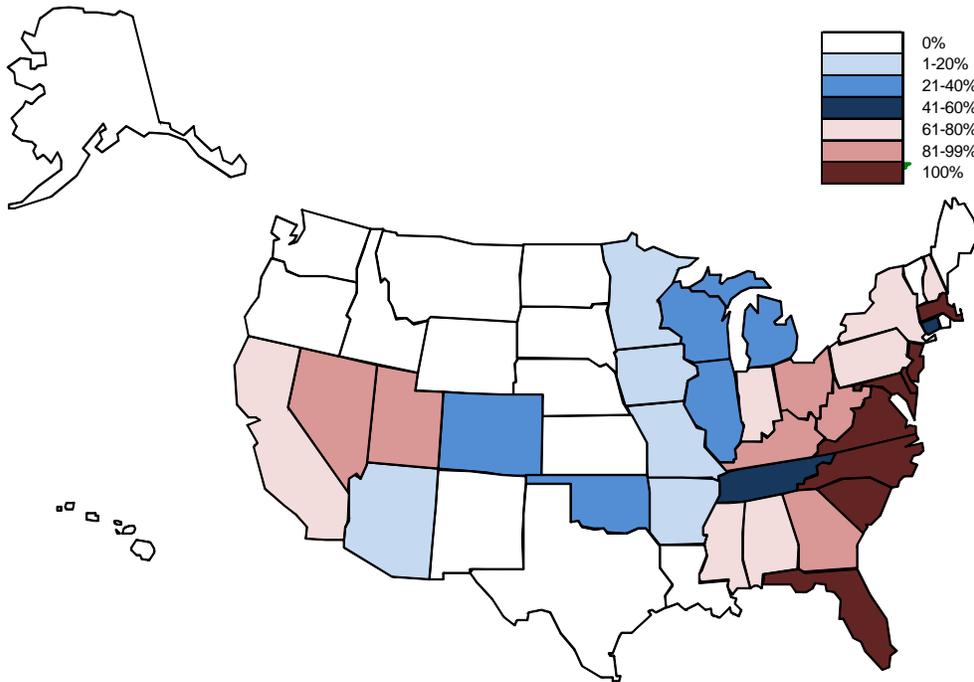
Coal rank	No. units	% of total units	MW	% of total MW
Bituminous	668	58.8%	181,438	53.6%
Subbituminous	406	35.7%	141,566	41.8%
Lignite	30	2.6%	13,564	4.0%
Other fuels	32	2.8%	2,201	0.6%
Total	1,136		338,769	



**Figure 1-2. Map of coal fields in the U.S. ([www.nationalatlas.gov](http://www.nationalatlas.gov))**

The geographical locations of boilers burning the major coal ranks are illustrated in Figure 1-3 through Figure 1-5. Eastern bituminous coal is burned in the eastern half of the U.S. It should be noted that boilers that import bituminous coal from South America have been included in Figure 1-3. In the Rockies and Intermountain West, western bituminous coal is

burned. Bituminous coal is more likely to be burned in the regions where it is mined, while subbituminous coal (primarily from Wyoming and Montana) is used in almost all regions of the U.S. except New England and the Atlantic States, as shown in Figure 1-4. Lignite is an important fuel in the regions where it is mined (Figure 1-5), but not elsewhere.



**Figure 1-3. Percent of coal-fired boilers in each state burning predominantly bituminous coal**

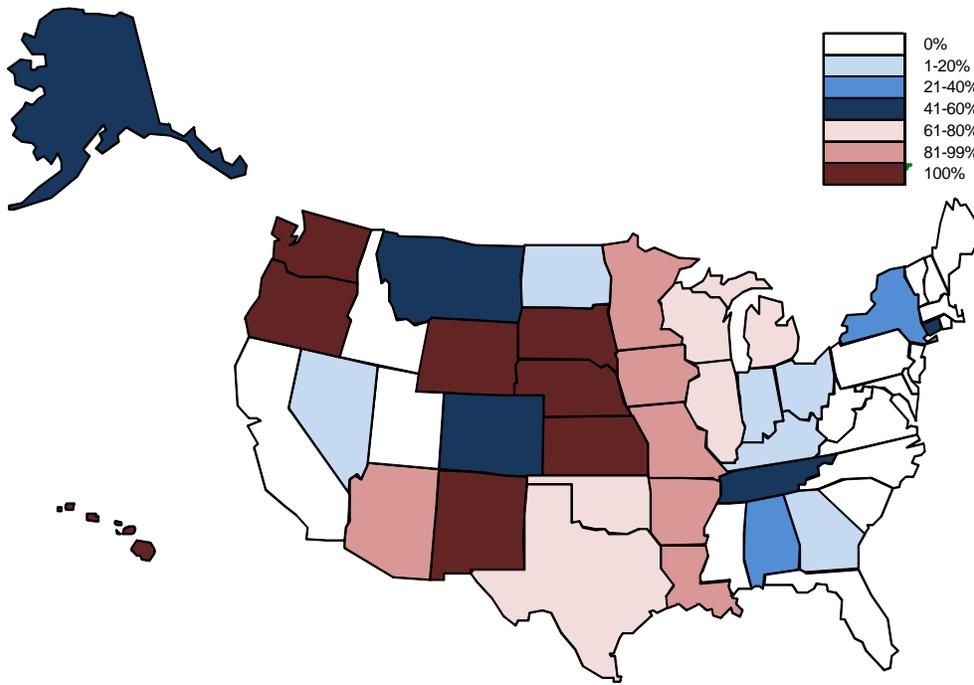


Figure 1-4. Percent of coal-fired boilers in each state burning predominantly subbituminous coal

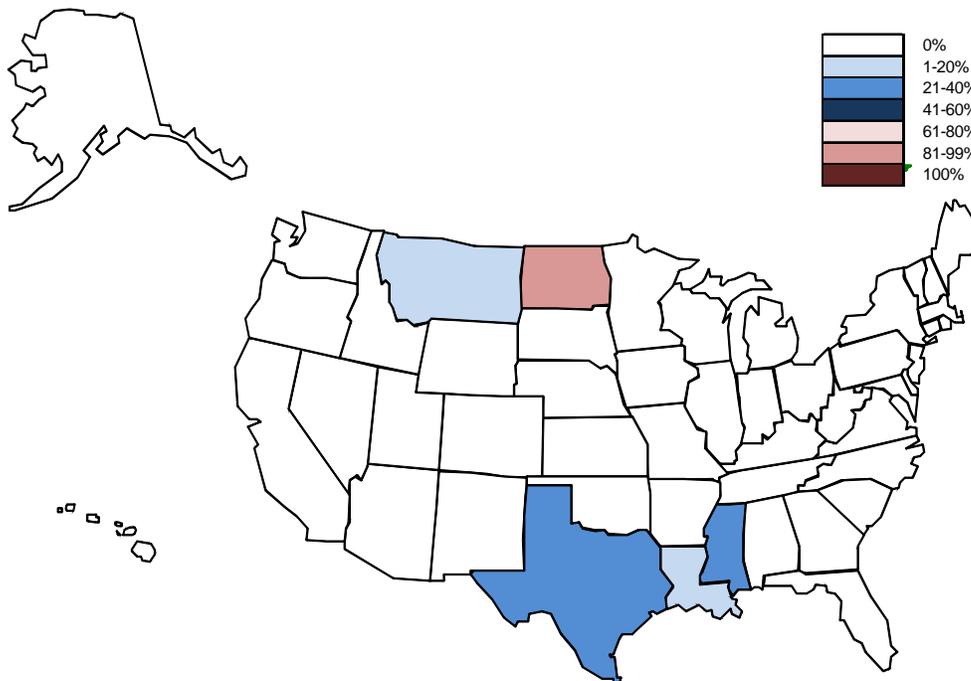


Figure 1-5. Percent of coal-fired boilers in each state burning predominantly lignite coal

The input mercury from these coals can vary widely; however, mercury content is not always an indication of mercury emissions. Native mercury removal (i.e., removal with existing APCDs without any mercury-specific technology) is influenced by coal composition and various APCDs installed for the reduction of NO<sub>x</sub>, SO<sub>2</sub>, or PM as discussed in Section 1.2. The coal-fired units in the U.S. were categorized based on type of PM control, SO<sub>2</sub> control, and type of post-combustion NO<sub>x</sub> control. An overall breakdown of the APCDs used in U.S. coal-fired boilers greater than 25 MW is shown in Table 1-2. Cold-side ESPs for particulate control are the most widely installed APCDs, followed by wet FGD units, SCR units, and FFs. While all units are equipped with particulate control, about a third of units have SO<sub>2</sub> control and about 25 percent have SCR post-combustion NO<sub>x</sub> control. In the next five years, this distribution is expected to shift, as more power plants install SCR units and wet or dry scrubbers to meet future federal regulations to lower SO<sub>2</sub> and NO<sub>x</sub> emissions.

**Table 1-2. Air pollution control devices on U.S. coal-fired boilers in 2010, number of boilers > 25 MW**

	Bituminous	Subbitum.	Lignite	Other <sup>#</sup>	Total
Particulate Control					
Cold-side ESP*	454	257	17	1	729
Fabric Filter**	120	112	12	31	275
Hot-side ESP	78	23	0	0	101
Other	16	14	1	0	31
Post-Combustion NO <sub>x</sub>					
SNCR	146	22	2	15	185
SCR	208	84	2	1	295
SO <sub>2</sub> Control					
Fluidized Bed***	20	4	7	29	60
Dry Sorbent Inject.	29	7	1	0	37
Spray Dryer	54	31	3	0	88
Wet FGD	255	89	16	1	361

<sup>#</sup>Includes waste coal and petcoke

\*Includes combinations of cold-side and hot-side

\*\*Includes combinations of ESP and FF

\*\*\*Includes in-bed capture in fluidized bed

## 1.2. Mercury Control Technologies

### 1.2.1. Introduction

Technologies to measure and control mercury emissions from coal-fired power plants are relatively new when compared to technologies to measure and control SO<sub>2</sub> and NO<sub>x</sub> emissions that have been commercially available for at least two decades. Section 112 of the 1990 CAAA triggered the requirement for the U.S. EPA to address hazardous air pollutants (HAPs) from coal-fired power plants including mercury. Much has been accomplished in the intervening years, certainly in terms of the technical learning curve. In this section, the impacts and

contributions of fuel and control equipment on mercury emissions and controls are briefly reviewed. It is relevant to this discussion to note that initially, the control of mercury emissions in the flue gas from coal-fired boilers presented some technical challenges due to the following considerations.

- *Very small quantities of Hg present* - Typical concentrations of mercury in the flue gas of a coal-fired power plant boiler are about 4 to 5 orders of magnitude (0.01 ppmv vs. more than 100 ppmv) lower than those of NO<sub>x</sub> or SO<sub>2</sub>.
- *Chemical speciation and physical forms of Hg present* - Unlike NO<sub>x</sub> or SO<sub>2</sub> (which are mostly present as gaseous NO or SO<sub>2</sub> in flue gases), mercury is present in both vapor form (as insoluble elemental mercury and as soluble ionic mercury (mercury chloride, mercuric sulfate, and mercuric oxide)) and in particulate form adsorbed on fly ash.
- *Measurement* - The very small quantities of various chemical forms of mercury present in the flue gas make it difficult to develop sufficiently accurate measurement devices.

These characteristics of mercury emissions and concentrations are well understood today, as reflected by the types and number of technology options available for controlling mercury emissions.

### **1.2.2. Impacts of Fuel on Mercury Speciation**

Mercury transformations in a coal-fired plant are complex and site-specific. As mercury leaves the boiler, it is present mostly in an elemental form (Hg<sup>0</sup>). As it proceeds through various components and APCDs of the plant, some of it is oxidized (Hg<sup>2+</sup>) and the rest remains in an elemental form. Both Hg<sup>0</sup> and Hg<sup>2+</sup> may be adsorbed on particulate matter (Hg<sup>P</sup>), although Hg<sup>2+</sup> is generally easier to adsorb. The amount of Hg<sup>0</sup> converted to Hg<sup>P</sup> and Hg<sup>2+</sup> depends on plant configuration and operating conditions as well as on flue gas composition. Hg<sup>2+</sup> is highly water soluble and is easily captured in scrubbers, whereas Hg<sup>0</sup> is not water soluble and is emitted from the stack. Hg<sup>P</sup> is frequently captured in an ESP or FF. This is important not only to the understanding and development of control technologies, but also to the broader environmental impact of the emissions. In this regard, it is noted that elemental mercury has a relatively long residence time in the atmosphere (1-2 years), while oxidized forms of mercury have lifetimes of only a few days as a result of the higher solubility of Hg<sup>+2</sup> in atmospheric moisture. Elemental mercury can thus be transported globally over long distances, whereas oxidized and particulate forms of mercury deposit locally or regionally within tens to a few hundreds of miles of the point of emission.<sup>3</sup>

Much has been learned since the late 1990s and early 2000s regarding the major contributors to mercury speciation in the flue gas. Chlorine in the coal which causes HgCl<sub>2</sub> formation in the flue gas, is the dominant contributor along with resultant oxidized species in the gas.<sup>4</sup> The key kinetic pathway to formation of HgCl<sub>2</sub> in flue gas is through the reaction of atomic chlorine (Cl) with elemental mercury.<sup>4,5</sup> Although the oxidation of elemental mercury in the convective section of a boiler is assumed to proceed primarily via gas-phase reaction, some fly ash can also catalyze oxidation of elemental mercury. Iron oxide and other constituents in the fly ash (carbon, calcium compounds) may also contribute to mercury oxidation. The presence of acid gases (HCl, SO<sub>2</sub>, NO, NO<sub>2</sub>) in the flue gas can also promote oxidation in the presence of fly ash.<sup>6,7</sup> Additionally, SCR technology for NO<sub>x</sub> control on bituminous coal-fired units has been observed to oxidize elemental mercury.<sup>8</sup> These reactions are further influenced by operating

conditions in the plant, specifically, gas temperatures (absolute and gradients), unburned carbon levels in the fly ash, and residence times.

In Section 1.1.3, the population distribution of coal-fired boilers in the U.S. was summarized. It is broadly distinguished by coal rank. Figure 1-6, Figure 1-7, and Figure 1-8 provide an overview of some of the key coal quality parameters and their distribution in U.S. coals, based on the data collected in Part 2 of the U.S. EPA's 1999 Information Collection Request (ICR). As stated above, chlorine plays a key role in the oxidation of  $\text{Hg}^0$  in the flue gas.

Mercury in coal translates directly to mercury in the flue gas, and therefore coal choice affects mercury emission levels, but the impact goes beyond the coal mercury content. Figure 1-8 shows the distribution of Cl in U.S. coals. It is relevant to note the range of Cl present primarily in bituminous coals, indicating that a significant portion of U.S. coals (on the order of 50%) have Cl concentrations between about 200  $\mu\text{g/g}$  (or ppmw) and 2000  $\mu\text{g/g}$ . This significant range of Cl content in coal results in varying Hg speciation in the flue gas. This, in turn, influences the choice of strategies and/or technologies for effective Hg emissions control. The distribution of sulfur in U.S. coals (Figure 1-7) varies even more than Cl. The sulfur content of the coal affects the choice of  $\text{SO}_2$  control technology, which in turn affects the potential for removal of mercury in the scrubber system. Furthermore, the amount of sulfur in the flue gas (as  $\text{SO}_2$  and  $\text{SO}_3$ ) can interfere with adsorption of mercury on carbon, as discussed below.

In summary, coal composition (primarily in terms of chlorine content and ash composition), the operation of the combustion system (primarily in terms of carbon left unburned in the ash), and the temperature and residence time of the exhaust gas in the particulate control device affect mercury speciation in the flue gas. These parameters and conditions affect the ultimate speciation of mercury in the flue gas, thereby influencing the choice of the most effective technology for removing mercury from the flue gas.

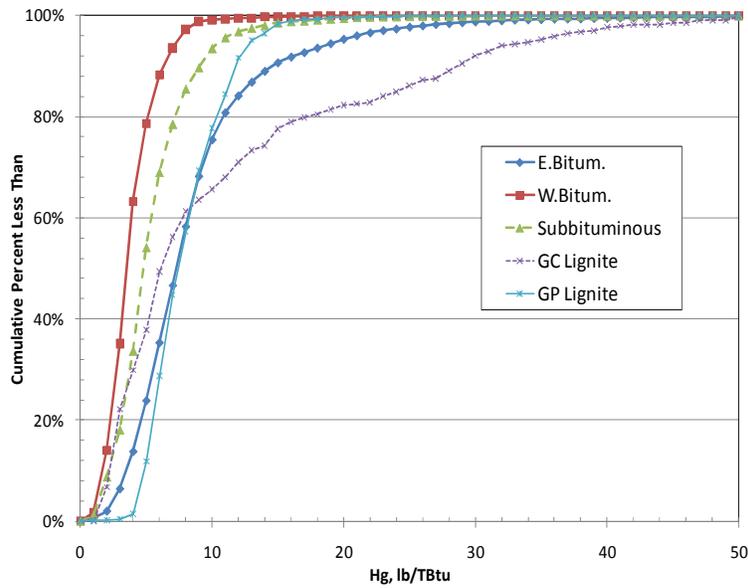


Figure 1-6. Distribution of mercury in coal burned at U.S. power plants from 1999 ICR Part 2

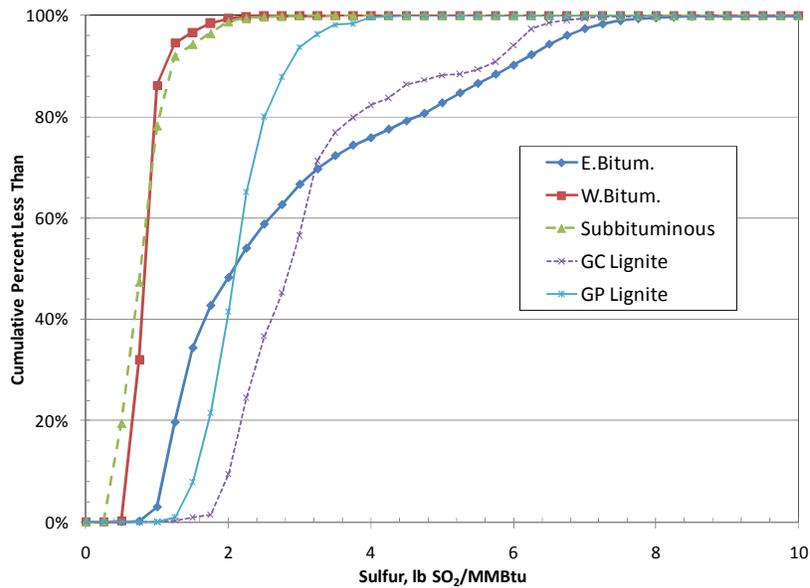
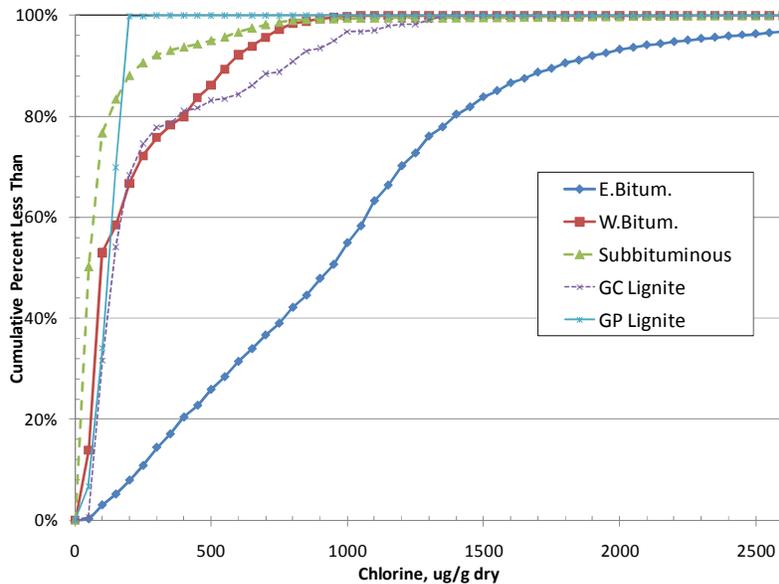


Figure 1-7. Distribution of sulfur in coal burned at U.S. power plants from 1999 ICR Part 2



**Figure 1-8. Distribution of chlorine in coal burned at U.S. power plants from 1999 ICR Part 2**

### 1.2.3. Impact of Air Pollution Control Devices

The various types of APCDs installed on coal-fired power plants include FFs and ESPs for particulate control, scrubbers for SO<sub>2</sub> control, and low-NO<sub>x</sub> burners, SCR or selective non-catalytic reduction (SNCR) for NO<sub>x</sub> control. Most of these APCDs have an unintended impact (positive or negative) on the behavior of mercury (speciation, capture).

The U.S. EPA’s Mercury ICR in 1999 was designed to provide useful information for making a regulatory determination about mercury emissions from coal-fired power plants. Table 1-3 shows the distribution of the various types of APCDs in the coal-fired power plants tested in Part 3 of the 1999 ICR. Part 3 included data from over 80 boilers, which were selected for mercury emission testing based on a representative sample of plant configurations, air pollution control equipment configurations, and coal types. In this table, low-rank coal denotes subbituminous and lignite coals.

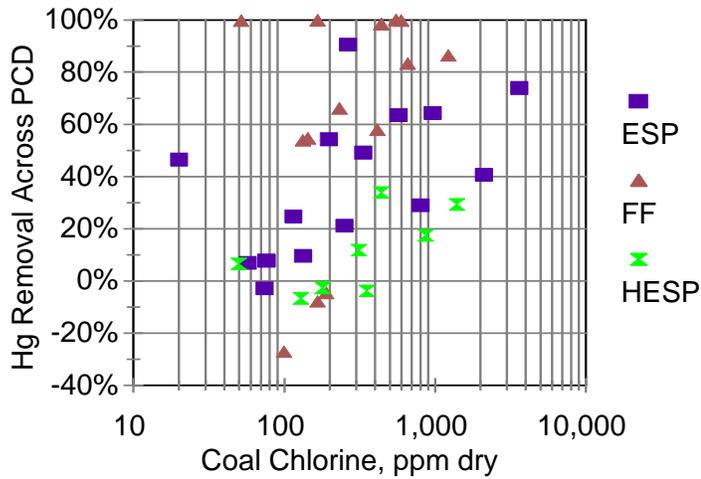
**Table 1-3. Summary of APCD and coal type information for 1999 ICR Part 3 data sets<sup>9</sup>**

APCD Equipment	Coal Type	%Units Tested in ICR Part 3	%Units in Population
Cold-side ESP	Bituminous	7.2	48.3
Cold-side ESP	Low-Rank	7.1	11.7
Hot-side ESP	Bituminous	7.2	6.6
Hot-side ESP	Low-Rank	3.6	2.4
Cold-side ESP+FGD	Bituminous	6.0	8.8
Cold-side ESP+FGD	Low-Rank	9.2	2.5
Hot-side ESP+FGD	Bituminous	4.8	0.7
Hot-side ESP+FGD	Low-Rank	3.6	1.0
FF	Bituminous	3.6	2.9
FF	Low-Rank	7.2	2.7
FF+FGD	Bituminous	7.2	1.6
FF+FGD	Low-Rank	3.6	1.6
SD-FF	Bituminous	3.6	2.9
SD-FF	Low-Rank	7.2	1.3
SD+ESP	Bituminous	2.4	0.2
SD+ESP	Low-Rank	3.6	0.3
FF+FBC	Bituminous	3.6	2.9
Other	Other	9.3	1.6

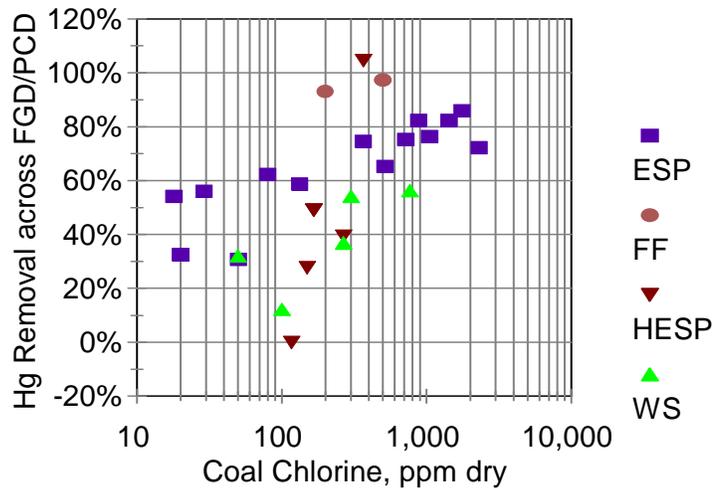
FBC=Fluidized bed combustor

SD=Spray dryer

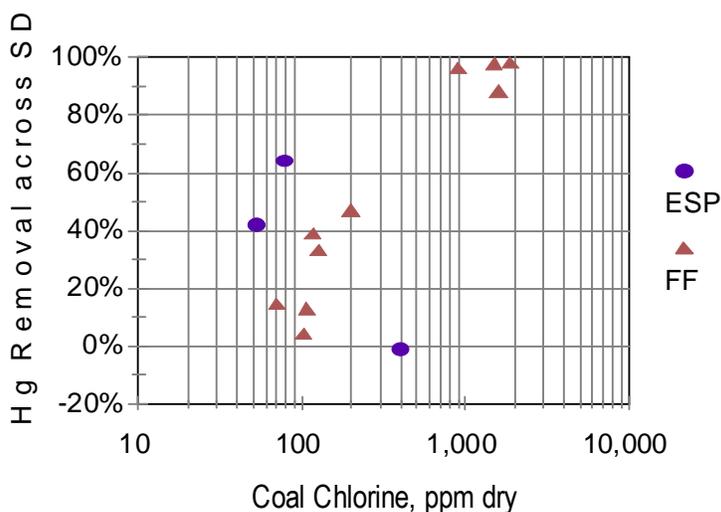
At each site, measurements were made to characterize the mercury reduction due to the particular site configuration and conditions. Analyses were conducted and the data obtained were reported.<sup>9</sup> These results, combined with more recent testing done at additional plants, have formed a basis for estimating the typical or average expected mercury capture associated with existing equipment (i.e., “co-benefit” control). Figure 1-9, Figure 1-10, and Figure 1-11 summarize the mercury removal observed by type of APCD and fuel rank. (In Figure 1-10, WS stands for wet particulate scrubber.) Mercury removal varied significantly among plants with similar equipment and chlorine content of the fuel. While Cl can be seen to have a positive effect in mercury removal in all three graphs, the otherwise significant scatter in the results amongst the various APCD types did not allow for strong, universal correlations to be drawn at that time.



**Figure 1-9. Hg removal across particulate control devices (PCDs) vs. chlorine in coal based on 1999 ICR Part 3 data<sup>9</sup>**



**Figure 1-10. Hg removal across wet FGD and particulate control devices (PCDs) vs. chlorine in coal based on 1999 ICR Part 3 data<sup>9</sup>**



**Figure 1-11. Hg removal across spray dryer (SD) and particulate control devices (PCDs) vs. chlorine in coal based on 1999 ICR Part 3 data<sup>9</sup>**

As the data show, although there are cases where the co-benefit control alone may be capable of greater than 90% reduction in mercury, this is not always true even for similar plant (boiler/APCD) and fuel configurations. Mercury reduction co-benefits can be exploited on a site-specific basis, but may not completely satisfy regulatory requirements, particularly stringent mercury emission limits. Therefore, this report focuses on dedicated or mercury-specific technologies, while co-benefits are discussed as appropriate.

Mercury transformations during the combustion process and subsequent flue gas path are driven by many complex factors, which ultimately yield mercury in elemental, oxidized and particulate forms. Particulate-bound mercury ( $Hg^P$ ) may be collected in particulate control devices such as ESPs and FFs. As has been stated previously,  $Hg^{2+}$  is the “easier” form (as opposed to  $Hg^0$ ) to remove from the flue gas, both through adsorption on particulate matter and through absorption in the wet FGD due to its water solubility.

In recognition of these considerations, technology developments over the last 15 plus years have concentrated on two major areas: 1) development of sorbents and associated systems (e.g., promoting the transformation of  $Hg^0$  and  $Hg^{2+}$  to  $Hg^P$ ); and 2) development of techniques and technologies to promote oxidation of  $Hg^0$  to  $Hg^{2+}$  in the flue gas.

The following sections present several technical approaches to enhanced and dedicated mercury controls. These include technologies that improve the mercury capture capabilities of existing equipment, primarily through methods that help oxidize increasingly larger fractions of the mercury in the flue gas (Section 1.3), as well as the use of dedicated sorbents in various system configurations (Section 1.4).

### **1.3. Oxidation Enhancement in Flue Gas**

Oxidation of  $\text{Hg}^0$  in the flue is affected by many factors as described previously. These include plant-specific equipment and operating conditions, as well as fuel quality characteristics. Increased oxidation can be promoted by several different methods. Most of the development has concentrated in two general areas: 1) chemical additives designed to maximize the oxidation of  $\text{Hg}^0$  in the flue gas; and 2) fixed bed oxidation catalysts.

The majority of the work involving enhanced oxidation techniques has been focused on plants with wet FGD systems, where the oxidized mercury is subsequently captured. The “re-emission” of  $\text{Hg}^0$  after  $\text{Hg}^{2+}$  has been captured and chemically reduced in the scrubber has been observed and can be addressed by the use of additives to the scrubber.

#### **1.3.1. Chemical Additives**

##### **Boiler Additives**

One approach for enhancing mercury oxidation in the flue gas is the use of boiler additives that may be applied to the coal and the flue gas to promote  $\text{Hg}^0$  oxidation. Much laboratory, pilot-scale and full-scale work has been done and reported on boiler additives.<sup>10-15</sup> NETL sponsored projects were awarded in three Phases, with the Phase I starting in 2000, Phase II in 2003 and Phase III in 2006.<sup>10</sup> Table 1-4 summarizes some of the more recent work in Phases II and III, as well as other relevant work.

Boiler additives for  $\text{Hg}^0$  oxidation are often referred to as sorbent enhancement additives (SEAs) or oxidation additives (OAs). Most of the testing of these additives undertaken under NETL sponsorship was conducted by the Energy & Environmental Research Center (EERC) and URS Corporation. These additives are typically sprayed onto the coal in an aqueous salt solution. Spraying the chemical on the coal prior to combustion maximizes the residence time for the reactions with  $\text{Hg}^0$  in the flue gas. When the boiler additives containing halogens (like chlorine or bromine) are applied to the coal, the results are often reported in terms of the weight of halogen per unit weight of coal, i.e., equivalent concentration in coal.

The tests at Milton R Young Unit 2 and Monticello Unit 3 were conducted at full scale and included several additives. Milton R Young Unit 2 used lignite coal in a cyclone boiler and was equipped with a cold-side ESP and wet FGD. Initially three boiler additives were tested: SEA1 (calcium chloride -  $\text{CaCl}_2$ ); 2) SEA2 (proprietary chemical); and 3) magnesium chloride ( $\text{MgCl}_2$ ). Total Hg capture in the ESP/wet FGD was 44% with the additive SEA2 at an injection level of 75 ppmw (equivalent concentration in coal). Injecting SEA2 at 50 ppmw and adding PAC at a rate of 1 pound per million actual cubic feet (lb/MMacf) resulted in total Hg removal of 60%. The SEA1 and  $\text{MgCl}_2$  additives at 500 ppmw (equivalent Cl in coal) only produced 20% mercury removal. In long-term tests (30 days), Hg capture across the ESP/wet FGD configuration ranged from 50 to 65% with SEA2 injection at 60-100 ppmw and activated carbon at 0.15 lb/MMacf.

**Table 1-4. Recently published testing with boiler additives to enhance Hg<sup>0</sup> oxidation<sup>10-15</sup>**

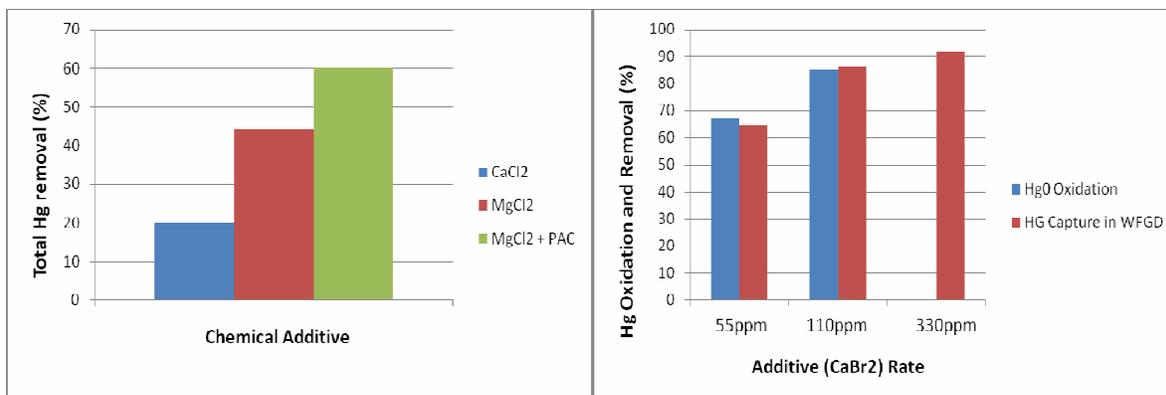
Project	Company	Unit (MW) (Date)	Coal	APCD Configuration
Mercury Oxidation Upstream of ESP and wet FGD	EERC	Milton R Young Unit 2 (475MW) (2005-07)	ND Lignite	Cold-side ESP - wet FGD
		Monticello Unit 3 (593MW) (2005-07)	TX Lignite/PRB Blends	Cold-side ESP - wet FGD
Field testing of FGD additives	URS	Monticello Unit 3 (590MW) (2005-07)	TX Lignite/PRB Blends	Cold-side ESP - wet FGD
		Plant Yates Unit 1 (120MW)	Low-sulfur Bituminous	Cold-side ESP - wet FGD
		Petersburg Unit 2 (470MW) (2005-07)	High-sulfur Bituminous	Cold-side ESP - wet FGD
Long-term demonstration of SEA technology for mercury control	EERC	Hawthorne Unit 5 (565MW)	PRB	SCR-SD-FF
		Mill Creek Unit 4 (545MW) (2006-07)	High-sulfur Bituminous	SCR-Cold-side ESP-wet FGD
Full scale results from Alstom's KNX <sup>TM</sup> technology	Alstom	Pleasant Prairie (600MW) (2007-08)	PRB	SCR-Cold-side ESP-wet FGD
Mercury control using B&W Absorption Plus(Hg) <sup>TM</sup>	B&W	Elmer Smith Station (440MW) (2008)	Bituminous	SCR-Cold-side ESP-wet FGD
Impact of HBr injection on Hg speciation and capture	ICSET	ICSET (slip stream) (2008)		SCR/ESP
Mercury oxidation upstream of ESP and wet FGD	EERC	Milton R Young Unit 2 (475MW) (2005-07)	ND Lignite	Cold-side ESP - wet FGD

EERC = Energy & Environmental Research Center

SEA = Sorbent enhancement additive

ICSET = Institute for Combustion Science and Environmental Technology at Western Kentucky University

Monticello Unit 3 burned blends of lignite and Powder River Basin (PRB) subbituminous coals and employed a similar ESP/wet FGD configuration to Milton R Young. Two additives were evaluated: OA1 (CaCl<sub>2</sub>); and OA2 (CaBr<sub>2</sub>). CaBr<sub>2</sub> proved very effective in parametric testing, yielding 72% Hg<sup>2+</sup> at the ESP outlet at an injection level of 100 ppmw (equivalent Br concentration in coal). Follow-up longer-term (two weeks) testing confirmed the expected performance of CaBr<sub>2</sub>. At a relative concentration of 55 ppmw coal equivalent Br, CaBr<sub>2</sub> resulted in 67% oxidation of Hg<sup>0</sup> upstream of the wet FGD and 65% total capture in the scrubber. Injection rates of 113 ppmw and 330 ppmw increased total capture in the scrubber to 86% and 92%, respectively. Figure 1-12 summarizes the key results from these programs. (Note: no data were reported for Monticello for Hg<sup>0</sup> oxidation at the 330 ppm CaBr<sub>2</sub> additive rate.)



**Figure 1-12. Hg removal and oxidation results with various additives at Milton R Young (left) and Monticello (right) power plants<sup>10</sup>**

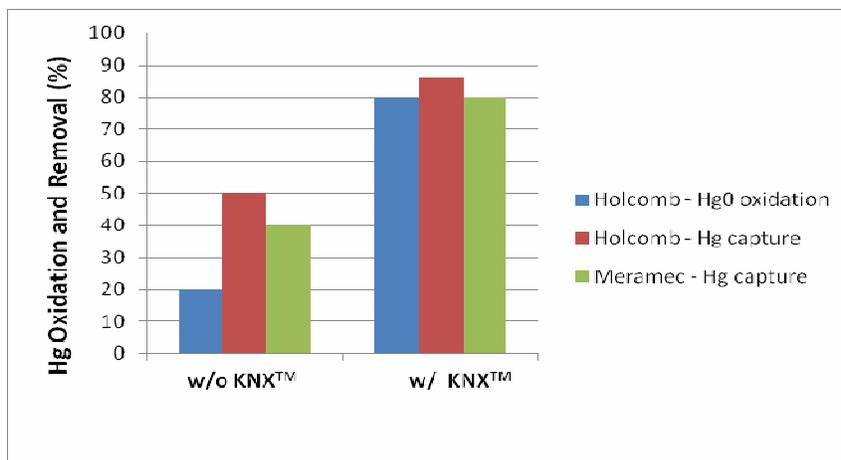
EERC conducted a test program at San Miguel station to evaluate several Hg sorbents and oxidation additives.<sup>11</sup> San Miguel station had a 450 MW boiler with an ESP-wet FGD configuration and fired Texas lignite coal. The full-scale portion of the test program followed a pilot-scale program where several chemicals (sorbents and boiler additives) were evaluated. For the full-scale tests, the focus was on additive SEA2 and PAC. The results showed Hg removal of up to 78% with SEA2 at 50 ppmw and PAC at 4 lb/MMacf injection rates.

At this plant, as at others, there was a significant *increase* in the concentration of Hg<sup>0</sup> at the wet FGD outlet as compared to the inlet with 3 µg/Nm<sup>3</sup> measured at the inlet and 7 µg/Nm<sup>3</sup> at the outlet. Wet FGDs are effective at absorbing oxidized Hg species from the flue gas. Some of the absorbed Hg<sup>2+</sup> can be reduced in the scrubbing solution to elemental Hg. Because Hg<sup>0</sup> is not very soluble in aqueous solutions, this Hg<sup>0</sup> goes into the gas phase in the outlet gas. This phenomenon has been called “Hg re-emission,” and it is evident in the San Miguel data.

Alstom’s KNX<sup>TM</sup> technology<sup>12,13</sup> is bromine-based (CaBr<sub>2</sub>) which has been shown to be quite effective. The additive was added to the coal prior to combustion in the boiler, typically sprayed on the coal either on the conveyor or at the coal feeders (upstream of the mills). As with any application of this type, it is important to ensure that the method of application yields a uniform distribution of the chemical on the coal.

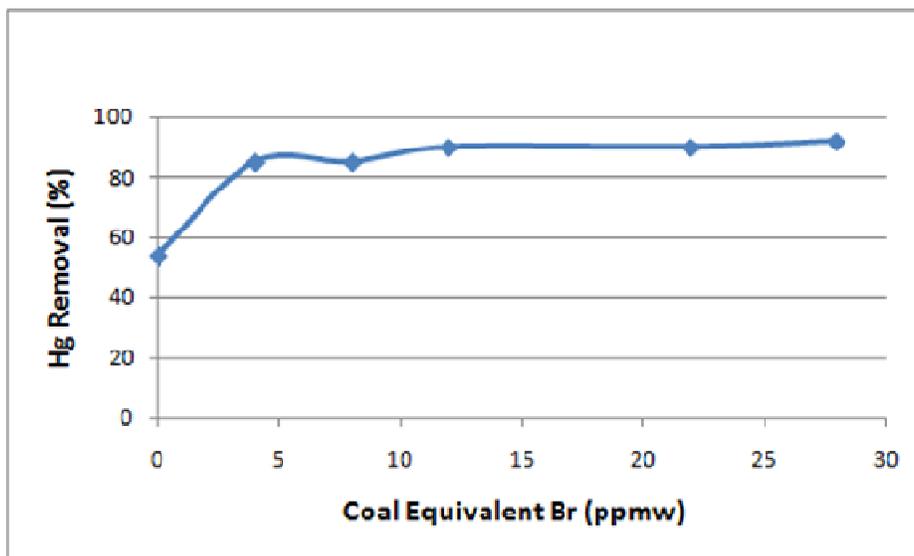
Tests at two PRB-fired boilers, Holcomb and Meramec, indicated KNX<sup>TM</sup> performance consistent with the results shown in Figure 1-13.<sup>14</sup> In these two cases, however the plant APCD configurations did not include a wet FGD. Holcomb employed a spray dryer-fabric filter (SD-FF) combination and had very low unburned carbon and low native Hg oxidation (about 20% at the APH outlet) and overall collection. PAC injection at the rate of about 1 lb/MMacf yielded Hg capture across the SD-FF of about 50%. KNX<sup>TM</sup> was successful in increasing Hg oxidation at the air preheater outlet to 80% and total Hg collection to 86%.

Meramec, on the other hand, had about 2% to 4% unburned carbon, which is high relative to typical PRB firing, and the boiler employed only an ESP for particulate control. The native Hg capture was about 40%. With KNX<sup>TM</sup> injection, the overall capture increased to over 80%. Figure 1-13 shows these results.



**Figure 1-13. Hg oxidation at air preheater outlet (Holcomb) and removal across APCDs at two PRB-fired plants with SD-FF (Holcomb) and ESP (Meramec)<sup>12</sup>**

More detailed tests were conducted by Alstom at Pleasant Prairie in Wisconsin, a plant with two 600 MW PRB coal-fired boilers equipped with SCR-ESP-wet FGD.<sup>13</sup> In these tests, varying concentrations of KNX™ were tested with the results shown in Figure 1-14. Mercury reductions of more than 90% were achieved with additive concentrations of less than 20 ppmw (coal equivalent Br).



**Figure 1-14. Mercury removal at Pleasant Prairie with KNX™ injection<sup>12,13</sup>**

CaBr<sub>2</sub> is an attractive boiler additive for oxidizing Hg in low-rank (subbituminous and lignite) coal applications. However, secondary effects of adding bromine to the coal need to be considered. For example, high-temperature corrosion of convective pass equipment (e.g., superheaters) due to high halogen-content fuels is well known. At coal chlorine levels below 2000 ppmw, this potential problem seems to be negligible. Most U.S. coals have Cl contents below 2000 ppmw (see Figure 1-8). Therefore, at these low levels of Br addition, it is expected

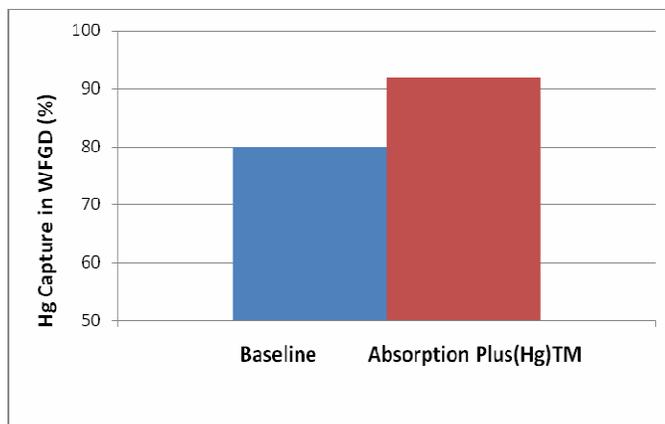
that no increased corrosion potential would result. However, long-term data on corrosion behavior when bromine compounds are injected to the boiler has not yet been collected.

Hydrogen bromide (HBr) has been investigated as a suitable boiler additive to affect the speciation of mercury in power plant flue gas.<sup>15</sup> Slip stream tests were conducted at the Institute for Combustion Science and Environmental Technology (ICSET) at the University of Western Kentucky to evaluate the potential of HBr to oxidize  $\text{Hg}^0$  in the flue gas and increase its capture in fly ash. Fly ash was injected into the slipstream reactor. The tests were conducted at two temperature regimes (350°C and 150°C) and used low-Cl coals (average concentrations between about 120 ppmw and 165 ppmw) as well as several fly ashes, to determine the effect on the capture of Hg. Hg measurements were conducted using the Ontario Hydro method as well as using a CEMS. Both  $\text{Hg}^0$  oxidation and in-flight Hg capture in fly ash were observed. The HBr rate of injection was up to 6 ppmw for the high temperature test (350°C) and up to 4 ppmw at the lower temperatures (150°C). HBr was injected in gaseous and solution forms. Lastly, corrosion test coupons (metal strips placed in the process stream to measure the state of corrosion) were used to address potential Br induced corrosion issues.

The results indicate that HBr was effective in oxidizing  $\text{Hg}^0$  and enhancing Hg capture in fly ash. Specifically,  $\text{Hg}^0$  oxidation rates of up to 60% and 90% were achieved at low and high temperature, respectively, with HBr injection rate of 4 ppmw. Further, Hg capture in fly ash yielded varying results for different fly ash types and fly ash concentrations ranging from about 40% to about 80%. Corrosion test coupons were analyzed by scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analysis and preliminary results suggested no negative impacts at the tested HBr concentration levels.

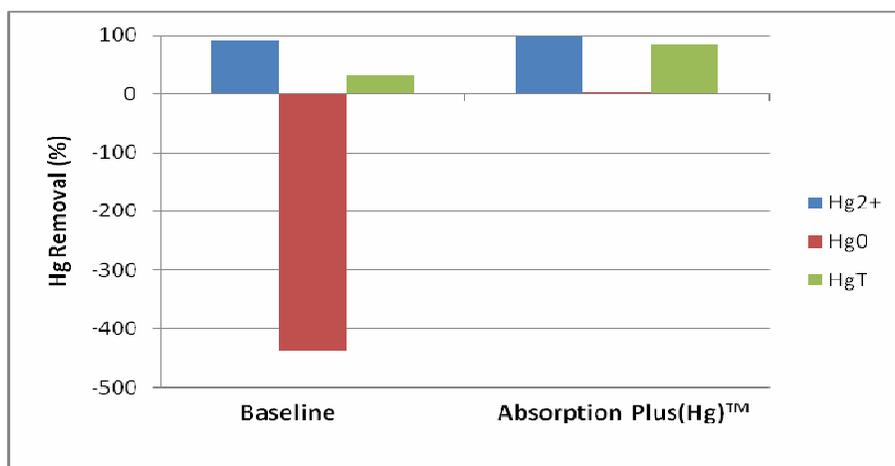
### **Wet FGD Additives**

Several additives have been tested to demonstrate their effectiveness in mitigating the re-emission of  $\text{Hg}^0$  in wet scrubbers. The additives help precipitate the absorbed Hg as a stable salt, minimizing the re-emission of  $\text{Hg}^0$  and lowering the concentration of Hg in the FGD liquor. As shown in Table 1-4, tests have been conducted at Monticello Unit 3 (pilot-scale), Plant Yates Unit 1 (pilot- and full-scale), Petersburg Unit 2 (full-scale), and Mill Creek Unit 4 (full-scale). Of the various additives tested, Babcock and Wilcox's (B&W's) Absorption Plus(Hg)<sup>TM</sup> yielded the most successful results during long-term testing, with Hg capture in the scrubber increasing from about 80% (without the additive) to 92%. Note that Mill Creek fired a bituminous coal with moderate chlorine, which resulted in a higher fraction of  $\text{Hg}^{2+}$  in the flue gas which explains the high baseline Hg removal (80%) in the scrubber. Figure 1-15 shows the results of the B&W Absorption Plus(Hg)<sup>TM</sup> technology at Mill Creek Unit 4 from the NETL test program.



**Figure 1-15. Test results for wet FGD Hg<sup>0</sup> re-emission additive at Mill Creek Unit 4<sup>16</sup>**

Another recent application of an Hg<sup>0</sup> re-emission additive was undertaken at Elmer Smith station.<sup>16</sup> The Elmer Smith station is a 445 MW station comprised of two boilers (one cyclone and one tangential-fired) firing eastern bituminous coal. The shared APCD configuration consists of SCR/SNCR, cold-side ESP, and wet FGD. The Absorption Plus(Hg)<sup>TM</sup> additive demonstrated its effectiveness in minimizing Hg<sup>0</sup> re-emissions from the wet FGD. The total Hg (HgT) capture in the scrubber increased from a baseline value of 31% to 83% with the additive, because there was less re-emission of Hg<sup>0</sup> when the additive was used. The capture of the Hg<sup>2+</sup> in the flue gas by the FGD was similar with and without the Hg<sup>0</sup> re-emission additive (91% baseline and 99% with the additive). The major change with the re-emission additive was that Hg<sup>0</sup> did not increase across the FGD. Operationally, the Hg<sup>0</sup> re-emission additive did not affect SO<sub>2</sub> removal or gypsum quality. Figure 1-16 summarizes these results.

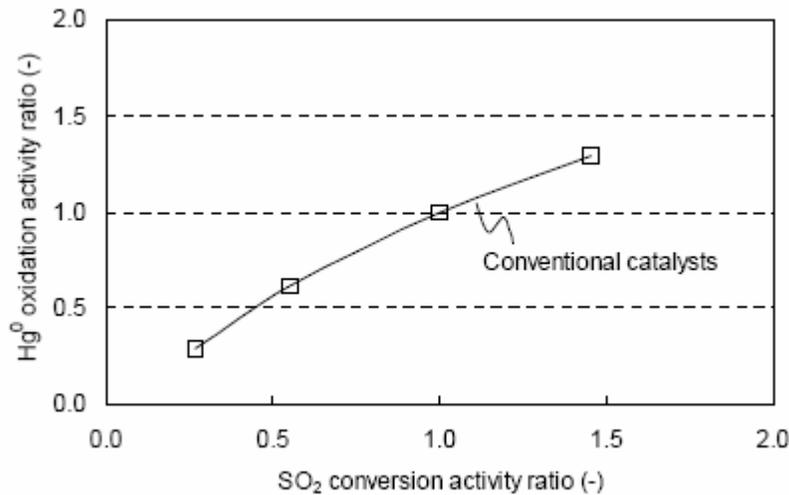


**Figure 1-16. Hg removal across the FGD and mitigation of Hg<sup>0</sup> re-emission with Absorption Plus(Hg)<sup>TM</sup> at Elmer Smith station<sup>16</sup>**

### 1.3.2. Fixed-bed Oxidation Catalysts

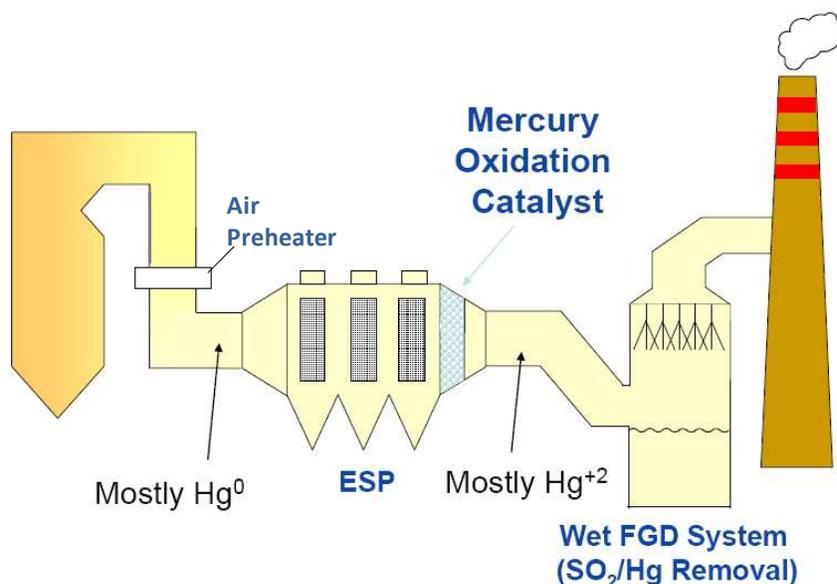
Fixed-bed Hg oxidation catalysts employ different catalyst materials including vanadium (V)/titanium (Ti), gold (Au), and palladium (Pd). Conventional SCR NO<sub>x</sub> catalysts have been shown to promote some oxidation of Hg<sup>0</sup>. However, typical formulations for SCR catalysts are developed to balance, among other things, NO<sub>x</sub> reduction while keeping the undesirable

oxidation of SO<sub>2</sub> to SO<sub>3</sub> to minimum levels. Unfortunately, Hg<sup>0</sup> oxidation and SO<sub>2</sub> conversion across the SCR catalyst are strongly correlated, as shown in Figure 1-17.<sup>17</sup> This has led to the development of dedicated Hg<sup>0</sup> oxidation catalysts.



**Figure 1-17. Relationship between SO<sub>2</sub> conversion and Hg<sup>0</sup> oxidation across SCR catalyst<sup>17</sup>**

The application of Hg oxidation catalysts is similar to that of commonly used SCR catalysts. Depending on catalyst formulation and other plant considerations, applications of dedicated Hg oxidation catalysts upstream (similar to SCR temperatures of 600°F to 700°F) and downstream of the air preheater (APH) at temperatures on the order of 300°F are possible. Figure 1-18 shows a sketch of a typical configuration downstream of the air preheater.<sup>19</sup> In general, other design and operating concerns associated with SCR are common to Hg<sup>0</sup> oxidation catalysts. These include gas flow conditions, such as uniformity and velocity, and control of ash deposition (i.e., sootblowers). Plant operators have significant experience with these concerns based on over 140 GW of operating SCR installations.



**Figure 1-18. Typical Hg<sup>0</sup> oxidation catalyst application in ESP-wet FGD plant<sup>19</sup>**

The current level of Hg<sup>0</sup> oxidation catalyst technology demonstrations is still relatively small compared to the more wide spread deployment of sorbent injection technologies (discussed in Section 1.4). However, much laboratory and pilot-scale work has been done and limited full-scale testing has been reported.<sup>10,17,18,19</sup> Table 1-5 summarizes the more recent work on Hg<sup>0</sup> oxidation catalysts.

**Table 1-5. Recent published testing with Hg<sup>0</sup> oxidation catalysts<sup>10,17,18,19</sup>**

Project	Company	Unit (MW) (Date)	Coal	APCD Configuration
Pilot/Full-scale testing of Hg Oxidation Catalyst	URS Group	Monticello Unit 3 (590MW) (2004-07)	Lignite/PRB	Cold-side ESP - wet FGD
		Plant Yates Unit 1 (120MW) (2004-07)	Low-sulfur Bituminous	Cold-side ESP - wet FGD
		Fayette Unit 3 (460MW) (2008)	PRB Blends	Cold-side ESP - wet FGD
Pilot/Full-scale testing of Hg Oxidation Catalyst	Hitachi Power Systems America	Northern U.S. Power Plant (640MW) (2006-08)	PRB	Cold-side ESP - wet FGD
Pilot-scale testing of Hg removal in CT-121 FGD (w/SCR)	Chiyoda Corporation/SCS	Plant Crist/MRC (~2MW) (2007-08)	(simulated flue gas)	SCR - Cold-side ESP - wet FGD

PRB = Powder River Basin

The results of the earlier pilot tests at both Monticello and Plant Yates, as well as the initial pilot tests at Fayette have been well documented and recently summarized.<sup>10</sup> These test

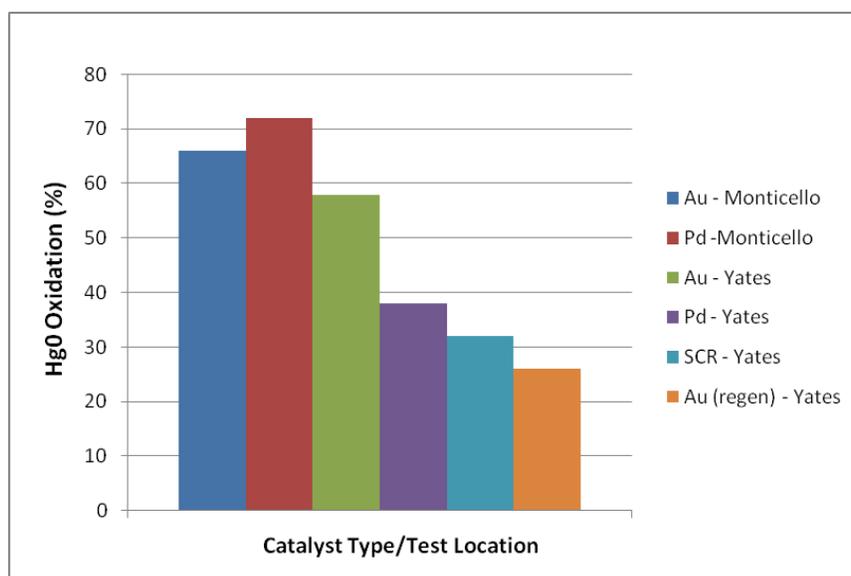
programs were sponsored by NETL under Phases II/III Field Testing and Mercury Control Technology projects. Highlights from these tests are summarized below.

Several Hg<sup>0</sup> oxidation catalysts were tested at Luminant’s Monticello Station Unit 3, which fires a blend of Texas (TX) lignite and PRB coals. In 2005, Hg<sup>0</sup> oxidation catalysts were installed downstream of the cold-side ESP and included the following catalysts: (1) Au; (2) V-Ti SCR; (3) regenerated Pd; and (4) fresh Pd.

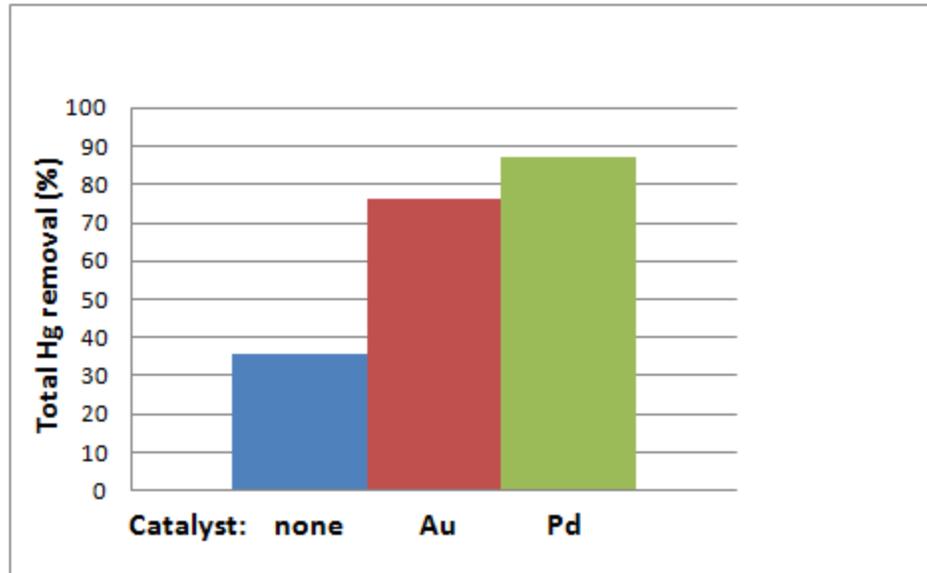
Results were encouraging with the Pd catalyst yielding about 72% Hg<sup>0</sup> oxidation, while the Au catalyst achieved 66% oxidation after about 17 months of operation. With respect to Hg capture in the wet FGD, the pilot-scale results ranged from 76% to 87%, a significant improvement compared to the baseline performance (e.g., no catalysts) of only about 36%.

At Plant Yates, firing low-sulfur bituminous coal, the menu of catalysts tested included Pd, fresh and regenerated Au, as well as SCR catalysts, located downstream of a cold-side ESP pilot unit. The results after about 11 months of operation showed Hg<sup>0</sup> oxidation ranging from 26% for the regenerated Au catalyst to 58% for fresh Au catalyst. The SCR and Pd catalysts yielded oxidation values of 32% and 38%, respectively.

Figure 1-19 and Figure 1-20 show these results graphically for Hg<sup>0</sup> oxidation across the catalysts and the resulting improvement in total Hg removal in the wet FGD.



**Figure 1-19. Summary of NETL Hg<sup>0</sup> oxidation catalyst test results from slipstream testing at Monticello and Yates power plants<sup>10</sup>**



**Figure 1-20. Impact of Hg<sup>0</sup> oxidation catalysts on total mercury removal by wet FGD, pilot-scale testing at Monticello<sup>10</sup>**

These results clearly indicate the importance of maximizing the Hg<sup>2+</sup> at the wet FGD inlet to enhance the overall Hg removal effectiveness of wet FGD. However, these are pilot-scale test results, intended to provide a basis for full-scale designs and applications. At present there is not a significant database of full-scale experience with Hg<sup>0</sup> catalysts. Two full-scale test programs have been reported recently that include some field test data. One is NETL's project at Fayette Unit 3. The other describes work performed by Hitachi Power Systems America at an undisclosed U.S. power plant. Brief summaries of the available results follow.

In May 2008, URS Corporation carried out a program at the Lower Colorado River Authority's (LCRA's) Fayette station Unit 3,<sup>19</sup> which was designed to evaluate catalyst performance in PRB coal flue gas, as well as to better understand full scale operation and maintenance (O&M) issues such as catalyst de-activation and ash deposition mitigation. The project involved the deployment and testing of an Hg<sup>0</sup> oxidation catalyst installed downstream of a cold-side ESP and upstream of one of three wet FGD modules at the station. This was nominally a 200 MW equivalent demonstration. The catalyst was a gold-plated, solid honeycomb type and was installed at the inlet to one of the scrubber modules (the diagram in Figure 1-18 depicts the overall configuration). The test plan required monitoring of the pressure drop across the catalyst over time and mercury measurements to determine Hg<sup>0</sup> oxidation, as well as total Hg removal in the wet FGD. The configuration permitted a direct comparison between the mercury removal across the two modules without the Hg<sup>0</sup> oxidation catalyst (A/B) and the test module (C). Tests were conducted using Ontario Hydro Method measurements. The key results between May 2008 and June 2009 are summarized in Table 1-6.

**Table 1-6. Hg oxidation and removal - summary of results at Fayette Unit 3**

PARAMETER	May 2008	Nov 2008	June 2009
Catalyst Inlet Oxidation (%)	35 ± 9	52 ± 7	44 ± 7
Predicted Hg oxidation (%)	81	81	81
Measured Hg oxidation (%)	80 ± 9	77 ± 4	52 ± 5
Hg oxidized at catalyst outlet (%)	86 ± 6	90 ± 1	74 ± 1
Hg removal - module C (w/ catalyst) (%)	80 ± 5	49 ± 4	71 ± 5
Hg <sup>0</sup> re-emission - module C – (% of Hg <sup>2+</sup> )	5 ± 11	41 ± 3	3 ± 9
Hg removal - modules A/B (w/o catalyst) (%)	34 ± 18	37 ± 9	44 ± 8
Hg <sup>0</sup> re-emission - modules A/B – (% of Hg <sup>2+</sup> )	23 ± 45	28 ± 9	2 ± 7
Hg removal – module C vs. A/B (% increase)	60 ± 13	18 ± 6	48 ± 11

While these results are not fully understood, some general comments can be made.

- Catalyst activity (i.e., measured Hg oxidation) dropped from about 80% to 52% over time. This was thought to be possibly driven by catalyst blockage due to fly ash deposition on the catalyst.
- Mercury removal across module C showed a significant increase from November 2008 to June 2009 (49% to 71%) which is consistent with the decrease Hg<sup>0</sup> re-emissions during the same period (41% to 3%). Hg<sup>0</sup> re-emissions result from reactions between the Hg<sup>2+</sup> absorbed in the liquor and sulfite/bisulfate in the liquor. It has been suggested that the higher levels of Hg<sup>2+</sup> in the FGD liquor in November 2008 as compared to May 2008 and June 2009 may explain the re-emission levels and associated overall mercury removal. Other variables can also account for re-emissions from wet FGD, including pH, chloride concentration, and the amount of slurry solids.
- Despite these uncertainties, the increased effectiveness in mercury removal from module C (w/catalyst) over modules A/B (w/o catalyst) was significant and supported the importance of minimizing the presence of Hg<sup>0</sup> for best mercury removal in wet FGD systems.

Operationally, it was reported that increased pressure loss across the catalyst due to fly ash build up required better sootblowing schemes and was likely to account for the loss in catalyst activity over the test period.

Hitachi also has developed a new SCR catalyst to enhance Hg<sup>0</sup> oxidation, while keeping SO<sub>2</sub>/SO<sub>3</sub> conversion low.<sup>17</sup> Its technology, TRAC<sup>TM</sup> (TRiple Action Catalyst) was tested at a power plant in the U.S., first in a slip-stream reactor and subsequently at full scale. The unit was a 640 MW, wall-fired boiler, firing PRB coal at an undisclosed location. The APCD equipment was configured in a conventional SCR-ESP-wet FGD arrangement.

The slip stream reactor included a four layer catalyst configuration and ran for about 8,000 hours. The results were very encouraging with Hg<sup>0</sup> oxidation rates ranging from about 95% initially to about 80% after 8,000 hours (see Figure 1-21).

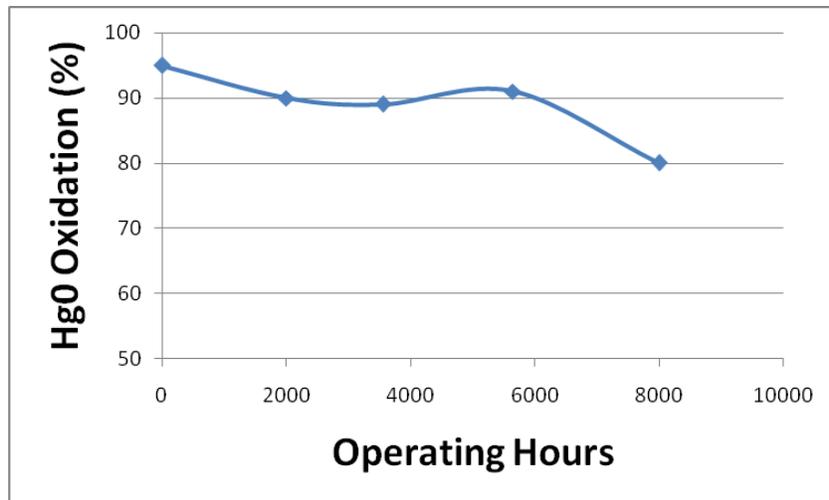


Figure 1-21. Slipstream TRAC™ catalyst performance Hg oxidation vs. time<sup>17</sup>

The full-scale application of TRAC™ involved replacing one of the three original catalyst layers with one layer of TRAC™ catalyst. The test program included measurements of Hg speciation at the inlet (through the plant’s Hg CEMS) and at the outlet of the wet FGD, and comparing results with similar testing prior to the TRAC™ installation. The results confirmed the slip stream tests and suggested the suitability of this approach to enhancing Hg<sup>0</sup> oxidation (and subsequent removal with wet FGD). Figure 1-22 summarizes the results. Hg<sup>0</sup> oxidation increased significantly. The percentage of oxidized mercury (Hg<sup>2+</sup>/Hg total) went from 40% before TRAC™ to about 70% with the TRAC™ catalyst, while overall mercury capture in the wet FGD increased from 30% to about 70%. It should be noted that the reported results represent short-term testing and do not address any potential long-term issues.

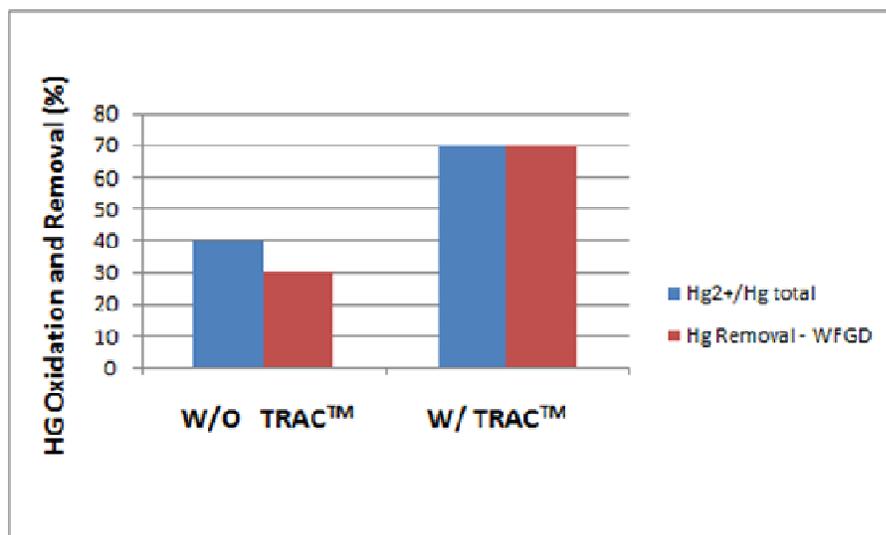
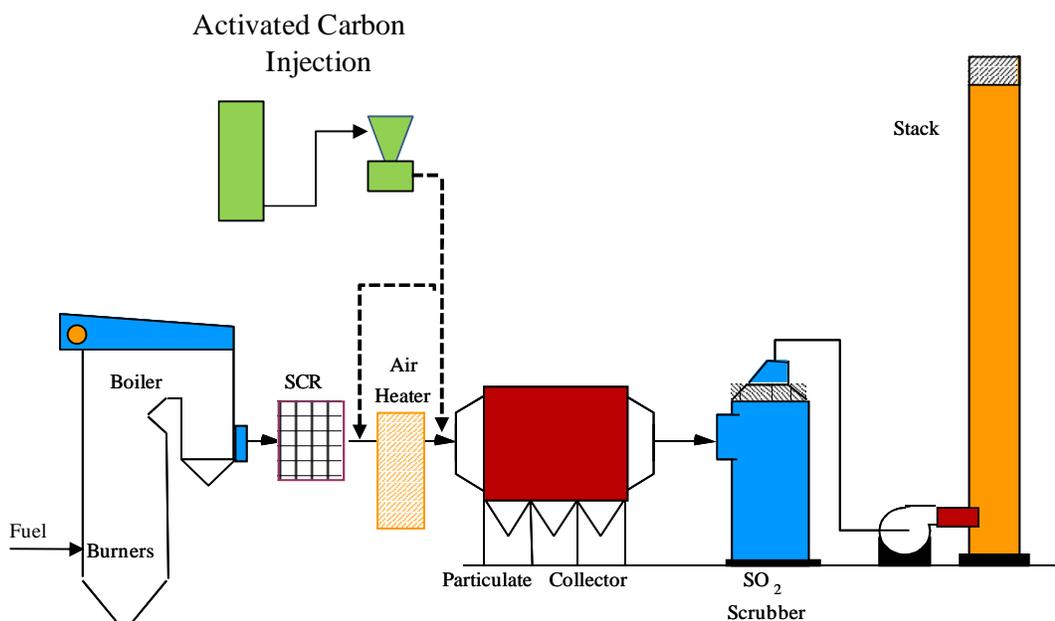


Figure 1-22. Hg oxidation and removal with full sale TRAC™ catalyst 640 MW, wall-fired boiler, firing PRB coal at an undisclosed location<sup>17</sup>

## 1.4. Sorbent Injection

### 1.4.1. Sorbents for Mercury Control

Injection of powdered sorbents upstream of particulate matter control devices is the most promising mercury capture technology for plants without FGD scrubbers. Powdered activated carbon (PAC) is the most widely studied sorbent, but other non-carbon based sorbents are also being developed. Activated carbon injection is relatively simple to install. The equipment consists of a silo, a feeder, a blower (for carrier air), hoses and injection lances. Activated carbon is typically injected either upstream or downstream of the air preheater, as shown in Figure 1-23, so that the sorbent can be collected in the particulate collector.



**Figure 1-23. Application of activated carbon injection**

Various mercury sorbents are described in Table 1-7. Mercury is readily adsorbed on carbon surfaces. PAC is a good adsorbent for mercury due to its large surface area (due to open pore structure and fine particle size). Activated carbons are made from coal or biomass and may be chemically treated to enhance mercury removal. Halogens (chlorine, bromine, iodine) and sulfur have been used as additives in activated carbons. Studies have shown that several factors influence the mercury adsorption capacity of PAC. These factors include temperature, mercury concentration and oxidation state, sorbent particle size, and flue gas composition (moisture, NO<sub>x</sub>, and most notably SO<sub>3</sub>).

**Table 1-7. Description of mercury sorbents**

<b>Sorbent</b>	<b>Vendor</b>	<b>Description</b>
Power Pac Premium	ADA-ES	Brominated activated carbon
Mer-Clean™	Alstom Power	Proprietary carbon-based, chemically treated sorbent
Amended Silicates™	Amended Silicates	Mineral-based sorbent
BS IAC (CB 200xF™)	Barnebey Sutcliffe	Iodated activated carbon manufactured from coconut shells
BS SAC (208CP™)	Barnebey Sutcliffe	Iodated super activated carbon manufactured from coconut shells
BASF (MS-200)	BASF	Mineral-based sorbent
Calgon HGR-LH™	Calgon Carbon	Iodated carbon
FLUEPAC® MC	Calgon Carbon	Activated carbon made from bituminous coal
FLUEPAC® -MC PLUS	Calgon Carbon	Brominated activated carbon
FLUEPAC® CF	Calgon Carbon	“Ash-Friendly” activated carbon
FLUEPAC® -CF PLUS	Calgon Carbon	“Ash-Friendly” activated carbon made with a proprietary ingredient
FLUEPAC® ST	Calgon Carbon	Activated carbon specially formulated for use in flue gas with elevated SO <sub>3</sub>
DARCO® Hg	Norit Americas	Activated carbon made from Texas lignite
Insul	Norit Americas	Fine particle size, chemically washed activated carbon
HydroDARCO-C	Norit Americas	Coarser version of DARCO Hg
DARCO® Hg XTR	Norit Americas	Low-activity lignite-based activated carbon
DARCO® Hg-LH	Norit Americas	Brominated activated carbon made from Texas lignite
DARCO® Hg E-XX	Norit Americas	Experimental sorbent
PAC2B	Norit Americas	Subbituminous/bituminous blend activated carbon
NH Carbon	Ningxia Huahui Activated Carbon Co., Ltd	Iodated activated carbon from China
Super HOK	RWE Rhinebraun	Activated carbon made from German lignite
B-PAC™	Albemarle	Brominated activated carbon
C-PAC™	Albemarle	Brominated activated carbon designed to have low impact on ash
H-PAC™	Albemarle	Brominated activated carbon optimized for hot-side ESP temperature regime
Q-PAC™	Albemarle	High performance brominated activated carbon
FF-PAC™	Albemarle	Brominated activated carbon designed for systems with FF

The U.S. Government Accountability Office (GAO) report in 2009 identified 14 coal-fired power plants that operate sorbent injection systems on 25 boilers.<sup>20</sup> Although injection of untreated carbon-based sorbents works well for plants burning bituminous coal, this control strategy is not as effective for plants burning subbituminous or lignite coals. Chemically treated sorbents are able to achieve high mercury reductions across all coal types (ranks). The U.S. GAO report also identified several power plant configurations for which mercury control by sorbent injection might be difficult, including units with high SO<sub>3</sub> concentrations in the flue gas (which prevents mercury from binding to carbon sorbents), hot-side ESPs (high temperatures reduce the ability of mercury to bind to sorbents), and those burning lignite coal (which releases

high levels of elemental mercury). These units might require alternate technologies for mercury control or improvements in existing technologies to achieve higher levels of mercury control.

A variety of companies design and install PAC injection systems for mercury control. Companies that produce PAC also design PAC injection systems, both permanent and temporary. ADA-ES claims to have sold over 140 PAC injection systems for mercury control in power plant boilers.<sup>21</sup> Albemarle Sorbent Technologies, another supplier of PAC, has started up over 50 PAC injection systems.<sup>22</sup> A number of equipment vendors that do not sell PAC do design and install injection systems. For example, Sargent & Lundy claims to have installed 57 PAC injection systems.<sup>23</sup>

#### **1.4.2. Sorbents Injection and Cold-Side ESPs**

The majority of boilers in the U.S. are equipped with cold-side ESPs. This configuration can offer several challenges for mercury control by sorbent injection. Demonstrations have been performed at several power plants with cold-side ESPs burning a variety of coals, as shown in Table 1-8. The biggest challenge arises with high levels of SO<sub>3</sub> in the flue gas, due either to burning high-sulfur eastern bituminous coal, oxidation of SO<sub>2</sub> in an SCR, or direct injection of SO<sub>3</sub> for improved ESP performance. Temperature and flue gas SO<sub>3</sub> concentrations directly influence the mercury removal efficiency of sorbent injection. The majority of full-scale tests have been done at plants where SO<sub>3</sub> concentrations limit sorbent injection mercury removal efficiencies. Based on the survey of the U.S. boiler population (Section 1.1.3), 15% of boilers in the U.S. use flue gas conditioning (FGC) on cold-side ESPs.

Several tests have been performed at various power plants to investigate alternatives to enhance mercury removal from flue gas with high SO<sub>3</sub> concentrations.<sup>24</sup> ADA-ES worked with DOE/NETL, EPRI, and several electric generating plant partners at the American Electric Power's (AEP) Conesville Unit 6 (high-sulfur coal), Public Service of New Hampshire (PSNH) Merrimack Unit 2 (medium-sulfur coal and SCR), and Ameren Labadie Unit 2 (SO<sub>3</sub> injection for flue gas conditioning). These three plants exemplify the possible causes of elevated SO<sub>3</sub> in the flue gas.

Conesville Unit 6 fired a high-sulfur coal (3-4%) and native mercury capture across the ESP was low (1% to 20%). There was typically 60% to 70% oxidized mercury at the ESP outlet, most of which was captured in the wet FGD. Native SO<sub>3</sub> concentration was typically above 20 ppmv. More than 20 sorbents or combination of sorbents were tested at injection rates of 9-18 lb/MMacf. Injection of 9.5 lb/MMacf DARCO® Hg resulted in 8% removal. The highest removal was 31% using DARCO® E12 (experimental lignite-based activated carbon chemically treated with basic materials to provide buffering against SO<sub>3</sub> condensation) at 12 lb/MMacf. No sorbent was able to achieve the goal of 50% removal at injection rates <10 lb/MMacf.

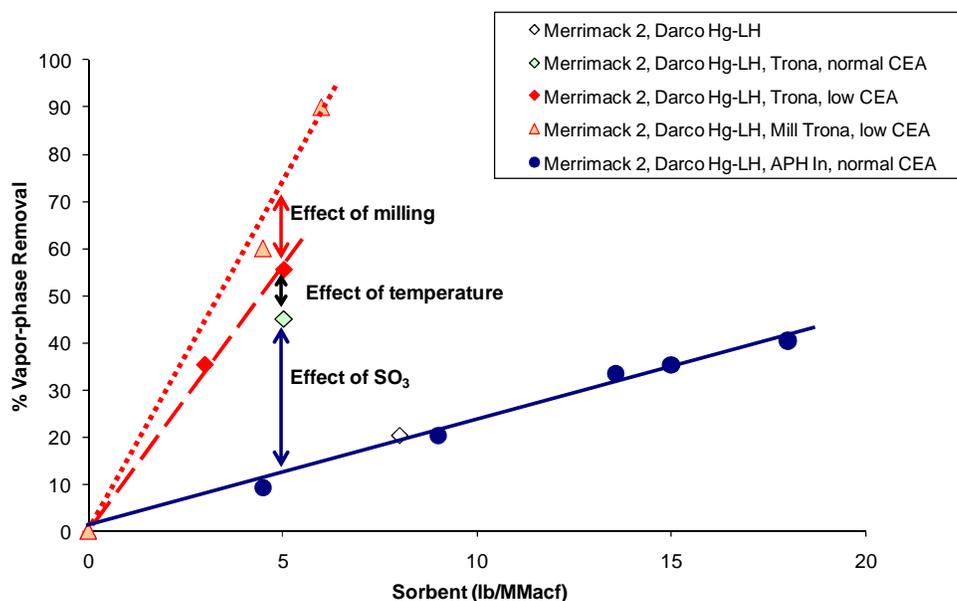
**Table 1-8. List of sorbent injection demonstration sites with cold-side ESPs**

Plant name	Blr ID	State	Unit MW	Primary boiler fuel	Particle Ctrl	ESP SCA, ft <sup>2</sup> /kacfm	FGC	SO <sub>2</sub> Ctrl	NOx Ctrl: Post-Combustion
Baldwin	3	IL	635	PRB	FF/CSE	247	Yes		
Brayton Point	1	MA	241	MSEB	FF/CSE	559	Yes	SDA	SCR
Coal Creek	1	ND	605	ND Lignite	CSE	599	No	wFGD	
Conesville	6	OH	444	HSEB	CSE	301	No	wFGD	SCR
Crawford	7	IL	239	PRB	CSE	112	No		
Victor J Daniel Jr	1	MS	500	PRB/LSEB	CSE	--	No		SNCR
Dave Johnston	3	WY	230	PRB	FF/CSE	629	No	wFGD	
Hoot Lake	3	MN	75	PRB	CSE	--	No		
Independence	2	AR	850	PRB	CSE	540	No		
Labadie	2	MO	574	PRB	CSE	279	Yes		
Lee	1	NC	75	MSEB	CSE	300	Yes		
Lee	3	NC	253	LSEB	CSE	300	Yes		
Leland Olds	1	ND	570	ND Lignite	CSE	320	No		
Limestone	1	TX	813	TX Lignite/PRB	CSE	--	No	wFGD	
Meramec	2	MO	138	PRB	CSE	376	No		
Merrimack	2	NH	346	MSEB	CSE	350	No		SCR
Miami Fort	6	OH	163	HSEB	CSE	353	No		SNCR
Milton R Young	2	ND	477	ND Lignite	CSE	375	No	wFGD	
Monroe	4	MI	817	PRB/MSEB	CSE	285	Yes		SCR
Pleasant Prairie	2	WI	617	PRB	CSE	468	Yes	wFGD	SCR
Portland	1	PA	172	HSEB	CSE	284	No		
Salem Harbor	1	MA	82	LSB (S.American)	CSE	474	No		SNCR
Shawville	3	PA	188	HSEB	CSE	--	No		SNCR
St Clair	1	MI	169	PRB/HSEB	CSE	467	No		
Stanton	1	ND	172	PRB	CSE	470	No		
Stanton	1	ND	172	ND Lignite, PRB	CSE	470	No		
Yates	2	GA	123	MSEB	CSE	149	Yes		
Yates	1	GA	123	MSEB	CSE	173	Yes	wFGD	

HSEB = High-sulfur eastern bituminous  
MSEB = Medium-sulfur eastern bituminous  
LSEB = Low-sulfur eastern bituminous  
PRB = Powder River Basin subbituminous

The SCR-generated SO<sub>3</sub> level at Merrimack Unit 2 was typically between 20 and 25 ppmv, which resulted in low native mercury removal usually less than 10%. The mercury capture was affected by the SO<sub>3</sub> concentration and the APH cold-end average (CEA) temperature. When the APH outlet temperature was lowered from approximately 330°F to 315°F, mercury removal increased, but reduction of SO<sub>3</sub> concentrations in the flue gas had a larger effect on Hg removal. Mercury removal by PAC was significantly increased with co-injection of SO<sub>3</sub> sorbent as shown in Figure 1-24. Trona injection reduced SO<sub>3</sub> concentration to 7-8 ppmv. Mercury capture can be improved with optimization of the trona injection system, but long-term balance of plant impacts must be considered. Balance of plant impacts seen at

Merrimack when injecting PAC and/or SO<sub>3</sub> sorbent included deterioration of ESP performance, increased pressure drop across the APH, increased sodium content in the fly ash when injecting trona (more limitation on fly ash utilization), and smoldering fly ash/PAC in the ESP hoppers.

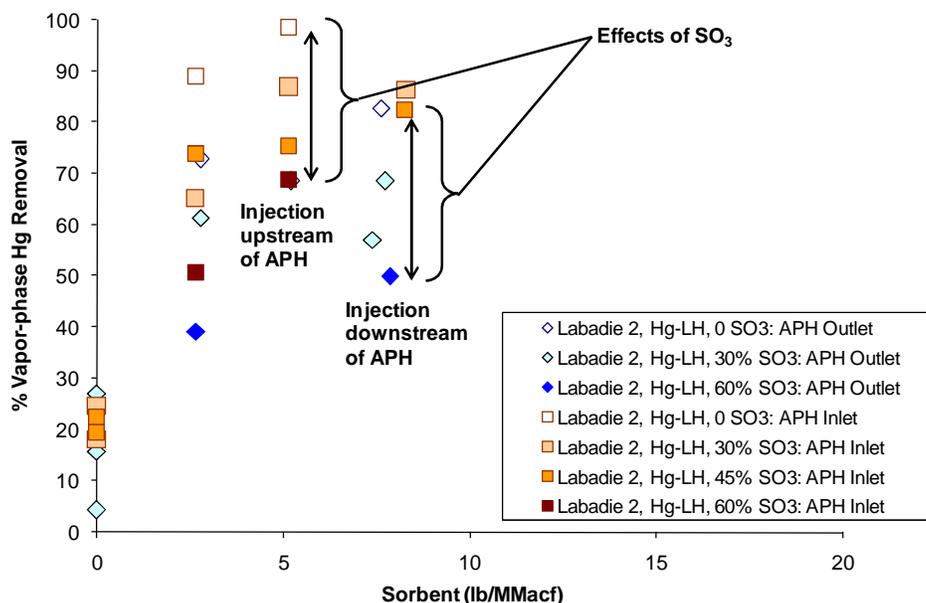


**Figure 1-24. Mercury removal across ESP at Merrimack Unit 2, combinations of Darco Hg-LH and trona sorbents**

Recent data on carbon injection presented by Sjoström et al.<sup>25</sup> showed that injection of activated carbon upstream of the air preheater does not always improve mercury removal in boilers using SO<sub>3</sub> injection for flue gas conditioning. Testing was carried out at a 200 MW PRB-fired boiler with a cold-side ESP. Parametric testing of brominated PAC injections showed mercury removals from 21% at 0.85 lb/MMacf to 58% at 8.2 lb/MMacf when injected at the APH inlet, with the FGC system in service. Mercury removals were similar when PAC was injected at the APH outlet. The air preheater outlet temperature was 350°F to 375° at full load at this plant. This high outlet temperature could have contributed to the lack of improvement of mercury removal when PAC was injected upstream of the air preheater: the temperature in the air preheater might have been too high for significant mercury removal. When the FGC system was not in service (i.e., no SO<sub>3</sub> injection), mercury removals from PAC injection increased. For example, at PAC injection rates of 3.3 and 4.1 lb/MMacf, mercury removals were 40% and 44%, respectively, with the FGC system in service; with the FGC system out of service, the mercury removals were 66% and 77%, respectively.

Sorbent injection testing at Labadie Power Plant illustrates the effect of injecting activated carbon in plants that use SO<sub>3</sub> injection for flue gas conditioning.<sup>25</sup> Native mercury removal across the ESP at Labadie was low and most of the mercury was in the elemental form. Figure 1-25 illustrates the results of SO<sub>3</sub> injected downstream of the air preheater and Norit Hg-LH sorbent injection upstream or downstream of the air preheater. Concentrations of SO<sub>3</sub> are given as percent of full scale on the sorbent injection system. Injection of activated carbon upstream of the air preheater has demonstrated higher Hg removal than injection downstream of the air preheater at plants that inject SO<sub>3</sub> downstream of the air preheater for flue gas

conditioning. This method of injection has not always worked at bituminous plants with high levels of SO<sub>3</sub> at the air preheater inlet. At Merrimack, for example, there was no improvement in Hg removal with DARCO Hg-LH injected upstream of the air preheater as compared to injection downstream.



**Figure 1-25. Removal across ESP at Labadie with injection of activated carbon as function of SO<sub>3</sub> injection and injection location<sup>25</sup>**

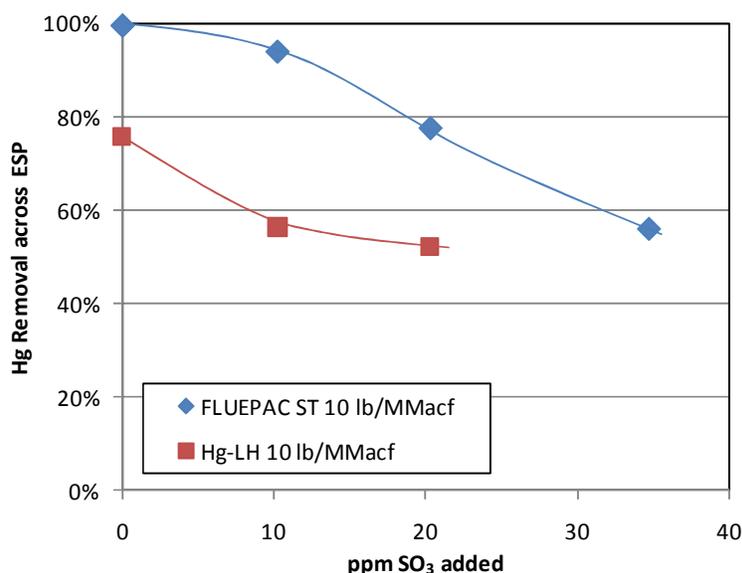
Figure 1-24 illustrates the improvement in ACI performance at Merrimack when the carbon was milled on-line. Further tests were performed at Independence Unit 2 and Labadie Unit 2 to investigate on-site milling of activated carbon.<sup>26</sup> At Independence, on-site milling also increased mercury removal from 40% to 75% with 0.5 lb/MMacf of DARCO® Hg-LH injected upstream of the APH and from 60% to 90% with 1 lb/MMacf DARCO® Hg-LH injected upstream of the APH.

Alstom’s Mer-Cure™ process was developed to improve mercury capture when activated carbon is injected upstream of the air preheater.<sup>27,28</sup> Mer-Cure™ uses a processor to mill the sorbent just before the point of injection, which leads to increase the mass transfer to the sorbent by reducing the size and by de-agglomerating sorbent at the injection point. Alstom reports that it has carried out more than 12 field test demonstrations of the Mer-Cure™ process. Some of these were carried out at plants burning low- to medium-sulfur bituminous coals. In recent results on bituminous-fired plants in Pennsylvania, Alstom reported approximately 90% removals of mercury at several plants with sorbent injection rates in the range of 4 to 6 lb/MMacf.

The effect of SO<sub>3</sub> sorbents on mercury removal by activated carbon was also studied at the Mercury Research Center (MRC) located at Gulf Power Company’s Plant Crist in Pensacola, Florida. This is a test facility that takes a slipstream of flue gas, equivalent to about 5 MWe, through a series of modules, including SCR, air preheater, ESP, FF, and wet scrubber. The facility can be configured to bypass some of the modules, in order to generate different APCD

configurations. The plant typically burns a low-sulfur bituminous coal (less than 1 wt% sulfur). The flue gas composition in the slipstream reactor can be changed to some extent by adding SO<sub>3</sub> or HCl.

Recent work at the MRC<sup>29</sup> tested several Calgon sorbents using PAC injection upstream of the ESP with SO<sub>3</sub> injection. Calgon FLUEPAC<sup>®</sup> ST, a new sulfur-tolerant sorbent, was tested against a standard brominated activated carbon (Norit DARCO<sup>®</sup> Hg-LH). The baseline SO<sub>3</sub> concentration in the flue gas was not given, but up to 34 ppmv of additional SO<sub>3</sub> was injected during the testing. The FLUEPAC<sup>®</sup> ST sorbent performed better than the standard brominated sorbents, although both sorbents were affected by SO<sub>3</sub> concentrations (as shown in Figure 1-26). The FLUEPAC<sup>®</sup> ST sorbent had an overall higher level of mercury removal and, therefore, maintained a higher level of Hg removal as SO<sub>3</sub> increased.



**Figure 1-26. Hg removal at MRC as a function of concentration of SO<sub>3</sub> injected into flue gas<sup>29</sup>**

Several potential solutions to the problem of SO<sub>3</sub> interference with ACI on cold-side ESPs have been proposed. SO<sub>3</sub>-friendly sorbents are being developed, such as Calgon’s FLUEPAC<sup>®</sup> ST.<sup>29</sup> New SCR systems often have improved catalytic control or novel catalysts<sup>30</sup> that can minimize the oxidation of SO<sub>2</sub> to SO<sub>3</sub>. In the case of SO<sub>3</sub> for FGC, other options for enhancing ESP performance are being explored, such as ammonia conditioning, water humidification, or rapid onset pulse energization, but these options also have disadvantages. As discussed above, sorbent injection upstream of FGC is a viable option if there is sufficient residence time for in-flight capture and mercury adsorbed onto the sorbent surface is not displaced by SO<sub>3</sub>. For cases where coal sulfur is the cause of SO<sub>3</sub> rather than FGC, co-injection of alkali minerals (trona, lime, magnesium oxide) to adsorb SO<sub>3</sub> may improve mercury capture on carbon as at Merrimack.<sup>24</sup> Bituminous plants that burn coal greater than 1.7 wt% S have scrubbers for SO<sub>2</sub> control and are more likely to use these scrubbers rather than sorbent injection to control mercury.

### 1.4.3. Sorbent Injection and Hot-Side ESPs

Other configurations that might have problems controlling mercury emissions by sorbent injection include units with hot-side ESPs. Hot-side ESPs operate at high flue gas temperatures (600-750°F), which limit mercury capture on sorbent surfaces. High-temperature sorbents are being developed, such as Albemarle Sorbent Technologies' H-PAC. Sorbent injection may be effective downstream of the hot-side ESP, although a dedicated particulate control device must also be installed. The TOXECON™ system (an EPRI-patented technology) involves injection of sorbent upstream of a dedicated FF.

A limited number of demonstrations have been conducted at units with hot-side ESPs (Table 1-9). All of these tests were conducted by Albemarle Sorbent Technologies. B-PAC™ was tested at Cliffside Unit 2<sup>31</sup> and H-PAC™ was tested at Buck Unit 6.<sup>32</sup> H-PAC™, an experimental low-cost version of H-PAC™, and DARCO® Hg-LH were tested at Progress Energy H.F. Lee Unit 2.<sup>33</sup> C-PAC™ was tested at Midwest Generation's Will County Unit 3.<sup>33</sup>

**Table 1-9. List of sorbent injection demonstration sites with hot-side ESPs**

Plant name	Blr ID	State	Unit MW	Primary boiler fuel	Particle Ctrl	ESP SCA, ft2/kacfm	SO <sub>2</sub> Ctrl	NO <sub>x</sub> Ctrl: Post-Combustion
Buck	6	NC	125	LSEB	HSE	240	--	SNCR
Cliffside	2	NC	40	MSEB	HSE	--	--	SNCR
Lee	2	NC	75	LSEB	HSE	--	--	--
Will County	3	IL	299	PRB	HSE	200	--	--

MSEB = Medium-sulfur eastern bituminous

LSEB = Low-sulfur eastern bituminous

PRB = Powder River Basin subbituminous

At Cliffside Unit 2, B-PAC™ was injected at various loads ranging from 12-40 MW.<sup>31</sup> Lower load corresponded to lower hot-side ESP inlet temperatures and lower flue gas flow rate. At high load (40 MW, 686°F injection temperature), mercury removal ranged from 16-39% with B-PAC™ injection rates of 1.8-5.7 lb/MMacf. At low load (12 MW, 530°F injection temperature), mercury removal was 78% with 6.2 lb/MMacf B-PAC™.

Mercury removal at Buck Unit 6 during parametric testing with 7 lb/MMacf H-PAC™ was 54-64% for loads between 60 MW (540°F injection temperature) and 140 MW (640°F injection temperature).<sup>32</sup> Removal at 140 MW using 7 lb/MMacf DARCO® Hg was only 3%. During longer testing, 50% removal was seen with 5 lb/MMacf H-PAC™ at 60 MW (540°F) and 140 MW (640°F). Mercury removal increased to 71% when the H-PAC™ injection rate was increased to 10 lb/MMacf (60 MW, 540°F). Mercury removal with fluctuating injection temperature seemed to be more stable using H-PAC™ instead of B-PAC™.

Further testing was conducted at Lee Unit 2 and Will County Unit 3.<sup>33</sup> The hot-side ESP inlet temperature at Lee averaged 798°F at full load (83 MW) and 564°F at reduced load (44 MW). At full load, injection of H-PAC™ at rates of 5 and 10 lb/MMacf resulted in mercury removals of 41% and 60% respectively. At reduced load, injection of 5-15 lb/MMacf H-PAC™ resulted in removals of 56-84%. The experimental low-cost version of H-PAC™ performed similarly at reduced load but showed significantly decreased mercury removal at full load (25%

at 5 lb/MMacf and 34% at 10 lb/MMacf), although it should be noted that the injection temperature was slightly higher during these tests (809-827°F). DARCO® Hg-LH did not perform as well as H-PAC™. Injection of 10 lb/MMacf DARCO® Hg-LH at full load gave removals in the range of 38-42%. Will County Unit 3 has two boilers: a “reheat” boiler and a “superheat” boiler. Testing was performed on the “superheat” boiler which has a hot-side ESP inlet temperature between 500°F and 700°F depending on load. Injection of C-PAC™ at rates of 3 and 5 lb/MMacf resulted in mercury reductions of 38% and 55%, respectively.

The dramatic effect of load illustrates the importance of temperature and residence time on mercury removal with sorbents. These data suggest that under normal operating conditions of a hot-side ESP, mercury removal by the current generation of activated carbon sorbents is limited and cannot achieve 90% removal without improvement in existing technology or development of new technologies.

#### 1.4.4. Sorbent Injection and Fabric Filters

Sorbent injection upstream of a fabric filter generally shows high mercury removal efficiency. The sorbent generally has a long contact time with the flue gas as sorbent builds up in the filter cake on the bags. Several demonstrations have been performed at units with FFs (Table 1-10), either as a primary particulate control device or in a COHPAC™ configuration (an EPRI-patented technology) in which the FF is installed downstream of another particulate control device. A COHPAC™ baghouse becomes a TOXECON™ configuration when sorbent is injected upstream of the baghouse.

**Table 1-10. List of sorbent injection demonstration sites with fabric filters**

Plant name	Blr ID	State	Unit MW	Primary boiler fuel	Particle Ctrl	SO <sub>2</sub> Ctrl	NO <sub>x</sub> Ctrl: Post-Combustion
E C Gaston	3	AL	272	MSEB	FF/HSE	--	SNCR
Presque Isle	7,6,9	MI	270	PRB	FF/HSE	--	--
Big Brown	2	TX	593	TX Lignite/PRB	FF/CSE	--	SNCR
Harrington	3	TX	360	PRB, TX Lignite/PRB	FF	--	--
Tolk	1	TX	568	PRB	FF	--	SCR

MSEB = Medium-sulfur eastern bituminous

PRB = Powder River Basin subbituminous

Harrington Unit 3 and Tolk Unit 1 both fired PRB coal and had FFs for particulate control. Seven sorbents were tested at Harrington and four were tested at Tolk.<sup>34</sup> At Harrington and Tolk, all brominated carbons tested (B-PAC™, DARCO® Hg-LH, FLUEPAC®-MC PLUS, and C-PAC™) performed well and were able to achieve greater than 80% removal at injection rates of less than 1 lb/MMacf. The non-carbon based sorbents (Amended Silicates and BASF MS200) did not perform as well at Harrington as the carbon based sorbents.

Alabama Power E.C. Gaston Unit 3 burned bituminous coal and controlled particulate matter with a hot-side ESP followed by a COHPAC™ baghouse. Three non-brominated carbons from Norit Americas were injected between the hot-side ESP and the baghouse: DARCO® Hg, PAC2B (subbituminous/bituminous blend activated carbon), and DARCO® Insul.<sup>35</sup> There was no discernable difference between the various carbons. Mercury removal increased linearly with activated carbon injection rate up to 2 lb/MMacf and then leveled off at about 90% removal.

Long-term injection of DARCO® Hg at 1.5 lb/MMacf resulted in an average removal of 78% (mercury removal over the 5-day tests ranged from 36% to 90%). The large range in removal was probably due to varying coal and operating conditions.

The TOXECON™ configuration was further tested at Luminant’s Big Brown Unit 2.<sup>36</sup> Big Brown burns a blend of PRB and Texas lignite coals. Activated carbon (DARCO® Hg or a proprietary EERC enhanced activated carbon) was injected at rates of 0.5-6.5 lb/MMacf. While injecting DARCO® Hg, mercury removal increased rapidly with activated carbon injection rates of up to 3 lb/MMacf (70% removal) and tapered to a maximum removal of 90% with 6.5 lb/MMacf. The enhanced activated carbon performed better and reached 90% removal with 2 lb/MMacf. Month-long injection of 1.5 lb/MMacf enhanced activated carbon resulted in an average removal of 75%.

WE Energies’ Presque Isle Power Plant burns PRB coal and has a TOXECON™ baghouse installed after the hot-side ESPs on units 7-9. DARCO® Hg and DARCO® Hg-LH were injected upstream of the baghouse.<sup>37</sup> DARCO® Hg-LH (60-95% removal with 0.5-3 lb/MMacf) slightly outperformed DARCO® Hg (45-90% removal with 0.5-3 lb/MMacf). DARCO® Hg was also more affected by elevated temperatures. DARCO® Hg showed a linear relationship between increasing temperature and decreasing Hg removal (at a given ACI rate, see Figure 1-27). Removal also decreased with an increase in time between bag cleaning (at a given ACI rate and temperature).

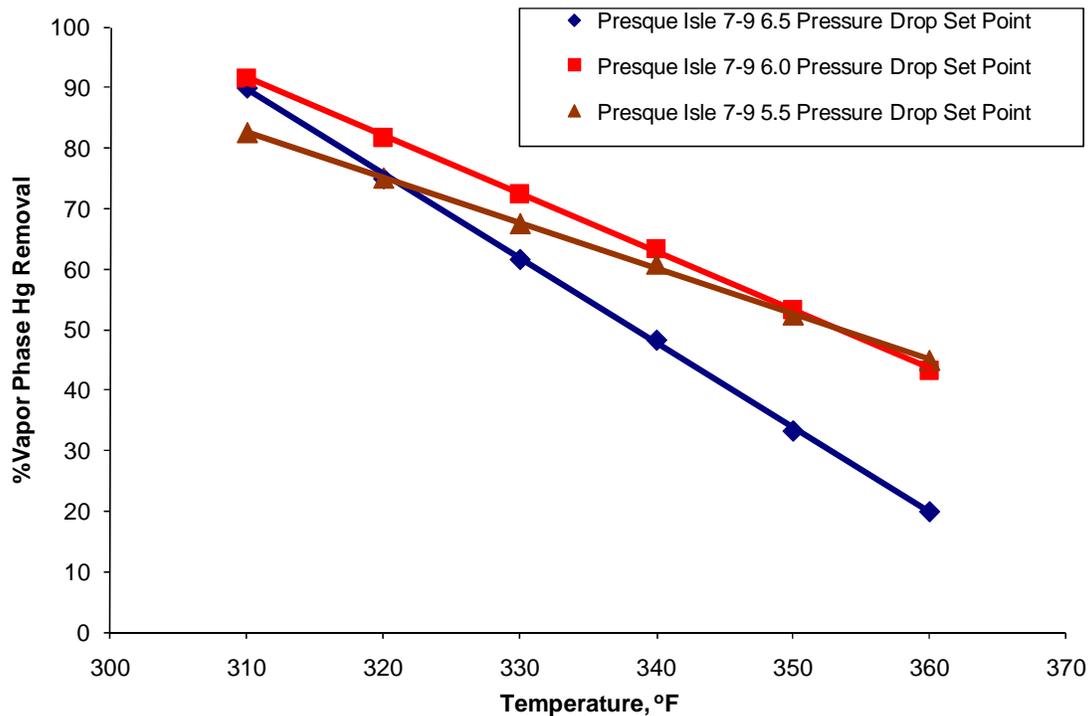


Figure 1-27. Removal of Hg across Presque Isle TOXECON™ baghouse via injection of Darco® Hg sorbent<sup>37</sup>

This technology has been set-up to operate on a long-term basis. The average mercury removal for 2007 was 90%, achieved using DARCO® Hg or DARCO® Hg-LH. Balance of plant impacts include smoldering fly ash/PAC in hoppers and fugitive dust emissions during transfer of fly ash/PAC to the ash silo.

Activated carbon injected upstream of a FF can achieve on the order of 90% mercury removal at plants burning bituminous and subbituminous coals, with less than 2 lb/MMacf of activated carbon. Removal across FFs can be sensitive to temperature. This level of performance has not been demonstrated to date on lignite plants. In general, less sorbent is required for the same level of mercury removal on a FF as compared to a cold-side ESP, all other things being equal.

### 1.4.5. Sorbent Injection and Spray Dryers

Spray dryers (SDs) are installed in combination with either a FF or ESP. Full-scale demonstrations have shown that plants with spray dryers and firing bituminous coal have high native mercury capture while units burning subbituminous or lignite coals do not. Thus several sorbent injection demonstrations have been performed at plants burning PRB or lignite coals with spray dryers in an effort to improve mercury capture (Table 1-11).

**Table 1-11. List of sorbent injection demonstration sites with spray dryers**

Plant name	Blr ID	State	Unit MW	Primary boiler fuel	Particle Ctrl	SO <sub>2</sub> Ctrl	NO <sub>x</sub> Ctrl: Post-Combustion
Laramie River	3	WY	570	PRB	CSE	SD	--
Stanton	10	ND	60	ND Lignite	FF	SD	--
Antelope Valley	1	ND	435	ND Lignite	FF	SD	--
Stanton	10	ND	60	ND Lignite, PRB	FF	SD	--
Holcomb	1	KS	349	PRB	FF	SD	--
Hardin	1	MT	116	PRB	FF	SD	SCR
Hawthorn	5A	MO	550	PRB	FF	SD	SCR

CSE = Cold-side ESP

PRB = Powder River Basin subbituminous

Stanton Unit 10 burned North Dakota lignite and was equipped with a spray dryer-fabric filter (SD-FF). Four carbon-based sorbents were tested at Stanton Unit 10: DARCO® Hg, Desorex HOK300S (German lignite-based carbon), Barnebey & Sutcliffe IAC (iodated carbon made from coconut shells), and LAC0101 (low-cost experimental carbon made from North Dakota lignite).<sup>38</sup> No native mercury removal was measured across the SD-FF. The three untreated carbons (DARCO® Hg, HOK, LAC) performed similarly but removal across the SD-FF was limited to 70% with 6.1 lb/MMacf. During long-term testing, the average removal with 6.1 lb/MMacf DARCO® Hg was 81%. The treated carbon (IAC) performed much better with removal greater than 90% at 0.7 lb/MMacf.

Sunflower Electric’s Holcomb Unit 1 and Missouri Basin Power Project’s Laramie River Unit 3 both fired PRB coal and had spray dryers for SO<sub>2</sub> control. Laramie River had an ESP for particulate control while Holcomb had a fabric filter. DARCO® Hg and DARCO® Hg-LH were injected at Laramie River while DARCO® Hg, Calgon’s 208CP, and DARCO® Hg-LH were tested at Holcomb.<sup>39</sup> Mercury removal was limited to 55% with 6 lb/MMacf DARCO Hg at Laramie River. The brominated DARCO® Hg-LH performed much better and reached greater

than 90% removal with 5 lb/MMacf. At Holcomb, the two non-treated activated carbons performed similarly. At injection rates of 1.0 lb/MMacf upstream of the SD, mercury removal was 50% to 54%. Mercury removal reached 90% with 5.7 lb/MMacf DARCO® Hg. Once again, DARCO® Hg-LH performed better and reached greater than 90% removal with 1 lb/MMacf.

Brominated carbon injection was tested at Rocky Mountain Power's Hardin Unit 1, which fired PRB coal and was equipped with an SCR for NO<sub>x</sub> control, an SD for SO<sub>2</sub> control, and a FF for particulate control.<sup>40</sup> At full load during baseline operation, little native mercury removal was seen across the SD-FF and there was no oxidized mercury at the SD inlet or the stack. With reduced load, as much as 50% removal was seen across the SD-FF corresponding to 50% SD inlet oxidized mercury. Significantly more mercury was oxidized across the SCR at reduced load caused by higher oxygen levels, lower temperatures, and longer residence time within the SCR. Two brominated carbons (DARCO® Hg-LH and FLUEPAC®-MC PLUS) were tested at Hardin. For both carbons, 90% mercury capture was obtained with injection of 1 lb/MMacf. During long-term testing, between 1.5 lb/MMacf and 2 lb/MMacf (up to 4 lb/MMacf at times) brominated carbon was required to maintain 90% removal.

Activated carbon in conjunction with a spray dryer-fabric filter is a promising technology for application on plants that combust subbituminous coal. This combination can achieve more than 90% mercury removal at injection rates that are comparable to those rates used with brominated carbons and FFs alone, that is, 1-2 lb/MMacf.

## **1.5. Other Hg Control Technologies**

As noted before, activated carbon injection is the most commercially mature control technology of those designed specifically to control mercury emissions from coal-fired boilers. Alternate sorbents and technologies are currently under development. Most of these are not ready for commercial deployment, but could become so by the time power plant owners are ready to deploy mercury control technologies. Therefore, alternate technologies are discussed briefly.

### **1.5.1. Pre-Combustion Removal**

Western Research Institute (WRI) patented a pre-combustion mercury removal technology (Patent No. 5,403,365) in which mercury is removed from coal in a two-stage thermal pre-treatment process.<sup>58</sup> The process also removes some of the coal moisture, which increases the heating value of the coal product, relative to the feed coal. This increase in heating value can be significant if the feedstock is a high-moisture subbituminous or lignite coal. This removal technology is best suited for plants that combust low-rank coals, because mercury in these coals is more likely to be found associated with the organic matrix and thus easily volatilized. By contrast, the mercury in bituminous coals is associated with minerals like pyrite. In WRI's process, the coal is first heated to remove moisture and then, in a second stage, heated to a temperature of approximately 550°F. At this temperature, 60% to 80% of the mercury in subbituminous and lignite coals is volatilized and removed by an inert sweep gas. The sweep gas stream containing the evolved mercury is cooled, passed to mercury capture equipment and the cleaned sweep gas is returned to the process. Bench-scale testing of seven low-rank coals demonstrated mercury removals in the range of 35% to 89%. A pilot-scale unit, which can handle up to 100 lb/hr of raw fuel, has been run using the same coals. It was reported that

similar levels of mercury removal were achieved in this pilot-scale unit. Costs have not yet been published for this process.

### **1.5.2. Fixed Adsorption**

Injecting activated carbon (or other sorbents) creates a waste stream, a mixture of sorbent and fly ash, that is enriched in mercury. As discussed below, the presence of activated carbon in fly ash can reduce the economic value of fly ash as a by-product. For these reasons, fixed substrates have been developed and tested for the removal of mercury from flue gas. Fixed substrates are located downstream of the particulate control device and thus preserve the economic value of the fly ash. Furthermore, fixed substrates could be regenerated and the mercury could be captured and segregated from the larger fly ash stream.

Considerable development effort was made in the MerCap™ process in which gold-coated structures were used to adsorb mercury. Slipstream evaluation of the MerCap™ process was carried out at Great River Energy's Stanton Station and Southern Company's Georgia Power Plant Yates.<sup>42</sup> The demonstrations used an electroplated layer of gold on a stainless steel screen (substrate). High levels of mercury removals were demonstrated in some cases. Mercury adsorption was affected by temperature and by the presence of acid gases. The captured mercury could be removed by a thermal treatment and collected using a carbon canister or cryogenic trap. Chemical desorption of the mercury from the gold-coated substrates could also be used as a regeneration technology.

Honeycomb substrates containing carbon-based sorbents were tested in laboratory and power plant slipstream reactors.<sup>43</sup> Two power plant slipstream tests demonstrated the ability to consistently remove 90% of the mercury from bituminous and subbituminous flue gas. Laboratory-scale experiments with simulated flue gas showed that mercury adsorption was not affected by up to 40 ppm SO<sub>3</sub> in the gas.

More recently, slipstream testing has been carried out on the MercScreen™ process, in which a thin bed of granular sorbent is located in the flue gas downstream of the ESP. Testing was carried out at Southern Company's Plant Yates and Plant Miller.<sup>44</sup> High levels of mercury removal were demonstrated. Estimates of the costs of the MercScreen™ process were competitive with the use of activated carbon and the TOXECON™ baghouse. Future testing is underway.

### **1.5.3. Multi-Pollutant Processes**

Powerspan developed the Electro-Catalytic Oxidation (ECO®) technology, which removes NO<sub>x</sub>, SO<sub>2</sub>, mercury and fine particulate matter, as well as heavy metals and other hazardous air pollutants.<sup>45</sup> The process is installed downstream of a coal-fired power plant's existing particulate control device. The three-step process includes 1) the ECO® Reactor, which oxidizes pollutants; 2) the absorber vessel, which cools the flue gas, removes SO<sub>2</sub>, NO<sub>2</sub>, and oxidized mercury and concentrates the fertilizer co-product; and 3) the wet electrostatic precipitator, which removes acid aerosols, air toxics, and fine particulate matter. The ECO® process produces a marketable fertilizer by-product. Powerspan has been operating a 50 MW commercial unit of the ECO® technology at FirstEnergy's R.E. Burger Plant in southeastern Ohio since February 2004.

J-Power EnTech developed the Regenerative Activated Coke Technology (ReACT).<sup>46</sup> This is a multi-pollutant control technology for control of SO<sub>x</sub>, NO<sub>x</sub>, mercury and particulate matter. There have been a number of industrial and power plant installations in Japan, including J-Power's (Electric Power Development Co.) Isogo and Takehara Power Stations. The process involves three steps: 1) adsorption, 2) regeneration, and 3) by-product recovery. The flue gas contacts a bed of activated coke pellets in an adsorption vessel where the pollutants are removed. The pellets are regenerated in a separate vessel. Removal efficiencies have been reported as up to 99.9% SO<sub>2</sub>, 20% to 80% NO<sub>x</sub>, and greater than 90% mercury. Although there are no installations of ReACT in the U.S., Hamon Research-Cottrell has recently entered into a license agreement with J-Power EnTech to market the ReACT technology in North America.

## **1.6. Coal Combustion Residues (CCRs)**

### **1.6.1. Impact of Hg Control Technologies on CCRs**

A possible problem with sorbent injection is its effect on fly ash. According to the American Coal Ash Association,<sup>41</sup> approximately 42% of fly ash produced by coal-fired power plants in 2008 (30 million out of 72 million tons) was used in commercial or engineering applications to avoid land disposal and to generate additional revenue for the power plant. Based on the power plant data in Section 1.1.3, plants that fire low-rank coal and sell their fly ash represent about 23% of boilers in the U.S., while 21% of plants that fire bituminous coal sell their fly ash.

The single most important usage category for fly ash is as a replacement for Portland cement in concrete manufacturing (42% of fly ash or 12.6 million out of 30 million tons per year). Other commercial applications include structural fill and other construction applications, raw material for cement (clinker) production, and mining applications. Many power plants sell their fly ash for use in concrete or cement manufacturing and construction (road fill, soil stabilization, etc.).

The U.S. EPA recently proposed regulating CCRs under the Resource Conservation and Recovery Act (RCRA) to address the risks from the disposal of CCRs.<sup>48</sup> The U.S. EPA proposed two a two-pronged approach on June 21, 2010. First, the U.S. EPA would list CCRs as special wastes subject to regulation under subtitle C of RCRA, when they are destined for disposal in landfills or surface impoundments. Second, the U.S. EPA would not change the May 2000 Regulatory Determination for beneficially used CCRs, which are currently exempt from the hazardous waste regulations under sec. 3001(b)(3)(A) of RCRA.

Sorbent injection can often make fly ash unsuitable for use in beneficial applications, specifically if the carbon content is too high from injection of carbon-based sorbents. The Foam Index test is often used to quantify the effect of activated carbon on fly ash destined for concrete production. In this test, a fly ash sample is mixed with water and a measured amount of a surfactant, or air-entraining agent (AEA). The solution is shaken to see if bubbles form as a result of the surfactant. More AEA is added and the solution is shaken again. This is repeated until bubbles are observed to form. The test mimics the use of AEAs in concrete production to create small air bubbles in the concrete. The high surface area of activated carbon, if present in the fly ash, requires the use of more AEA, and this can make mixtures of fly ash and PAC unsuitable for concrete production.

Segregation of fly ash and carbon is one method to preserve the value of fly ash. Other possible solutions to mitigate the effect of sorbent injection of fly ash include reducing the amount of sorbent needed or using “ash-friendly” sorbents such as C-PAC™ or FLUEPAC®-CF PLUS.

The use of a TOXECON™ baghouse downstream of a particulate collection device allows segregation of fly ash and activated carbon, as discussed previously. However, the capital cost of a baghouse is high. A less expensive solution for units with cold-side ESPs is injection of sorbent mid-field in the ESP, a technology called TOXECON II™ (an EPRI patented technology). The first few fields in the ESP remove most of the fly ash. There is no sorbent present in this fly ash, making it suitable to sell. The last fields collect remaining fly ash and the sorbent. This technique is only suitable for boilers that have ESPs with a relatively large specific collection area (SCA), larger than 400 ft<sup>2</sup> per 1000 acfm.

TOXECON II™ was demonstrated at Entergy’s Independence Steam Electric Station Unit 2, which fired PRB coal and had a cold-side ESP for particulate control.<sup>29</sup> Several lance designs were used at Independence in an effort to maximize sorbent distribution. The coverage area inside an ESP is at least 10 times larger than the cross-sectional area of the inlet ductwork, and this creates difficulties in the injection and distribution of the carbon in the flue gas. Mercury removal of 78% was achieved using 5 lb/MMacf DARCO® Hg-LH.

Reducing the amount of sorbent needed to achieve a given level of mercury emissions is another method of preserving the economic value of fly ash. NRG’s Limestone Station burned a mixture of Texas lignite and PRB subbituminous coals. The fly ash at this plant was sold for concrete manufacture. Testing carried out in 2009 at Limestone<sup>31</sup> showed that ash generated during injection of 2 lb/MMacf DARCO® Hg-LH carbon was not suitable for sale to the concrete industry, but ash generated during injection of 0.5 lb/MMacf of the same sorbent was acceptable for sale.

Injecting a finer grind of sorbent has been tested as a means to increase mass transfer and reduce the amount of sorbent required.<sup>31</sup> On-site milling of the activated carbon injected in the TOXECON II™ configuration at Independence achieved 78% removal with only 2 lb/MMacf. Tests were performed at Independence Unit 2 and Labadie Unit 2 to investigate the effect of on-site milling of activated carbon.<sup>26</sup> At Independence, on-site milling also increased mercury removal from 40% to 75% with 0.5 lb/MMacf of DARCO® Hg-LH injected upstream of the APH and from 60% to 90% with 1 lb/MMacf DARCO® Hg-LH injected upstream of the APH. At Labadie, more than 10 lb/MMacf FLUEPAC®-MC PLUS was required to achieve 85% mercury removal. When the carbon was milled, only 4.1 lb/MMacf was required to achieve similar mercury removal, which was a 60% reduction in carbon usage.

Injection of PAC upstream of the air preheater is another method to reduce the amount of sorbent required (see Figure 1-25). Alstom has demonstrated 90% removal with the Mer-Cure™ process on PRB-fired units (without FGC) using injection rates of less than 1 lb/MMacf.<sup>28</sup>

Another possible solution to mitigate the effect of sorbent injection of fly ash is to use “ash-friendly” sorbents such as C-PAC™ or FLUEPAC®-CF PLUS.

Recent testing at the Boardman Plant<sup>51</sup> focused on DARCO® Hg-LH sorbent as compared to several experimental sorbents designed to be more compatible with concrete applications. The plant burned PRB coal and had a cold-side ESP. Powdered activated carbon was injected

upstream of the ESP. Foam Index Tests of sorbent-fly ash mixtures showed that the experimental sorbents required about one-quarter of the amount as compared to DARCO® Hg-LH. A “pass” on the Foam Index Test means that the amount of AEA required is below a certain level, generally set by the buyer of the fly ash for concrete applications. At moderate levels of ACI, approximately 2 lb/MMacf, some of the experimental sorbents mixed with fly ash showed a Foam Index test result that was similar to the fly ash alone or to Portland cement. However, concrete air stability testing, in which the PAC-fly ash mixtures were substituted for 20% of the cement in concrete mixtures, showed that the air content of the concrete decreased with time. This could cause difficulties for providers of concrete because the time from initial mixing of concrete to use is variable. If properties of concrete change with time because of the presence of PAC, then this will make it less likely that PAC-containing fly ash will be used for concrete manufacture.

Injection of FLUEPAC®-CF PLUS upstream of the APH at Labadie Unit 2<sup>26</sup> produced removals similar to injection of DARCO® Hg-LH at the same location indicating no decrease in performance due to the ash-compatible carbon. Ash samples, collected while injecting FLUEPAC®-CF PLUS at rates from 1.5 to 2.0 lb/MMacf, were analyzed using the Foam Index Test. The samples passed the test and were deemed suitable for concrete, although it was noted that the ash had a dark color that would probably not be acceptable for some concrete applications.

C-PAC™, a product of Albemarle Sorbent Technologies, has been tested at a number of plants. A recent review of C-PAC™ testing<sup>49</sup> highlighted results from Crawford Station Unit 7, a PRB-fired boiler with a cold-side ESP. At an average injection rate of 4.6 lb/MMacf, over 80% mercury removal was achieved for a month-long period. The resulting fly ash, containing C-PAC™, was extensively tested for use in concrete. Based on the Foam Index Test, the fly ash was shown to be usable for concrete production. Testing at another PRB-fired unit, Corrette Station, showed that a C-PAC™ injection rate of 3 lb/MMacf resulted in 85% mercury removal and that the resulting fly ash could be used in concrete manufacture, again based on the Foam Index Test.

There are several strategies that are currently being tested to allow sorbent injection for mercury removal while preserving the economic value of the fly ash. Several companies are developing non-carbon, mineral-based sorbents.<sup>52,53</sup> These can remove mercury while not increasing the carbon content of the fly ash collected in the particulate control device. Other strategies involve using activated carbon for mercury removal while making changes to the sorbent or the process. Segregation of the fly ash from the activated carbon using separate collection devices or different fields in the ESP has been demonstrated. In configurations in which fly ash is commingled with activated carbon, specialized sorbents have been developed to minimize the impact of activated carbon on concrete properties. Another approach is to reduce the amount of carbon required, either by on-line milling or by injection upstream of the air preheater.

### **1.6.2. Environmental Stability of Hg in CCRs**

A wide range of mercury concentrations have been found in fly ash. One reference<sup>53</sup> summarized several studies, which reported an average Hg concentration of 527 ng/g, and a range of 16 to 1530 ng/g. Some uses of fly ash may involve high-temperature processing that may increase the potential for release of mercury and other metals. In cement manufacturing, for

example, fly ash can be raw feed for producing clinker in cement kilns. Virtually all mercury will be volatilized when fly ash is used as feedstock to cement kilns as a result of high operating temperatures (1450°C).<sup>56</sup> Curing of concrete can also involve temperatures on the order of 80°C. In a laboratory simulation experiment, mercury emissions during steam-curing of concrete were measured at 0.4 to 5.8 ng of mercury/kg of concrete. The study reported that the Hg flux from exposed concrete surfaces did not exceed mercury fluxes from soils (4.2 ng m<sup>-2</sup>h<sup>-1</sup>). The study concluded that less than 0.022% of the total quantity of Hg present in concrete was released during the curing process. Therefore greater than 99% of the Hg was retained in the concrete under the conditions tested.<sup>57</sup>

There has also been concern raised for other processes, such as the production of asphalt. Using 13 different CCRs, including fly ash containing activated carbon, a laboratory simulation was conducted on asphalt production at 170°C.<sup>56</sup> The results suggest that volatilization of mercury is less than 10% except for one CCR where results suggested volatilization of 92% to 100%.

When there is no beneficial use for fly ash, it is placed in landfills or ponds, where mercury (and other trace metals) might be leached out. Laboratory studies and field measurements of solid-gas exchange between fly ash and fly ash mixed with FGD solid mixtures have been conducted.<sup>58</sup> These studies have shown that fly ashes from bituminous and subbituminous coals act as a sink for atmospheric mercury, while lignitic fly ash may emit mercury to the atmosphere. In the field, mercury fluxes (solid to gas) from both uncovered landfills and vegetated, topsoil-covered landfills containing bituminous or mixed subbituminous-bituminous fly ash were determined to be lower than the mercury fluxes from the surrounding soils. Mercury fluxes from a landfill containing FGD solids mixed with lignitic fly ash were estimated to be about four times higher than the surrounding soil.<sup>58</sup>

## **1.7. Costs of Mercury Reduction**

### **1.7.1. Basis for Cost Calculations**

Assessing costs of new emission control technologies has traditionally been a challenging task. Many factors contribute to this, including business confidentiality concerns, early stage technology questions (e.g., short vs. long-term performance, expected market penetration, regulatory uncertainty), vendor vs. user perspectives, etc. Confidence in cost estimates typically grows with statistically significant, actual cost data. Also, developing “universal” cost estimates for broad technical and policy decisions represents a different effort and approach than, for example, developing a site-specific cost estimate for a given technology.

Universal technology cost estimates are typically accomplished through algorithm-based analyses, using a combination of assumptions and empirical data and using procedures and tools such as NETL’s cost analyses framework<sup>59,60</sup> and the U.S. EPA’s CUECost.<sup>61</sup> On the other hand, site-specific costs can be estimated with more or less precision ranging from full-fledged engineering designs to more general “order-of-magnitude” estimates depending on the particular objectives.

In this section of the report no attempt is made to conduct either of the above types of analyses. The objective is to provide a summary of the most recent data available with respect to costs of mercury control technologies. To that extent, the information in this section is very

consistent with the earlier technical sections in this report, in that it is based on researching and summarizing recently published data. Specifically, this includes algorithm-based cost information developed by NETL,<sup>59,60</sup> as well as plant survey-based actual costs gathered by the GAO.<sup>20</sup> These recent studies, conducted in 2007-2009, represent a reasonable basis for the current status of estimates of mercury control costs, specifically because they included several key components necessary for such analyses: actual cost and performance data from well monitored and documented test programs, generally accepted cost factors for power plant economics (e.g., taxes, interest rates, contingencies, retrofit assumptions, labor and material costs, etc.), a consistent “study-level” methodology throughout (all these common to the NETL cost analyses), as well as actual reported costs from commercially operating plants under the U.S.GAO study/survey. In addition, other specific costs available in the literature are included as well.

As stated previously, this report addresses dedicated mercury control technologies, even though mercury capture can and does occur in other plant APCDs (co-benefits). Hence, in this section, the focus remains on dedicated mercury control costs and not those associated with co-benefits. For example, the costs of an SCR or WFGD, both of which can affect the overall mercury capture in a plant, are not part of this report. The costs reported in the NETL and the U.S. GAO studies focus on the mercury control technologies described in this report (sorbents, oxidation catalysts and additives). It is important to recognize that the effect of mercury reduction co-benefits can have a major impact of the actual cost of mercury reductions (\$/lb Hg removed). This is similar to the impact of varying mercury levels in the coal, in that the actual reductions in pounds, for a given level of control (i.e., percent reduction) are proportionally higher or lower with the respective higher or lower initial mercury level concentrations. This real, but potentially misleading, reporting of control costs is avoided when costs are presented in terms of their impact on the plants’ resulting cost of electricity (COE). As such, the NETL analyses presents costs in both formats – cost of mercury removed (\$/lb) and 20-year levelized COE (mills/kWh).

A potentially very large factor affecting mercury control costs is the impact of sorbents (activated carbon) on the resulting fly ash from the plant. This comes from the fact that many plants sell their fly ash for beneficial reuse (e.g., concrete industry) and the addition of the sorbent may render the fly ash undesirable for that market. In such cases, the revenue represented by the sale of fly ash is replaced by the cost of its disposal. Given the potentially large cost of these scenarios, the NETL studies include analyses with and without fly ash (or “by-product”) impacts.

It should be noted that although both NETL cost studies<sup>59,60</sup> were based on results from its Phase II field test programs, representing mostly short-term results, subsequent longer-term testing (as described in the technical sections above) have for the most part corroborated the earlier tests, providing additional confidence that these costs remain relevant. Comparisons with the U.S. GAO commercial plant surveys lend further credibility to the cost analyses. In addition, it should be noted that the NETL studies present several cost scenarios for various coals, configurations and levels of mercury control. For the sorbent technology (ACI), the analyses include 50%, 70% and 90% control scenarios for bituminous, subbituminous and lignite coals; for the oxidation technologies (catalysts and additives), the analyses include subbituminous and lignite coals and mercury reduction levels of 73% (for the catalysts and additive - CaBr<sub>2</sub>) and 85% for CaBr<sub>2</sub>.

The U.S. GAO survey provides a much different level of cost detail. Only average cost and ranges are provided. Further they are not directly linked to the plants identified in the survey; hence there is no direct opportunity to analyze those results in a more detailed manner. However, using the U.S. power plant information described in Section 1.1.3, it was possible to develop nominal costs for comparison with the NETL estimates.

**1.7.2. National Energy Technology Laboratory (NETL) Costs Summary for ACI**

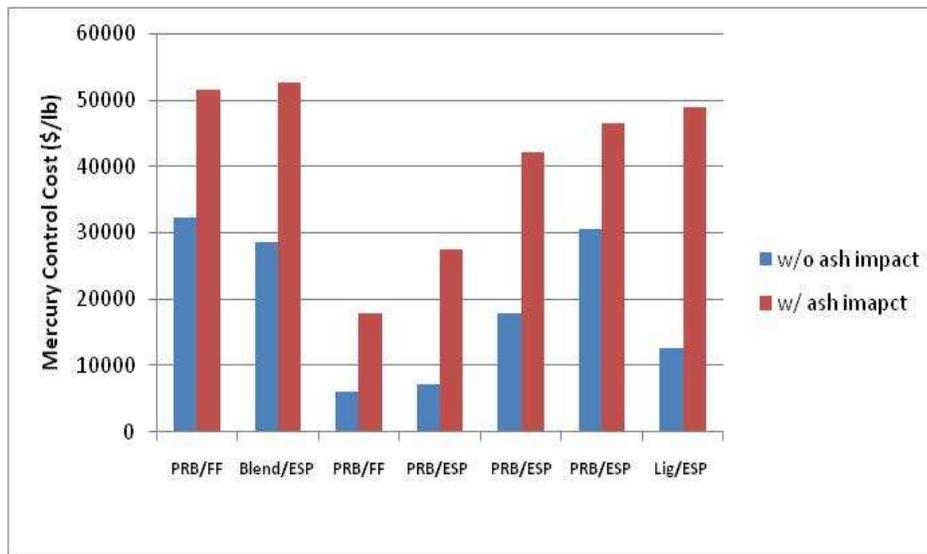
ACI technology costs are primarily driven by the cost of the sorbent. Hence, quantity (injection rate, plant size) and quality (type of sorbent –treated or untreated) of the sorbent are the key factors in the total sorbent cost. Sorbent costs varied between about \$0.40/lb and \$1.35/lb.

Total installed capital costs ranged from about \$3.6/kW to about \$9.2/kW reflecting primarily the wide range of unit sizes in the study (from 140 MW to 360 MW). Table 1-12 summarizes the configurations of APCDs and coal rank for the units in the cost study at the 90% Hg control level.

**Table 1-12. Configurations of units in NETL cost study and capital cost of ACI for 90% Hg removal<sup>59</sup>**

Coal Type	Bit	Bit/PRB	PRB	PRB	PRB	PRB	LIG
Size (MW)	172	145	360	240	140	150	220
APCD	ESP	ESP	SD-FF	ESP	ESP	ESP	ESP
Hg in coal, (lb/TBtu)	8.23	5.66	10.36	7.17	7.83	5.5	8.66
ACI, (lb/MMacf)	5.34	2.31	1.03	0.55	2.4	3.65	1.64
Capital (\$/kW)	8	8.79	3.63	8	9.16	8.5	8

Figure 1-28 and Figure 1-29 summarize mercury control costs (\$/lb Hg) and 20-year levelized COE (mills/kWh), with and without an impact on ash (i.e., lost sales of fly ash as a by-product), for the various units and coal types. As can be seen in the figures, when the combined cost of not selling the fly ash and paying for its disposal is factored in to the cost of mercury control, the cost of control (in \$/lb Hg) and cost of electricity (mills/kWh) are higher.



**Figure 1-28. Cost of 90% mercury control with and without impact of lost sales of fly ash as a by-product<sup>59</sup>**

These results indicate costs ranging from about \$6,000/lb to \$30,000/lb when by-product contamination/sales are not a factor and between about \$18,000/lb and \$50,000/lb if ash revenue is lost. These numbers correspond to 20-yr levelized COE ranging from about 0.35 mills/kWh to 2 mills/kWh (0.035 to 0.2 cents/kWh) without by-product penalty and about 1 mill/kWh to 3.5 mills/kWh (0.1 to 0.35 cents/kWh) if by-product impacts are present.

As already discussed, the cost of sorbent injection technology is largely driven by the cost of sorbent, and the costs are thereby influenced by the price of the sorbent and especially its consumption requirements. Figure 1-30 shows the relative impact of capital cost (a), plant size (b) and sorbent consumption on COE. There is a direct relationship between sorbent consumption and control cost, while plant size and capital cost have minor impact on the ultimate COE.

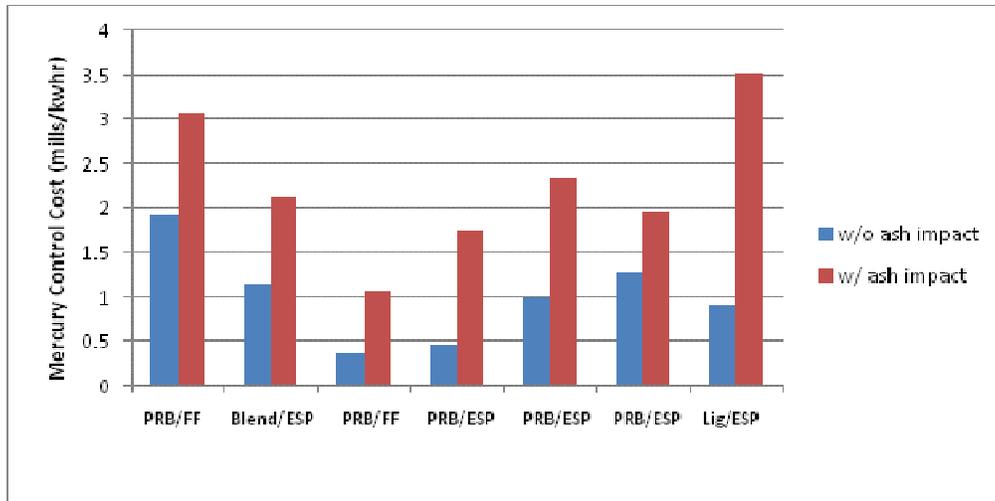


Figure 1-29. Incremental cost of electricity (COE) for 90% mercury control with and without impact of lost sales of fly ash as a by-product<sup>59</sup>

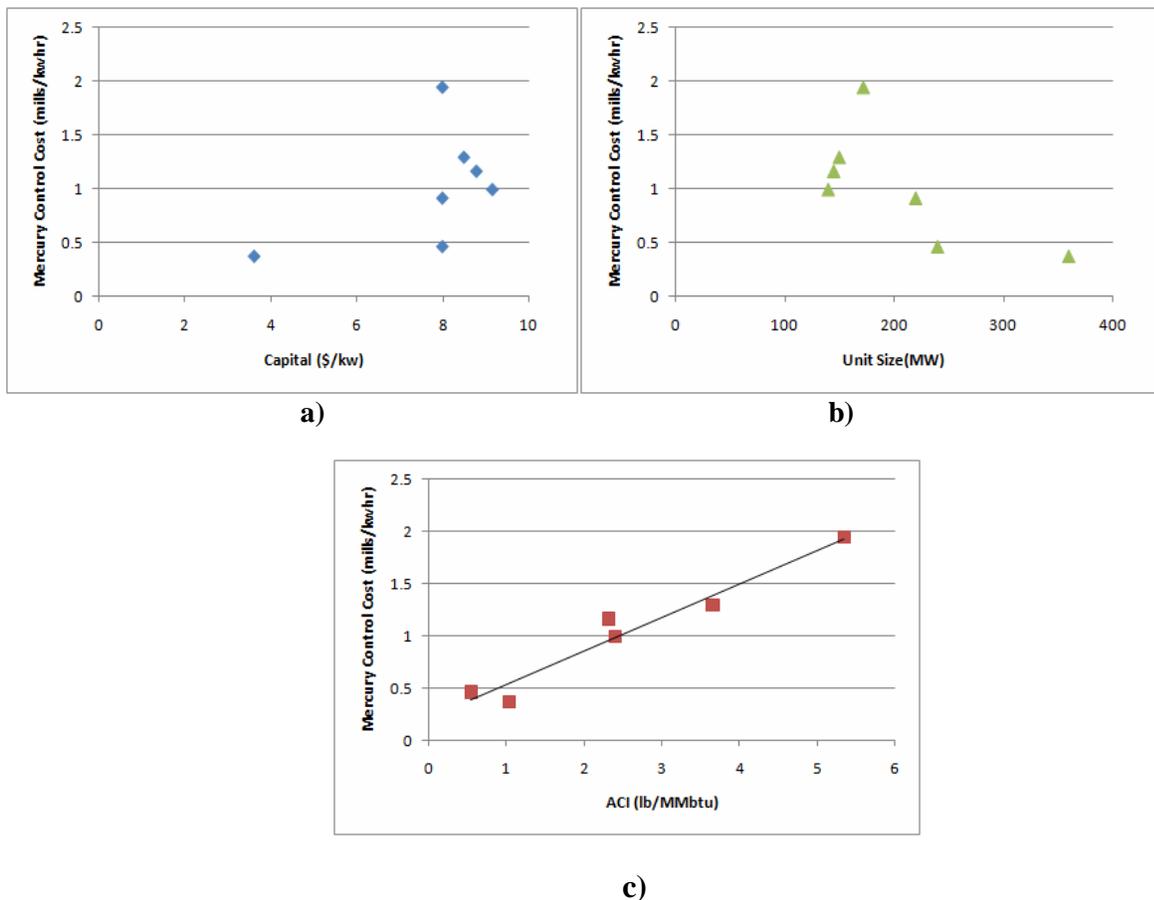


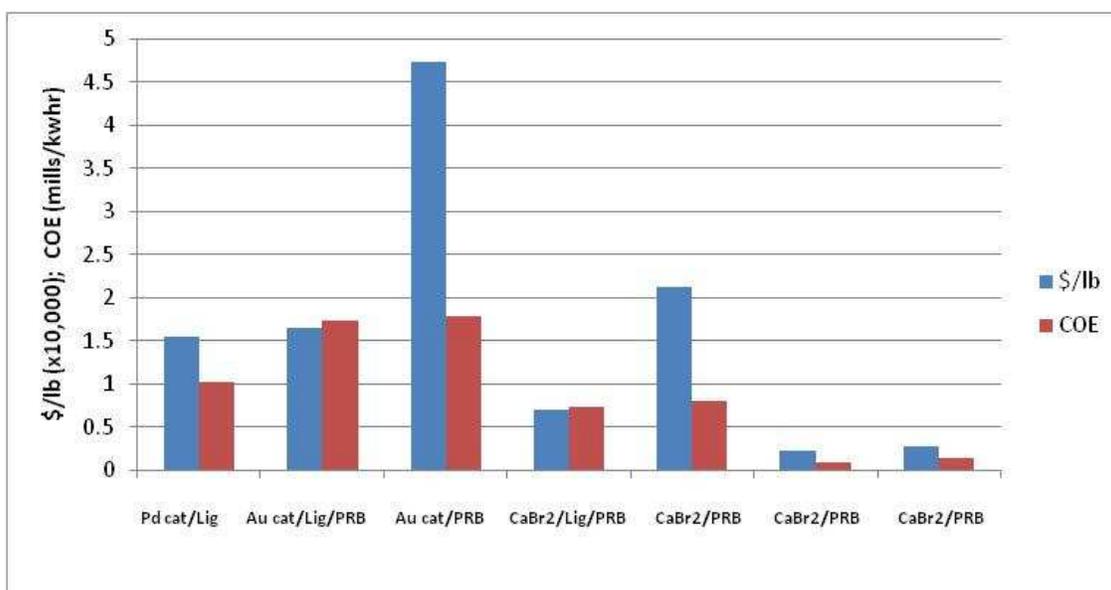
Figure 1-30. Cost of 90% mercury reduction vs. a) capital cost b) plant size; and c) sorbent consumption<sup>59</sup>

### 1.7.3. National Energy Technology Laboratory (NETL) Cost Summary for Oxidation Technologies

The two types of Hg oxidation technologies (catalysts and additives) have different cost components: catalysts are primarily driven by the initial capital and re-generation costs, while additive technology is not capital-intensive, but as with the ACI technologies, is driven by chemical costs. Unlike the analyses above for ACI technologies, the oxidation technology costs were estimated based on pilot-scale results and applied to a nominal 500 MW plant. Table 1-13 summarizes the major parameters for the units in the cost study. Figure 1-31 summarizes the costs of mercury reduction for Hg oxidation technologies in \$/lb of mercury removed and 20-year COE.

**Table 1-13. List of key parameters in NETL cost study of oxidation technologies combined with FGD<sup>60</sup>**

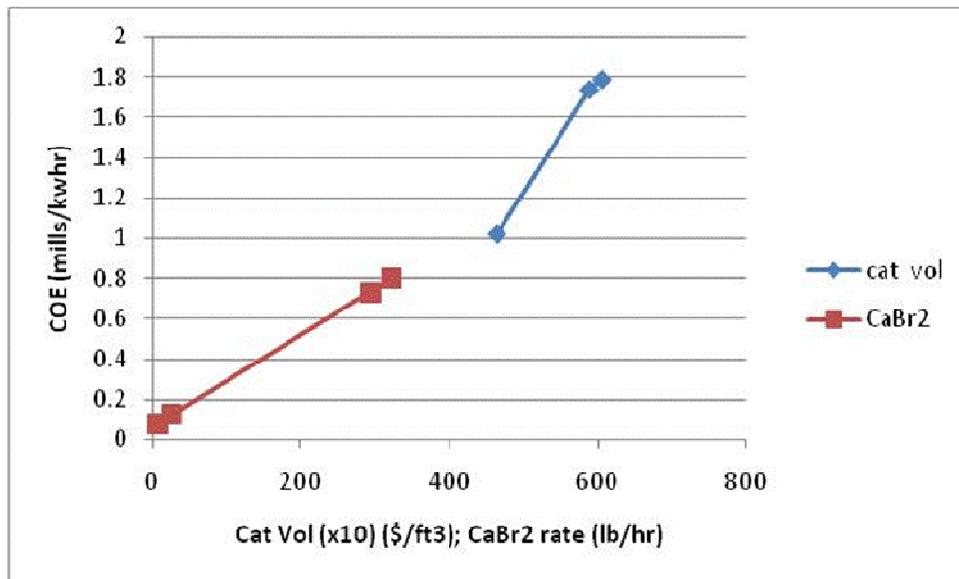
Technology	Pd Catalyst	Au Catalyst	Au Catalyst	CaBr <sub>2</sub>	CaBr <sub>2</sub>	CaBr <sub>2</sub>	CaBr <sub>2</sub>
Coal type	ND Lig	TX Lig/PRB	PRB	TX Lig/PRB	PRB	PRB	PRB
Hg control (%)	73	73	73	73	73	73	85
APCD	ESP, wFGD	ESP, wFGD	ESP, wFGD	ESP, wFGD	ESP, wFGD	SCR, wFGD	SCR, wFGD
Hg in coal (lb/TBtu)	10.5	16.98	6	16.98	6	6	6
CaBr <sub>2</sub> rate (lb/hr)	NA	NA	NA	294	322	5.9	25
Catalyst volume (ft <sup>3</sup> )	4,640	5,890	6,060	NA	NA	NA	NA
Capital (\$/kW)	2.69	3.42	3.53	1.56	1.56	1.56	1.56



**Figure 1-31. Cost of mercury reduction using oxidation technologies combined with FGD<sup>60</sup>**

It can be seen from the graph in Figure 1-31 that the costs are comparable to those for sorbent injection technologies. Specifically, the incremental COE in the range of 1.0 to

1.8 mills/kWh is about the same as that for the ACI technologies shown in Figure 1-29 when by-product impacts are not included. It should be pointed out that Hg oxidation technologies do not impact fly ash (or scrubber waste) and are not therefore subject to by-product impact costs as with ACI technologies. It is also important to note that the costs for oxidation technologies were based on lower level of Hg reductions (73% and 85%) than for ACI (90%). Another important observation is the impact of SCR on the overall COE with CaBr<sub>2</sub>. The last two bars in Figure 1-31 show the low COE (~1 mill/kWh) due to the lower injection rate required for CaBr<sub>2</sub> because of the Hg oxidation impact of the SCR co-benefit. As shown in Table 1-13, capital costs are low for these technologies. Figure 1-32 below shows the key cost components affecting both catalyst and additive oxidation technologies. For the ranges of oxidation catalyst volume and CaBr<sub>2</sub> injection rates cited in the NETL study, COE is considerably higher when an oxidation catalyst is used to oxidize mercury upstream of a wet FGD. From a cost perspective, bromine injection appears to be advantageous relative to oxidation catalysts, assuming that the desired level of Hg oxidation can be obtained.



**Figure 1-32. Cost of mercury reduction for oxidation technologies vs. catalyst and chemical costs<sup>60</sup>**

#### **1.7.4. U.S. Government Accountability Office (GAO) Mercury Control Study**

The U.S. GAO study focused on a plant survey/interview process designed to obtain current performance and cost data from plants operating mercury control technologies. The plants/units included in the survey employed sorbent injection technologies (ACI), but exhibited different APCD configurations. The majority of the applications were on units equipped with ESPs, although several had FFs. Further, there were several units with SD-FF configurations, presumably for compliance with other regulatory requirements (e.g., SO<sub>2</sub>). As already stated, the data presented in the U.S. GAO report were used here in conjunction with the databases described in Section 1.1.3. Table 1-14 summarizes the information obtained from this analysis. It should be noted that these estimates represent nominal values, because no direct comparison between the U.S. GAO data and individual units can be made. However, the results are very

consistent with the overall cost estimates in the NETL cost studies (capital and COE) and are further corroborated in that the capital cost for both ACI and FF technologies agree well with the NETL estimates for ACI, as well as with other available cost data for FFs.<sup>61</sup>

**Table 1-14. Summary of results from U.S. GAO Hg control survey<sup>20</sup>**

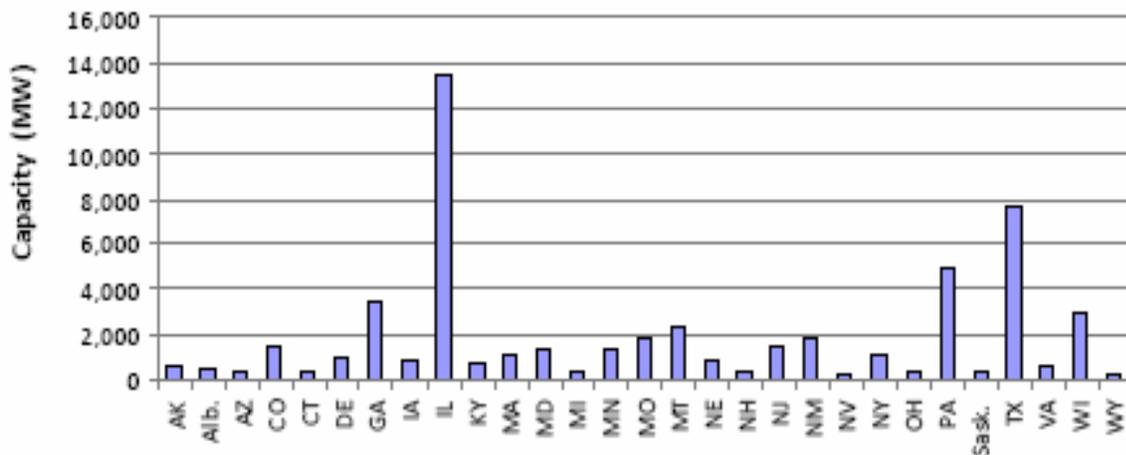
Technology	MW range	MW avg.	ACI Capital (\$/kW)	FF Capital (\$/kW)	COE (mills/kWh)
ACI/ESP	80-375	240	11-15	NA	1.2
ACI/FF	75-350	260	10-14	140-200	NA
ACI/SD-FF	250-790	430	NA	190-210	NA

Additionally, the reported O&M costs (sorbent costs) range from about \$1/kW-yr to \$5/kW-yr. This also compares well with the NETL costs for ACI, which ranged from about \$1.2/kW-yr to \$9/kW-yr. These results represent real, commercial operating data and appear to corroborate with the NETL costs quite well.

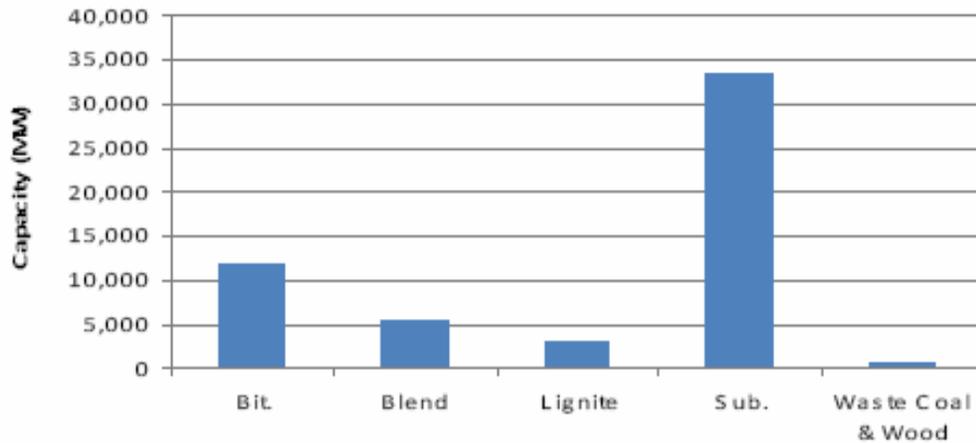
One last commercial data point, included in the U.S. GAO survey, but not identified individually, is the operation of ACI with FF (TOXECON<sup>TM</sup>) at Presque Isle power plant. The 270 MW project reported a capital cost of \$128/kW and an overall mercury removal cost of \$67,000/lb Hg.<sup>63</sup> These correlate well with the NETL and the U.S. GAO estimates.

### 1.8. Commercial Experience with Sorbent Injection Technologies

The penetration of mercury control technologies into the U.S. electric power marketplace has grown rapidly in the recent past, mostly as a result of various state regulations and initiatives. The Institute of Clean Air Companies (ICAC) has collected information relative to the current and projected deployment of mercury controls.<sup>64</sup> At present about 25 units representing about 7,500 MW are using commercial ACI technologies for mercury control. In addition, about 55,000 MW of new bookings are reported by ICAC. Figure 1-33 and Figure 1-34 summarize these data by state and by coal type, respectively.



**Figure 1-33. Mercury control systems orders booked by state<sup>64</sup>**



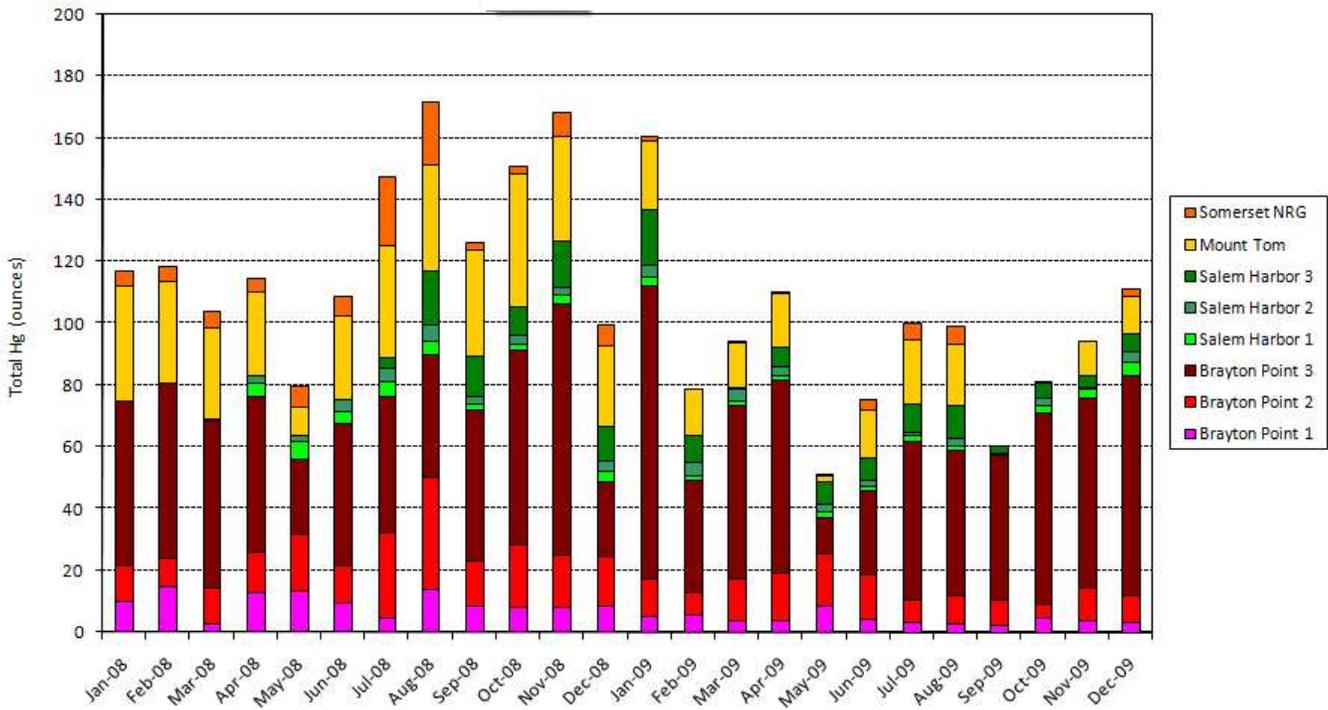
**Figure 1-34. Mercury control systems orders booked by coal rank burned at plant<sup>64</sup>**

NESCAUM has received, courtesy of the New Jersey Department of Environmental Protection,<sup>65</sup> Hg emission data from several sites, based on stack testing data. Selected data from this information are summarized in Table 1-15. Data were selected for sites reporting percent mercury reduction for the years 2008 to 2009. The sites in the table include dedicated mercury control technologies (ACI) as well as those whose mercury reductions are solely attributable to co-benefits through other installed APCD equipment.

**Table 1-15. Summary of New Jersey stack test mercury emissions for 2008 and 2009<sup>65</sup>**

<b>Unit/APCD</b>	<b>Test Date</b>	<b>Load (MW)</b>	<b>ACI (lb/hr)</b>	<b>Hg Reduction (%)</b>
Mercer 1/SCR-FF-ACI	Jun-08	325	603	92
	Sep-08	325	607	56
	Dec-08	215	98	99
Mercer 2/ FF-ACI	Jun-08	260	478	95
	Sep-08	324	643	59
	Dec-08	317	643	98
Carney's Point 1/SCR-SD-FF	Feb-08	139	NA	98.4
	Jun-08	139	NA	96.9
	Sep-08	139	NA	97.2
Carney's Point 2/SCR-SD-FF	Feb-08	138	NA	98.5
	Jun-08	138	NA	97.1
	Sep-08	138	NA	97.4
Logan 1/SCR-SD-FF	Mar-08	224	NA	99.9
	Jun-08	223	NA	96.2
	Sep-08	222	NA	96.5
	Nov-08	219	NA	97.8
B L England 2/SNCR-SD-ESP-ACI	Mar-08	160	414	96.7
	Jun-08	163	337	97.8
	Sep-08	167	373	91.2
	Nov-08	167	365	99.1
	Mar-09	165	209	83.8
	Jul-09	169	362	99.5

Information from the Massachusetts Department of Environmental Protection was also obtained, including a summary of the 2008-2009 Hg emissions data from the coal-fired plants in Massachusetts (Figure 1-35), as well as the formal compliance reports submitted by two of the plants in the state: Salem Harbor<sup>66</sup> and Brayton Point.<sup>67</sup>



**Figure 1-35. Summary of Hg emissions from coal-fired power plants in Massachusetts, 2008-2009<sup>66,67</sup>**

The required Hg reductions in Massachusetts are based on baseline Hg emissions from a historical 12-month period; hence it is not possible to infer the performance of the Hg controls from the available data. It is, however, important to note that Salem Harbor does not have dedicated Hg controls (e.g., reductions are through co-benefits only), while Brayton Point employs SD-FF with ACI for multi-pollutant control in Units 1 and 2, and has an SCR and ESP in Unit 3. Table 1-16 and Table 1-17 present the data provided for Salem Harbor and Brayton Point, respectively.

**Table 1-16. Dominion Energy Salem Harbor Station 2009 reported Hg emissions<sup>66</sup>**

			1/09	2/09	3/09	4/09	5/09	6/09	7/09	8/09	9/09	10/09	11/09	12/09	Total/Average	
Unit 1	Net Generation	MWh	51,845	37,354	42,001	34,430	27,839	22,265	16,298	30,035	351	27,258	30,539	39,231	395,446	
	Emissions	pounds	0.172	0.108	0.095	0.064	0.138	0.084	0.112	0.074	0.011	0.179	0.171	0.251	1.458	
	Monthly Rate	lb/GWh	0.0033	0.0029	0.0023	0.0019	0.0049	0.0038	0.0068	0.0025	0.0321	0.0066	0.0056	0.0064	0.0041	
Unit 2	Net Generation	MWh	43,732	41,515	42,820	34,381	20,096	11,887	5,817	16,299	0	12,166	1,588	37,712	268,013	
	Emissions	pounds	0.250	0.254	0.240	0.200	0.157	0.138	0.081	0.163	0.000	0.132	0.034	0.227	1.877	
	Monthly Rate	lb/GWh	0.0057	0.0061	0.0056	0.0058	0.0078	0.0116	0.0140	0.0100	0.0000	0.0109	0.0215	0.0060	0.0070	
Unit 3	Net Generation	MWh	101,316	81,851	22,717	54,591	59,828	55,467	58,199	62,525	11,816	36,876	33,543	81,843	660,572	
	Emissions	pounds	1.109	0.559	0.035	0.388	0.456	0.427	0.549	0.656	0.169	0.308	0.236	0.342	5.235	
	Monthly Rate	lb/GWh	0.0109	0.0068	0.0015	0.0071	0.0076	0.0077	0.0094	0.0105	0.0143	0.0084	0.0070	0.0042	0.0079	
Total - Units 1,2,3	Net Generation	MWh	196,893	160,720	107,538	123,402	107,763	89,619	80,314	108,859	12,167	76,300	65,670	158,786	1,288,031	
	Emissions	pounds	1.532	0.921	0.369	0.652	0.751	0.650	0.742	0.893	0.180	0.619	0.441	0.820	8.570	
	Monthly Rate	lb/GWh	0.0078	0.0057	0.0034	0.0053	0.0070	0.0072	0.0092	0.0082	0.0148	0.0081	0.0067	0.0052	0.0067	
	7.29 Allowable	lb/GWh	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	
	12-month Rolling Rate	lb/GWh	0.0073	0.0071	0.0068	0.0068	0.0069	0.0070	0.0071	0.0067	0.0066	0.0067	0.0066	0.0065		
	7.29 Allowable Removal Rate	%	85%	85%	85%	85%	85%	85%	85%	85%	85%	85%	85%	85%	85%	
12-month removal from baseline	%	92%	92%	91%	91%	91%	91%	91%	91%	92%	92%	93%	93%	93%		



## **2. Continuous Mercury Monitoring Technologies**

There are two forms of continuous mercury monitoring systems (CMMS), devices that continuously sample mercury emissions and provide a measurement of mercury emissions over time. They are

- Analyzer-based CEMS; and
- Sorbent traps (STs).

Hg CEMS are analyzers that continuously sample the stack gases and provide an indication of mercury concentration in the stack flu gas within minutes of the gas being sampled. In this respect, the Hg CEMS provide information to the operator about mercury emissions on a near real-time basis, or at least in a timely fashion that provides emissions data for a particular hour or day. The total mass emissions rate of mercury is determined by multiplying the measured concentration of mercury in the flue gas times the measured flue gas flow rate.

Sorbent traps provide an indication of cumulative mercury mass emissions over a period of time that could be hours, days, or even weeks. Gas is pulled through a set of traps filled with sorbent that captures mercury. The gas flow rate drawn through the sorbent is varied at a rate that is in proportion to the flue gas flow rate, and must be isokinetic if there is significant amount of particulates in the flue gas. After a period of time, the sorbent traps are removed and replaced. The used sorbent traps are analyzed for total mercury. The mass of mercury trapped can be used to determine the average mercury emission rate over that period of time.

This Chapter focuses on methods that are intended for permanent installation and continuous monitoring of mercury emissions. For continuous monitoring and reporting for the purpose of regulatory compliance there are requirements imposed that assure the reliability and accuracy of the measurement. The same technologies as discussed in this Chapter have been used for short term test programs spanning hours, days, or even weeks. Many of the method requirements that are discussed in this Chapter that are necessary for a method designed for regulatory compliance purposes would not be necessary if the same methods were used for a short-term test.

### **2.1. Hg CEMS Technology Overview**

Currently in the U.S, the two principal suppliers of Hg CEMS technology are ThermoFisher Scientific and Tekran Instruments. These two suppliers have supplied nearly every Hg CEMS ordered for power plants. This Chapter, therefore, focuses on the technologies offered by these two companies.

Each company has been working to address the specific challenges associated with measuring mercury in flue gas. Some of these challenges include:

- Mercury is present in much smaller concentrations than typical criteria pollutants, (i.e., concentration measured in parts per trillion versus parts per million). Although ambient monitors are capable of measuring mercury concentrations to much lower levels than what is experienced in power plant flue gases, some of the particular characteristics of mercury and power plant flue gas – such as interferences and reactivity – make the concentration of mercury in power plant flue gas especially difficult to measure at such low levels.

- Ionic mercury is a reactive material that tends to react with or adhere to other materials, and thereby may be lost in sample handling unless special precautions are taken.
- Elemental mercury tends to form an amalgam with metals. So, to avoid loss of sample, metal surfaces in the sampling system must be coated and temperature maintained at 180°C.

The challenge faced by the Hg CEMS suppliers has been to design a monitoring system that is reliable while also addressing the above difficulties unique to mercury measurement in flue gas.

## **2.2. Hg CEMS Suppliers**

### **2.2.1. ThermoFisher Scientific Hg CEMS**

ThermoFisher Scientific has shipped more than 450 Hg CEMS.<sup>68</sup> Figure 2-1 shows how the ThermoFisher Hg CEMS is configured. The key components are the Sample Extraction & Conversion System, the Probe Controller, the Cold-Vapor Atomic Fluorescence (CVAF) Analyzer, and the Calibration System.

#### **Sample Extraction and Converter**

Flue gas is sampled from the stack by the probe and is typically diluted at a 40:1 ratio with air (or in some cases with nitrogen). Within the probe is a converter that converts oxidized mercury, which is mostly in the form of  $\text{HgCl}_2$ , to elemental mercury. Therefore, all of the mercury sent into the lines to the analyzer is in the form of elemental mercury. This makes the sample somewhat easier to transport and also puts the mercury in a form that the analyzer is capable of measuring. The sample line from the probe to the analyzer must be heated to 120°C (248°F) in order to ensure that sample integrity is preserved. The probe also provides the means to convert elemental Hg gas from the calibrator to oxidized mercury for the purpose of system integrity checks.

#### **Probe Controller**

The Probe Controller sends signals to the probe that control the oxidized Hg to elemental Hg converter and the elemental Hg to oxidized Hg converter, nitrogen supply and other functions performed within the probe. It also controls probe and sample line temperature.

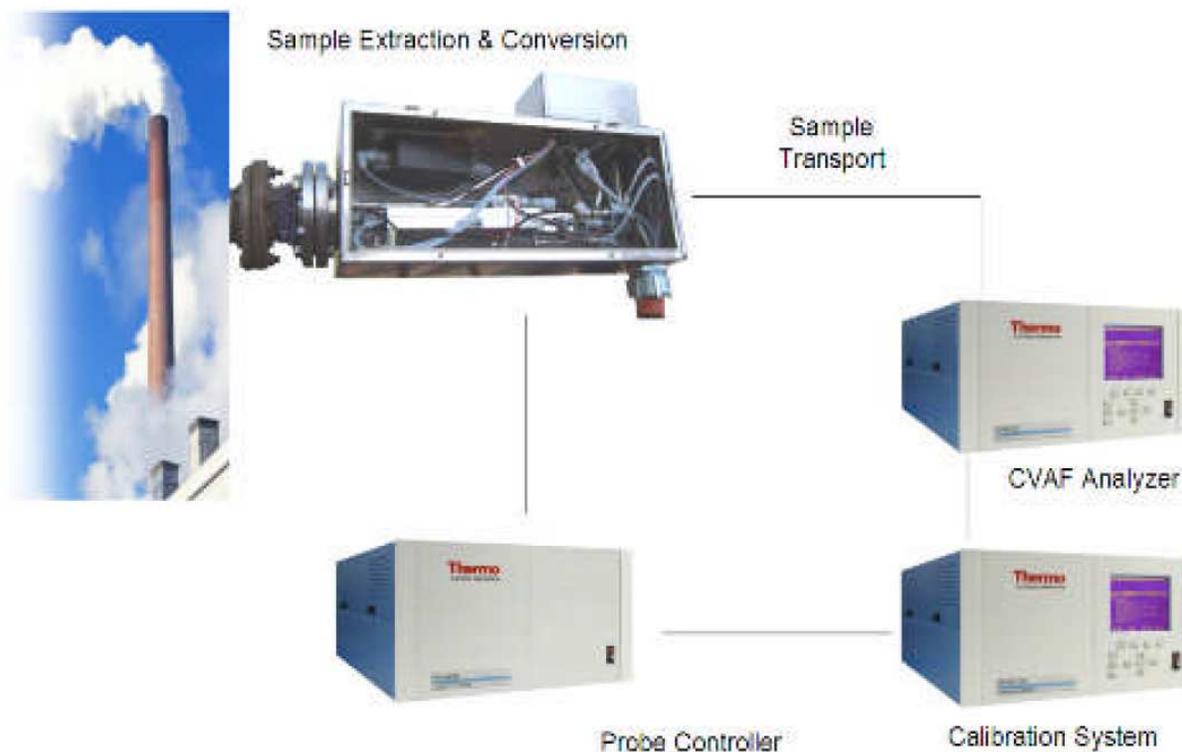


Figure 2-1. ThermoFisher Scientific Mercury Freedom System<sup>68</sup>

### CVAF Analyzer

Within the analyzer the sample is continuously measured using CVAF. In the CVAF method, free mercury atoms (elemental mercury) in a carrier gas are excited by an ultraviolet light source. The excited mercury atoms re-radiate their absorbed energy (fluoresce). The fluorescence intensity is related to the amount of mercury present. The technique is sensitive, selective, and linear over a wide range of concentrations; however, molecular gases (such as oxygen and nitrogen) present in the carrier gas quench the fluorescence signal, which reduces instrument sensitivity.

The analyzer provides a measure of total mercury and cannot speciate mercury on its own. In order to measure mercury speciation, it is necessary to take two measurements – one with the converter in the probe operating (for total mercury) and another with the converter bypassed and with  $\text{HgCl}_2$  removed from the gas (to arrive at elemental Hg). The difference between the amount of total mercury and the amount of elemental mercury equals the amount of oxidized mercury. When used for regulatory purposes, CEMS are not typically operated in speciating mode, but rather used to measure total mercury only.

The gas in the analyzer is maintained at a vacuum to suppress quenching and improve sensitivity. Sensitivity of the analyzer's CVAF measurement can be improved roughly five-fold by using nitrogen as the dilution gas in the probe rather than air because oxygen has a greater tendency to quench the atomic fluorescence than nitrogen.<sup>68</sup> Therefore, for low concentration measurements (less than  $2 \mu\text{g}/\text{m}^3$ ), nitrogen dilution gas is recommended by the manufacturer.

The analyzer has digital outputs for various data protocols. The advantage of digital output is that, with the high degree of linearity expected from the CVAF analysis method combined with digital output, good linearity over a broad dynamic range is expected.

### **Calibration Gases and Standards**

It is periodically necessary to verify the accuracy of the Hg CEMS using calibration gases that have known concentrations of both elemental and oxidized mercury. As an alternative to commercial, bottled calibration gases, the Hg CEMS manufacturers have been working with the U.S. EPA and NIST on traceable methods for the instruments to produce elemental mercury calibration gases utilizing known relationships for mercury vapor pressure.<sup>69</sup> The elemental mercury calibration gas generators for both suppliers operate by carefully controlling a sample of Hg and dilution gas to a specific temperature and pressure that is determined by the desired vapor pressure. In this manner, the mercury concentration of the gas exiting the calibration gas generator is determined by the mercury vapor pressure relationship. The calibrator output is NIST-traceable.

It is important that the Hg CEMS measure all forms of mercury accurately. A system integrity check is performed to verify the accurate measurement of oxidized mercury. For system integrity checks it is necessary to have oxidized mercury calibration gas provided to the probe tip where it is drawn through the probe and through the converter and to the analyzer. To do this, the ThermoFisher Hg CEMS adds chlorine to the elemental Hg calibration gas at the probe in order to convert the elemental mercury from the elemental mercury gas generator to oxidized mercury. It is necessary to have a bottle of chlorine gas at the probe for this system integrity check. The probe has a converter that converts the oxidized mercury back to elemental mercury, which is then transported to the analyzer for measurement. So, for system integrity checks on ThermoFisher's Hg CEMS, elemental mercury calibration gas is oxidized with chlorine, sent through the probe tip, and then the oxidized mercury is converted back to elemental mercury before leaving the probe.

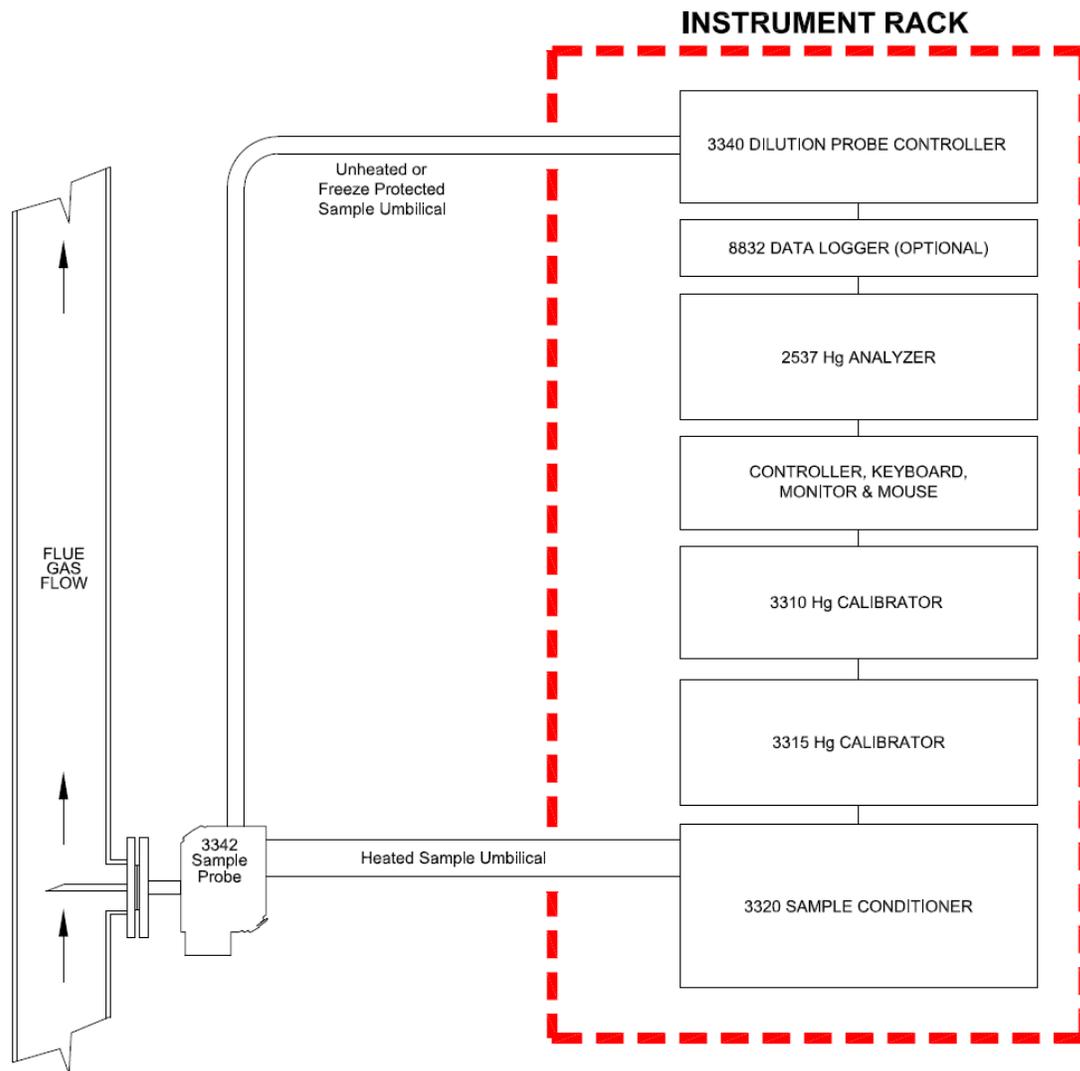
### **2.2.2. Tekran Instruments Hg CEMS**

Tekran Instruments has sold roughly 175 Hg CEMS to power plants plus additional systems sold for the purpose of mercury monitoring for control technology test programs, for research or for other purposes. The Tekran Instruments Hg CEMS, shown schematically in Figure 2-2 has some similarities and some significant differences with the ThermoFisher Hg CEMS; these will be discussed below.

#### **Sample Extraction**

The Tekran probe extracts sample from the stack and dilutes it with air at roughly a 30:1 ratio. The probe is heated. The portion of the probe that is in the gas stream is made of Hasteloy (a corrosion-resistant metal) coated with a thin quartz layer. The probe body is made of coated stainless steel. The filter is titanium. Unlike the Thermo Fisher analyzer, which conditions the sample at the probe, the Tekran sample is sent in its sampled form to the sample conditioner, which is near the analyzer. The sample line from the probe to the sample conditioner is maintained at about 180°C (356°F) to avoid loss of ionic or elemental mercury or plating out of selenium. If selenium were allowed to build up in the sample line, the elemental mercury would be lost in the line because elemental mercury reacts with condensed selenium. If this takes place after the converter, it will result in a low bias for the total Hg measurement. An unheated line is

also used in some cases to carry air for the probe. The unheated line does not carry sample or calibration gas.



**Figure 2-2. Schematic of Tekran Hg CEMS<sup>70</sup>**

**Sample Conditioner**

The sample conditioner converts the oxidized mercury to elemental mercury using a pyritic converter. Also, acid gases (and selenium), which could induce mercury recombination reactions and could adversely affect analyzer reliability, are scrubbed out using deionized (DI) water. The conditioner therefore provides an acid gas-free stream with elemental mercury and other gases to the analyzer. The sample conditioner facilitates speciation by providing one of two gas streams to the analyzer: 1) 100% of the flue gas mercury after having converted any ionic mercury to elemental mercury; and 2) a sample with the ionic mercury removed so that only the elemental mercury from the flue gas remains. Similar to the ThermoFisher analyzer, ionic mercury is determined in the Tekran analyzer by subtracting the elemental mercury concentration from the total mercury concentration.

### CVAF Analyzer

Both the ThermoFisher instrument and the Tekran instrument use CVAF for analysis. However, Tekran's analyzer uses a gold amalgam to collect and concentrate the mercury prior to analysis. This also permits the mercury to be re-released into an inert gas (argon) atmosphere. The argon gas ensures that fluorescence is not quenched by molecular gases that are present in the boiler flue gas. The gold amalgam concentration method and the use of inert gas help the analyzer to provide high sensitivity. The analyzer consumes argon gas; one tank of argon is expected to last roughly six weeks. Like the ThermoFisher analyzer, the Tekran analyzer produces an output concentration of total mercury. Speciation is performed in concert with the sample conditioner.

### Calibrators

The Tekran Hg CEMS has two calibrators – one for elemental mercury and another for ionic mercury. The elementary mercury calibrator produces a gas stream with a known concentration of elemental mercury in a similar manner as the ThermoFisher analyzer – by carefully controlling the temperature and pressure of a sample of mercury and dilution gases to provide a gas with a well-controlled elemental mercury vapor pressure.

Tekran also has an oxidized mercury calibrator, which generates a defined mixture of air and water vapor and mercuric chloride by evaporating a controlled amount of aqueous mercury chloride solution of known concentration into a carefully controlled gas volume, as shown in Figure 2-3. Because this approach starts with oxidized mercury in a NIST-traceable aqueous solution, there is assurance that only oxidized mercury is produced. Also, because the solution and the hardware are NIST-traceable, the amount of oxidized mercury is NIST-traceable. This method of generating oxidized mercury does require transporting the oxidized Hg from the generator, up a heated umbilical to the probe tip, through the probe, and back through a heated umbilical to the sample conditioner for the system integrity check.

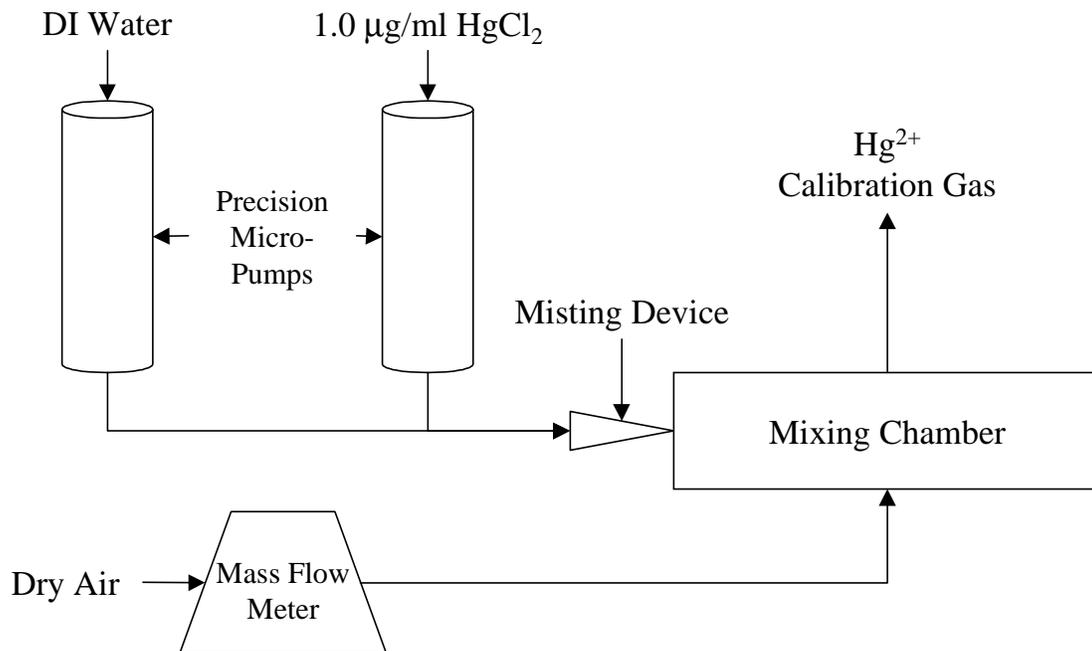


Figure 2-3. Simplified diagram of the Tekran Model 3315 Ionic Mercury Calibrator

### **2.2.3. Other suppliers of Hg CEMS**

Three other suppliers of Hg CEMS have been identified: PS Analytical, Cemtrex and Ohio Lumex. PS Analytical's Sir Galahad mercury CEMS uses an amalgamation method combined with CVAF, the same general method as the Tekran CEMS. The Cemtrex and Ohio Lumex CEMS analyze the gas using the method of atomic absorption spectroscopy (AAS). In AAS, a light source is scanned at a wavelength where elemental mercury vapor absorbs light. The amount of light that is absorbed is related to the amount of mercury in the light path. This Chapter focuses on the results achieved so far with the more widely used ThermoFisher and Tekran analyzers.

### **2.3. Approximate Costs of Hg CEMS**

ThermoFisher and Tekran confirmed that the initial cost of an Hg CEMS is typically on the order of \$500,000.<sup>68,71</sup> These costs include:

- Approximately \$200,000 for system including startup and training;
- Another \$200,000-\$300,000 for site preparation.

Costs will vary somewhat from this \$500,000 figure. The heated umbilical alone is a significant cost item that might cost anywhere from about \$10,000 for a short stack to over \$100,000 for a very tall stack. Other factors that affect cost include the number of Hg CEMS located at the site, site conditions, and local climate.

Typical annual operating costs are more difficult to estimate, because there has been limited experience with the learning curve associated with the use of Hg CEMS and the actual quality assurance (QA) and reporting requirements are not certain. Midwest Generation estimates that it takes three times as many labor hours to support the Hg CEMS as traditional NO<sub>x</sub> and SO<sub>2</sub> CEMS.<sup>72</sup> Using the U.S. EPA's CEMS cost estimating tool, there is roughly \$20,000 in annual plant labor charges for a typical power plant CEMS with NO<sub>x</sub>, SO<sub>2</sub>, opacity, and flow, and total annual costs including Relative Accuracy Test Audits (RATAs), reporting, parts and consumables, and other costs of about \$65,000. The U.S. EPA CEMS cost model<sup>73</sup> would suggest that Midwest Generation's annual labor charges have been in the range of about \$60,000 for the Hg CEMS. Due to the learning curve with these instruments, experience to date should not represent long-term estimates.

According to ThermoFisher, the long-term operating requirements are expected to approach those of the dilution CEMS that most power plants currently have installed for NO<sub>x</sub> and SO<sub>2</sub>.<sup>74</sup> This is consistent with information from Tekran that labor costs should ultimately approach those of the existing NO<sub>x</sub> and SO<sub>2</sub> CEMS; but that total annual costs will be somewhat higher when including RATAs, reporting, parts and consumables, NIST traceability and other costs for a total of about \$100,000 or more.<sup>75</sup> These estimates are based upon the Part 75 mercury monitoring requirements of the vacated Clean Air Mercury Rule (CAMR).<sup>\*</sup> The actual costs of monitoring will depend upon the requirements of any future monitoring rule.

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<sup>\*</sup> On March 15, 2005, EPA issued CAMR to permanently cap and reduce mercury emissions from coal-fired power plants for the first time ever. Included in the rule were mercury monitoring and reporting requirements under Part 75. Appendix K of Part 75 set forth the mercury monitoring and reporting requirements for Sorbent Trap Monitoring Systems. On February 8, 2008, the D.C. Circuit vacated EPA's rule removing power plants from the Clean Air Act list of sources of hazardous air pollutants. At the same time, the Court vacated CAMR. Because the mercury monitoring and reporting requirements were part of CAMR, they too were vacated. EPA is

## **2.4. Operating Issues of Hg CEMS**

Although ambient mercury analyzers have been available and operating well for many years, Hg CEMS for power plant or other combustion exhaust gases are new. There are numerous challenges in accurately and reliably measuring mercury emissions from power plants that do not exist for ambient analyzers. These include:

- Transporting the sample from the stack to the analyzer while preserving sample integrity;
- Measuring small amounts of mercury in the presence of large amounts of combustion gases that may interfere with the measurement;
- Measuring mercury that may exist in multiple chemical forms;
- Having the means to verify the accuracy of the measurement for the purpose of assuring that the instrument is providing reliable measure of emissions compliance; and
- Doing all of this while having a system that is not unduly expensive or difficult to use under the harsh industrial conditions at a power plant.

The suppliers of mercury analyzers have made great progress in addressing these issues. The following sections examine the key issues relating to operation of Hg CEMS, including:

- Reliability;
- Calibration and NIST traceability;
- Measurement bias and bias adjustment factor;
- Accuracy and precision at low concentrations; and
- Availability and data substitution.

### **Reliability**

Because Hg CEMS are fairly new devices, there is reasonable concern regarding the reliability of the devices for power plant applications. In some cases product development has been occurring concurrently with implementation of Hg CEMS at power plants. As challenges associated with these applications have been encountered, design changes have been implemented to address them. Recognizing that these systems have been under development and that some of the problems encountered a few years ago have been addressed, the focus here is on issues that may continue to have an impact on reliability.

### **Umbilical Failure**

The umbilical is the heated sample line(s) from the probe to the analyzer or sample conditioner. It is often several hundred feet long. Failure of the umbilicals has been a problem. Dominion Generation stated that 5 of 13 umbilicals on its Tekran systems installed in Illinois and

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now developing air toxics emissions standards for power plants under the Clean Air Act (section 112), consistent with the D.C. Circuit's opinion regarding CAMR. EPA intends to propose air toxics standards for coal- and oil-fired electric generating units by March 10, 2011 and finalize a rule by November 16, 2011.

Massachusetts had failed.<sup>76</sup> These failures are mostly due to overheating. Midwest Generation noted similar experiences with the umbilicals of its ThermoFisher analyzers installed on boilers in Illinois and Pennsylvania, with 6 of 13 umbilicals failing. Midwest Generation also noted that there were approximately 50 umbilical failures industry-wide.<sup>72</sup> This is roughly consistent with information on umbilical reliability from other sources. Tekran stated that about 10% of umbilicals have failed, which has led to new designs for umbilicals with better temperature control.<sup>71</sup> This is consistent with information from Dekoron/Unitherm, the primary manufacturer of these umbilicals for both Hg CEMS suppliers, who reported a failure rate of 8.4%.<sup>77</sup>

The causes of umbilical failures have varied. According to Dekoron/Unitherm, about half of the failures were field repaired; the balance required replacement. In some cases there was an installation error, as installers were not accustomed to installations of several hundred to a thousand feet of this type of heated and insulated sample line. Failure modes varied from leads being pulled apart during installation, to short circuits of heaters, and in a small number of cases, fires. (Again, according to Dekoron/Unitherm, every one of the cases in which there were fires was the result of faulty installation, i.e., no ground fault protection despite recommendation by the manufacturer and requirements of the National Electric Code.) The other causes of the failures included improper installation, incomplete information at the time of design, defective heater elements (that were ultimately replaced by the manufacturer), and lack of individual and high limit temperature control (a heater controller design issue). To address these causes, there have been design changes to eliminate the failure modes, education of installers to reduce risk of damage during installation or failure upon start up, and education of all parties involved to improve specification, design and installation to reduce risk of failure.<sup>77</sup> In addition, many facilities have installed redundant umbilicals to provide a backup in the event of an umbilical failure.

As a result of the improvements made by the various companies involved in the manufacture, supply and installation of the umbilicals, it is anticipated that umbilical failures should be less troublesome in the future.

### **System Integrity Tests**

System integrity tests exercise the entire sampling, conditioning, analysis, and calibration gas generating system. A shortcoming in any one of the associated components will result in a failed system integrity test. According to Dominion,<sup>76</sup> this was the most frequently failed quality assurance (QA) test. Also, unlike the calibration tests, the system integrity test requires use of oxidized mercury calibration gases, which are more difficult to assure because oxidized mercury is so reactive that it can be lost easily in sample streams after leaving the calibration gas generator (such as in the Tekran instrument), or the conversion rate of elemental to oxidized Hg in the probe (in the case of ThermoFisher) may be difficult to verify. Dominion recorded 80-150 hours of down time per Hg CEMS in 2008 as a result of failed system integrity tests.<sup>76</sup> Dominion has found that it is beneficial to perform the system integrity test manually to ensure that a technician can observe the physical process and identify problems during the test, which has proven to be helpful in avoiding false failures of the test.<sup>78</sup> This is consistent with the experience of Midwest Generating, who reported that its Hg CEMS do not have a good record at passing system integrity tests.<sup>72</sup> At this point, it appears that the equipment associated with the system integrity tests may not yet be at the point where the test can be performed in an automated fashion with high reliability. This affects how the tests can be scheduled because a technician needs to be available to monitor them.<sup>78</sup>

The difficulty of system integrity tests is closely related to the development of NIST traceable oxidized Hg standards, which are explored more fully in the following section.

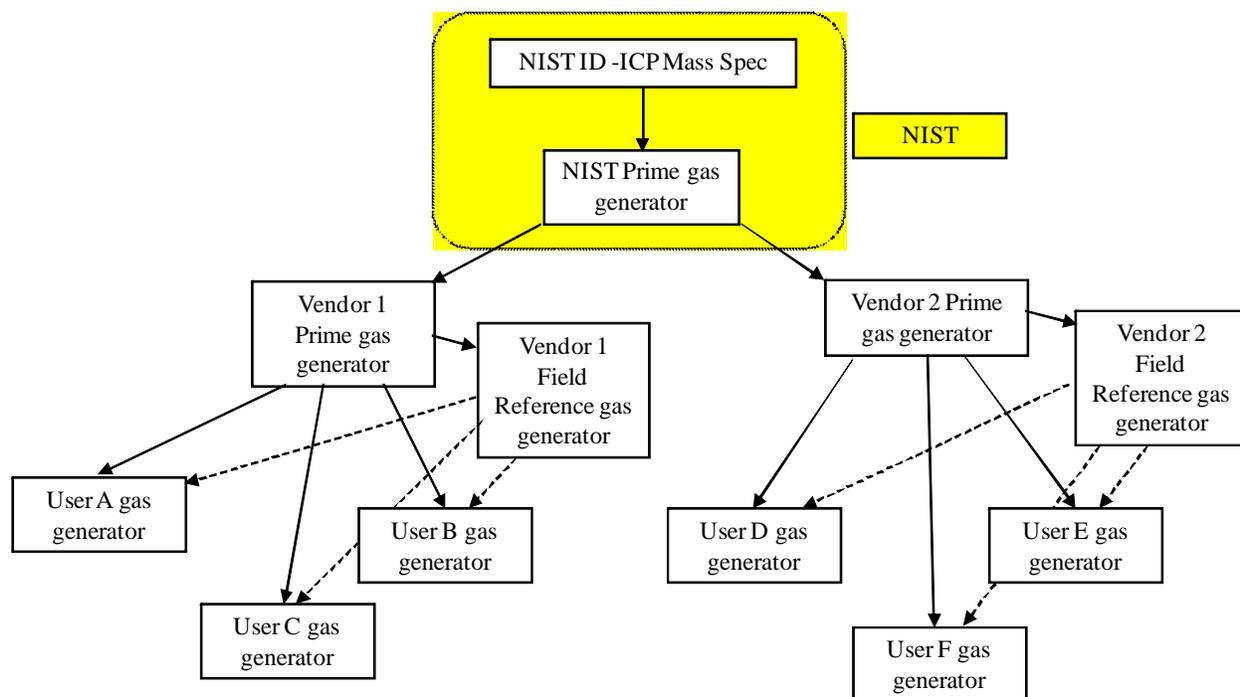
## **Calibration and NIST Traceability**

For regulatory compliance purposes, it is important that emissions monitors provide measurements with accuracy that can be traced back to verifiable NIST standards. This is done through regular calibration checks of the Hg CEMS against gases of a known mercury concentration.

### **Elemental Mercury Calibration Standards**

Traceability of the elemental mercury measurement of each Hg CEMS is to be performed using a calibration gas generator that is certified by NIST. The U.S. EPA has established interim traceability protocols for elemental gas generators, which provide procedures to: “(1) establish the quantitative output of elemental Hg generators; and (2) determine the expanded, combined uncertainty values of the gas standards produced by the elemental Hg generators.”<sup>80</sup> The protocol also specifies the maximum allowable uncertainty for the elemental Hg gas standards. Elemental mercury is also available as a bottled gas, but the U.S. EPA has not yet established traceability protocols for gas cylinders.

The NIST certification is achieved through an unbroken chain of comparison of one elemental mercury calibration gas generator to another and eventually to a NIST-verified standard. An interim traceability protocol has been developed to provide for this and was promulgated by the U.S. EPA on July 1, 2009.<sup>79</sup> In this protocol, NIST uses isotope dilution inductively coupled plasma mass spectrometry (ICP-MS) as the fundamental measurement to certify the NIST Prime elemental mercury calibration gas generator. This NIST Prime calibration gas generator is used to certify Vendor Prime calibration gas generators. The Vendor Prime calibration gas generators are used to certify user calibration gas generators that are sent to the vendors for certification. In cases where a user cannot send in their calibration gas generator to the vendor for certification, a Field Reference calibration gas generator, which is certified against the Vendor Prime calibration gas generator, can be used at the user’s site to certify the user calibration gas generator. Figure 2-4 shows how this approach produces an unbroken chain of measurement comparisons for certification back to a NIST-verified standard.



**Figure 2-4. General approach for elemental mercury calibration gas generator certification**

Certification of gas generators is valid for a period of time, and each calibration gas generator needs to be periodically recertified. The NIST Prime gas generator needs to be periodically recertified against ICP-MS (or another method determined by NIST). Vendor Prime gas generators are periodically sent to NIST for recertification against the NIST Prime gas generator, and User and Field Reference gas generators need to be periodically recertified against the Vendor Prime gas generators. As a result, this will become a regular requirement for all companies involved in mercury monitoring.

### Oxidized Hg Calibration Gas Standards

The interim oxidized Hg NIST traceability protocol was promulgated on July 1, 2009.<sup>80</sup> The interim oxidized Hg gas traceability protocol provides procedures for: “(1) establishing the NIST traceability and quantitative performance of key components of  $\text{HgCl}_2$  generators; (2) determining the uncertainty contributed by each of these components; and (3) calculating certified output concentrations and expanded, combined uncertainty values for the gas standards produced by the generators.”<sup>69</sup> Oxidized mercury must be used for system integrity checks. There are no gas cylinders for oxidized mercury, so the two CEMS manufacturers have developed different generators for oxidized Hg calibration gas.

The ThermoFisher Hg CEMS starts with elemental mercury, transports it to the probe, oxidizes it to  $\text{HgCl}_2$  in the probe using chlorine that is added at that location, and sends the oxidized Hg sample to the probe tip. Certification of the ThermoFisher oxidized mercury generator is related to the elemental gas generator.<sup>81</sup> The combined uncertainty of the  $\text{HgCl}_2$  calibration standards is calculated based on the uncertainty of the elemental Hg generator, the water vapor dilution (if applicable), and the chlorine dilution. In the interim oxidized Hg protocol, the oxidation efficiency of ThermoFisher systems is not included in the overall

combined uncertainty calculation. However, the apparent percent conversion of elemental Hg to HgCl<sub>2</sub> is calculated as part of the periodic QA (data quality) assessments.<sup>82</sup>

For the Tekran's oxidized mercury calibrator that uses an evaporative gas generator, NIST traceability may be achieved in a different manner because NIST-traceable solutions are available and it is possible to verify the precision of the metering pumps, etc., used in the device. For a reason that is not clear, comparisons of this type of oxidized Hg gas generator (Tekran 3315 or any other evaporative type) against elemental gas generators have shown a fairly consistent difference of about 8% to 9%, with the ionic calibrator always producing a lower level. Because of the consistency of this difference, this type of oxidized Hg calibration gas generator can be certified by NIST.<sup>83</sup> This approach does not involve an actual measurement to verify the output concentration, but relies on the calibrated, theoretical value.

### **Measurement Bias and Bias Adjustment Factor**

When a measurement device indicates a different value than a reference method (RM) and that difference is consistent, the difference is regarded as bias. To correct for this difference and make the reported values consistent with the RM, bias adjustments (up or down) may be made. Part 75 requires bias adjustments for SO<sub>2</sub>, NO<sub>x</sub>, and volumetric flow rate monitoring systems, based on data collected during relative accuracy test audits (RATAs), but Part 60 does not require such adjustments.

When compliance is achieved under a trading mechanism, the measurements provide the "currency" used in the allowance market and an excess in emissions can be made up through purchase of allowances in the market. Bias adjustments may, at the discretion of the regulatory agency, be required if the RM shows a consistently higher value than the monitor during the RATA (i.e., the CEMS is biased low) and the difference is statistically significant. The regulatory agency may require the subsequent data from the CEMS to be adjusted upward to agree with the RM; consequently, the reported emissions will be higher than would otherwise be indicated by the monitor. Similarly, downward bias adjustment may be required if the CEMS consistently reads higher than the RM. Under the Acid Rain Program, the U.S. EPA has, since 1993, required bias adjustment of SO<sub>2</sub>, NO<sub>x</sub>, and volumetric flow rate data only in one direction (i.e., upward), to correct for low bias. However, under a compliance mechanism where trading is not an option, there may be an argument to require bias adjustments in both directions, rather than adjusting only for low bias. This is because there is no ability to sell excess allowances or to purchase allowances that are needed. The potential problem if there is no requirement to adjust for low bias is that it could open an opportunity for sources to deliberately adjust their Hg CEMS to read below the reference method, while staying marginally within the percent relative accuracy requirements when performing a RATA. This could result in under-reporting of emissions.<sup>77</sup>

The issue of bias adjustment was raised in testimony before the Illinois Pollution Control Board by representatives of electric generators.<sup>76</sup> The Illinois EPA subsequently agreed to remove bias adjustments from its rule.<sup>85</sup> However, for the most part the Illinois power plants are complying with a percent reduction requirement or alternatively with a technology-based standard and therefore have been given the option of quarterly stack tests rather than Hg CEMS. This is a different situation than would exist with an annual mass emission limit where the argument in favor of bias adjustments is stronger. As a result, the argument in favor of bias adjustments is not as great under Illinois' rule.

## **Accuracy/Precision at Low Concentrations**

Accurate and precise mercury measurements are becoming increasingly important at low mercury concentrations because some APCDs (or combinations of APCDs) are capable of producing removal efficiencies of mercury that can result in emissions concentrations well below  $1.0 \mu\text{g}/\text{m}^3$ . Furthermore, some states have required 90% and greater removal of mercury from flue gases. Accuracy relates to how close the measurement is to the actual number. Precision relates to how repeatable a measurement is at a given level. Both qualities are desirable.

The CVAF method is capable of measuring mercury concentrations at levels far lower than what is seen in flue gas, as demonstrated in its use in ambient monitoring. However, there is some concern regarding its accuracy and precision at low concentrations when it is used to analyze flue gas samples that are transported through a probe, sample line, sample conditioning, etc. Also, there is concern about the ability to verify low Hg concentrations against a RM, such as Ontario Hydro or Method 30B (STs), which may have poorer accuracy and precision at lower concentrations.

As shown in Figure 2-5, Hg CEMS have demonstrated the ability to measure mercury concentrations well below  $1.0 \mu\text{g}/\text{m}^3$  and to agree with the Ontario Hydro Method (the RM) measurements within about  $0.09 \mu\text{g}/\text{m}^3$ . The trend shown indicates good precision when compared against the RM, and an accuracy that has a relatively steady offset that is generally under  $0.10 \mu\text{g}/\text{m}^3$ . Figure 2-6, which shows data taken from a stack with a wet scrubber, shows that good agreement between Hg CEMS and Method 30B has also been achieved at levels well under  $1.0 \mu\text{g}/\text{m}^3$ .

Because the absolute difference between the RM and the Hg CEMS at low concentrations may be a significant percentage of the average RM value, this can be an issue of concern when calculating the percent relative accuracy of the CEMS and when making bias adjustments (if such adjustments are required). If, during a RATA, the measurements are expected to be well under  $1.0 \mu\text{g}/\text{m}^3$ , as shown in Figure 2-5 and Figure 2-6, it may be difficult to achieve a particular relative accuracy (RA) percentage (e.g., 20% RA). Therefore, an alternative RA standard, in terms of the absolute difference between the RM and CEMs mean values is sometimes needed. At these low concentration levels, the error band allowed by the alternative RA specification should be sufficiently large to ensure that well-running instruments will pass the RATAs, yet not so great as to make it impossible to fail the test. In the original requirements under CAMR, the alternative RA specification was  $1 \mu\text{g}/\text{m}^3$  absolute difference. That specification was based on an initial assumption that a low emitting source would have Hg concentrations of about  $5 \mu\text{g}/\text{m}^3$ . At the time CAMR was published, the U.S. EPA could not have anticipated the extremely low Hg concentration levels that have since been observed at many units equipped with wet scrubbers. For concentrations of  $1 \mu\text{g}/\text{m}^3$  or less, the alternative RA specification in the vacated CAMR is obviously too wide; a specification on the order of 0.3 to  $0.5 \mu\text{g}/\text{m}^3$  would appear to be more appropriate.

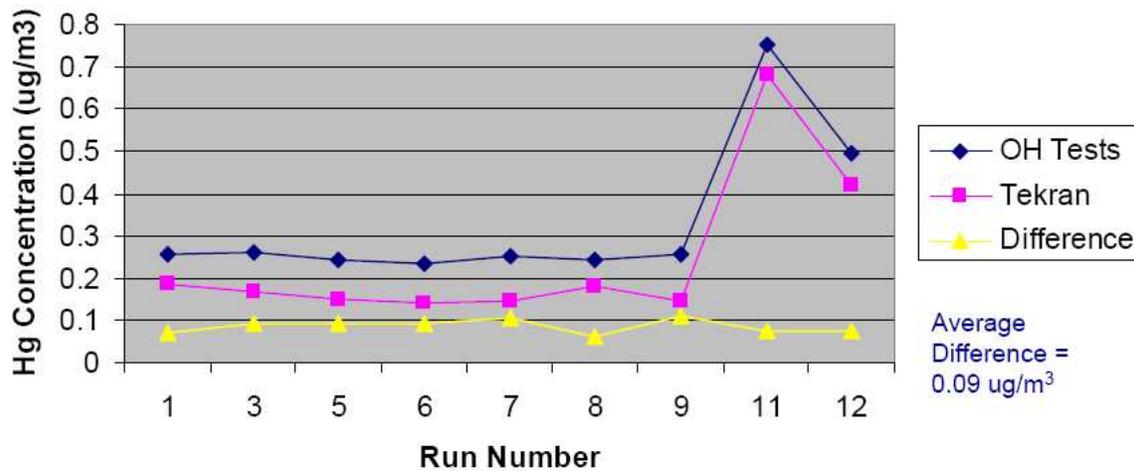


Figure 2-5. RATA results at low mercury concentrations<sup>71</sup>

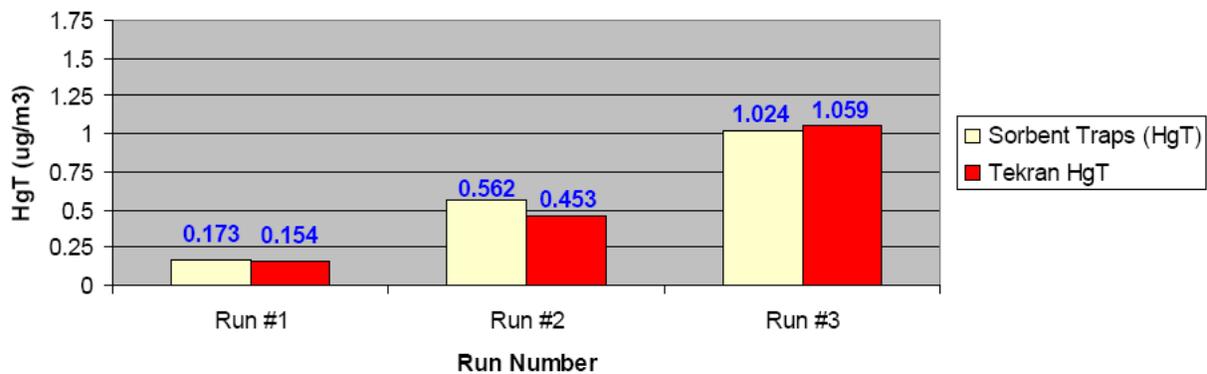


Figure 2-6. Low level Hg CEMS accuracy check against sorbent traps on a stack that follows a wet scrubber or wet stack<sup>71</sup>

### Availability and Data Substitution

Availability is a measure of the number of hours in an operating period that the monitoring system is providing reliable data, and is generally expressed as a percentage of the operating hours. Data substitution is sometimes required for periods in which a monitored facility is operating, but the emissions monitoring system is not providing reliable data (not available). For example, the Acid Rain Program requires substitute data to be reported in the periods of time when the monitoring system is not available. The monitoring requirements under the vacated CAMR required the use of missing data substitution for Hg concentration. The substitute data values became increasingly more conservative (i.e., conservatively high) as the percent monitor data availability (PMA) dropped and the length of the missing data period increased. If the PMA ever dropped below 70%, the maximum potential Hg concentration would have been reported.

Even absent trading, due to the variability in mercury emissions, there is an argument for maintaining high data availability. Mercury emissions are sensitive to many factors that can vary routinely for a power plant, such as furnace oxygen (through its impact on fly ash carbon), soot blowing, coal mercury levels and other factors.

Figure 2-7 shows results of a RATA at Nebraska Public Power’s Sheldon Unit 2. Measured mercury concentrations varied by more than a factor of two over the period of the RATA, comparing an Hg CEMS (shown in figure as HgT) versus sorbent traps as the reference method (shown as 30B). As a result, data substitution can be inaccurate and periods of lost data should be minimized.

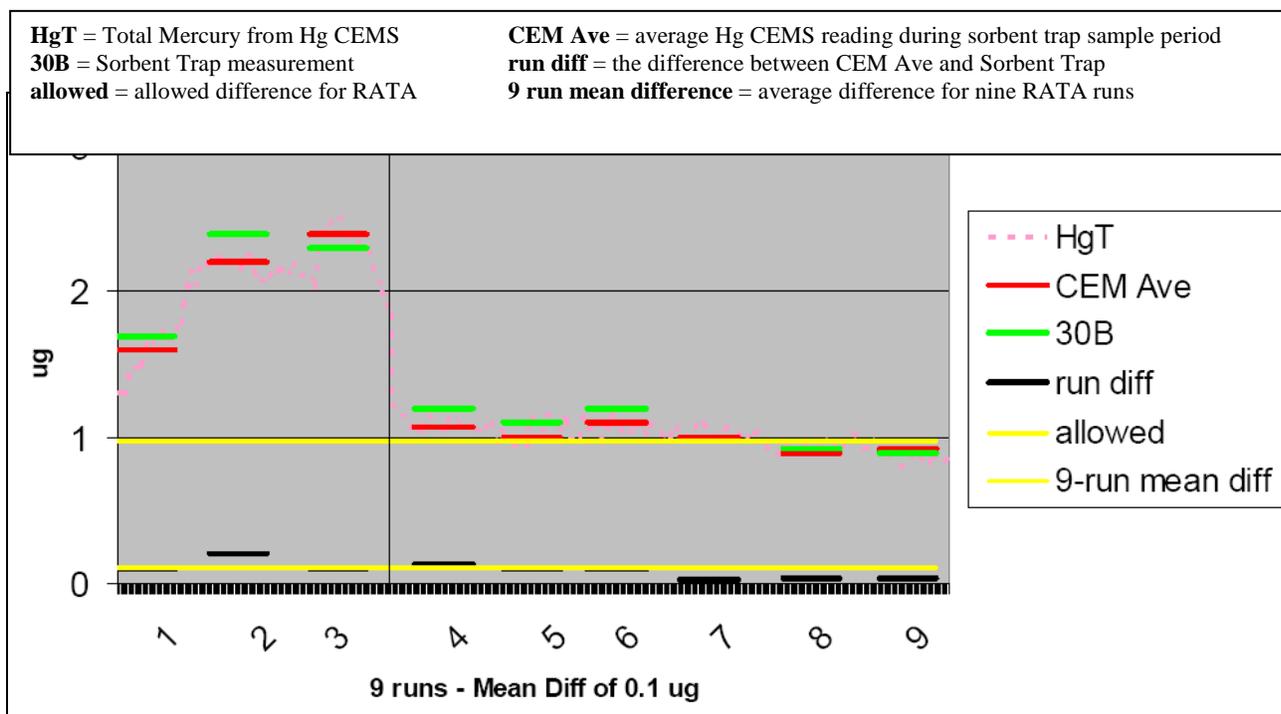


Figure 2-7. Nebraska Public Power Sheldon 2 RATA results<sup>86</sup>

There are several factors that affect Hg CEMS availability, including the following:

- Stringency of Regulation – If QA testing requirements are stringent, then there is likely to be more down time because failure of a QA test will require troubleshooting.
- Technician Skill Level – This will vary from plant to plant. The higher the skill level of the technicians, the faster they will be able to restore an instrument to service in the event of a failure.
- Priority of Preventive Maintenance (PM) Program – Is the PM program at the plant a management priority that has adequate resources? If not, then maintenance in general for all equipment will be poor and uptime will suffer.

- Spare Parts Stocking – If spares are on hand, the instrument can be restored to service faster than if parts must be ordered.

According to ThermoFisher, customers that are conscientiously operating and maintaining the equipment, even with no current reporting requirements, have been able to keep the instruments operational about 90-98% of the time.<sup>33</sup>

Availability is a concern for new technology. Although few states require reporting of availability, Massachusetts did request that the coal plants in Massachusetts report availability of their Hg CEMS. As shown in Table 2-1, the Hg CEMS at the Brayton Point station reported availability ranging from 88% to 94%.<sup>87</sup> The Mount Tom generating station reported 98% availability.<sup>88</sup>

Strictly speaking, the reported availability statistics in Table 2-1 for Hg CEMS in Massachusetts are not subject to the Part 75 requirements of CAMR because those requirements were vacated when the CAMR was vacated. Also, there are some aspects of the original Part 75 CAMR that have since evolved out of technical necessity, particularly with regard to the move to on-site calibration gas generators that will be NIST-traceable rather than use of NIST-traceable compressed gas cylinders. The reported data are not QA-tested by the Massachusetts Department of Environmental Protection (DEP) in exactly the same manner as the U.S. EPA would have done under a Part 75 requirement because the U.S. EPA – who has the capability to perform Part 75 data QA - lost the authority to perform data QA when CAMR was vacated. According to the Massachusetts DEP,<sup>89</sup> the Massachusetts requirements under 310 CMR 7.00 et al. are otherwise identical to those of the now-vacated Part 75 CAMR requirements. The units in Massachusetts must undergo the same daily calibration checks, weekly system integrity checks, quarterly linearity checks, RATAs, and other requirements of the now vacated Part 75, and these availability statistics and the good quality emissions data being generated are a strong indication of the industry’s efforts and ability to operate Hg CEMS.

**Table 2-1. Availability of Hg CEMS at Dominion Brayton Point power plant in 2008<sup>86</sup>**

		Quarter 1	Quarter 2	Quarter 3	Quarter 4	Overall
Unit 1	Operating Hours	1,536	2,076	2,102	2,159	7,873
	Out of Service Hours	96	223	87	52	458
	Availability, %	93.7	89.3	95.9	97.6	94.2
	Year-to-date Availability, %	93.7	91.17	92.89	94.2	
Unit 2	Operating Hours	2,184	2,116	1,994	2,208	8,501
	Out of Service Hours	140	123	415	346	1,024
	Availability, %	93.6	94.2	79.2	84.3	88.0
	Year-to-date Availability, %	93.6	93.88	89.23	88.0	
Unit 3	Operating Hours	2,170	1,422	1,929	2,072	7,593
	Out of Service Hours	359	253	55	104	771
	Availability, %	83.5	82.2	97.1	95.0	89.8
	Year-to-date Availability, %	83.5	82.96	87.92	89.8	

Missing data are normally substituted under a Part 75 system because trading programs rely on knowing the total mass emissions. Under a rule where a percent reduction or implementation of a specific control technology is required, it could be argued that data substitution may not be necessary. On the other hand, in the case where there is a mass emissions limit, it could be argued that data substitution should be performed to ensure that mass

emissions are not under-reported. Also, data substitution for missing data provides motivation for maintaining a high availability of the instrument.

## **2.5. Sorbent Trap Method**

### **2.5.1. Sorbent Trap Method Description**

The ST method is an approach to measuring total mercury emissions over a period of time. The continuous measurement method was addressed by Appendix K of the Part 75 requirements of the now vacated CAMR. The U.S. EPA Method 30B has replaced Appendix K and is a reference method that can be used for RATAs as well as for monitoring. The ST method is pictured in Figure 2-8. Gas is drawn through two separate traps concurrently. Two traps are necessary for the purpose of quality assurance, and agreement must be within prescribed levels or the sample fails QA. The two traps can be installed within the same probe or in separate probes. The mercury traps must also be installed in the probe such that gas is pulled directly into the traps. The method assumes that there is not a significant concentration of particulate matter in the flue gas. A common trap sorbent material is activated carbon impregnated with iodine or another halogen, such as bromine. For continuous monitoring each trap must have the sorbent configured into three sections that can be tested independently. The first section is for primary mercury collection. The second section is to provide an indication of mercury breakthrough. If there is too much breakthrough, the sample fails QA. The third section is for spike recovery testing using a spiked mercury sample gas. Analysis of the third section must show good recovery of the spiked sample for acceptable results. After a period of sampling, the traps are removed and analyzed to measure the total amount of mercury in the traps. The mercury found in the traps divided by the total gas flow over the period of the sampling indicates mercury concentration in the gas.

The balance of the sampling system includes a moisture removal system, dry gas flow pump, and dry gas flow meter (or other equivalent mass flow equipment), and related instrumentation. The flow meter and associated instrumentation (barometer and temperature indication) must be regularly calibrated to ensure that they are reporting the correct volume of gas. The flow meter must also have a variable flow control to maintain sample flow rate in proportion with load.

Because of the QA requirements that could cause a sample to be rejected, most users replace traps every four to seven days. This assures that if a sample is rejected for QA reasons, only four to seven days of data are lost.<sup>90</sup>

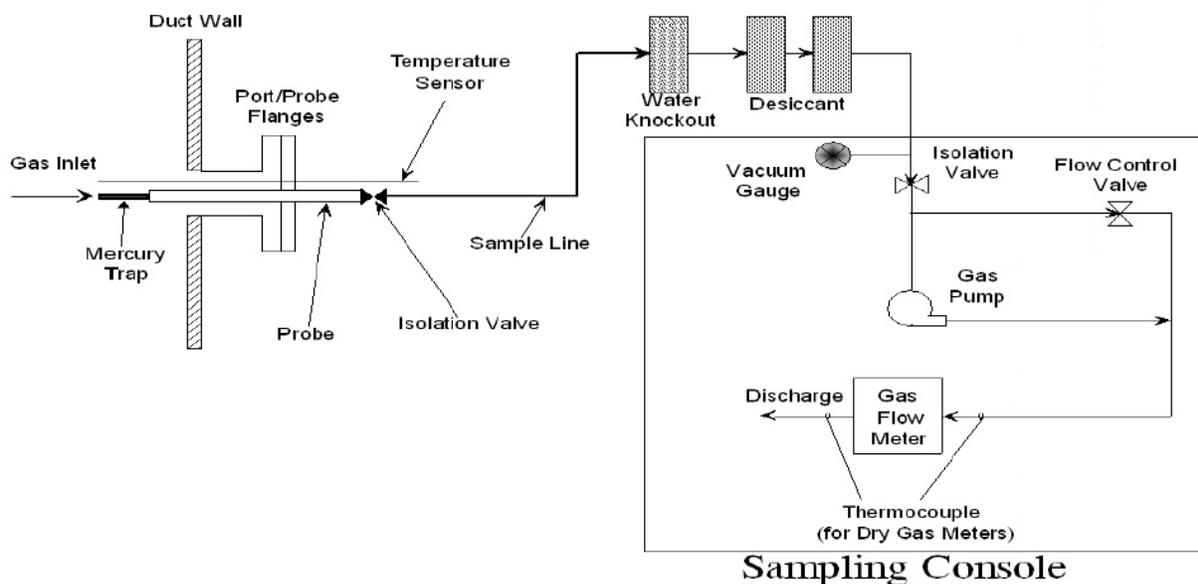


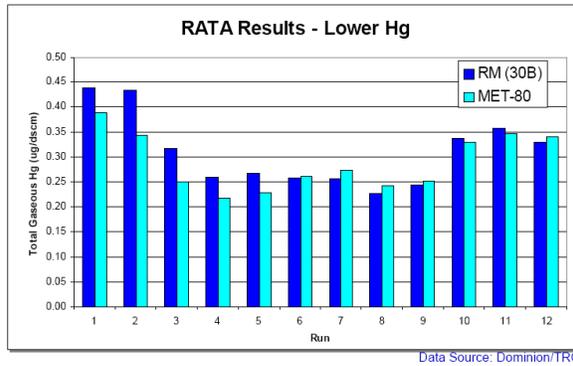
Figure 2-8. Method 30B sorbent trap equipment<sup>91</sup>

The two most widely used approaches to analyzing the traps for mercury are: 1) a wet digestion method using atomic absorption or fluorescence analysis; and 2) thermal release with atomic absorption analysis. The latter approach can be done on site with the proper equipment. However, it has the disadvantage that the sample is destroyed, so that if there is a problem with the analysis it cannot be checked again.

Sorbent traps can be used as a reference method against a CMMS or as a CMMS. Sorbent trap requirements as CMMS were defined under CAMR as Appendix K. As a reference method, STs are the U.S. EPA Method 30B. Because it is used as a reference method, Method 30B has different QA requirements than Appendix K in terms of spike recovery, etc., and is somewhat different in procedure.

### 2.5.2. Sorbent Trap Accuracy/Precision

The ST method for measuring mercury generally has good measurement accuracy down to relatively low mercury concentrations well under  $1 \mu\text{g}/\text{m}^3$ . This can be influenced by sample time, trap size and other parameters that the user can control depending upon their needs. Figure 2-9<sup>92</sup> and Figure 2-10<sup>93</sup> show results from six different RATA's from six different power plants, in each case (a), (b) and (c) showing results for low concentrations (under  $1 \mu\text{g}/\text{m}^3$ ), moderate concentrations (about  $1 \mu\text{g}/\text{m}^3$ ), and higher concentrations (over  $1 \mu\text{g}/\text{m}^3$ ), respectively. Relative accuracy can be more difficult at the lower concentrations because there appears to be more variation in concentration on a percent of value basis at these low levels of mercury. The sorbent trap CMMS in the figure being compared to a sorbent trap reference method (Method 30B) follow the Appendix K protocol. In these cases both sorbent trap methods (either Appendix K or Method 30B) were being drawn at the same time. Therefore, in each case there was a comparison of total mercury collected in the traps over the same period.

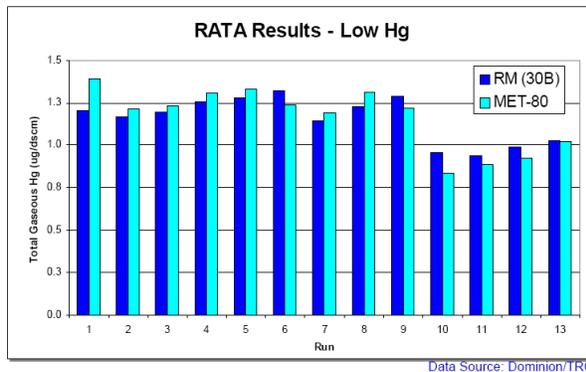


> Bit.Coal  
Unscrubbed  
CMMS: MET-80  
AppK Traps: FGS  
AppK Anlys: EPA 1631  
30B Traps: FGS  
30B Anlys: EPA 1631

Data Source: Dominion/TRC

Relative accuracy = 13%

(a)

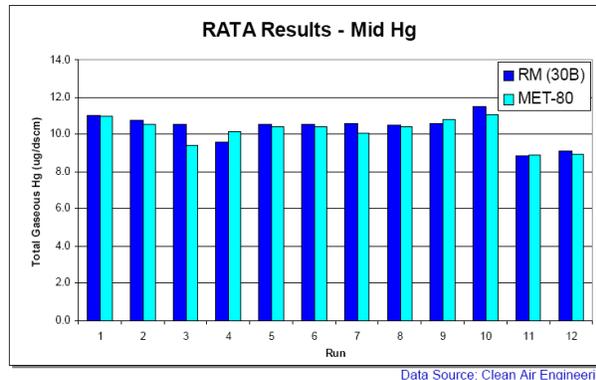


> Bit.Coal  
Unscrubbed  
CMMS: MET-80  
AppK Traps: FGS  
AppK Anlys: EPA 1631  
30B Traps: FGS  
30B Anlys: EPA 1631

Data Source: Dominion/TRC

Relative accuracy = 4.5%

(b)



> Eastern Bit.Coal  
Unscrubbed  
CMMS: MET-80  
AppK Traps: SKC  
AppK Anlys: Thermal  
30B Traps: OH Lumex  
30B Anlys: Thermal

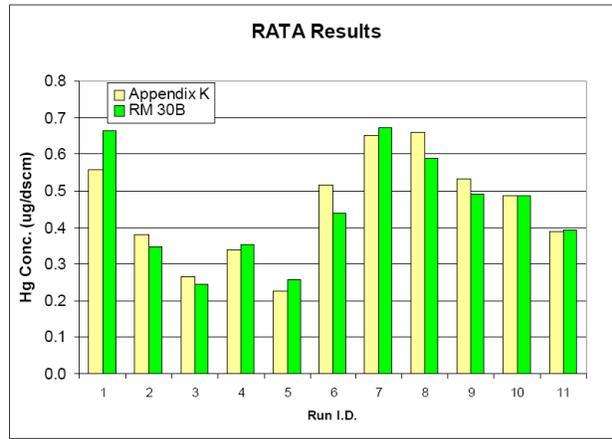
Data Source: Clean Air Engineering

Relative accuracy = 2.3%

(c)

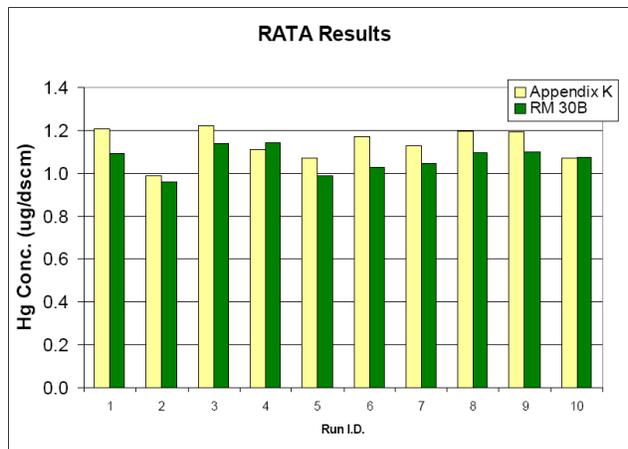
Figure 2-9. RATA results reported by Wright and Schmid<sup>92</sup> with (a) concentrations under 1 µg/m<sup>3</sup>; (b) concentrations near 1 µg/m<sup>3</sup>; and (c) concentrations over 1 µg/m<sup>3</sup>

RM = 0.43  $\mu\text{g}/\text{m}^3$   
Diff = 0.035  $\mu\text{g}/\text{m}^3$   
RA = 8.2%  
No Bias



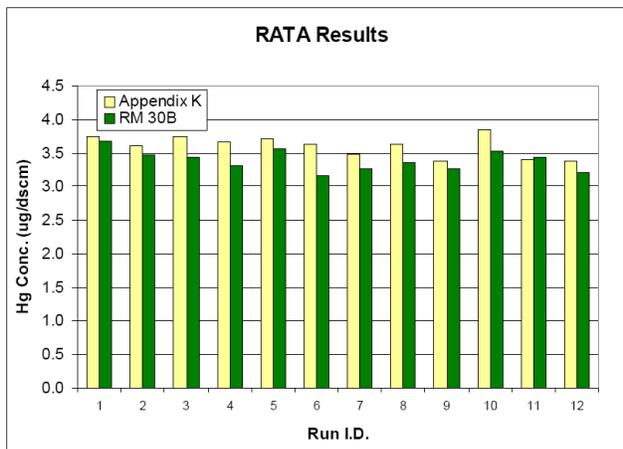
(a)

RM = 1.07  $\mu\text{g}/\text{m}^3$   
Diff = 0.06  $\mu\text{g}/\text{m}^3$   
RA = 9.3%  
No Bias



(b)

RM = 3.4  $\mu\text{g}/\text{m}^3$   
Diff = 0.16  $\mu\text{g}/\text{m}^3$   
RA = 7.4%  
No Bias



(c)

Figure 2-10. RATA results reported by Wright<sup>93</sup> with (a) concentrations under 1  $\mu\text{g}/\text{m}^3$ ; (b) concentrations near 1  $\mu\text{g}/\text{m}^3$ ; and (c) concentrations over 1  $\mu\text{g}/\text{m}^3$

## **2.6. Approximate Costs of Sorbent Trap Systems**

The initial installed cost of a sorbent trap system is on the order of \$150,000. Operating costs entail roughly \$500 to \$700 per week for traps and analysis (\$26,000 to \$36,000 per year).<sup>66,75</sup> The cost of labor for operating the traps corresponds to about two people for half a day per stack every four to seven days.<sup>93</sup> At \$50/hr for labor, that is roughly another \$21,000 to \$36,000 per year.

## **2.7. Advantages/Disadvantages of Sorbent Traps When Compared to Hg CEMS**

The advantages of STs versus Hg CEMS are:

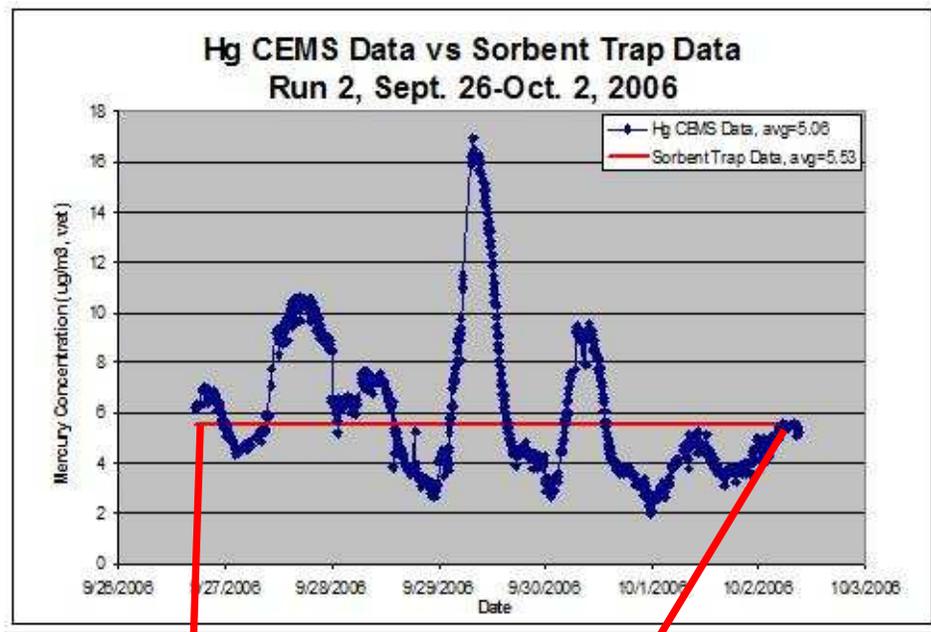
- Significantly lower capital cost - The principal advantage of STs over Hg CEMS is much lower capital cost – about \$150,000 versus about \$500,000.
- Simpler system to operate and maintain – Sorbent trap systems are less complex than Hg CEMS and do not require as sophisticated a technical staff to support. However, the personnel involved in STs do need training on how to properly handle the traps to avoid contamination and other problems that could introduce errors.
- Lower concentrations - In principal, STs may be able to measure to lower concentrations than Hg CEMS, but this is very methodology dependent. Furthermore, Hg CEMS are improving their ability to measure to low levels such that any advantage in this respect may be small.

Disadvantages of STs versus Hg CEMS are:

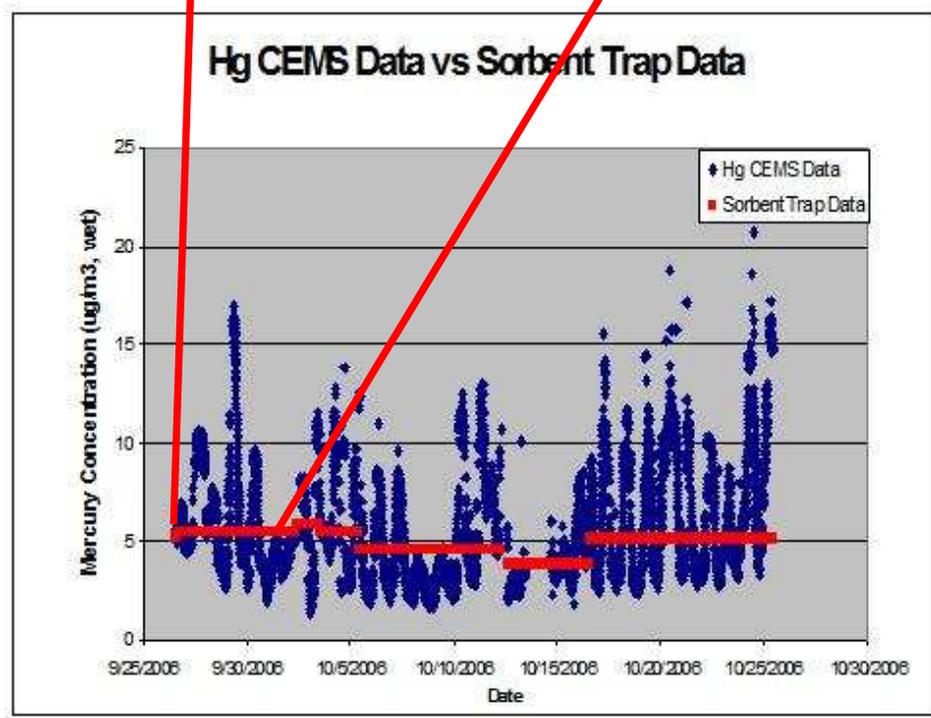
- No real-time, or near real-time data – This is the principal technical advantage of Hg CEMS over STs. The information is available in minutes, which enables the performance of Hg emission control processes to be monitored in near real time and can thereby offer advantages in Hg control. Figure 2-11 shows how Hg CEMS data and ST data compare at one facility equipped with a wet scrubber over a period of 5 days and 30 days, respectively. As shown, there was a wide variation in Hg emissions that was not evident in the ST results, since the latter were inherently averaged over the trap sample time.
- Higher Labor Costs - This may not have been realized yet since Hg CEMS have been coming down a fairly steep learning curve, which means that owners have had to dedicate more hours to service and support than they ultimately will in the future. Sorbent traps, on the other hand, will always require regular trap replacement and testing (typically every four to seven days) and the labor associated with replacing and testing the traps is not likely to drop very much.
- Loss of Data – If there is a problem with a ST sample, it may not be discovered until after the sample is completed, and when ST samples fail the quality control tests, the data are lost for the full sampling period. For this reason, ST systems have quality control procedures in place to minimize this risk, and in practice samples are limited to about four to seven days. For Hg CEMS the existence of a problem that would cause lost data is generally apparent right away, so that

corrective action can be immediately taken to restore the instrument to a fully functioning state.

- Personnel Safety – STs require that personnel regularly go up to the sampling point to remove and replace sorbent traps. This creates an added concern for personnel safety.
- Speciation – Although only total Hg emissions would have been reported under the vacated Part 75 CAMR requirements, oxidized Hg and elemental Hg do behave differently in terms of capture and in terms of how they behave once released to the environment. Therefore, there is a benefit with respect to emissions control and with respect to understanding environmental impact in having speciated Hg emissions information. Although speciated Hg measurement approaches are available using STs, they are difficult to conduct due to the reactivity of oxidized mercury. Additionally, there is limited experience with taking speciated ST measurements.
- Process Steps - There can be many people and steps necessary to assure a good measurement; a mistake at any point in the process could introduce error.
- Hazardous Wastes - Hazardous wastes can be generated from the analysis methods that need to be disposed of in accordance with procedures for handling and disposing of hazardous materials.
- Trap Analysis - The analysis of the trap (thermal desorption or wet chemical analysis) destroys the sample, so that it can not be checked in the event of an analysis error.



(a)



(b)

Figure 2-11. Hg CEMS performance compared with Sorbent Traps<sup>94</sup>

## 2.8. Availability of Sorbent Traps used as CMMS

Because reporting of Hg monitoring data has not been required in many states, there are limited data on reported availability of the method. However, information on short-term experience (under six months) using Part 75 availability requirements has shown availability generally over 90%. Figure 2-12 shows availability data over several months for eight different STs. Also, as shown in

Table 2-2, year-long data from Dominion reported to Massachusetts on its Salem Harbor Units 1 through 3 CMMS show availability of 89% to 96%.<sup>94</sup>

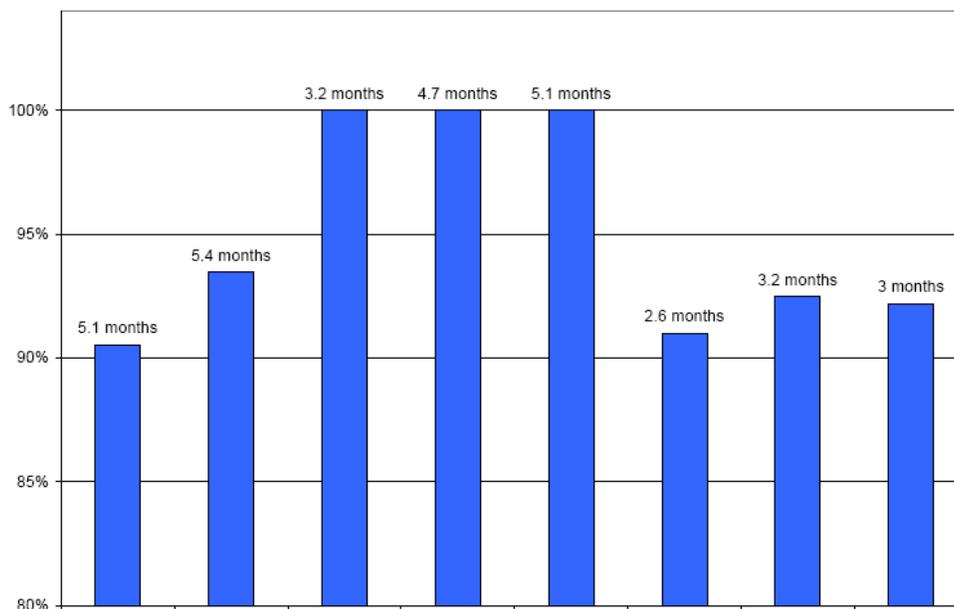


Figure 2-12. Sorbent Trap availability reported by Wright and Schmid<sup>96</sup>

Table 2-2. Availability information for Dominion Salem Harbor Units 1, 2, 3 CMMS<sup>94</sup>

	Unit 1	Unit 2	Unit 3
Online operating hours	5,922	6,209	3,620
Monitored hours	5,263	5,587	3,480
Total operating hours of downtime	659	622	140
Availability	89%	90%	96%
Missing data caused by:			
Monitor not operated*	269	82	0
Monitor malfunction/maintenance	12	74	129**
Trap QA/QC***	360	429	0
Trap change out	5	17	3
Monitor calibration	13	12	8

\* Early in the monitoring program the monitor operating parameters (e.g., vacuum, trap flow) were not well enough understood to use as predictive information to change out traps in a timely manner to avoid the monitor shutting down on its own. Automated alerts were not sufficient. The issue has since been resolved.

\*\* One recurring maintenance issue caused the bulk of this downtime. The issue has since been resolved.

\*\*\* Initially the sorbent traps were not able to sample for longer than three days due to a loss of spike recover. In June 2008, the design of the traps was improved, which allowed the duration of the run to increase. Subsequently, data loss due to trap quality assurance/quality control (QA/QC) has been greatly reduced.

### **Strictly speaking, the reported availability statistics in**

Table 2-2 for the STs in Massachusetts are not subject to the Part 75 requirements of the CAMR because those requirements were vacated when the CAMR was vacated. And as discussed previously, some changes from the original Part 75 CAMR protocol have been made out of technical necessity. In other words, these changes would have occurred even if CAMR were still in place. According to the Massachusetts DEP,<sup>89</sup> the Massachusetts requirements under 310 CMR 7.00 et al. are otherwise identical to those of the now vacated Part 75 CAMR requirements, and these availability statistics and the good quality emissions data being generated are a strong indication of the industry's efforts and ability to use STs for the continuous monitoring of mercury emissions.

## **2.9. Approximate Number of Units Installed/In Operation**

According to ThermoFisher, over 450 of its Hg CEMS systems have been shipped to date. Of the 450, more than 160 systems were installed directly by ThermoFisher, and the balance of the Hg CEMS were installed by CEMS system integration companies – other companies that purchase the analyzer from ThermoFisher and install it at the customer's site. Because the manufacturers, ThermoFisher and Tekran, sell spare parts, provide service, and in many cases monitor instruments remotely, they can estimate the number of Hg CEMS in operation. Of the total 450 Hg CEMS, ThermoFisher estimates that about 375 are actively in operation in the U.S.<sup>33</sup> About 75 of the ThermoFisher systems are not active at least in part because some owners do not currently have a need to monitor mercury emissions and are choosing to avoid the cost of operating the systems. According to Tekran, of the 175 systems sold, approximately 140 are in operation and 100 have completed RATA testing. The balance of the systems represents later orders that are still in the process of installation and startup.<sup>75</sup>

In 2009, NESCAUM surveyed nine states and one city as to the purchase and usage of Hg CMMS. These data are summarized in Table 2-3. In these states, 116 CEMS and 44 ST systems had been purchased. Most of the CEMS (73%) were installed and operating, but only a third of the ST systems were installed and operating. Half of the states required the collection of Hg emissions data and information on the availability of the CMMS.

A CMMS being active does not mean that the company is reporting data. The reason many companies operate Hg CMMS (even without a current requirement to operate them or to report data) is because of the anticipated need to do so in the future and the benefit gained from the experience of operating them prior to facing a regulatory requirement.

With few exceptions, RATA tests and other tests such as system integrity tests have been performed for the purpose of verifying that the systems met their contractual performance requirement rather than an emissions reporting requirement imposed by a regulation. Therefore, the results of these tests are not publicly available unless they were published in a paper or other forum.

**Table 2-3. NESCAUM 2009 survey of Hg CMMS in nine states and one city**

<b>Data Summary</b>	
Number of states surveyed	9
Number of cities surveyed	1
States/city collecting Hg data	5
States collecting monitoring reliability/availability data	4
<i>Hg CEM Prevalence</i>	
CEMS purchased	116
CEMS installed	99
CEMS operating	85
<i>ST Prevalence</i>	
STs purchased	44
STs installed	20
STs operating	14
<i>Number of Units Sold per Vendor:</i>	
Thermo Fisher Hg CEMS	34+
Tekran Hg CEMS	9+
Apex STs	5
Frontier Geosciences STs	1
<i>Monitors' First Year of Use</i>	
2006	3
2007	1
2008	41+
2009	28+

## 2.10. Summary

This Chapter examined the technologies for continuous monitoring of mercury emissions from power plant stacks, including continuous analyzers, or mercury CEMS and sorbent trap methods. Both Hg CEMS and STs are currently being applied to over 700 coal-fired power plant stacks, with over 600 Hg CEMS and about 100 STs.

The findings of this Chapter with regard to Hg CEMS are summarized below:

- Hg CEMS, at roughly \$500,000 of capital cost per site (with some variation due to site specifics), are the more costly of the two approaches to install, but offer advantages that are listed below. There has been a significant learning curve with Hg CEMS, with the technology advancing rapidly and many of the technical challenges that existed with the technology only a few years ago having been addressed.
- Many issues affecting reliability of Hg CEMS have been addressed, and it is expected that design changes implemented over the past few years as Hg CEMS have been installed will improve reliability going forward. Although only a small percentage of Hg CEMS have reported annual emissions data to state agencies,

the reported availability is 90% or greater. In other states, power plant owners may be operating Hg CEMS in anticipation of requirements to report such data; however, official availability statistics have not been made available from these states. As more state mercury emission rules take effect, more data should become available.

- Accuracy at low mercury levels has improved. Data indicate that Hg CEMS may offer reliable measurements to well below  $1.0 \mu\text{g}/\text{m}^3$ , which is important for situations where Hg emission controls are in place.
- Mercury calibration gas standards (generators) that are traceable to NIST measurements have been developed. Interim calibration protocols have been established.

The findings of this Chapter with regard to ST methods are summarized below:

- Sorbent traps, at about \$150,000 of capital cost per site (with some variation on this cost due to site specifics), are a lower capital cost alternative to Hg CEMS. However, STs require regular replacement and testing (roughly every four to seven days) of the sorbent traps, which entails additional labor and cost that will continue at that level.
- Although only 3 of the more than 100 installed STs have reported annual emissions data to state agencies (Massachusetts), the reported availability has been 90% or greater. As more state mercury emission rules take effect, more availability data should become available.
- STs appear to offer reliable measurements to well below  $1.0 \mu\text{g}/\text{m}^3$ , which is important for situations where Hg controls are in place.
- In addition to lower capital cost, STs offer the advantage of requiring less sophisticated technical support than that needed for Hg CEMS.
- Hg CEMS offer results in minutes, while STs offer information in days.

### **3. Conclusions**

#### **3.1. Outlook for Control Technologies**

Two general approaches for mercury control have, to date, proven capable of effectively reducing mercury emissions at levels of control of 90% or greater on combinations of coal type and APCDs that represent the majority of coal-fired boilers. These approaches involve use of either existing APCDs or dedicated mercury control technology, primarily powdered activated carbon injection.

There are cases where the co-benefit of existing APCDs alone may be capable of greater than 90% reduction in mercury, but this is not universally true even for similar plant/fuel configurations. The use of oxidation additives or dedicated mercury catalysts has been demonstrated to increase the removal of mercury by wet FGD systems, which is the leading method of obtaining removal of high levels of mercury with existing APCDs.

Powdered activated carbon (PAC) is the most widely used mercury sorbent, and in the majority of coal-fired power plants, injection of PAC can achieve mercury removal of 90% or greater. In order for activated carbon to achieve such high levels of removal, special sorbents have been developed for low-halogen environments, for environments with high concentrations of SO<sub>3</sub>, for plants in which fly ash is sold for concrete manufacture, etc. Different methods of introducing activated carbon into flue gas have also been developed, including the Mer-Cure™ process and the TOXECON™ and TOXECON II™ processes.

The combination of a wet scrubber and an FGD has demonstrated mercury removal in the range of 70% to 90% on plants burning high-sulfur bituminous coal. Activated carbon has been shown to be cost-effective for high levels of mercury removal at boilers with a cold-side ESP or baghouse that burn low-sulfur bituminous coal, subbituminous, or lignite coal, as long as the plant does not use flue gas conditioning with the ESP. The U.S. GAO, in its report to Congress,<sup>20</sup> concluded:

While sorbent injection technology has been shown to be effective with all coal types and on boiler configurations that currently exist at more than three-fourths of U.S. coal-fired power plants, DOE tests show that some plants may not be able to achieve mercury reductions of 90% or more with sorbent injection systems alone.

The situations that the U.S. GAO identified as falling short of 90% mercury reduction with sorbent injection alone were: plants burning lignite, plants with hot-side ESPs, and plants with high levels of SO<sub>3</sub> in the flue gas.

Lignite burning coal plants are not a very large category, comprising approximately 3% of the boilers greater than 25 MW in size in the U.S. Sorbents are currently under development specifically for lignite-fired boilers.

Hot-side ESPs are the only particulate control device on about 9% of boilers; these boilers burn both bituminous and subbituminous coals. There have been a limited number of full-scale demonstrations of activated carbon specifically designed for hot-side ESPs. Unless sorbents can be found that are effective at temperatures greater than about 700°F, the best current control option for hot-side ESPs would be to install a fabric filter for use with sorbent injection.

High levels of SO<sub>3</sub> are produced at plants that burn high-sulfur bituminous coal (defined as greater than 1.7 wt% sulfur) or that have an SCR and burn bituminous coal. At present, only 17% of boilers burn high-sulfur bituminous coals. Some of the plants that burn high-sulfur bituminous coal have both an SCR and an FGD, and this combination of APCDs might achieve 90% Hg removal. The high-sulfur bituminous plants that have a cold-side ESP or FF without both SCR and FGD make up only 11% of the US boiler population. This percentage is expected to shrink in the next several years as more bituminous-fired plants install advanced NO<sub>x</sub> and SO<sub>2</sub> controls. Injection of alkaline sorbents, like trona, can be used to reduce SO<sub>3</sub> in the flue gas and improve the performance of activated carbon. Furthermore, new carbon-based mercury sorbents are being developed that are tolerant of higher levels of SO<sub>3</sub>.

The other category of plants that have relatively high levels of SO<sub>3</sub> are plants burning low-sulfur bituminous, subbituminous or lignite coal with cold-side ESPs that require flue gas conditioning to meet limits on stack opacity. Approximately 24% of boilers with cold-side ESPs use flue gas conditioning, which represents 15% of the overall boiler population. As noted above, SO<sub>3</sub>-tolerant sorbents are being developed to address the difficulty in achieving 90% mercury removal in these systems. Trona injection has been proposed as an alternative to SO<sub>3</sub> as a flue gas conditioning agent and there are other alternative flue gas conditioning agents under development. Another, but more expensive alternative, is to install a fabric filter after the ESP and to inject the sorbent into the fabric filter.

Another consideration in the implementation of activated carbon injection for mercury control is the potential loss of revenue for plants that sell their fly ash for concrete manufacture. Plants that fire low-rank coal and sell their fly ash represent about 23% of boilers in the U.S., while 21% of plants that fire bituminous coal sell their fly ash. Forty-two percent of the fly ash sold in the U.S. goes toward the production of concrete. Adding enough activated carbon to achieve 90% removal can ruin the economic value of the fly ash, if the fly ash is sold for concrete manufacture. The Mer-Cure™ process, which requires low activated carbon injection rates to achieve high levels of removal, might allow for the sale of fly ash. Several sorbent vendors offer activated carbon that is specially treated to allow the fly ash-sorbent mixtures to be made into acceptable concrete. An alternative is to segregate the fly ash collection from the sorbent collection by using the TOXECON™ or TOXECON II™ configurations.

Regarding the cost of mercury controls, the detailed, test data-based NETL cost analyses compared well with the recent U.S. GAO survey-based costs for sorbent technologies (ACI). Sorbent-based Hg reduction costs should range between about \$6000/lb to \$30,000/lb when by-product contamination/sales are not a factor and between about \$18,000/lb and \$50,000/lb if ash revenue is lost (note that ash revenues/losses can vary greatly across geographical areas and its impact can deviate from these values depending on site-specific market conditions). These estimates correspond to 20-year levelized COE of 0.35 to 2 mills/kWh and 1 to 3.5 mills/kWh respectively. Capital costs for sorbent injection technologies were found to be in the \$5/kW to \$15/kW range, while special applications, such as fabric filter-based TOXECON™, are likely to cost \$120/kW to \$150/kW.

Mercury oxidation technologies, catalysts and additives primarily used in wet FGD plants have lower capital costs, about \$1-\$2/kW for additives and \$2-\$4/kW for catalysts. Twenty-year levelized COE is under 1 mill/kWh for additives and between 1 and 2 mills/kW-hr for catalyst technologies.

### **3.2. Outlook for Measurement Systems**

CMMS are currently deployed on a subset of coal-fired power plants in the U.S. There are two types of CMMS: 1) CEMS, which measure mercury in the gas phase using CVAF or AAS, and 2) STs, which collect mercury on substrate and then analyze the mercury in the substrate after collection.

Hg CEMS, at roughly \$500,000 of capital cost per site, are the more costly of the two approaches to install. Many issues affecting reliability of Hg CEMS have been addressed, and it is expected that design changes implemented over the past few years as Hg CEMS have been installed will improve reliability going forward.

Although only 5 of the more than 600 Hg CEMS have reported annual emissions data to state agencies, they have reported availability of about 90% or greater. In other states power plant owners may be operating Hg CEMS in anticipation of requirements to report such data; however, official availability statistics have not been made available from these states. As more state mercury emission rules take effect, more data should become available.

There has been a significant learning curve with Hg CEMS with the technology advancing rapidly. Many of the technical challenges that existed with the technology only a few years ago have now been addressed. Accuracy at low mercury levels has improved. Data indicate that Hg CEMS may offer reliable measurements to well below  $1.0 \mu\text{g}/\text{m}^3$ , which is important for situations where Hg emission controls are in place. Calibration gas standards and calibration gas generators that are traceable to NIST measurements have been developed. Interim calibration protocols have been established.

Sorbent traps, at about \$150,000 of capital cost per site, are a lower capital cost alternative to Hg CEMS. However, STs require regular replacement and testing (roughly, every four to seven days) of the sorbent traps, which entails additional labor and cost that will continue at that level. Thus, the operating costs of STs might be higher than those of Hg CEMS.

Although only 3 of the more than 100 installed STs have reported annual emissions data to state agencies (Massachusetts), the reported availability is 90% or greater. As more state mercury emission rules take effect, more availability data should be reported. STs appear to offer reliable measurements to well below  $1.0 \mu\text{g}/\text{m}^3$ , which is important for situations where Hg controls are in place. In addition to lower capital cost, STs offer the advantage of requiring less sophisticated technical support than that needed for Hg CEMS.

The choice between Hg CEMS or STs for continuous mercury monitoring will be influenced by a number of factors that are specific to a particulate plant. Hg CEMS offer results in minutes, while STs offer information in days. If information on Hg emissions is desired on a daily basis in real-time, then a CEMS are a better choice. At present, Hg CEMS require more technical training and sophistication for the operator than STs, although this distinction might fade as manufacturers of CEMS improve the product offerings. The level of technical training of plant personnel is therefore an issue in selecting a CMMS. Sorbent traps are able to measure mercury with good accuracy to well below  $1.0 \mu\text{g}/\text{m}^3$ . If the mercury concentration in the stack is well below  $1.0 \mu\text{g}/\text{m}^3$ , then an ST system is at present a better choice. As Hg CEMS vendors continue to improve the detection limits of the instruments, this distinction might disappear in the future. Finally, the capital and operating costs of the two approaches might also influence the decision for a power plant.

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