WASTE ISSUES RELATED TO MERCURY CONTROL

The mercury control strategy implemented at a facility may have an effect on: 1) the quantity of waste produced by a facility, 2) the mercury content of the waste produced, and 3) the physical properties of the wastes produced, including the chemical availability of mercury. The Department believes that there are currently, and will continue to be, safe options for the disposal and/or management of waste generated from coal-fired power plants. The Department will consider issues such as landfill capacity and ultimate fate of mercury, including water quality and coal ash re-use options, as it proceeds with developing a mercury standard. A more detailed discussion of these issues can be found in Appendix D.

SUMMARY

The Department plans, pursuant to the requirements of 310 CMR 7.29, to propose a mercury emissions standard for power plants within six months of the date of this report. In doing so, it will rely, in part, on the technical information presented herein. The Department has completed a review of the scientific and technological research relating to mercury control in order to assess the current state of methods and technologies for reducing mercury emissions. While the Department's review is not exhaustive as to either the current research or the applicability of all technologies to the affected facilities, the Department's thorough review of an extensive number of studies and reports has allowed it to draw conclusions relating to the feasibility of mercury emission reduction and controls.

There is substantial evidence that some technologies are currently available and that additional technologies will be available for implementation at the affected facilities in order to meet the proposed compliance date of October 1, 2006. The Department believes that there is strong evidence to conclude that the capture of at least 85-90+% of flue gas mercury is technologically and economically feasible for coal-fired power plants at the present time. The Department is not concluding that each of the affected facilities will be required to achieve 85-90+% capture of flue gas mercury; nor is the Department making any determination as to the appropriate level or form of the mercury standard that will be proposed. The Department will consider multiple factors, including the contents of this report, when it proposes standards for mercury emissions from Massachusetts' power plants.

UNITS AND ACRONYMS

AC – activated carbon
ADA-ES – ADA Environmental Solutions, LLC
ADP – acid dew point
AECDP – Advanced Emissions Control Development Program
APCD – Air Pollution Control Device
BUD – Beneficial Use Determination
°C – degrees Celsius
Ca – calcium
$CaSO_4$ – calcium sulfate
CCR – Coal Combustion Residue
CEMS – Continuous Emissions Monitoring System
CFBA – circulating fluidized-bed absorber
Cl – chlorine
CMR – Code of Massachusetts Regulations
CO_2 – carbon dioxide
COALQUAL – National Coal Resources Data System, US Coal Quality Database
COHPAC – compact hybrid particulate collector
CS-ESP – cold-side electrostatic precipitator
CVAAS – Cold Vapor Atomic Abortion Spectroscopy
DEP – Massachusetts Department of Environmental Protection
DOE – Department of Energy
DOE/NETL – DOE National Energy Technology Laboratory
DSI – dry sorbent injection
E-beam – electron beam radiation
ECP – Eastern Canadian Premiers, Emission Control Plan
EDTA – ethylene diamine tetra-acetic acid
EPA – Environmental Protection Agency
EPRI – Electric Power Research Institute
ESP – electrostatic precipitator
ETV – Environmental Technology Verification
°F – degrees Fahrenheit
FF – fabric filter
FGD – flue gas desulfurization
FGR – flue gas recirculation
g – gram
H_2S – hydrogen sulfide
H_2SO_4 – sulfuric acid
HCl – hydrochloric acid
Hg – mercury
Hg^0 – gaseous elemental mercury
Hg^{2+} – gaseous oxidized mercury
Hg_p – particle-bound mercury
Hg_T – total mercury
$HgCl_2$ – mercury chloride
HNO_3 – nitric acid
HS-ESP – hot-side electrostatic precipitator
ICR – information collection request
IGCC – integrated gasification combined cycle
kW – kilowatt

lbs/hr – pounds per hour
LNB – Low NO_x Burners
LOI – Loss On Injection
MA – Massachusetts
MACT – Maximum Achievable Control Technology
µg – microgram
mg/L – milligrams per liter
MW – megawatt
MWC – municipal waste combustor
MWe – megawatt electrical
N_2 – nitrogen
NAS – National Academy of Sciences
NEG – New England Governors
NESCAUM – Northeast States for Coordinated Air Use Management
NH_3 – ammonia
NO – nitric oxide
NO_2 – nitrogen dioxide
N_2O_4 – nitrogen tetroxide
N_2O_5 – nitrogen pentoxide
NO_x – oxides of nitrogen
O_2 – oxygen
O_3 – ozone
OH – Ontario Hydro method
P2 – pollution prevention
PAC – powdered activated carbon
PC – pulverized coal
PCD – pollution control device
PM – particulate matter
ppm – parts per million
PRB – Powder River Basin coal
PS – particulate scrubber
RA – Relative Accuracy
RACT – Reasonably Available Control Technology
RATA – Relative Accuracy Test Audit
RCRA – Resource Conservation and Recovery Act
SC – spray cooling
SCR – selective catalytic reduction
SDA – spray dryer absorber, semi-dry absorption
SNCR – selective non-catalytic reduction
SNO_x – trade name emission control technique
SO_2 – sulfur dioxide
SO_3 – sulfur trioxide
TCLP – EPA Toxicity Characteristic Leaching Procedure
US – United States
USGS – United States Geological Survey
WFGDS – wet flue gas desulfurization system

APPENDIX A: MERCURY CONTROL AND CONTROL TECHNOLOGIES

1. Introduction

The Department has reviewed the scientific and technological research relating to mercury control in order to assess the current state of methods and technologies for reducing mercury emissions. While the Department's review is not exhaustive as to either the current research or the applicability of all technologies to the affected facilities, the Department's thorough review of an extensive number of studies and reports has allowed it to draw conclusions relating to the feasibility of mercury emission reduction and controls.

2. Background

Mercury is a naturally occurring impurity in coal in trace amounts. It generally occurs in several forms and is associated with both inorganic minerals in coal (i.e., the materials that generate ash when the coal is burned) as well as with the organic fraction in coal (i.e., the carbon portion of the coal that generates heat).

2.1 Coal Types and Coal Preparation

In the United States, coals are classified based on the geological age of the coal and the conditions under which the coal was formed (i.e., the degree of metamorphism), and are divided into four major categories called “ranks.” Each rank is further subdivided into groups. The basic classification criteria are coal heating value, volatile matter content, carbon content, and agglomerating behavior. These coal ranks are: anthracite, bituminous, subbituminous, and lignite. The combustion properties and the characteristics of the coal combustion byproducts depend on coal properties. The Massachusetts coal-fired facilities subject to 310 CMR 7.29 burn bituminous coal.

According to a study that evaluated the Hg content of coals representing major coal producing regions in the United States (using the USGS COALQUAL database), the average concentration of Hg in the (in-ground) coal samples ranged from 0.08 to 0.22 µg/g. The data show that the Hg content of coals is not constant but varies depending on the coal deposit. Also, the Hg content of the coal is not a function of the coal rank.

The Hg concentrations in different coals cannot be directly related to the amount of Hg emitted from boilers burning these coals. In other words, one cannot conclude that burning a coal with higher as-mined Hg concentration will necessarily result in higher Hg emissions from a coal-fired electric utility boiler in the absence of applying any Hg emissions controls. Other coal properties as well as how the coal is prepared prior to firing in a boiler (i.e., coal cleaning) affect the theoretical potential level of Hg emissions.

After coal is mined, it is often first processed at a coal preparation plant to remove mineral matter (i.e., a source of coal combustion ash) and mineral bound sulfur (pyrite). This “coal cleaning” increases the heating value of coal and produces a coal with certain combustion specifications. A portion of mercury and other trace metals that are associated with the mineral fraction of the coal are also removed by the coal cleaning process.

Mercury reduction in the coal cleaning process is believed to be a function of the type of process used to clean a given coal and the proportion of Hg in the coal that is present in combination with pyrite. The existing commercially available coal cleaning methods remove only a portion of the Hg associated with the non-combustible mineral matter in the coal; they do not remove the Hg associated with the organic carbon structure of the coal (i.e., the material that generates the heat during the combustion process). In some coals, large portions of Hg are associated with the organic fraction of the coal. Hg removal in these cases is expected to be substantially lower.

2.2 Mercury Speciation in Coal Combustion Systems

As coal is burned in an electric utility boiler, due to the high temperatures in the coal combustion process, mercury (Hg) contained in coal volatilizes[21] to form gaseous elemental mercury (Hg^0). In the subsequent cooling of the combustion gases, the interaction of the elemental mercury with other combustion products results in a portion of the mercury being converted into gaseous oxidized forms[22] of mercury (Hg^{2+}) and particle-bound mercury (Hg_p).[23] Thus, mercury exists in elemental, oxidized, and particulate-bound forms in coal combustion gas. The term *speciation* is used to denote the existence of mercury in various forms and the relative amounts of these three forms of mercury in the flue gas. The total mercury in flue gas (Hg_T) is the sum of Hg_p, Hg^{2+}, and Hg^0.

The particulate-bound form of mercury can be readily captured in the particulate matter (PM) control devices, i.e., electrostatic precipitators (ESPs) and fabric filters (FFs). The predominant oxidized mercury compounds in coal flue gas are water-soluble, and the more soluble species can be generally captured in wet flue gas desulfurization (WFGD) scrubbers. Elemental mercury is insoluble in water and cannot be captured in wet scrubbers. Both elemental and oxidized mercury adsorb onto porous solids such as fly ash, powdered activated carbons (PAC), or calcium-based acid gas sorbents for subsequent collection in a PM control device. Oxidized mercury is generally easier to capture by adsorption than elemental mercury.

The control of flue gas mercury depends on mercury speciation. Factors that affect the speciation and capture of mercury in coal-fired combustion systems include: the type and properties of coal, the combustion conditions, the types of flue gas cleaning technologies employed, and the temperatures at which the flue gas cleaning systems operate.

2.3 Other Factors Affecting Hg Speciation

The amount of mercury present in the flue gas and its speciation depends on the coal type and its properties. In addition to different levels of mercury, different coals contain different levels of other trace elements and chemical constituents. Chlorine, calcium oxide/carbonate, and iron oxide content of coal can affect mercury oxidization.[24] Additionally, the quality of the fly ash (such as pore structure and carbon content) and its mercury adsorption capacity depend on the type of coal. Combustion and the operational conditions, as well as the gas cleaning technologies employed, affect the physical and chemical properties of the system and thus influence mercury speciation. The level of unburned carbon left in the fly ash, the temperature and residence time of the exhaust gas in the particulate control device, and the presence of oxygen (O_2), ozone (O_3), and acid gases (HCl, SO_2, NO, NO_2) in the flue gas are among factors that impact mercury speciation.

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[21] Essentially most of the mercury in coal is volatilized (as elemental mercury) and negligible amounts are left in the solid residue from the gasification process (i.e., bottom ash).

[22] The extent of oxidation varies and has a broad range, and can vary from <10% to as high as 70% of the total mercury upstream of the control device (Ref. 1).

[23] Both oxidized and elemental forms of mercury may be adsorbed onto the particulates present in the combustion gases to form particulate-bound mercury. In this document, oxidized and elemental mercury refer to their vapor-phase forms unless specifically stated otherwise.

[24] It is believed that calcium oxide/carbonate reduces mercury oxidation.

Many basic physical and chemical phenomena affecting mercury speciation and adsorption are not well understood yet. However, basic and applied research to develop insight into these fundamental processes has been undertaken and is in progress.

2.4 Overview of Control Strategies

The pollution control devices (PCDs) that are utilized on coal-fired utility boilers for reducing NO_x, SO_2, and PM affect mercury speciation and are effective in reducing mercury emissions to varying extents. New technologies that specifically aim at addressing mercury emissions have recently been under investigation and development. Additionally, certain conventional air pollution technologies that have not been traditionally employed in control of emissions from coal-fired utility boilers (such as wet electrostatic precipitators) have recently received attention and are under evaluation for their potential in application to mercury emissions reduction. The mercury control issues, the different approaches to reducing mercury emissions, and the various control technologies are further discussed in the following sections.

2.5 Challenges in Control Of Mercury Emissions

Control of mercury emissions from coal-fired utility boiler flue gas poses a more challenging problem compared to SO_2 and NO_x due to the following factors:

- Low concentration – Mercury concentrations in utility boiler flue gas are significantly (4-5 orders of magnitude) (typically 0.01 vs. 100+ ppm) lower compared to concentrations of SO_2 or NO_x (Ref. 2, 3). The interaction of mercury with sorbents is essentially limited by mass transfer.[25] Addressing this issue has proved technically challenging.

- Presence of chemical speciation and different physical forms – In contrast to NO_x and SO_2, which are mostly present in gaseous form in the flue gas, mercury exists both in vapor (as elemental and ionic mercury) and particulate forms. Because current control technologies and technologies under development do not have the same capture efficacy on different mercury forms, an understanding of the physical and chemical apportionment of mercury in the system is essential in development and deployment of control systems. It is also important to understand physical and chemical interactions of mercury at various points in the boiler unit.

These issues have been under investigation by researchers and are being addressed in the development of mercury control technologies.

3. Pollution Control Options

In general, two approaches can be adopted to reducing mercury emissions from coal-fired utility boilers: pollution prevention[26] (P2) and post combustion pollution control. Pollution prevention, in some cases, involves commercially available technologies, which do not require capital investment (e.g., using cleaned coal with lower mercury content, or fuel-blending in place of using coal alone for facilities that allow this option). Pollution prevention has been cost effective in SO_2 control for some facilities and this may be the case for mercury control as well.

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[25] Mass transfer refers to the ability of the sorbent particles to contact the Hg in the flue gas.

[26] Pollution prevention aims at reducing or eliminating the pollutant at the source. Options such as energy efficiency and power plant production efficiency improvement fall under pollution prevention approach but are not specifically discussed in this document.

Many of the conventional post combustion control technologies used on coal-fired power plants to control SO_2, and PM have the co-benefit of reducing Hg emissions. Certain NO_x control technologies (such as Low-NO_x burners (LNB) and selective catalytic reduction (SCR) in certain plant configurations) enhance mercury removal. A combination of some of these control devices[27] can achieve high (above 95%) mercury control.

A number of mercury-specific control technologies are under investigation and several of these have reached more advanced stages of testing (i.e., pilot- and full-scale tests in coal-fired utility plants) and development. At least one mercury-specific control technology (powdered activated carbon injection) has the potential for commercialization in the near future. Additionally, several post combustion multi-pollutant technologies are being developed. Several of these multi-pollutant technologies have been tested in pilot-scale tests. One multi-pollutant technology (Electron Beam Irradiation) has been commercially available since the 1980s and is currently used in Japan and China. The commercial demonstration of another multi-pollutant technology (Power Span's ECO^{TM}) has been planned.

In the following sections, the pollution prevention options and post combustion control technologies for mercury control are presented. The status of each technology with regards to its testing and demonstration has been noted in these discussions.

3.1. Pollution Prevention

Two pollution prevention options are available: fuel switching, and additional coal cleaning. Advanced coal cleaning technologies are available and can achieve further reduction of mercury in coal (30% to >60% reduction in mercury content of coal). However, depending on the required level of mercury control, coal cleaning alone may not be sufficient to achieve the mercury emissions reduction objectives of a facility. Use of post-combustion control technologies may be necessary in conjunction with coal cleaning. Fuel switching/blending has the potential to reduce other pollutants in addition to mercury. Improvements in generation and power plant efficiency can also reduce the mercury emission rate per unit of power generated, and should be explored, although these options will not be discussed here in detail.

Fuel Switching

Mercury emissions can be reduced by limited fuel switching (generally not more than 10 to 20% of fuel) or installation of new gas-fired units or integrated gasification combined cycle (IGCC) units. The mercury reduction is incremental and limited to the difference in the mercury emissions of the two fuels. Installation of new gas-fired units or IGCC units would result in significant reduction of Hg and co-benefits in reductions of other pollutants. Co-firing or switching to natural gas may be an option for some facilities. Major considerations in switching to natural gas are: the availability of natural gas, the differential cost of natural gas versus coal, and the configuration of the existing units.

Coal Cleaning

Reducing the amount of mercury in the coal that is burned in electric utility boilers reduces the level of mercury emissions from these boilers. Also, for two coals with the same mercury content but different heating values, burning the coal that has a higher heating value would reduce the mercury emitted in boiler combustion gases per unit of electricity output because less coal would be burned in the boiler on a mass basis to produce a given electricity output. However, most coal-fired plants have a limited range of

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[27] Such as a combination of SCR (for NO_x control) and WFGD (for SO_2 control) systems.

fuel properties (e.g., heating value, ash content, sulfur) that are acceptable. Consequently, replacing the coal type may not be feasible in all cases.

Coal cleaning can reduce the Hg content of the coal fired in the boiler. Approximately 80% of bituminous coals from mines in the Eastern and Midwestern United States are cleaned prior to shipment to an electric utility power plant. The subbituminous and lignite coals from mines in the Western United States are not routinely cleaned; however, these types of coals can also be cleaned. Currently, the available data on the level of Hg removed by conventional coal cleaning methods is limited. It has been estimated that conventional coal cleaning results in an average mercury reduction of about 37 percent (Ref. 1).

Mercury concentration of the coal can be further reduced by advanced coal cleaning technologies (30 to greater than 60 percent (Ref. 1). The combination of conventional with advanced coal cleaning technologies removes from 40 to 82 percent of the Hg contained in samples of raw coal according to the results of bench scale studies (Ref. 2).

In the conventional coal cleaning processes, separation of the organic fraction of the coal from the mineral materials is based on the density or surface characteristics of the different materials. Several advanced physical coal cleaning processes are now being developed that use selective agglomeration or column froth flotation.

Microcel™ and Ken-Flote™ are two types of commercially available new coal cleaning technologies that are based on column froth flotation techniques. Microcel™ is available through ICF Kaiser and Control International and has been sold for commercial operation in Virginia, West Virginia, and Kentucky.

Under DOE-funded bench scale studies, advanced coal cleaning processes that use naturally occurring microbes and mild chemical treatments to reduce the mercury content of coal have been investigated and indicate potential for further reduction of mercury. However, DOE has viewed these processes as potentially high-cost control technologies and is not currently funding development of these types of coal cleaning technologies (Ref. 2).

In the near-term, some reduction of the Hg content in certain coals is achieved by physical coal cleaning processes. As mentioned previously, the extent of mercury removed from coal in the cleaning process depends not only on the process used to clean a given coal but also on the proportion of Hg in the coal that is present in combination with mineral matter (pyrite). Because there is a variation in mercury content and its form of association in the coals of even the same rank, coal deposits or coal types that would reliably benefit from cleaning with respect to reducing Hg content cannot be easily identified. Additionally, significant quantities of Hg will remain in the coal after cleaning. Consequently, although coal cleaning can be used as a mercury reduction technique, it is very probable that use of post combustion control techniques would be necessary to achieve additional levels of reduction in mercury emissions. Advanced coal cleaning technologies are being developed and can achieve further reduction of mercury in coal but do not offer the potential of significant additional reductions in the near term.

The coal cleaning processes transfer the mercury that is removed from coal to the coal cleaning wastes. Proper management of the mercury in this waste is necessary. Waste issues are addressed later in this document.

3.2. Post Combustion Control Options

Flue gas cleaning technologies that are applied on combustion sources employ three basic methods to capture mercury:

- Capture of particulate-bound mercury in particulate matter control devices,
- Adsorption of elemental and oxidized mercury onto entrained sorbents for subsequent capture in particulate matter control devices; and
- Solvation of oxidized mercury in wet scrubbers.

Most of the new technologies under development use measures to enhance mercury capture through one of these methods or a combination of them. The currently available (conventional) air pollution control technologies and their impacts on mercury reduction, the new technologies under development specifically for mercury control, and the technologies aimed at multi-pollutant control are discussed below.

3.2.1. Conventional Control Technologies

The pollution control devices that are commercially available and can be utilized on coal-fired utility boilers for reducing sulfur dioxide (SO_2), nitrogen oxides (NO_x), and particulate matter (PM) affect mercury speciation and emissions. A number of these control systems (alone or in combination) can significantly reduce mercury emissions (in some cases above 95%).

The extent to which an existing post combustion control device is effective in mercury capture depends on mercury speciation at the inlet to the control device and the type of technology used in that device. In general, various types of coal, owing to the variation in their constituents, generate combustion gases with different levels of oxidized mercury and coal ashes with different mercury adsorption capabilities. A control device can itself affect the speciation of mercury. Consequently, the overall level of mercury control in a system depends on the combination of the control devices used as well as on the boiler and the coal type effects.

Combustion of bituminous coal results in a flue gas that contains moderate to high levels of Hg^{2+}. In contrast, subbituminous and lignite coals typically generate relatively low concentrations of Hg^{2+} and high concentrations of Hg^0 in the flue gas. The bituminous coals contain relatively high concentrations of chlorine and lower amounts of alkaline material (calcium and sodium) compared to both subbituminous and lignite coals. The high chlorine concentration in the bituminous coal is believed to result in the oxidization of Hg^0 to form Hg^{2+}, primarily $HgCl_2$. The flue gas from combustion of subbituminous and lignite coals tends to have relatively low concentrations of Hg^{2+} because chlorine in the flue gas of these coals tends to react with the alkaline materials resulting in little, if any, chlorine being available for the oxidization of Hg.

The oxidization of Hg^0 can occur from gas-phase reactions or gas/solid reactions with fly ash (and sorbents when these are injected into the system) or surface deposits in power plants. The unburned carbon in fly ash can oxidize Hg^0 or adsorb gas-phase Hg.[28] $Hg^{2+}$is believed to be more readily captured by adsorption than Hg^0.

As a result of US EPA's coal-fired utility boiler Information Collection Request (ICR), which was undertaken in anticipation of the utility MACT standards development by EPA, certain mercury related data has been collected from a number of coal-fired utility boilers. The average total mercury emission reductions obtained from the EPA ICR data for boiler units with pulverized coal type burner and various conventional post combustion control technologies are summarized in the following table.

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[28] The properties of the ash, which are dependent on the coal type, affect this oxidization and adsorption. The fly ash from lignite and subbituminous coals is more effective in this oxidization/adsorption process.

Table A-1. Mean mercury reduction for pulverized-coal-fired boilers.[29]

Post-combustion Emission Controls Used for Pulverized Coal Boiler		Average Total Mercury Emission Reduction (%)(a)		
		Bituminous Coal	Subbituminous Coal	Lignite Coal
PM Control Only	CS-ESP	36 %	3 %	-4 %
	HS-ESP	9 %	6 %	not tested
	FF	90 %	72 %	not tested
	PS	not tested	9 %	not tested
PM Control and Spray Dryer Adsorber	SDA + ESP	not tested	35 %	not tested
	SDA + FF	98 %	24 %	0 %
	SDA + FF + SCR	98 %	not tested	not tested
PM Control and Wet FGD System	PS + FGD	12 %	-8 %	33 %
	CS-ESP + FGD	75 %	29 %	44 %
	HS-ESP + FGD	49 %	29 %	not tested
	FF + FGD	98 %	not tested	not tested

Key: (a) Mean reduction from test 3-run averages for each PC boiler unit in Phase III EPA ICR database.
CS – cold side; ESP – electrostatic precipitator; FF – fabric filter; FGD – flue gas desulfurization; HS – hot side; PM – particulate matter; PS – particulate scrubber; SDA – spray dryer absorber; SCR – selective catalytic reduction.

Massachusetts coal-fired utility boiler units that are subject to the provisions of 310 CMR 7.29 regulations have pulverized coal boilers and burn bituminous coal. These facilities do not currently have, and are not expect to deploy in future, HS-ESP and/or PS particulate control devices (due to lower control efficiencies of these systems). The ICR data indicates that, for pulverized coal boilers burning bituminous coal and excluding units with the PS and HS-ESP control systems, the emission reductions averages range from 36% to 98% nationwide. The different types of post-combustion air pollution control devices (for PM, SO_2, and NO_x) and their impacts on mercury capture are discussed below.

3.2.1.a. PM Control Devices

Particulate control devices are used to capture particulate matter and reduce the opacity of air emissions from utility boilers. A PM control device can readily capture the particulate-bound form of mercury. Gaseous mercury (both Hg^0 and Hg^{2+}) can potentially be adsorbed on fly ash and subsequently be collected in a PM device. The level of this adsorption depends on the speciation of mercury, the flue gas concentration of fly ash, and the properties of fly ash. It is currently believed that mercury is primarily adsorbed onto the unburned carbon in fly ash (Ref. 2). The concentration of the unburned carbon in the fly ash depends on the type of the coal fired and the coal burner type. The use of low NO_x burners tends to increase the amount of unburned carbon and the potential for capturing gas-phase Hg. The amount of Hg captured in a PM control device is higher for bituminous coal than for either subbituminous coal or lignite, because as mentioned above, the bituminous coal flue gas contains higher levels of Hg^{2+} and fly ash with unburned carbon (Ref. 2).

The conventional particulate matter control technologies currently used in control of utility boiler emissions include electrostatic precipitators (ESPs), fabric filters (FFs) (also called “baghouses”), and particulate scrubbers (PS). Generally, FFs are the most effective PM control systems for mercury reduction because they can achieve a higher level of particulate control. Two factors contribute to the relative higher capture efficiency of FFs. The first factor is that generally a fabric filter can capture a higher level of fine particulates compared to other PM control devices. The second factor is that in a FF, when the gaseous mercury passes through the filter cake, the filter cake can adsorb (and also oxidize) the

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[29] Table from the Reference (2) of the Reference list for this section, pp. ES-10.

mercury that has not already been adsorbed on the entrained fly ash upstream of the device. Mercury control capability has been shown to be respectively lower for units with ESPs, PS, and mechanical collectors.

ESPs and FFs fall into two classifications, coldside (CS) or hotside (HS), depending on whether they are installed after an air heater, where flue gas temperatures range from 284 to 320ºF (140 to 160°C), or before an air heater, where flue gas temperatures range from 662 to 842ºF (350 to 450°C). Currently available data indicate that mercury capture in HS-ESPs is very low.

PS systems, primarily venturi scrubbers, are used on some boiler units to control PM emissions. Only soluble Hg compounds such as $HgCl_2$ can be captured in such systems. Because PS systems typically do not collect fine PM effectively, capture of mercury associated with fine PM is poor in such scrubbers. Since Hg^0 is insoluble in water, it will not typically be captured by the scrubber. Hg^{2+} can be captured in the wet scrubbers, but the scrubber chemistry, and the manner in which the scrubber is operated, will determine whether it is effectively removed and/or stripped from the scrubbing liquor. Hg^{2+} can be stripped if it is not adsorbed on the particles, or reacted chemically with liquid-phase reactants within the scrubber.

Mechanical collectors such as cyclones are poor fine PM control devices. Mercury capture in these control devices is generally limited to the Hg_p associated with particles larger than 10 μm.

According to the ICR data, the average Hg emission reductions for plants that employ only post-combustion PM controls range from 0 to 90 percent. For bituminous coal (i.e., the type of coal currently used in the Massachusetts coal-fired utility boiler units subject to 310 CMR 7.29 regulations) and excluding the PS and HS-ESP systems (i.e., PM control system types that do not currently exist, and are not expected to be deployed in the future, at the affected coal-fired facilities), the emission reductions average for plants that employ only post-combustion PM controls ranges from 36% to 90% according to the ICR data.

Research is ongoing in improving particulate control efficiency and devices. A number of new systems have been developed that are based on the currently available particulate device control technologies and concepts, such as pulsed FFs, and hybrid ESP/FFs. Certain PM control systems such as wet ESPs (horizontal as well as tubular wet ESPs) that have been used in other industries (e.g., chemical processing) have been under evaluation and optimization for use in coal-fired boiler systems. Already progress has been made in improving PM control efficiency and several of these new technologies and new applications seem promising. Improvements in PM control efficiency, and especially improvements in fine PM control efficiency, will result in significant improvements in mercury control.

3.2.1.b. SO_2 Control Devices

SO_2 control may be achieved through pollution prevention (P2) and/or post-combustion methods. Using coal with lower sulfur content (a P2 approach) has been cost-effective for many facilities in achieving their SO_2 reduction goals. SO_2 post-combustion control technologies fall into three classifications: wet, semi-dry, or dry systems. An SO_2 control system always operates in conjunction with a PM control device.

The wet flue gas desulfurization (FGD) scrubbers remove SO_2 by dissolving it in a solution. A PM control device is always installed upstream of (i.e., prior to) a wet scrubber to reduce the solids in the scrubbing solution and prevent chemistry problems that may be associated with fly ash. PM devices that may be used with wet FGD scrubbers include a FF, CS-ESP, HS-ESP, or PS.

Semi-dry scrubbers include spray dryer absorbers (SDA). In these systems, a wet slurry is sprayed into the flue gas prior to the particulate control device. The SO_2 is adsorbed on the slurry sorbent, which is dried prior to collection by a PM control device.

In dry sorbent injection (DSI) systems, a dry powdered sorbent such as lime is directly injected into the flue gas. In many cases, water is injected upstream of the sorbent injection location to increase the flue gas moisture, which reduces the flue gas temperature and increases sorbent reactivity. An ESP or a FF is always installed downstream of a semi-dry scrubber or dry injection point to remove the sorbent from the flue gas.

The conventional SO_2 control devices achieve some level of mercury reduction. In certain cases, the Hg reduction levels can be quite high (98%). Table A-1 shows the average efficiency ranges for these devices obtained from the ICR data. SO_2 control systems in conjunction with sorbent injection and other possible modifications (such as addition of oxidant materials to the slurry) can provide further Hg reductions.

Wet Flue Gas Desulfurization Systems (WFGD)

In wet scrubbers, the gaseous species that must be removed are mixed with a liquid in which they are soluble; the solution is then removed and treated for disposal. WFGD scrubbers use a caustic slurry, typically water and limestone or water and lime, for SO_2 adsorption.[30]

The level of mercury capture in WFGD systems depends on the relative level of Hg^{2+} present in the flue gas that enters the FGD system. The gaseous Hg^0 is insoluble in water and therefore does not absorb in such slurries. The majority of Hg^{2+} species in the flue gas are soluble in water. After they are dissolved in the FGD solution, these mercury compounds are believed to react with dissolved sulfides from the flue gas, such as H_2S, to form mercuric sulfide (HgS), which precipitates from the liquid solution as sludge (Ref. 2). The adsorption of oxidized mercury in WFGD appears to be strongly correlated with the mass-transfer of gas to liquid in the scrubber and weakly dependent on the pH of the scrubber solution (Ref. 4).

When sufficient sulfides are not present in the liquid solution, a competing reaction that reduces/converts dissolved Hg^{2+} to Hg^0 is believed to take place. This newly formed (insoluble) Hg^0 is transferred to the flue gas passing through the wet FGD system, increasing the concentration of gaseous Hg^0 in the flue gas exiting the wet FGD compared to that entering. Transition metals in the slurry (originating from the flue gas) are believed to play an active role in this conversion reaction since they can act as catalysts and/or reactants for reducing oxidized species (Ref. 2). In many of the samples taken at the outlet of WFDG systems, an apparent increase from 7 to 40% in a non-Hg^{2+}, possibly Hg^0, has been indicated (Ref. 1).[31]

The level of Hg^{2+} that enters the WFGD system depends on the flue gas as well as the control systems upstream of the WFGD system (for example a FF and a SCR, used for NO_x control, oxidize the elemental mercury). A PM control device always precedes a wet FGD scrubber. Four types of PM control devices are commonly used upstream of the WFGD systems: FFs, CS-ESPs, HS-ESPs, and PM scrubbers (PS). In systems with a FF upstream of the FGD system, an increase in mercury reduction is observed across the FGD system due to the oxidization of elemental mercury that occurs on the fabric filter cake. Units equipped with FF+WFGD achieve the highest Hg reduction followed by units with CS-ESP, HS-ESP, and PS. Units with HS-ESPs operate at temperatures where the oxidization and capture of Hg is limited; therefore, a lower mercury reduction across the system is achieved. Systems with PS+WFGD have the

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[30] These scrubbers also eliminate other acid (e.g., hydrochloric and hydrofluoric) gases.

[31] Results from testing additives upstream and within a pilot-scale WFGD system has indicated no appreciable increase in the Hg^0 compared to tests with no additives.

lowest Hg removal efficiency (ICR data contains only a single test unit with a Hg_T capture of 12%) (Ref. 2).

According to the ICR data, average Hg captures in wet FGD scrubbers ranged from 23 percent (for a PC-fired HS-ESP+FGD unit burning subbituminous coal) to 97 percent (for a PC-fired FF + FGD unit burning bituminous coal) (Ref. 2).[32] According to the EPA-collected data, in the United States, generally more than 90% of the oxidized mercury that enters the wet limestone scrubbers for SO_2 control is captured. Total mercury reductions ranges from 20% to over 80% depending on the speciation of the Hg in the inlet flue gas (Ref. 2).

In general, the ability of SO_2 scrubbers to reduce total mercury is well established (Ref. 1, 2). However, it is difficult to generalize the effectiveness of the scrubbers for removing total mercury without an understanding of mercury speciation in the system. Increasing the oxidized mercury that reaches the inlet of the WFGD control device or modifying the liquid phase of the scrubber to cause oxidation to occur would result in an increase in mercury capture across WFGD. Currently research is being conducted to understand the conversion of Hg^0 to Hg^{2+} upstream of WFGD inlets, the conversion through injection of novel additives in the flue gas upstream of and directly into the WFGD systems, and the re-emission of Hg^0 from WFGD systems (for more information, please refer to the discussion under Capture of Mercury in WFGD Scrubbers in this report).

Conversion of Hg^0 to Hg^{2+} has been demonstrated in both laboratory- and small pilot-scale tests using catalysts. The decrease in the re-emission of Hg has been demonstrated in a pilot-scale WFGD system. Longer-term catalysts tests, and demonstration of additive injection at full scale is needed to further demonstrate viability and cost-effectiveness of these technologies (for more information, please refer to the discussion under Capture of Mercury in WFGD Scrubbers in this report).

Stability tests conducted on WFGD waste solids from a full-scale coal-fired power plant indicated that mercury concentrations of the WFGD samples remained below detection limits after the EPA Toxicity Characteristic Leaching Procedure (TCLP) tests,[33] with the mercury being below the analytical detection limit of 0.01 mg/L. Based on these tests, it has been concluded that Hg contained in the WFGD solids is in a non-leachable form (e.g., chemically bound possibly with $CaSO_4$). The WFGD materials would be classified as non-hazardous based on the Resource Conservation and Recovery Act (RCRA) criteria for mercury (i.e., a limit of 0.20 mg/L) (Ref. 1).

WFGD waste samples have also been tested to determine whether the captured Hg could be desorbed or re-emitted (volatilized). It has been concluded that Hg did not re-volatilize when exposed to temperatures up to 140°F.[34]

With further oxidization of the elemental Hg (as a result of new technologies which focus on this approach for mercury reduction) and higher capture of Hg^{2+} across the WFDG, the Hg in the WFGD solids would be increased. The increase in the Hg content of the WFGD waste may affect the stability of Hg in these wastes. Consequently, although the WFGD wastes can be currently considered stable under certain conditions (as discussed above), further research is needed to demonstrate the stability of the Hg associated with WFGD wastes for conditions other than those already tested (e.g., longer test periods) and

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[32] The nominal Hg removal for WFGD systems on units firing bituminous coal(s), based on mercury sampling results, is approximately 55% ±10% of the total Hg, with an associated removal for Hg^{2+} of between 80 to 95% (Ref. 1).

[33] TCLP test is used to assess whether the toxic substance can leach from the waste sample. If the toxic substance can leach, the waste would be considered as hazardous.

[34] The testing period was 11 weeks.

in situations when the wastes contain higher Hg levels. Suitability of these wastes for use in certain applications may be affected, if they could not be considered stable in those applications. Waste issues are further discussed under the Ash Issues section of this document.

Spray Dryer Adsorbers (SDA)

Spray Dryer Adsorber systems operate on the same basic principle as wet FGD systems. However the scrubbing agent (generally a fine mist of lime slurry) is sprayed into the flue gas and is mixed with the flue gas.[35] The SO_2 in flue gas is absorbed in the slurry and reacts with the hydrated lime reagent to form solid calcium sulfite and calcium sulfate. The high temperatures of the flue gas cause the water in the mist to evaporate, leaving dry solid particles of calcium sulfite and calcium sulfate. In some cases, water-soluble sodium-based sorbents are used instead of calcium-based sorbents. The PM control device (either an ESP or FF) downstream of the SDA captures the entrained particles (un-reacted sorbent particles, reaction products, and fly ash). Other dry sorbents for Hg control can be co-injected into the SDA systems (along with SO_2 control sorbents) for achieving multi-pollutant control.

The SDA systems on coal-fired boilers typically operate about 20^oF (11^oC) above the water vapor saturation temperature[36] in order to achieve optimal SO_2 reduction. This decrease in the flue gas temperature (compared to SDA inlet flue gas temperature) increases the potential for mercury capture, because mercury capture in general is dependent on temperature and increases with a decrease in temperature. The optimal flue gas temperature for SDA operation is determined by factors such as the buildup of moist fly ash deposits, which can plug the SDA reactor and coat downstream surfaces.

Both Hg^0 and Hg^{2+} can potentially be adsorbed on fly ash, calcium sulfite, or calcium sulfate particles in the SDA. Gaseous Hg^{2+} may also be absorbed in the slurry droplets and react with the calcium-based sorbents within the droplets. Hg^0 and Hg^{2+} can be adsorbed and captured as the flue gas passes through the PM control device (ESP or FF). Nearly all of the Hg_p can be captured in the downstream PM control device. When a FF is used, additional capture of gaseous mercury occurs as the flue gas passes through the bag filter cake.

Based on the limited test data available, mercury capture (i.e., percent reduction) in PC-fired units equipped with SDA seem to be similar to wet limestone scrubbers on a percentage reduction basis (Ref. 2). Further testing is needed to characterize the effects of fuel, combustion conditions, and APCD conditions on the speciation and capture of Hg.

Dry Sorbent Injection (DSI)

In this process dry powdered sorbent (lime or another suitable sorbent) is directly injected into the ductwork upstream of a PM control device. Some systems use spray humidification (for cooling of the flue gas) followed by dry injection. The SO_2 is adsorbed and reacts with the powdered sorbent. The entrained dry solids and the fly ash are collected by the downstream PM control device. The slurry production and handling equipment required for wet scrubbers and spray dryers is eliminated in this process. Additionally, the waste products of the process are dry and easier to manage for disposal. The SO_2 reduction efficiencies for the existing dry injection systems range from 40 to 60 percent. The dry sorbent injection systems also provide the opportunity for co-injection of sorbents for multi-pollutant control.

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[35] In wet scrubbing system flue gas passes through a bulk liquid slurry.

[36] This is called a 20^oF (i.e., 11^oC) approach to saturation temperature.

Circulating fluidized-bed adsorber (CFBA)

A circulating fluidized-bed adsorber (CFBA) system is a type of sorbent injection system with simultaneous gas cooling, sorbent injection and recycle, and gas sorption by flash drying of wet sorbent reagent. By allowing the flue gas to flow upward and adjusting the gas flow rate to sufficiently support the particles, but not carry them out of the system, a fluid-like condition in the bed is produced. Characteristic high heat and mass transfer (due to high mixing rates and particle-to-gas contact) allow the sorbent particles to remove a sorbate from the gas stream with high effectiveness. The sorbent material can be treated before it is re-injected into the bed.

CFBAs are currently used with limestone and ash as sorbents for SO_2 control, but they can also be used for simultaneous control of several pollutants (by co-injecting sorbents). The SO_2 removal for CFBAs ranges from 80 to 98 percent (Ref. 2).

Owing to their improved sorbent utilization (by re-injection and recycle), and flash evaporative cooling, CFBAs are believed to have the potential for controlling Hg emissions at lower costs than those associated with use of DSIs. Utilization of advanced sorbents with these systems appears to be more favorable (Ref. 2).

3.2.1.c. NO_x Control Devices

Combustion and post-combustion control measures can be used to reduce NO_x. Combustion techniques for NO_x reduction employ modifications that reduce the peak temperatures and excess air in the furnace. More than one combustion technique[37] can be combined to reduce NO_x emissions. Certain combustion modification techniques increase the unburned carbon in fly ash and increase the adsorption of Hg onto collectable fly ash.

Nationally, a very small percentage (~ 3% in 1999) of boilers use post-combustion control technologies for NO_x reduction (Ref. 2). However, the application of these post-combustion NO_x controls will become more prevalent as EPA's SIP call for summertime NO_x control in 22 states takes effect. NO_x post-combustion control technologies include selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) processes. In both methods a reducing agent such as ammonia or urea is used to reduce NO_x to N_2 and H_2O. SCR operates at lower temperatures than SNCR and is more effective at reducing NO_x, but it is more expensive.

In the SCR process a catalyst (such as vanadium, titanium, platinum, or zeolite) is used in a bed reactor, and the NO_x reduction occurs at the surface of the catalyst bed with the help of a reducing agent (diluted ammonia or urea, which generates ammonia in the process). Ammonia dilution is achieved by introducing air or steam into the gas stream. The ammonia mixture is injected into the flue gas upstream of the metal catalyst bed reactor, which is located upstream of a PM or SO_2 control device (usually between the economizer outlet and air heater inlet, where temperatures range from 230 to 400°C, i.e., 450 to 750°F)(Ref. 2).

The SNCR process does not require the use of a catalyst to prompt the reduction reactions. However, the reduction can only occur in a specific temperature range (870 to 1090°C, i.e., 1,600 to 2,000°F) and the reducing agent can only be injected into the flue gas stream in a location that supports the temperature requirements. When the ammonia is injected above this temperature range, oxidation of the ammonia

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[37] These techniques include low NO_x burners, overfire air, off-stoichiometric firing, selective or biased burner firing, reburning, burners-out-of-service, flue gas recirculation (FGR), and staged combustion (also called air staging). Please see Reference (2) for more detail on these techniques.

forms more NO_x. At lower temperatures outside the optimum temperature window, the efficiency of the NO_x reduction process is significantly reduced. By adding hydrogen gas or other chemical enhancers, the reduction process can be sustained at lower temperatures (down to approximately 700°C, i.e.1300°F) [38] (Ref. 2).

ICR data regarding the potential effects of these post-combustion NO_x controls on Hg capture is limited. ICR data revealed that SCR application with SDA at one plant firing bituminous coal resulted in greater than 95 percent mercury removal. Recent pilot-scale tests indicate that SNCR and SCR systems may enhance Hg capture under some conditions by oxidizing Hg^0 (Ref. 2).

The effects of SNCR on mercury oxidization have not been documented in the open literature. Oxidation of elemental mercury in SCR systems has been documented in the literature (Ref. 5). EPRI has investigated mercury reactions in (actual) flue gas at conditions expected for certain NO_x processes including SCR (Ref. 6). Results indicate that some commercial SCR catalysts are capable of oxidizing elemental mercury. Oxidation is affected by the operating conditions and the flue gas properties. The effect of the ammonia on fly ash mercury reactions has also been investigated. Research is ongoing on the impacts of low NO_x burners, SCR, and SNCR on conversion of Hg^0 to Hg^{2+}, and possible mercury reductions (Ref. 6). In systems that burn bituminous coal, a combination of SCR and WFGD can achieve significant (above 95%) mercury reduction in certain cases (depending on several operational factors).[39]

3.2.2. Mercury-Specific Control Technologies

A number of technologies have been under development specifically to address mercury control and are in various stages of research, development, and testing. They include use of sorbents (processes that use injection and fixed-bed configurations), mercury oxidation materials, and mercury oxidation catalysts. A number of these technologies can be used in plants equipped with a PM control device (ESP and/or FF). The application of others requires a SO_2 scrubber. Certain technologies have been demonstrated at pilot- and full-scale applications and are closer to commercialization (such as activated carbon injection), while others are still in laboratory testing stage. A number of these technologies have indicated the potential to achieve mercury reduction levels above 90% (variation depends on the plant specifics such as other air pollution control devices already deployed, the type of coal fired, and the firing conditions). A brief explanation of these mercury-specific technologies follows.

3.2.2.a. Sorbents

Sorbents that can adsorb mercury can be injected into the duct in the form of a powder. An alternative approach that has been investigated is passing the gas through a fixed bed of a noble-metal-based sorbent.

Since 1995, EPRI has supported a sorbent development program for removal of Hg emissions from coal-fired electric utility power plants at several research organizations. The main objective of this program is development of effective sorbents that can be produced at lower costs (Ref. 2, 7, 8). Research has included investigation of preparation methods and the effects of sorbent properties. A number of promising low-cost sorbents have been further evaluated in actual flue gas at several full-scale coal-fired electric utility power plants.

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[38] Currently, two SNCR processes are commercially available: the THERMAL DeNOx and the NOxOUT.
[39] Research in this area and the operational factors that affect mercury oxidization by SCR is still on going.

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3.2.2.a.i. Sorbent Injection

Mercury can be captured and removed from gas by injection of a sorbent into the exhaust system and subsequent collection of the particulates in a PM control device. Availability of low-cost and efficient sorbents and effective particulate collection are key in implementation of this type of mercury control. There is active research both in development and evaluation of mercury sorbents and enhancement of particulate collection methods (Ref. 2).

Certain physical and chemical sorbent characteristics affect its mercury adsorption capacity. These include surface area of the sorbent (especially surface area in the micro-pore structure of the sorbent for the removal in the part per billion mercury concentration range typical of coal combustion gases), pore size distribution, particle size distribution, and the sorbent content of certain chemicals (e.g., sulfur, iodine, chlorine, and water content of activated carbon), and certain chemical functional groups (e.g., carbonyls, carboxyl, phenol, etc.). Understanding these sorbent characteristics in the context of mercury adsorption would lead to development of better sorbents and is currently an active area of research.

Various types of sorbents have been under investigation. These include various types of activated carbon, calcium-based and sodium-based (trona) sorbents, various clays and zeolites, alkaline-earth sulfides, as well as lime and lime-silica multi-pollutant sorbents. Activated Carbon and calcium-based sorbents have been the most actively researched and tested sorbents. However, new classes of mercury sorbents and improvements in the mercury adsorption of the current sorbents can be expected because currently much research is taking place in this field.

In the near term, activated carbon seems the most likely technology to be commercialized for mercury control because there have been full-scale tests of this technology that have generated promising results. However, other sorbent technologies also offer certain advantages. A concern associated with use of activated carbon sorbents is the potential increase in the carbon content of the fly ash, which can affect the use of this waste in certain products (such as cement). Non-carbon-based sorbents eliminate this concern. Some of the non-carbon based sorbents (such as calcium-based sorbents) may prove cheaper than activated carbon.

Increased removal of mercury from gas has been demonstrated by co-injection of activated carbon and calcium-based sorbents in spray dryer adsorber systems in full-scale coal-fired power plants (Ref. 9), up stream of a baghouse in pilot tests (Ref. 10), and in a specialized fluidized bed reactor (Ref. 11). Activated carbon combined with hydrated lime has been shown to reduce the amount of carbon required by one half to one third compared to activated carbon alone (Ref. 1, 3). For eastern bituminous coals, injection of limestone into the furnace followed by a cyclone separator has shown good mercury removal in full-scale tests (Ref. 2, 12). A brief discussion of sorbents that have been under extensive investigation is given below.

Powdered Activated Carbon

Activated carbon (AC) has been the most extensively studied sorbent for mercury adsorption. Currently, AC seems to be the most likely candidate to reach commercialization for mercury removal in the near future. Mercury adsorption on activated carbon is affected by the following major factors: Temperature and composition of the gas (including the concentration of acid gases), the concentration of Hg in the gas exhaust system, the residence time in the duct and the dispersion of the sorbent in the gas, and the chemical and physical properties of the activated carbon (or the impregnated activated carbon). The effect of factors such as acid gases (SO_2) and temperature on adsorption of elemental and oxidized mercury is not identical (Ref. 2, 3). Sorption studies have suggested that it is more difficult to control Hg^0 emissions than $HgCl_2$ (Ref. 2).

Activated carbon has been successfully commercialized in municipal waste combustor (MWC) applications and is capable of removing >90% of the mercury at very modest carbon-to-mercury ratios, with a fraction of a pound increase in carbon injection rate increasing mercury removal from the gas by much as 30% (Ref. 1). However, differences between municipal and coal-fired utility boiler gases affect the performance of activated carbon in these two environments. These differences include a lower concentration of mercury, a higher concentration of acid gases, and a lower residence time (the time available for the mercury to contact the AC particle) in coal-fired utility boiler gas. Consequently, transfer of the AC technology commercialized for MWCs to utility boilers has required further investigation and optimization. Extensive tests have been performed at the bench, laboratory, pilot, and full scale for application of AC in the coal-fired utility boiler gas. The results of these tests will be discussed in the following section.

Modified activated carbons (i.e., doped with sulfur, iron, chlorine, and iodine), as well as activated carbon derived from a variety of materials (such as biomass, waste tire, carbon fibers, char produced from corn-to-ethanol production process byproducts, fly ash, and coal) have been studied. Preliminary evaluations have shown that activated carbon derived from some materials such as lignite coal fly ash and corn waste[40] may provide economic advantage compared to the currently commercially available activated carbon. Doped activated carbons can provide higher mercury adsorption capacity, but often have higher production costs that should be considered in the evaluation studies. As research in production and sorbent application methods continues, some of the cost issues associated with impregnated activated carbons may be addressed.

For example, it is believed that sulfur impregnation[41] increases the capacity of activated carbon for both elemental and oxidized mercury adsorption (Ref. 13). However, the cost of this material may be substantially higher than undoped available activated carbons. Research has been done on processes for impregnation and preparation of the sulfur-doped activated carbon because these processes affect the physical and chemical properties of the impregnated sorbent and its mercury adsorption capacity (Ref. 14). Due to higher production cost for sulfur-impregnated AC, the cost of mercury control using this type of powdered AC injection may be substantially higher compared to the undoped activated carbon. However, in an effort to investigate potential means of reducing costs associated with using this material, cloth made with activated carbon fiber was impregnated with sulfur and was tested for adsorption of mercury in simulated gas (Ref. 14). Bench-scale studies indicated a high capacity for Hg^0 capture, and a potential for the fabric filter to have a lower cost than the injection of activated carbon (Ref. 3).

Residence time and temperature of the flue gas prior to entering the particulate device control (where AC is injected) are two critical factors in improving the efficiency of the mercury capture with AC. Reducing gas temperatures (by spray cooling or use of heat exchangers) has promoted higher capture efficiencies of mercury with AC injection. However, operating at reduced temperatures may result in formation of sulfuric acid (and possibly hydrochloric acid) mist. Temperature reduction would not pose any operational concerns for facilities burning (low sulfur) subbituminous coals. For facilities that use coals with high sulfur content and humidification for flue gas cooling, formation of sub-micron sulfuric acid mist as a result of sulfur trioxide (SO_3) condensation at or below the acid dew point[42] (ADP) of the gas

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[40] The corn-derived activated carbon showed a Hg^0 adsorption capacity over twice that of the commercial activated carbon sorbent, after the char was activated (in CO_2 at 865°C for 3.5 hour) (Ref. 15).

[41] According to the document in Reference (2), the most effective sorbents were obtained by sulfur impregnation of activated carbons derived from waste material and carbon fibers (Ref. 2, 15).

[42] The acid due point (ADP) is the temperature of the flue gas at which the acidic components will condense.

can result in degradation of the ductwork and pollution control system. Formation of SO_3 may be a result of coal combustion, or sulfuric acid gas may be injected separately or in combination with ammonia for enhancing fine particle collection (this occurs mainly when PRB and other subbituminous coals are used). Also, pilot-scale tests have indicated that certain carbons convert SO_2 to SO_3 while the carbon is captured on the filter of the baghouse. Some options are available to address acid mist formation problem. In general, the system can be operated at a temperature above the ADP to avoid this problem.[43]

According to prior investigations, rather high carbon-to-mercury weight ratios are needed to achieve a high level of mercury removal. In order to reduce the carbon injection rates and the operating cost of the process, it is necessary to develop either a more efficient sorbent (i.e., lower carbon-to-mercury injection) or a lower-cost sorbent (or possibly both). Carbon impregnation and use of ultra fine activated carbon, as well as improvements in particulate collection have been investigated to address this issue.

A chlorine-impregnated activated carbon was produced and studied (Ref. 16). An inexpensive virgin activated carbon was used in a cost-effective impregnation process. Bench scale tests and cost analyses have shown that this Cl-impregnation process can produce a very efficient and cost effective activated carbon that can be used as a sorbent in ESP-equipped coal-fired boilers. Preliminary cost estimates have indicated 53 percent reduction in total annual cost of mercury control compared to using virgin activated carbon (with a removal efficiency of 80%). The Cl-impregnated AC will be investigated in a pilot-scale test (a 21-kW boiler fired with pulverized coal) (Ref. 2, 16).

Recent investigations have indicated that the composition of the flue gas affects the mercury adsorption capacities of the activated carbons. This is a result of complex interactions between the flue gas components, such as acid gases, and the surface characteristics and properties of the carbon sorbent. The observed varying effects of acid gases on Hg adsorption behavior of the carbon sorbents can be attributed to these complex physical and chemical interactions (Ref. 2, 8, 17).

The micropore surface area of sorbent is believed to be an important physical property for vapor-phase mercury adsorption. Recent research has indicated that relatively low surface area microporous activated carbon sorbents derived from bio-mass materials, such as pistachio nut shells and corn fibers, are as effective as the commercial (FGD activated carbon) sorbent for mercury adsorption (Ref. 8). It has been suggested that the presence of active surface functional groups (such as sulfur) in the micropores of the activated carbon are likely to provide the most reactive sites for Hg adsorption from the coal combustion flue gas (Ref. 18). Consequently, it is believed that sorbent-impregnation should focus on highly microporous sorbents.[44] The importance of active functional groups in micropores for vapor-phase Hg adsorption was demonstrated in an EPA study (Ref. 22) by treating the as-received activated carbon with sulfuric acid to increase its micropore functional groups. The Hg^0 adsorption capacity of the treated sorbent was much improved. Most of the commercial activated carbons have been developed for liquid-phase applications and contain large mesopore surface areas (in addition to micropores), which are less effective for adsorption of ppb levels of mercury from coal combustion gas (Ref. 2).

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[43] Often a temperature of ADP+10°C is adopted. A higher temperature may be necessary in some cases to prevent acid formation. Operating in a higher temperature range, based on the costs modeling studies, would result in increased total annual mercury control costs for plants firing bituminous coals and decreased costs for plants firing subbituminous coals (Ref. 2).

[44] It has been demonstrated that impregnation of activated carbon with heteroatoms such as sulfur and chloride is an effective method to improve the vapor-phase Hg adsorption capacities of AC (Ref. 2, 19, 20). Recently, EPA researchers have suggested that the Hg^0 adsorption capacity of an activated carbon is correlated with the concentration of the oxygen (another heteroatom) functional groups in the activated carbon (Ref. 21).

Research in understanding and improving mercury adsorption efficiency of activated carbons has been ongoing with the goal of improving carbon to mercury injection rates and reducing control costs. In general, the efficiency of sorbent use can also be increased by recycling and re-injecting sorbent and fly ash collected in the PM control device(s) located downstream of the injection point because sorbent capacity may be maximized through this recycling.

Successful implementation of full-scale tests for commercially available activated carbon has been demonstrated. Although these tests have had fairly short time frames and more extensive tests are needed for commercialization of this technology, the activated carbon injection technology appears to be promising. Issues such as potential increase in carbon content of the fly ash; SO_3 mist formation; and high carbon-to-mercury injections required for high levels of mercury reduction are being investigated and will potentially be addressed through measures such as sorbent modification (e.g., use of modified sorbents with higher capture efficiency), implementation of appropriately designed equipment (e.g., implementation of systems that can address SO_3 mist formation), and selection of the appropriate combination of APCD control devices (e.g., implementing an additional FF control device to reduce the carbon injection rate). In summary, activated carbon in conjunction with the capture of mercury by native fly ashes[45] and with enhancements for particle collection has potential application in coal-fired utility boilers to reduce mercury emissions (Ref. 2).

Field Demonstration of Mercury Control Using Activated Carbon Injection Control Technologies

Activated carbon injection technology has been demonstrated (under DOE-funded grants) in four coal-fired utility plants at pilot- and full-scale level tests. These tests were performed at the following plants: Pleasant Prairie Station (in Wisconsin), Alabama Power E.C. Gaston Station (in Alabama), Brayton Point Station (in Massachusetts), and Salem Harbor Station (in Massachusetts). In order to obtain AC injection technology performance data under various deployment conditions, facilities with different configurations and operational conditions were selected, and the tests were performed under varying testing conditions. The preliminary results of these field tests demonstrate successful application of mercury-specific control technology at mercury removal levels greater than 90% for boilers burning bituminous coals. Details on these field demonstration tests are discussed in Appendix F.

Calcium-Based Sorbents

Recent investigations of mechanisms involved in mercury adsorption of Ca-based sorbents have indicated the potential for efficient use of such sorbents in a range of applications (Ref. 23). It has been shown that injection of calcium-based sorbents into gas can result in significant removal of mercury (Ref 24, 25).[46,47] Other benefits associated with the use of limestone injection for mercury control include a high probability of SO_3 removal and an incremental SO_2 capture.[48] Relatively large quantities of Ca are required for SO_2 control at coal-fired utility boilers. The investigation results suggest that Ca-based sorbents, modified by reaction with fly ash, can be used to control total Hg and SO_2 emissions cost-effectively. Calcium-based sorbents that have significant pore volume (for elemental mercury capture)

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[45] The fly ash that is generated by any coal combustion process and enters into the flue gas.

[46] In a pilot-scale test, under high-temperature/short-gas-phase residence time for Illinois #6 coal, 77% of total mercury was removed from the gas (Ref.2).

[47] This work has been a collaboration between EPA and ARCADIS Geraghty & Miller, Inc (funded by the Illinois Clean Coal Institute).

[48] Additionally, injection of calcium-based sorbents eliminates the potential concern associated with use of AC sorbents. Injection of AC sorbents might in some cases increase the carbon content of the fly ash beyond what would be appropriate for its use in certain products such as cement.