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**CONTROL OF MERCURY EMISSIONS FROM  
COAL-FIRED ELECTRIC UTILITY BOILERS \*/**

Note prepared by the secretariat based on information provided  
by the delegation of the United States of America

**Introduction**

1. At the thirty-third session of the Working Group on Strategies and Review, the delegation of the United States informed the Working Group that its work on mercury was currently focusing on developing technology to reduce emissions from coal-fired power plants. In response to a question, the delegation offered to prepare a note on this work in consultation with the secretariat (EB.AIR/WG.5/70, para. 37).
2. In accordance with article 3, paragraph 1, of the 1998 Aarhus Protocol on Heavy Metals, Parties to that Protocol will have to reduce their emissions of mercury (Hg) into the atmosphere by taking effective measures, appropriate to their particular circumstances, unless, according to paragraph 6, they cannot achieve this after applying the best available techniques (BAT) to major stationary sources and the product measures required under the Protocol. Annex II to the Protocol lists, as a stationary source category, combustion installations with a net rated thermal input exceeding 50 MW. Annex III provides guidance on BAT for this category and annex V sets a limit value of 50 mg/m<sup>3</sup> for particulate emissions for solid and liquid fuels for this category.

\*/ Note: In the present document, the term “ton” refers to short tons, i.e. 2000 lb. or 907.19 kg.

Documents prepared under the auspices or at the request of the Executive Body for the Convention on Long-range Transboundary Air Pollution for GENERAL circulation should be considered provisional unless APPROVED by the Executive Body.

3. This note summarizes an interim report that documents current knowledge on the emission and control of mercury (Hg) from coal-fired electric utility plants. The purpose of the interim report was to provide information on the status of government and industry efforts in the United States in developing improved technologies for the control of Hg emissions. The interim report contains information available in the public domain prior to June 2001 and can be accessed on the Internet at <http://www.epa.gov/appcdwww/aptb/EPA-600-R-01-109corrected.pdf> (or at <http://www.epa.gov/appcdwww/aptb/publications.htm>, last document under "Miscellaneous").

4. The 1990 United States Clean Air Act Amendments required the United States Environmental Protection Agency (USEPA) to study the health and environmental impacts of hazardous air pollutants (HAPs) emitted from electric utility boilers. The Agency was also required to conduct a study of the potential health and environmental impacts of Hg emitted from anthropogenic sources in the United States. USEPA subsequently published an eight-volume Mercury Study Report to Congress in December 1997 and a Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units-Final Report to Congress in February 1998. The Hg report to Congress identified coal-fired utility boilers as the largest single anthropogenic source of Hg emissions in the United States. The utility HAP report indicated that there was a plausible link between Hg emissions from coal-fired boilers and health risks posed by indirect exposure to methylmercury. In December 2000, USEPA announced its intent to regulate HAP emissions from coal- and oil-fired electrical generating stations.

## **I. ELECTRIC UTILITY COAL COMBUSTION AND AIR POLLUTION CONTROL TECHNOLOGIES**

5. The USEPA Information Collection Request (ICR) effort was conducted in three phases. In phase I, information was collected on the fuels, boiler types and air pollution control devices used at all coal-fired utility boilers in the United States. In phase II, coal data were collected and analysed by the utility industry for 1,140 coal-fired and three integrated gasification, combined cycle (IGCC) electric power generating units. Each coal sample was analysed for Hg content, chlorine (Cl) content, sulphur (S) content, moisture content, ash content and calorific value. In phase III, flue gas Hg measurements were made using the modified Ontario-Hydro (OH) method for total and speciated Hg. Additional coal samples were collected and analysed in conjunction with the OH method measurements.

6. The USEPA ICR data indicated that, in 1999, coal-fired steam electric generating units in the United States burned 786 million tons of coal, of which about 52 per cent was bituminous and 37 per cent was Sub-bituminous. Other fuels included lignite, anthracite coal, reclaimed waste coal, mixtures of coal and petroleum coke (pet-coke), and mixtures of coal and tyre-derived fuel (TDF). Pulverized coal-fired (PC) boilers represent approximately 86 per cent of the total number

and 90 per cent of total utility boiler capacity. Based on capacity, other types of boilers include cyclone-fired boilers (7.6 per cent), fluidized-bed combustors (1.3 per cent) and stoker-fired boilers (1.0 per cent).

7. The 1999 USEPA ICR responses indicate that a variety of emission control technologies are used to meet requirements for sulphur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM). Most utilities control NO<sub>x</sub> by combustion modification techniques and SO<sub>2</sub> by the use of compliance coal. For post-combustion controls, 77.4 per cent of the units have PM control only, 18.6 per cent have both PM and SO<sub>2</sub> controls, 2.5 per cent have PM and NO<sub>x</sub> controls, and 1.3 per cent have three post-combustion control devices.

8. The different types of post-combustion control devices are listed below:

(a) **Particulate matter control technologies** include electrostatic precipitators (ESPs), fabric filters (FFs) (also called “baghouses”) and particulate scrubbers (PS). ESPs and FFs may be classified as either hot-side (HS) devices, installed upstream of the air heater where flue gas temperatures range from 662 to 842 °F (350 to 450 °C), or cold-side (CS), installed downstream of the air heater and operating at temperatures ranging from 284 to 320 °F (140 to 160 °C). Based on current information, it appears that little Hg can be captured in HS-ESPs;

(b) **SO<sub>2</sub> post-combustion control technologies** are systems that are classified as wet flue gas desulfurization (FGD) scrubbers, dry scrubbers or dry injection. Wet FGD scrubber controls remove SO<sub>2</sub> by dissolving it in a solution. A PM control device is always located upstream of a wet scrubber. PM devices that may be used with wet FGD scrubbers include a PS, CS-ESP, HS-ESP or FF baghouse. Dry scrubbers include dry sorbent injection (DSI) and spray dryer absorption (SDA). Dry injection involves injecting dry powdered lime or other suitable sorbent directly into the flue gas. SDA systems, which are also called wet-dry systems, involve the injection of an aqueous slurry (or solution) into a reaction vessel where the water is evaporated. A PM control device (ESP or FF) is always installed downstream of a DSI location or a SDA to remove fly ash and spent sorbent from the flue gas;

(c) **NO<sub>x</sub> post-combustion control technologies** include selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) processes. With both of these methods, a reducing agent such as ammonia or urea is injected into the duct to reduce NO<sub>x</sub> to N<sub>2</sub>. SCR operates at lower temperatures than SNCR and is more effective at reducing NO<sub>x</sub>, but it is more expensive.

9. For PM control, ESPs are used on 84 per cent of the existing electric utility coal-fired boiler units, and FF baghouses are used on 14 per cent of the utility units. Post-combustion SO<sub>2</sub> controls are less common. Wet FGD systems are used on 15.1 per cent of the units; and dry scrubbers, predominantly spray dryer absorbers (SDA), are used on 4.6 per cent of units that were surveyed. While the application of post-combustion NO<sub>x</sub> controls is becoming more prevalent, only 3.8 per cent of units used either SNCR or SCR systems in 1999.

## II. MERCURY MEASUREMENT METHODS

10. When the coal is burned in an electric utility boiler, the resulting high combustion temperatures vaporize the Hg in the coal to form gaseous elemental mercury (Hg<sup>0</sup>). Subsequent cooling of the combustion gases and interaction of the gaseous Hg<sup>0</sup> with other combustion products result in a portion of the Hg being converted to gaseous oxidized forms of mercury (Hg<sup>2+</sup>) and particle-bound mercury (Hg<sub>p</sub>). The term 'speciation' is used to denote the relative amounts of these three forms of Hg in the flue gas. The total Hg in flue gas (Hg<sub>T</sub>) is the sum of Hg<sub>p</sub>, Hg<sup>2+</sup> and Hg<sup>0</sup>. It is the ability to measure these forms of Hg, either collectively or individually that distinguishes the capabilities of available measurement methodologies.

11. The Hg in flue gas can be measured either by manual sampling methods or by the use of a continuous emission monitor (CEM). Manual methods are available for the measurement of Hg<sub>T</sub> and the speciation of Hg, including Hg<sub>p</sub>. CEMs are now available to measure gas-phase Hg<sub>T</sub>.

### A. Manual test methods

12. Manual sampling methods for measuring Hg<sub>T</sub> from combustion processes are well established. USEPA methods 101A and 29 are routinely used to measure Hg<sub>T</sub> in flue gas from incineration and coal combustion. While a validated reference method for the measurement of the speciated forms of Hg does not exist, the Ontario-Hydro (OH) method is the de facto method of choice.

13. Generally, sampling trains used to collect flue gas samples for Hg analysis consist of the same components: a nozzle and probe operated to extract a representative sample from a duct or stack; a filter to collect PM; and a series of impingers with liquid reagents to capture gas-phase Hg. Sampling trains used for speciation measurements sequentially capture Hg<sup>2+</sup> and Hg<sup>0</sup> in different impingers. After sampling, the filter and sorption media are prepared and analysed for Hg in a laboratory.

14. While several research methods exist for performing speciated Hg measurements, the OH method is currently the method of choice for measuring Hg species in the flue gas from coal-fired

utility plants. The OH method has been shown to provide valid Hg speciation measurements when samples are taken downstream of an efficient PM control device. However, the OH method can give erroneous speciation measurements for locations upstream of PM control devices because of sampling artefacts.

15. Fly ash captured by the sampling train filter can absorb  $\text{Hg}^{2+}$  and  $\text{Hg}^0$ . Catalytic properties of the fly ash can also oxidize  $\text{Hg}^0$ , resulting in physical and chemical transformations within the sampling train. Transformations caused by the sampling process are called artefacts, and the resulting measurements do not accurately reflect critical properties of Hg at the locations where the samples were taken. Sampling methods have not yet been developed to overcome measurement artefacts associated with high flue gas concentrations of fly ash.

### **B. Continuous emission monitors**

16. Continuous emission monitors (CEMs) are in some respects superior to manual measurement methods. CEMs provide a rapid real-time or near real-time response, which can be used to characterize temporal process variations that cannot be measured with manual measurement methodologies. Mercury CEMs are similar to most combustion process CEMs in that a flue gas sample must be extracted from the stack and then transferred to the analyser for detection. However, Hg monitoring is complicated by the fact that Hg exists in different forms and that quantitative transport of all forms is difficult.

17. CEMs designed to measure total gas-phase Hg ( $\text{Hg}^{2+}$  and  $\text{Hg}^0$ ) are now routinely used in Europe and Japan to measure Hg emissions from incinerators. The Hg concentrations in the stack gas from well-controlled emission sources contain negligible amounts of  $\text{Hg}_p$ , and the measurement of gas-phase Hg downstream of the emission control devices can be considered to be equivalent to the measurement of  $\text{Hg}_T$ .

18. The detectors in Hg CEMs typically measure  $\text{Hg}^0$  by the use of cold vapour atomic absorption spectroscopy or cold vapour atomic fluorescence spectroscopy.  $\text{Hg}_T$  concentrations are measured by converting (reducing) all of the  $\text{Hg}^{2+}$  in the sample to  $\text{Hg}^0$  before it enters the detector. Various conversion techniques exist, including thermal, catalytic and wet chemical methods. The wet chemical technique is currently used in commercial monitors that are capable of speciation measurement. The use of wet chemical reagents results in high operating costs, which are the primary limitation to the use of Hg CEM as a compliance tool.

19. Speciating Hg CEMs are highly valuable as research tools. Several commercially available  $\text{Hg}_T$  CEMs have been modified to indirectly measure  $\text{Hg}^{2+}$  by determining the difference between gas-phase  $\text{Hg}_T$  and  $\text{Hg}^0$ . Hg CEMs are susceptible to the same PM-related measurement artefacts

associated with manual measurements, and users of Hg CEMs in high dust conditions must consider this problem.

20. Regardless of the sampling method, the key to reliable and accurate Hg sampling and continuous monitoring is maintaining sample integrity. Flue gases may contain particles that change the species of Hg within the sampling train or CEM system. While this does not change the total Hg measurement, it may bias the determination of Hg vapour species, which may be used to estimate the potential for Hg capture, as well as to assess the performance of control devices. Similarly, common flue gas constituents, such as SO<sub>2</sub>, HCl and NO<sub>x</sub>, may affect quantitative measurement performance.

21. Additional research is needed to investigate and overcome measurement obstacles so that speciating CEMs can serve as process monitors and as a research tool for evaluating the effectiveness of emission controls. Such research can also provide a better understanding of the factors that affect Hg speciation and capture.

### **III. SPECIATION AND CAPTURE OF MERCURY IN FLUE GAS**

#### **A. Mercury speciation**

22. The capture of Hg by flue gas cleaning devices is dependent on Hg speciation. Both Hg<sup>0</sup> and Hg<sup>2+</sup> are in vapour phase at flue gas cleaning temperatures. Hg<sup>0</sup> is insoluble in water and cannot be captured in wet scrubbers. The predominant Hg<sup>2+</sup> compounds in coal flue gas are weakly to strongly soluble, and the more-soluble species can generally be captured in wet FGD scrubbers. Both Hg<sup>0</sup> and Hg<sup>2+</sup> are adsorbed 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. Hg<sup>2+</sup> is generally easier to capture by adsorption than Hg<sup>0</sup>. Hg<sub>p</sub> is attached to solids that can be readily captured in an ESP or FF.

23. Flue gas cleaning technologies that are applied on combustion sources use three basic methods to capture Hg:

- (i) Capture of Hg<sub>p</sub> in PM control devices;
- (ii) Adsorption of Hg<sup>0</sup> and Hg<sup>2+</sup> onto entrained sorbents for subsequent capture in an ESP or FF. Alternatively Hg may be captured in a packed carbon bed; and
- (iii) Solvation of Hg<sup>2+</sup> in wet scrubbers.

24. The factors that affect the speciation and capture of Hg in coal-fired combustion systems include the type and properties of coal, the combustion conditions, the types of flue gas cleaning technologies used and the temperatures at which the flue gas cleaning systems operate.

25. Oxidation reactions that affect the speciation of Hg include homogeneous, gas-phase reactions and heterogeneous gas-solid reactions associated with entrained particles and surface deposits. Suspected flue gas oxidants involved in Hg<sup>0</sup> oxidation include oxygen (O<sub>2</sub>), ozone (O<sub>3</sub>), hydrochloric acid (HCl), chlorine (Cl), nitrogen dioxide (NO<sub>2</sub>) and sulphur trioxide (SO<sub>3</sub>). Many of these oxidants are also acid species, which may be significantly impaired by the presence of alkaline species, such as sodium, calcium and potassium, in fly ash. Heterogeneous oxidation reactions may be catalysed by metals such as iron, copper, nickel, vanadium and cobalt. Conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> may be followed by adsorption to form Hg<sub>p</sub>.

26. The determination of which mechanisms, oxidants and catalysts are dominant is crucial in developing and implementing Hg control strategies. For example, the impaired oxidation of Hg in sub-bituminous coals and lignites is probably related to lower concentrations of HCl in flue gas and high alkalinity of the fly ash. PM collectors and scrubbers reflect this in the low removals of Hg in the ICR database.

## **B. Fundamentals of sorption**

27. Sorbents used for the capture of Hg can be classified as Hg sorbents or multi-pollutant sorbents. Sorbents evaluated for Hg capture have been manufactured from a number of different materials such as lignite, bituminous coal, zeolites, waste biomass and waste tyres. The manufacturing process typically involves some type of thermal treatment. Additives are often used to produce impregnated sorbents.

28. For coal-fired electric utility boiler applications, the use of sorbents to capture gas-phase Hg (or gas-phase Hg and acid gases) is limited to the use of finely ground powdered sorbents. These sorbents can be injected upstream of PM control devices to collect the sorbent and adsorbed Hg. The development of improved sorbents is needed because of poor sorbent utilization that results from low flue gas concentrations of Hg and short sorbent exposure times in units equipped with CS-ESPs. The performance of a sorbent is related to its physical and chemical characteristics. The best performing sorbents must be carefully matched to performance requirements as defined by the application for which it is to be used. For example, properties and performance requirements of sorbents used for the capture of SO<sub>2</sub> and Hg<sup>0</sup> are quite different. In a similar fashion, the performance criteria for sorbents used with flue gas from bituminous coal will probably be different from the sorbents used with sub-bituminous coals.

29. Sorbents are porous materials. The most common physical properties related to sorbent performance are surface area, pore size distribution and particle size distribution. The capacity for Hg capture generally increases with increasing surface area and pore volume. The ability of Hg and other sorbates to penetrate into the interior of a particle is related to pore size distribution. The pores of the sorbent must be large enough to provide free access to internal surface area by  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  while avoiding excessive blockage by previously adsorbed reactants. As particle size decreases, access to the internal surface area of the particle increases, along with potential adsorption rates. Powdered activated carbons used for Hg control typically have diameters of 44  $\mu\text{m}$  or smaller.

30. Mercury can be either physically or chemically adsorbed. Physical adsorption (physisorption) typically results from van der Waals and Coulombic (electrostatic) interactions between the sorbent and the sorbate. The resulting bonds are weak (typically  $< 10\text{-}15$  kcal/mole) and are easily reversed.

31. Chemical adsorption (chemisorption) involves the establishment of a chemical bond (as the result of a chemical reaction, electron transfer). Chemisorption results in stronger bonds than physisorption and is not necessarily reversible. Chemical adsorption is also dependent on the presence of chemically active sites where the sorbate is chemically bound. Some of the chemical constituents of activated carbons influencing Hg capture include: sulphur content, iodine content and chlorine content. Impregnation of carbons with sulphur, iodine or chlorine can increase the reactivity and capacity of sorbents.  $\text{Hg}^0$  is likely oxidized and sorbed in a rapid two-step reaction, either chemically by reaction with strong ionic groups such as  $\text{Cl}^-$ ,  $\text{I}^-$  or  $\text{S}^{2-}$  or physically through interaction with functional groups in sorbent pores.

32. The  $\text{HgCl}_2$  is readily adsorbed onto both carbon- and calcium-based sorbents, probably by acid-base reactions. The full report details the fundamental research to develop carbon and calcium sorbents for Hg vapour capture.

### **C. Evaluation of sorbents**

33. Sorbents may be evaluated by bench-, pilot-scale or full-scale experiments. The initial screening of sorbents has typically been conducted using bench-scale, packed-bed experimental reactors. These reactors are used to evaluate the adsorption capacity of sorbents exposed to Hg in a synthetic flue gas made from compressed bottled gases. The reactor is held at a predetermined temperature and either  $\text{Hg}^0$  or  $\text{HgCl}_2$  is fed into the synthetic flue gas upstream of the reactor. An on-line Hg analyser is used to continuously monitor the Hg content of the inlet flue gas and of that after exposure to the sorbent fixed bed. These reactors are used to determine the effects of

temperature and flue gas composition on the performance of sorbents. These reactors provide results that are primarily applicable to the capture of Hg in FF baghouses.

34. Flow reactors that expose sorbents to flue gas during short residence experiments can be used to simulate conditions associated with ESPs. These reactors can be used to explore the rates of Hg adsorption and determine the effects of temperature and flue gas composition. The most effective screening tests are conducted with reactors that are installed on a slip stream from a pilot-scale or full-scale coal combustion system. Large pilot-scale or full-scale tests must be used to assess the effects of mass transfer limitations (i.e. mixing and diffusion of flue gas constituents) and long-term equipment operability.

#### **D. Wet FGD scrubbers**

35. Oxidized mercury compounds such as  $\text{HgCl}_2$  are soluble in water and alkaline scrubbing solutions. Thus, the oxidized fraction of Hg vapours in flue gas is effectively captured when a power plant is operated with wet or semi-dry scrubbers for removing  $\text{SO}_2$ . The elemental fraction, on the other hand, is insoluble and is not removed to any significant degree. The challenge to Hg removal in wet FGD scrubbers, then, is to find some way to oxidize the elemental Hg vapour before or after it reaches the scrubber.

### **IV. EVALUATION OF DATA ON MERCURY CONCENTRATIONS**

36. The methods used to evaluate the ICR data were based on two interrelated objectives. The first method was to estimate the speciated amount and the geographical distribution of national Hg emissions from coal-fired power plants in 1999 in the United States. The second method was to characterize the effects of coal properties, combustion conditions and flue gas cleaning methods on the speciation and capture of Hg.

#### **A. Mercury capture by existing air pollution control devices**

37. The air pollution control technologies now used on pulverized-coal (PC) fired utility boilers exhibit average levels of Hg control that range from 0 to 98 per cent, as shown in table 1. The best levels of control are generally obtained by emission control systems that use FFs. The amount of Hg captured by a given control technology is better for bituminous coal than for either sub-bituminous coal or lignite.

38. The lower levels of Hg capture in plants firing sub-bituminous coal and lignite are attributed to low fly ash carbon content and the higher relative amounts of  $\text{Hg}^0$  in the flue gas from combustion of these fuels. The average capture of Hg based on OH method inlet measurements in

PC-fired plants equipped with a cold-side ESP is 35 per cent for bituminous coal, 3 per cent for sub-bituminous coal and near zero for lignite.

Table 1. Mean mercury emission reduction for pulverized-coal-fired boilers

Post-combustion emission controls used for PC boiler		Average mercury emission reduction (%) <sup>a/</sup>		
		Bituminous-coal-fired	Sub-bituminous-coal-fired	Lignite-fired
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 dry FGD system	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

a/ Mean reduction from test 3-run averages for each PC boiler unit in ICR phase III database.

39. Plants that use only post-combustion PM controls display average Hg emission reductions ranging from 0 per cent to 89 per cent. The highest levels of control were observed for units with FFs. Decreasing levels of control were shown for units with ESPs, PS scrubbers and mechanical collectors.

40. Units equipped with lime spray dryer absorber scrubbers (SDA/ESP or SDA/FF systems) exhibited average Hg captures ranging from 98 per cent for units burning bituminous coals to 3 per cent for units burning Sub-bituminous coal. The predominance of Hg<sup>0</sup> in stack gas units that are fired with Sub-bituminous coal and lignite results from low levels of Hg<sup>0</sup> oxidation.

41. The capture of Hg in units equipped with wet FGD scrubbers is dependent on the relative amount of Hg<sup>2+</sup> in the inlet flue gas and on the PM control technology used. Average Hg captures in wet FGD scrubbers ranged from 23 per cent for one PC-fired HS-ESP + FGD unit burning sub-bituminous coal to 97 per cent in a PC-fired FF + FGD unit burning bituminous coal. The high Hg capture in the FF + FGD unit is attributed to increased oxidation and capture of Hg in the FF.

42. Mercury captures in PC-fired units equipped with spray dry scrubbers and wet limestone scrubbers appear to provide similar levels of control on a percentage reduction basis. However, this observation is based on a small number of short-term tests at a limited number of facilities.

Additional testing will be required to characterize the effects of fuel, combustion conditions and air pollution control device conditions on the speciation and capture of Hg.

### **B. National emission estimates**

43. The data used for estimating the national Hg emissions in the United States were: (i) the mean Hg content of coal burned in any given unit during 1999; (ii) the amount of coal burned in that unit during 1999; and (iii) best match coal-boiler-control device emission factor for the unit. The results of these estimates indicated that:

- (a) Coal and related fuels burned in coal-fired utility boilers in 1999 contained 75 tons of Hg; and
- (b) Coal-fired utility power plants emitted 48 tons of Hg to the atmosphere in 1999.

### **C. Multi-pollutant controls**

44. The USEPA ICR data indicate that technologies currently in place for the control of criteria pollutants achieve reductions in Hg emissions that range from 0 to > 90 per cent. Current levels of Hg control can be increased by applying retrofit technologies or methods designed to increase capture of more than one pollutant. This multi-pollutant approach can utilize the synergisms that accrue through the simultaneous application of technologies for NO<sub>x</sub> and Hg control, SO<sub>2</sub> and Hg control, or SO<sub>2</sub>, NO<sub>x</sub> and Hg control.

45. Bench-scale and pilot-scale tests have shown that Hg capture in PM control devices generally increases as the carbon content of fly ash increases. Increased use of combustion modification techniques that increase ash carbon content will generally increase the amount and capture of Hg<sub>p</sub>.

46. The USEPA ICR data indicate that SCR systems may enhance the oxidation and capture of Hg. Recent pilot-scale and full-scale tests on bituminous-coal-fired units equipped with SNCR + CS-ESP and SCR + SDA/FF systems have confirmed these results. However, improvement in Hg capture appears to be highly dependent on the type of coal burned, and the design and operating conditions of SCR systems. The potential in increased Hg capture associated with the NO<sub>x</sub> control system cannot be quantified at present. It is believed, however, that the use of combustion modification techniques and post-combustion NO<sub>x</sub> control technologies on NO<sub>x</sub> state implementation plan (SIP) units will also increase the capture of Hg in these units.

47. The retrofit of coal-fired electric utility boiler units to control emission of SO<sub>2</sub> and fine PM is also expected to provide co-benefits in the control of Hg. This is apparent from the increased control of Hg on units equipped with FFs, dry FGD scrubbers and wet FGD scrubbers. Mercury or

multi-pollutant sorbents will add minimal capital costs to units that are retrofitted with FFs or SDA/FF for the control of other pollutants. The use of multi-pollutant sorbents would be more costly, but the incremental costs of Hg control would be modest. Technologies designed for use on existing wet FGD units could also be used for new scrubbers that are intended to control SO<sub>2</sub> and the precursors to secondary fine PM.

48. Generally, the control of Hg emissions via multi-pollutant control technologies can provide a cost-effective method for collectively controlling the various pollutants of concern.

## **V. POTENTIAL RETROFIT MERCURY CONTROL TECHNOLOGIES**

49. A practical approach to controlling Hg emissions at existing utility plants is to minimize capital costs by adapting or retrofitting the existing equipment to capture Hg. Potential retrofit options for the control of Hg were investigated for units that currently use any of the following post-combustion emission control methods: (i) ESPs or FFs for the control of PM; (ii) dry FGD scrubbers for the control of PM and SO<sub>2</sub>; and (iii) wet FGD scrubbers for the control of PM and SO<sub>2</sub>.

### **A. ESP and FF systems**

50. The least costly retrofit options for the control of Hg emissions from units with ESP or FF are believed to include:

(a) Injection of a sorbent upstream of the ESP or FF. Cooling of the stack gas or modifications to the ducting may be needed to keep sorbent requirements at acceptable levels;

(b) Injection of a sorbent between the ESP and a pulse-jet FF retrofitted downstream of the ESP. This approach will increase capital costs but reduce sorbent costs;

(c) Installation of a semi-dry circulating fluidized-bed absorber (CFA) upstream of an existing ESP used in conjunction with sorbent injection. The CFA recirculates both fly ash and sorbent to create an entrained bed with a large number of reaction sites. This leads to higher sorbent utilization and greater fly ash capture of Hg and other pollutants.

51. Units equipped with a FF require less sorbent than units equipped with an ESP. ESP systems depend on in-flight adsorption of Hg by entrained fly ash or sorbent particles. FFs attain the same in-flight Hg adsorption as ESPs and additional adsorption as the flue gas passes through the FF cake.

52. In general, the successful application of cost-effective sorbent injection technologies for ESP and FF units will depend on: (i) the development of lower-cost and/or higher-performing

sorbents; and (ii) appropriate modifications to the operating conditions of equipment currently being used to control emission of PM, NO<sub>x</sub>, and SO<sub>2</sub>.

### **B. Semi-dry FGD systems**

53. SDA systems that use calcium-based sorbents are the most common dry FGD systems used in the electric utility industry. An aqueous slurry containing the sorbent is sprayed into an absorber vessel where the flue gas reacts with the drying slurry droplets. The resulting particle-laden, dry flue gas then flows to an ESP or a FF where fly ash and SO<sub>2</sub> reaction products are collected.

54. CFAs are “vertical duct absorbers” that allow simultaneous gas cooling, sorbent injection and recycle, and gas absorption by flash drying of wet lime reagents. It is believed that CFAs can potentially control Hg emissions at lower costs than those associated with the use of spray dryers.

55. Dry FGD systems are already equipped to control emissions of SO<sub>2</sub> and PM. The modification of these units by the use of appropriate sorbents for the capture of Hg and other air toxics is considered to be the easiest retrofit problem to solve.

### **C. Wet FGD systems**

56. Wet FGD systems are typically installed downstream of an ESP or FF. Wet limestone FGD scrubbers are the most commonly used scrubbers on coal-fired utility boilers. These FGD units are expected to capture more than 90 per cent of the Hg<sup>2+</sup> in the flue gas entering the scrubber. Consequently, existing wet FGD scrubbers may lower Hg emissions between 20 and 80 per cent, depending on the speciation of Hg in the inlet flue gas.

57. Improvements in wet scrubber performance in capturing Hg depend primarily on the oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup>. This may be accomplished by (i) the injection of appropriate oxidizing agents or (ii) the installation of fixed oxidizing catalysts upstream of the scrubber to promote oxidation of Hg<sup>0</sup> to soluble species.

58. An alternative strategy for controlling Hg emissions from wet FGD scrubbing systems is to inject sorbents upstream of the PM control device. In wet FGD systems equipped with ESPs, performance gains are limited by the in-flight oxidation of Hg<sup>0</sup> and the in-flight capture of Hg<sup>2+</sup> and Hg<sup>0</sup>. In systems equipped with FFs, increased oxidation and capture of Hg can be achieved as the flue gas flows through the FF. Increased oxidation of Hg<sup>0</sup> in the FF will result in increased Hg removal in the downstream scrubber.

#### **D. Multi-pollutant control methods**

59. From a long-term perspective, the most cost-effective Hg controls will be those implemented with a multi-pollutant emission control scheme, wherein Hg sorbents also remove other pollutants, and catalysts and absorbers are employed to remove bulk contaminants such as NO and SO<sub>2</sub>. Mercury is also removed as a consequence of using particular bulk gas sorbents, catalysts, particle collectors and absorbers. Therefore, while sorbents injected upstream of PM collectors may be readily used for Hg control, the best long-term schemes will result from modifying or adding control systems for other pollutants that also control Hg emissions.

### **VI. COSTS OF RETROFIT MERCURY CONTROL TECHNOLOGIES**

60. Preliminary annual costs of Hg controls using powdered activated carbon (PAC) injection have been estimated based on recent pilot-scale evaluations with commercially available adsorbents (see table 2). These control costs range from 0.03 to 0.4 US cents/kWh, with the highest costs associated with plants having hot-side electrostatic precipitators (HS-ESPs). For plants representing 89 per cent of current capacity and using controls other than HS-ESPs, the costs range from 0.03 to 0.2 US cents/kWh. Assuming a 40 per cent reduction in sorbent costs by the use of a composite lime-PAC sorbent for Hg removal, cost projections range from 0.02 to 0.2 US cents/kWh, with higher costs again being associated with plants using HS-ESPs.

Table 2. Estimates of current and projected annual operating costs for retrofit mercury emission control technologies

Coal type (sulphur content)	Existing air pollution control device <sup>a/</sup>	Retrofit mercury control <sup>b/</sup>	Current cost (cents/kWh)	Projected cost (cents/kWh)
Bituminous (3% S)	CS-ESP+FGD	PAC	0.07 – 0.12	0.04 – 0.07
	FF+FGD	PAC	0.03 – 0.05	0.02 – 0.03
	HS-ESP+FGD	PAC+PFF	0.15 – NA <sup>c/</sup>	0.09 – NA <sup>c/</sup>
Bituminous (0.6% S)	CS-ESP	SC+PAC	0.1 – 0.18	0.06 – 0.1
	FF	SC+PAC	0.4 – 0.08	0.03 – 0.05
	HESP	SC+ PAC+PFF	0.18 – 0.38	0.1 – 0.23
Sub-bituminous (0.5% S)	CS-ESP	SC+PAC	0.12 – 0.19	0.07 – 0.11
	FF	SC+PAC	0.04 – 0.11	0.03 – 0.07
	HESP	SC+PAC+PFF	0.14 – 0.27	0.09 – 0.16

<sup>a/</sup> CS-ESP = cold-side electrostatic precipitator; HS-ESP = hot-side electrostatic precipitator; FF= fabric filter; FGD = flue gas desulphurization

<sup>b/</sup> PAC=powdered activated carbon; SC=spray cooling; PFF=polishing fabric filter

<sup>c/</sup> NA = not available

61. In comparison, the estimated annual costs of Hg controls, as a function of plant size, lie mostly between the costs for low-NO<sub>x</sub> burners (LNBS) and selective catalytic reduction (SCR) systems. The costs of Hg control will dramatically diminish if retrofit hardware and sorbents are used for the control of other pollutants such as NO<sub>x</sub>, SO<sub>2</sub> or fine PM.

62. The performance and cost estimates of PAC injection-based Hg control technologies presented in this document are based on relatively few data points from pilot-scale tests and are considered to be preliminary. However, based on pilot-scale tests and the results of ICR data evaluations, better sorbents and technologies now being developed will reduce the costs of Hg controls beyond current estimates.

63. Within the next two to three years, the evaluation of retrofit technologies at plants where co-control is being practised will lead to a more thorough characterization of the performance and costs of Hg control. Future cost studies will focus on the development of performance and cost information needed to refine cost estimates for sorbent-injection-based controls, will develop cost estimates for wet scrubbing systems that use methods for oxidizing Hg<sup>0</sup> and will determine the costs of various multi-pollutant control options.

64. The issue of Hg in residues will also be examined to address concerns related to the release of captured Hg species into the environment. These evaluations will be conducted in conjunction with the development and evaluation of air pollution emission control technologies.

## **VII. COAL COMBUSTION RESIDUES AND MERCURY CONTROL**

65. The operation of power plants results in solid discharges including fly ash, bottom ash, boiler slag, and FGD residues. These residues already contain Hg, presumably bound Hg that is relatively insoluble and non-leachable. In 1998, utility boilers in the United States generated approximately 108 million tons of coal combustion residues (CCRs). Of this amount, about 77 million tons were landfilled and about 31 million tons were utilized.

66. Increased control of Hg emissions from coal-fired power plants may change the amount and composition of CCRs. Such changes may increase the potential for release of Hg to the environment from either landfilling or uses of CCRs. Mercury volatilization from CCRs in landfills and/or surface impoundments is expected to be low due to the low temperatures involved and the relatively small surface area per unit volume of residue. For Hg control retrofits involving dry or wet FGD scrubbers, the residues are typically alkaline and the acid leaching potential of Hg from these residues is expected to be minimal.

67. There are several commercial uses of CCR where data needed to characterize the Hg emission potential are lacking. The following CCR uses are given a priority for developing additional data in order to characterize the ultimate fate of Hg:

- (a) The use of fly ash in cement production;
- (b) The volatilization and leaching of residues used for structural fills;
- (c) Leaching of residues exposed to the acidic conditions from disposal in abandoned mines;
- (d) Volatilization of Hg during the production of wallboard from gypsum in wet scrubber residues;
- (e) Mercury volatilization during the production and application of asphalt with fly ash fillers; and
- (f) Leaching or plant uptake of Hg from fly ash, bottom ash and FGD sludge that are used as soil amendments.

### **VIII. CURRENT AND PLANNED RESEARCH**

68. The United States authorities, the utility industry and the control technology industry are funding research on the control of Hg emissions from coal-fired boilers. These research efforts will be used to:

- (a) Develop hazardous air pollution maximum achievable control technology (MACT) requirements for electric utility generating units;
- (b) Optimize control of Hg emissions from units that must comply with more stringent NO<sub>x</sub> emission requirements under the revised State implementation plans; and
- (c) Develop technologies that can be used to control emissions under multi-pollutant control legislation options that are currently being considered.

69. Current Federal research efforts include three full-scale test projects, six new pilot-scale test projects on coal-fired units, the evaluation of Hg CEMs, supporting research on the speciation and capture of Hg, and research on CCRs and CCBs. This research includes:

- (a) One full-scale ESP sorbent-injection project with tests at four sites;
- (b) One full-scale wet FGD scrubber project at two sites;

- (c) One full-scale project on the effects of SNRC, SCR and SO<sub>3</sub> conditioning systems at five sites;
- (d) On going research on the development and use of Hg CEMs;
- (e) On going speciation, capture and sorbent development research; and
- (f) Small Business Administration projects on the development of sorbents and measurement methods.

70. Six new pilot-scale projects by the United States Department of Energy were announced in 2001. These are:

- (a) Advance particulate collector with sorbent injection (North Dakota-EERC);
- (b) Evaluation of Hg<sup>0</sup> oxidation catalysts (URS Radian Group);
- (c) Spray cooling and multi-pollutant sorbents (CONSOL);
- (d) Evaluation of multi-pollutant sorbents and CFBA (SRI);
- (e) Electrical discharge multi-pollution control system (Power Span);
- (f) Evaluation of advanced sorbents (Apogee Scientific).

## IX. CONCLUSIONS AND RECOMMENDATIONS

71. Additional efforts are planned to characterize the behaviour of Hg in coal combustion systems. Further research is needed on the speciation and capture of Hg and on the stability of Hg in CCRs and residue by-products. Studies on the control capabilities and costs of potential Hg retrofit technologies currently under pilot-scale development are being continued and appropriate control technologies are to be evaluated on full-scale units. Additionally, an evaluation of the co-control of Hg with available PM, SO<sub>2</sub> and NO<sub>x</sub> controls is needed.

72. Mercury measurement and monitoring capabilities must be consistent with the regulatory approaches being considered; e.g. speciated vs. total Hg emissions. Field activities need to be coordinated to (i) improve the emissions database; (ii) develop the most appropriate technologies (e.g. Hg-specific vs. multi-pollutant); and (iii) refine cost data and cost-performance models based on actual field experience.

73. Current and future research should focus on:

- (a) Control of emissions for units with ESPs;
- (b) Control of Hg emissions from Sub-bituminous coals and lignite;
- (c) Evaluation of CFA systems;
- (d) Demonstration of Hg control for units with SDA/ESP and SDA/FF systems;

- (e) Development of Hg<sup>0</sup> oxidizing methods for wet FGD systems;
- (f) Evaluation additives for the oxidation of Hg<sup>0</sup> and the sequestration of Hg<sup>2+</sup> in wet scrubbers;
- (g) Enhancement of fly ash capture by combustion modification techniques;
- (h) Optimization of NO<sub>x</sub> controls for Hg control;
- (i) Control of Hg and other toxic air emissions from units equipped with SCR and wet FGD scrubbers;
- (j) Use and evaluation of Hg CEMs;
- (k) Tests with CEMs to study the variability of Hg emissions;
- (l) Effects of coal blending on Hg capture; and
- (m) Effects of cyclone-, stoker-, and fluidized-bed combustion on Hg control.