

**Guidance on best available  
techniques and best  
environmental practices**

**Coal-fired power plants and  
coal-fired industrial boilers**

**UN Environment**

**2016**

## **Coal-fired power plants and coal-fired industrial boilers**

### **Guidance on Best Available Techniques and Best Environmental Practices to Control Mercury Emissions from Coal-fired Power Plants and Coal-fired Industrial Boilers**

#### **Summary**

Coal-fired power plants and coal-fired industrial boilers constitute a large and important source of atmospheric mercury emissions. In 2010, coal burning was responsible for the emission of some 475 tons of mercury worldwide, the majority of which was from power generation and industrial boiler use (UNEP, 2013a). This represents about 40 per cent of the total global anthropogenic emissions. Coals used for combustion throughout the world contain trace amounts of mercury that, when uncontrolled, are emitted into the atmosphere.

This chapter provides guidance on best available techniques (BAT) and best environmental practices (BEP) for controlling and, where feasible, reducing mercury emissions from coal-fired power plants and coal-fired industrial boilers, which are covered by Annex D of the Convention.

Most coal-fired power plants are large electricity-producing plants; some also supply heat. Industrial boilers provide heat or process steam to meet the needs of the facility where they are installed.

Mercury emissions from coal-fired combustion plants are affected by a number of variables, including mercury concentration and speciation in coal; coal type and composition; type of combustion technology; and control efficiency of existing pollution control systems. Mercury emission control technologies are generally similar for all coal-fired boilers, however, regardless of their application at power plants or industrial facilities.

Air pollution control systems are already widely used in a number of countries to reduce emissions of traditional air pollutants other than mercury, such as particulate matter, oxides of nitrogen, and sulfur dioxide. Even when not primarily designed for mercury capture, these systems provide the co-benefit of reducing mercury emissions, as they are able to capture some of the mercury in the flue gases. Dedicated mercury control techniques have been developed and are being applied in a number of countries to provide additional mercury control in cases where co-benefit techniques are not able to provide sufficient and reliable mercury reductions.

This chapter discusses a variety of BAT used for mercury control and provides indicative information on their emission performance and estimated costs. It also describes important components of BEP for the operation of coal-fired facilities. Finally, it presents selected emerging mercury emission control techniques and discusses mercury emission monitoring in the specific context of coal-fired plants.

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## **List of acronyms and abbreviations**

|      |  |
|------|--|
| APCS | Air pollution control system               |
| BAT  | Best available technique                   |
| BEP  | Best environmental practice                |
| COP  | Conference of parties                      |
| ESP  | Electrostatic precipitator                 |
| FF   | Fabric filter                              |
| FGD  | Flue gas desulfurization                   |
| ID   | Induced draft                              |
| O&M  | Operation and maintenance                  |
| PAC  | Powdered activated carbon                  |
| PC   | Pulverized coal                            |
| PM   | Particulate matter (sometimes called dust) |
| SCR  | Selective catalytic reduction              |
| UBC  | Unburned carbon                            |

# 1 Introduction

This section provides guidance on best available techniques (BAT) and best environmental practices (BEP) for controlling and, where feasible, reducing mercury emissions from coal-fired power plants and coal-fired industrial boilers, which are covered by Annex D of the Convention.

Coal-fired power plants and coal-fired industrial boilers are a large source of local, regional, and global atmospheric mercury emissions, emitting over 470 metric tons of mercury worldwide (UNEP, 2013a). Coals used for combustion throughout the world contain trace amounts of mercury that, when uncontrolled, are emitted (along with other pollutants) during the combustion process.

Most coal-fired power plants are large electricity-producing plants; some also supply heat (combined heat and power plants, district heating, etc.). Industrial boilers provide the heat or process steam necessary for local production at a facility where they are installed. Boilers in coal-fired power plants typically consume more coal than the majority of coal-fired industrial boilers, with a potential increase in mercury emissions. However, the number of industrial boilers is usually larger than the number of power plants. Another difference is that coal-fired power plant boilers are mostly single fuel, while coal-fired industrial boilers are often designed for and use a more diverse mix of fuels (e.g., fuel by-products, waste, wood) in addition to coal (Amar et al., 2008).

From the standpoint of their technical feasibility, the same technologies can be used for controlling mercury emissions from all coal-fired boilers, whatever their function. In a number of countries, power plants and large industrial boilers are already equipped with air pollution control systems (APCSs) as a result of air pollution policies. Even when not designed for mercury capture, these APCSs are capable of capturing some of the mercury output from combustion with the direct effect of reducing the release of mercury to the atmosphere (the so-called mercury co-benefit of APCSs). Smaller coal-fired industrial boilers, on the other hand, are often not equipped with efficient emission control devices, and this will affect the consideration of how to address mercury emissions from these plants.

Several factors affect the amount of mercury that might be emitted by similar plants burning comparable amounts of coal. These factors include:

- Mercury concentration in coal
- Coal type and composition
- Type of combustion technology
- Presence and mercury removal efficiency of an APCS

The above factors will be considered in the remainder of this document in greater detail in the context of BAT/BEP determination.

## 2 Processes used in coal-fired power plants and coal-fired industrial boilers, including consideration of input materials and behaviour of mercury in the process

### 2.1 Coal properties

Coal is a complex energy resource that can vary greatly in its composition, even within the same seam. The quality of coal is determined by its composition and energy content. Ranking of coal is based on the degree of transformation of the original plant material to carbon. The American Society for Testing and Materials (ASTM) defines four basic types of coal: lignite, subbituminous, bituminous, and anthracite (ASTM D388). In some countries lignite and subbituminous coal are termed “brown coal”, and bituminous and anthracite coal “hard coal”. The ASTM nomenclature will be used throughout this document.

**Lignite** typically contains 25–35 per cent fixed carbon (w/w) and has the lowest energy content (below 19.26 MJ/kg gross calorific value). It is generally used for electricity generation or district heating in the vicinity of the mines.

**Subbituminous coal** typically contains 35–45 per cent fixed carbon (w/w) and has a heating value between 19.26 and 26.80 MJ/kg gross calorific value. It is widely used for electricity generation, and also in industrial boilers.

**Bituminous coal** contains 45–86 per cent fixed carbon (w/w) and has a heating value between 26.80 and 32.66 MJ/kg gross calorific value. Like subbituminous coal, it is widely used to generate electricity and in industrial boilers.

**Anthracite** contains a very large amount of fixed carbon, as high as 86–97 per cent (w/w). It is the hardest coal and gives off the greatest amount of heat when burned (more than 32.66 kJ/kg gross calorific value). It is the most difficult coal fuel to burn, however, owing to its low volatile content.

Figure 1 presents typical use of different types of coal (WCA, 2014). As shown in that Figure 1, combined bituminous and subbituminous coals used in electricity-generating power plants and in industrial boilers are estimated to constitute over 80 per cent of known coal reserves worldwide.

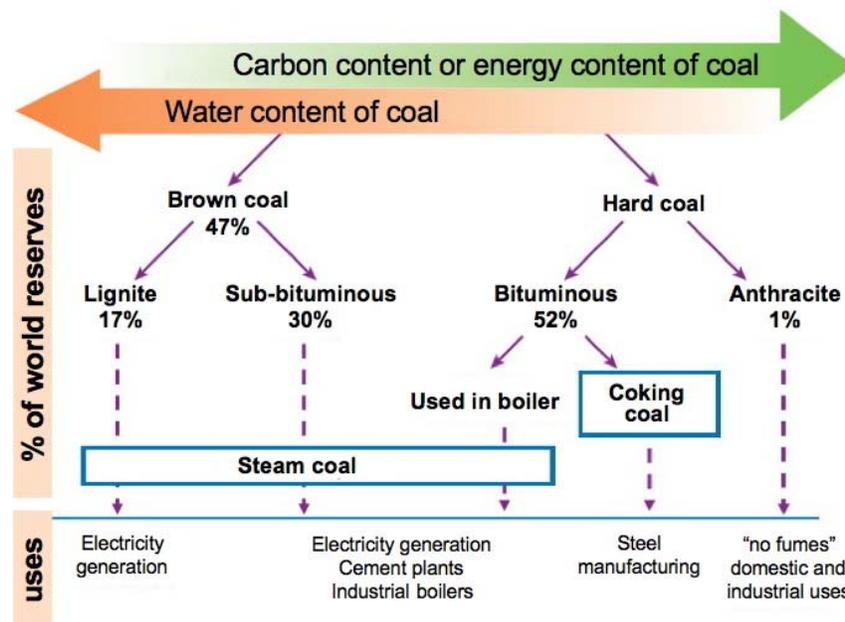


Figure 1. Use of different ranks of coal (WCA 2014)

Mercury content is a key parameter affecting the amount of uncontrolled mercury emission. Table 1, adopted from Tewalt et al. (2010), presents publicly available data on the mercury content of coal.

**Table 1**

Mercury content in coals (mg/kg)

| Country        | Coal type                              | Average of all samples  | Range  | Reference  |
|----------------|--|-------------------------|--|--|
| Australia      | Bituminous                             | 0.075                   | 0.01-0.31  | Nelson, 2007; Tewalt et al., 2010                    |
| Argentina      | Bituminous                             | 0.19                    | 0.02-0.96 (8)                                      | Finkelman, 2004; Tewalt et al., 2010                 |
| Botswana       | Bituminous                             | 0.10                    | 0.04-0.15 (28)                                     | Finkelman, 2004; Tewalt et al., 2010                 |
| Brazil         | Bituminous<br>Subbituminous            | 0.20<br>0.3             | 0.04-0.81 (23)<br>0.06-0.94 (45)                   | Finkelman, 2004; Tewalt et al., 2010                 |
| Canada         |  | 0.058                   | 0.033-0.12 (12)                                    | Tewalt et al., 2010                                  |
| Chile          | Bituminous<br>Subbituminous            | 0.21<br>0.033           | 0.03-2.2 (19)<br>0.022-0.057 (4)                   | Tewalt et al., 2010                                  |
| China          | Bituminous/Subbituminous               | 0.17                    | 0.01-2.248 (482)                                   | Zhang et al., 2012; UNEP, 2011                       |
| Colombia       | Subbituminous                          | 0.069                   | >0.02-0.17 (16)                                    | Finkelman, 2004                                      |
| Czech Rep.     | Lignite<br>Bituminous                  | 0.338<br>0.126          | <0.03-0.79 (16)<br>0.03-0.38 (21)                  | Finkelman, 2003<br>Tewalt et al., 2010               |
| Egypt          | Bituminous                             | 0.12                    | 0.02-0.37 (24)                                     | Tewalt et al., 2010                                  |
| France         | Bituminous                             | 0.044                   | 0.03-0.071 (3)                                     | Tewalt et al., 2010                                  |
| Germany        | Bituminous<br>Lignite                  | 0.05                    | 0.7-1.4<br>Max: 0.09                               | Pirrone et al., 2001<br>MUNLV 2005                   |
| Hungary        | Bituminous<br>Subbituminous<br>Lignite | 0.354<br>0.138<br>0.242 | 0.091-1.2 (5)<br>0.04-0.31 (19)<br>0.075-0.44 (12) | Tewalt et al., 2010                                  |
| India          | Bituminous<br>Lignite                  | 0.106<br>0.071          | 0.02-0.86 (99)<br>0.053-0.093 (8)                  | Tewalt et al., 2010; UNEP, 2014                      |
| Indonesia      | Lignite<br>Subbituminous               | 0.11<br>0.03            | 0.02-0.19 (8)<br>0.01-0.05 (78)                    | Finkelman, 2003; Tewalt et al., 2010<br>US EPA, 2002 |
| Iran           | Bituminous                             | 0.168                   | 0.02-0.73 (57)                                     | Tewalt et al., 2010                                  |
| Japan          | Bituminous                             | 0.0454                  | 0.01-0.21 (86)                                     | Ito et al., 2004                                     |
| Kazakhstan     | Bituminous                             | 0.08                    | <0.03-0.14 (15)                                    | Tewalt et al., 2010                                  |
| New Zealand    | Bituminous<br>Subbituminous            | 0.073<br>0.082          | 0.03-0.1 (5)<br>0.062-0.13 (9)                     | Tewalt et al., 2010                                  |
| Mongolia       | Bituminous                             | 0.097                   | 0.02-0.22 (36)                                     | Tewalt et al., 2010                                  |
| Peru           | Anthracite+Bituminous                  | 0.27                    | 0.04-0.63 (15)                                     | Finkelman, 2004                                      |
| Philippines    | Subbituminous                          | 0.04                    | <0.04-0.1  | Finkelman, 2004                                      |
| Poland         | Bituminous                             | 0.085                   | 0.013-0.163  | Bojkowska et al., 2001                               |
| Romania        | Lignite+Subbituminous                  | 0.21                    | 0.07-0.46 (11)                                     | Finkelman, 2004                                      |
| Russia         | Bituminous/<br>Subbituminous           | 0.12                    | <0.02-0.25 (23)                                    | UNEP, 2013b<br>Romanov et al., 2012                  |
| Slovak Rep.    | Bituminous<br>Lignite                  | 0.08<br>0.057           | 0.03-0.13 (7)<br>0.032-0.14 (8)                    | Finkelman, 2004<br>Tewalt et al., 2010               |
| South Africa   |  | 0.157                   | 0.023-0.1 (40)                                     | Leaner et al., 2009; Tewalt et al., 2010             |
| Tanzania       | Bituminous                             | 0.12                    | 0.03-0.22 (75)                                     | Finkelman, 2004                                      |
| Thailand       | Lignite                                | 0.137                   | 0.02-0.6 (23)                                      | Tewalt et al., 2010                                  |
| Turkey         | Lignite                                | 0.12                    | 0.03-0.66 (149)                                    | Tewalt et al., 2010                                  |
| United Kingdom | Bituminous                             | 0.216                   | 0.012-0.6 (84)                                     | Tewalt et al., 2010                                  |

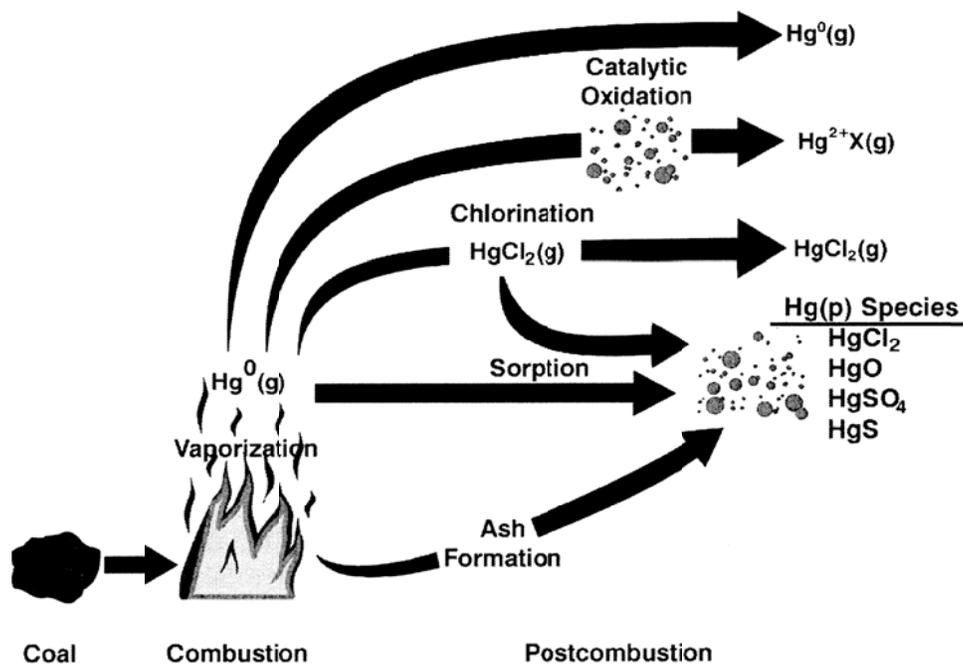
| Country  | Coal type     | Average of all samples | Range            | Reference           |
|----------|---------------|------------------------|------------------|---------------------|
| USA      | Subbituminous | 0.1                    | 0.01-8.0 (640)   | US EPA, 1997        |
|          | Lignite       | 0.15                   | 0.03-1.0 (183)   | US EPA, 1997        |
|          | Bituminous    | 0.21                   | <0.01-3.3 (3527) | US EPA, 1997        |
|          | Anthracite    | 0.23                   | 0.16-0.30 (52)   | US EPA, 1997        |
| Vietnam  | Anthracite    | 0.348                  | <0.02-0-34 (6)   | Tewalt et al., 2010 |
| Zambia   | Bituminous    | 0.6                    | <0.03-3.6 (14)   | Tewalt et al., 2010 |
| Zimbabwe | Bituminous    | 0.08                   | <0.03-0.15 (6)   | Tewalt et al., 2010 |

Note: Caution should be used when interpreting the above mercury concentration information, as populations of coal samples for different countries vary widely. In addition, information is not universally available to indicate whether the reported concentrations of mercury are based on dry coal or as-received coal figures. These data may not be representative of coal from the as-burned standpoint. The number in parentheses in the 'range' column reflects the number of samples.

## 2.2 Mercury transformations during combustion of coal

The principal combustible constituents of coal are elemental carbon and hydrogen, and their compounds.

The physical and chemical transformations that mercury undergoes during coal combustion, and subsequently in the resulting flue gas, are shown schematically in Figure 2 (Galbreath and Zygarlicke, 2000). Mercury is associated primarily with the inorganic mineral components of coal, although an association with the organic components of coal as organo-mercuric compounds has been suggested (Swaine, 1990; Groen and Craig, 1994; Finkelman, 1994). Accordingly, pyrite ( $\text{FeS}_2$ ) is the dominant mineral host for mercury in coal. In rare cases with anomalous mercury enrichment, cinnabar ( $\text{HgS}$ ) may also be present (Kolker et al. 2006; Kolker, 2012 and references therein). As the mineral (and possibly organo-mercuric) hosts of mercury decompose during combustion ( $>1400\text{ }^\circ\text{C}$ ), mercury evolves as elemental mercury ( $\text{Hg}^0$ ). The mode of occurrence of mercury in coal does not affect this initial combustion transformation mechanism.



**Figure 2.** Potential mercury transformations during combustion and post-combustion (Galbreath and Zygarlicke, 2000)

Mercury emissions from coal-fired boilers can be classified into three main forms: gaseous elemental mercury ( $\text{Hg}^0$ ), gaseous oxidized mercury ( $\text{Hg}^{2+}$ ), and particulate-bound mercury ( $\text{Hg}_\text{p}$ ) which may be elemental or oxidized mercury. The relative amounts of these three main forms of mercury in the flue gases are the so-called mercury speciation. Mercury bromination or chlorination is assumed to be the dominant mechanism of mercury chemical transformation affecting the speciation of mercury. Other potential mechanisms involve mercury

interactions with ash particle surfaces where reactive chemical species, catalysts, and active sorption sites are available to convert elemental to oxidized mercury, and also elemental and oxidized mercury to particulate-bound mercury (Galbreath and Zygarlicke, 2000).

Gas phase oxidation occurs primarily via chlorine species originally present in the coal, as the gases cool down through the air preheater and air pollution control devices. The extent of gas phase mercury oxidation is highly dependent upon the coal rank, the concentration of chlorine present in the coal, and the operating conditions of the boiler (e.g., air-to-fuel ratio and temperature). For example, a study of mercury speciation measurements from 14 different coal combustion systems reported from 30 to 95 per cent oxidized mercury upstream of the air pollution control devices (Prestbo and Bloom, 1995). A literature survey reveals that mercury oxidation falls primarily in the range of 45–80 per cent, with the oxidized form of mercury mostly being mercury chloride (Senior et al., 2004).

Different combustion or firing methods of coal are used in power plants and industrial boilers. These methods include:

- Suspension firing of pulverized coal (pulverized coal firing)
- Stoker firing (i.e., firing on a slowly moving or fixed grate)
- Fluidized bed firing (in either a bubbling type or a circulating fluidized bed)
- Cyclone firing of crushed coal

Most large steam generation at power plants is produced through the pulverized coal firing. In a pulverized coal boiler, finely ground coal is pulverized to a fine powder and blown directly to individual burners where it is mixed with preheated combustion air and combusted in a flame. The heat energy from the combustion process is used to produce steam, which drives a turbine-generator set to produce electricity. Field tests indicate that the speciation profile varies considerably among the tested pulverized coal boilers (Wang et al., 2010).

Stoker firing is still in use in some parts of the world, mostly in smaller boilers. In stoker firing, heated air passes upward through apertures in the grate. Dampers are positioned in under-grate zones in order to achieve proper biasing of the airflow. Over-fire combustion (air added above the grate) adds turbulence to gases coming from the grate and supplies the required air for the portion of fuel that burns in suspension. In general, stokers produce less particulate matter (PM) per unit of fuel fired, and coarser particulates compared with pulverized coal firing, because combustion takes place in a quiescent fuel bed without significant ash carry-over into the exhaust gases.

Fluidized bed firing is particularly useful for handling low-grade coals (no need for drying). In a fluidized bed combustor of the bubbling-bed type, coal particle size and vertical air velocity are regulated to establish a discrete horizontal plane that divides the active bed from the entrained-flow open furnace above. The basic mechanism for the control of bed temperature and heat transfer to the walls of the combustor, and to any immersed heating surface in the bed of a fluidized-bed boiler, is the variation in the total solids inventory. The temperature in a fluidized-bed combustor is controllable in a narrow range. On-site measurement of mercury concentrations from a circulating fluidized bed boiler shows that particulate mercury is the dominant mercury species in the boiler's flue gas (Duan et al., 2010).

In cyclone firing, crushed (but not pulverized) coal is burned in a swirling combustion chamber at high temperatures, making a liquid slag out of most of the mineral matter in the coal. The hot gases then enter the furnace where they radiate heat to the furnace walls and convect heat to generate steam, which drives a turbine generator set to produce electricity. Cyclone boilers generate less fly ash per unit coal burned than pulverized coal boilers, because most of the mineral matter in a cyclone boiler becomes a liquid slag that is collected from the bottom of the cyclonic combustion chamber.

### 3 Menu of mercury emission reduction techniques

This section describes mercury emission reduction approaches and control technologies that could be considered for the determination of BAT by a given party or facility (see section 5 below). They include coal treatment, co-benefit mercury removal, and technologies dedicated to the removal of mercury.

#### 3.1 Coal washing

Coal washing reduces ash content and improves its heating value, thus increasing boiler efficiency (Satyamurty, 2007). Coal washing, while primarily targeting the minimization of ash and sulfur content of coal, can also decrease the mercury content of coal, and this is already done in some cases. Raw coal contains mineral impurities such as rock and clay that are referred to as ash. Where appropriate, this raw coal should be processed (or cleaned) to reduce the ash content, to increase the heating value, and to reduce the particulate matter (PM), sulfur and, potentially, mercury content to ultimately lower emissions when the coal is burned in the boiler. In addition, the removal of mineral impurities also reduces operation and maintenance costs and slows the deterioration of the boiler system. It should be noted, however, that most lignite and brown coals are not amenable to conventional coal washing (Institution of Chemical Engineers, 1997).

Conventional coal washing methods may also remove some of the mercury associated with the incombustible mineral materials. However, they will typically not remove the mercury associated with the organic carbon structure of the coal (USEPA, 2002). One review quotes test data for 26 bituminous coal samples from the United States with a wide range in the amount of mercury removed by coal washing (USEPA, 1997). This trend was confirmed by another study (USGS, 2014), which concluded that coal washing was effective in reducing the concentrations of pyrite-associated elements such as mercury. Yet another study reported average mercury reduction on an energy basis of 37 per cent (Toole-O'Neil et al., 1999).

The variation in mercury reductions quoted above might be a function of the type of process used to wash a given coal, the coal rank, and the nature of mercury in the coal matrix. In summary, removal of some of the mercury from coal is feasible when conventional coal washing methods are used. The effectiveness of mercury removal during conventional coal washing, however, varies widely depending on the source of the coal and on the nature of the mercury within it.

##### *Cross-media effects of coal washing*

Coal washing generates waste slurry which contains mercury. There is potential soil or groundwater contamination if coal washing slurry is not safely managed

#### 3.2 Contribution of APCs in terms of mercury removal

The APCs installed primarily for control of SO<sub>2</sub>, NO<sub>x</sub>, or particulate matter (PM) remove mercury from the flue gas. This is called the co-benefit mercury removal. Co-benefit mercury removal by non-mercury air pollution control equipment is most often accomplished in two fundamental modes: removal of oxidized mercury in a wet flue gas desulfurization (wet FGD) scrubber and removal of PM-bound mercury in a PM control device, such as an electrostatic precipitator (ESP) or fabric filter (FF). Co-benefit removal of mercury can also be accomplished in spray dryer absorbers. Depending on the configuration of pollution control equipment, varying amounts of mercury removal could be accomplished. An overview of the magnitude of co-benefit mercury removal for different configurations of existing APCs is provided in Table 2 (Srivastava et al., 2006; EIPPCB, 2013). It should be noted that the co-benefit removal as shown in Table 2 will vary depending on coal properties and operational parameters of the APCs.

**Table 2**

Overview of co-benefit mercury removal in APCs

| Existing control equipment | Qualitative mercury capture  |
|----------------------------|--|
| ESpC only                  | Good capture of particulate-bound; better capture for high chlorine coals than low rank coals.   |
| ESPh only                  | Low capture  |
| FF only                    | Good capture of oxidized mercury   |
| ESpC + wet FGD             | Generally, good capture for high chlorine coals thanks to presence of soluble oxidized mercury in the flue gas. Relatively poor capture for low rank coals. Elemental mercury re-emission may decrease the amount of co-benefit. |
| ESPh + wet FGD             | Generally, good capture for high chlorine coals thanks to presence of soluble oxidized mercury in the flue gas. Relatively poor capture for low rank coals. Elemental mercury re-emission may decrease the amount of co-benefit. |

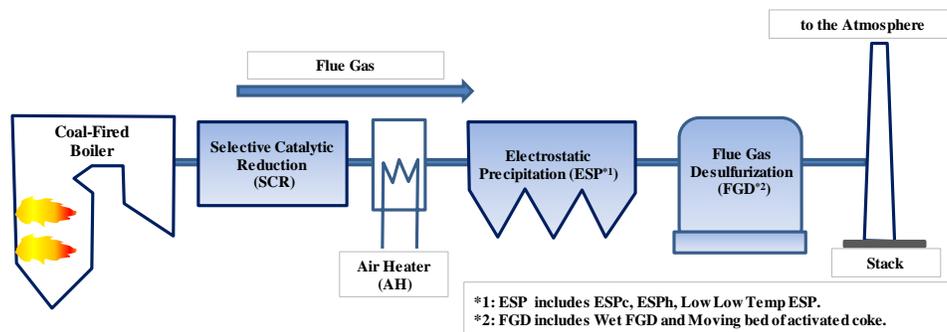
|                               |   |
|-------------------------------|---|
| SDA + FF                      | Generally good capture for high chlorine coals; less co-benefit capture expected for low rank coals.  |
| FF + Wet FGD                  | Generally, good capture for high chlorine coals thanks to presence of soluble oxidized mercury in the flue gas. Relatively poor capture for low rank coals. Elemental mercury re-emission may decrease the amount of co-benefit. Elemental mercury may be oxidized across the FF and captured in the wet scrubber.  |
| SCR + ESPc                    | Good capture of particulate-bound mercury, better capture for high chlorine coals than low rank coals   |
| SCR + ESPh                    | Low capture   |
| SCR + ESPc + wet FGD          | Good capture for high chlorine coals thanks to increased amount of soluble oxidized mercury in the flue gas which is promoted by the SCR. Improved capture for low rank coals thanks to greater amount of soluble oxidized mercury in the flue gas. Elemental mercury re-emission may decrease the amount of co-benefit. Good capture of particulate-bound mercury.   |
| SCR + HEX + LLT-ESP + wet FGD | Very high capture for high chlorine coals thanks to increased amount of soluble oxidized mercury in the flue gas which is promoted by the SCR. Improved capture for low rank coals thanks to greater amount of soluble oxidized mercury in the flue gas. Elemental mercury re-emission may decrease the amount of co-benefit. Combination of heat exchanger and low-low temperature ESP enhances capture of particulate and vapour phase mercury. |
| SCR + SDA + FF                | Generally good capture for high chlorine coals, less for low rank coals. SCR enhances capture by oxidizing elemental mercury to oxidized mercury form, given availability of chlorine in the flue gas.  |
| SCR + ESPh + wet FGD          | Good capture for high chlorine coals thanks to increased amount of soluble oxidized mercury in the flue gas which is promoted by the SCR. Improved capture for low rank coals thanks to greater amount of soluble oxidized mercury in the flue gas. Elemental mercury re-emission may decrease the amount of co-benefit.  |
| SCR + FF + wet FGD            | Good capture for high chlorine coals thanks to increased amount of soluble oxidized mercury in the flue gas which is promoted by the SCR. Improved capture for low rank coals thanks to greater amount of soluble oxidized mercury in the flue gas. Elemental mercury re-emission may decrease the amount of co-benefit. Good capture of particulate-bound mercury;   |

**Key:**

ESP = electrostatic precipitator; ESPc = cold side ESP; ESPh = Hot side ESP; FF = fabric filter; SCR = selective catalytic reduction; SDA = spray dryer absorber (dry scrubber); Wet FGD = wet flue gas desulfurization scrubber; HEX = heat exchange; LLT-ESP= low-low temperature ESP

Low means less than 30 per cent control, high/good means more than 70 per cent control, moderate means 30 to 70 per cent control.

One of the APCS configurations presented in Table 2 (SCR+ESPc+FGD) is shown schematically in Figure 3 below (Ito et al., 2006). For example, such a combination in Japan achieved an average mercury removal efficiency of 74 per cent (Ito et al., 2006). Co-benefit techniques can, therefore control multiple air pollutants, including mercury.

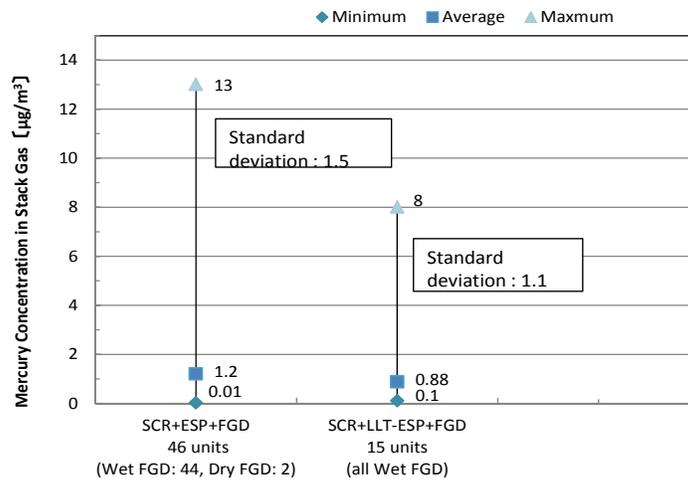


**Figure 3. Process diagram of a typical configuration of coal-fired power plants in Japan (Ito et al., 2006) (revised)**

High-level co-benefit removal of mercury can be achieved by combining selective catalytic reduction (SCR), cold side electrostatic precipitator (ESPc) and flue gas desulfurization scrubber (FGD). The combination of these techniques is quite typical at advanced coal-fired power plants in some countries and is widely used, for

example in Japan, as shown in Figure 3. The combination of SCR, ESP and FGD as shown in these examples can achieve removal efficiencies of 50–90 per cent for NO<sub>x</sub>, more than 99 per cent for PM, and 76–98 per cent for SO<sub>2</sub>, along with high-level mercury removal efficiency at on average 74 per cent, which results in 1.2 µg/m<sup>3</sup> of mercury concentration in the flue gas in this example. Furthermore, the combination of SCR, low-low temperature ESP (LLT-ESP), whose operating temperature is 90°C, and wet FGD can achieve mercury removal efficiency of quite a high level, at on average 87 per cent, which results in 0.88 µg/m<sup>3</sup> of mercury concentration in the flue gas for this specific case. The LLT-ESP, which requires flue gas cooling, improves particulate control through reduced gas volume and lower ash resistivity due to SO<sub>3</sub> condensation and moisture adsorption to fly ash, and increases mercury adsorption on fly ash due to lower flue gas temperature. It also avoids costs associated with flue gas reheat or wet stack retrofits. In cases where reheating wet FGD exhaust is not needed, the recovered heat can be used in the boiler or steam turbine to improve the efficiency of the unit, thus increasing net output (Nakayama et al, 2006, Iwatsuki et al 2008).

The mercury concentrations in figure 4 show a wide range. This is because these units include older or smaller units which provide the higher concentrations. On the other hand, the two units with the moving bed of active coke (Peters, 2010), which is a dry FGD, show higher performance than the wet FGD. The performance is higher than the combination with the LLT-ESP and the wet FGD (CRIEPI and FEPC, 2012).



Note: ESP in SCE+ESP+FGD includes ESPh includes ESPh, ESPc and LLT-ESP  
 Operating temperature ESPh 300–400°C, ESPc 130–180°C, LLT-ESP 90–100°C

**Figure 4. Mercury concentrations in flue gas from coal-fired power plants with SCR+ESP+FGD and SCR+LLT-ESP+FGD**

Table 3 summarizes the mercury removal efficiencies of APCDs for coal combustion plants in China. It shows that, in some cases, the combination of ESP and wet FGD achieves mercury removal efficiencies of up to 88 per cent. The combination of SCR, ESP and wet FGD, which is widely used in Chinese coal-fired power plants, can accomplish a higher mercury removal efficiency, for example, of up to 95 per cent. High mercury removal efficiencies are also observed for the combination of SCR, FF and wet FGD.

**Table 3**

Mercury removal efficiency by typical APCD combinations in China (in percentages) (Zhang et al., 2015)

| APCD combination | Mean | Min | Max | Standard Deviation | Number of tests |
|------------------|------|-----|-----|--------------------|-----------------|
| Wet PM Scurbber  | 23   | 7   | 59  | 18                 | 8               |
| ESPc             | 29   | 1   | 83  | 19                 | 64              |
| FF               | 67   | 9   | 92  | 30                 | 10              |
| ESPc+wFGD        | 62   | 13  | 88  | 22                 | 19              |
| FF+wFGD          | 86   | 77  | 97  | 10                 | 3               |
| SCR+ESP+wFGD     | 69   | 36  | 95  | 24                 | 4               |

|                 |    |    |    |   |   |
|-----------------|----|----|----|---|---|
| SCR+FF+wFGD     | 93 | 86 | 99 | 9 | 2 |
| ESPC+CFB-FGD+FF | 68 | 68 | 68 |   | 1 |

Table 4 below shows measurement values of mercury emissions for different coal-fired power plants, achieved through co-benefits for pollution controls. The selected examples in this table show that co-benefit control techniques in some cases achieve low mercury concentrations in the flue gas.

**Table 4**

Emission levels achieved with co-benefit techniques (data compiled by ZMWG, 2015)

| <i>Plant</i>                                   | <i>Coal type</i> | <i>Emission level (<math>\mu\text{g}/\text{Nm}^3</math>)<br/>(normalized to 6 % <math>\text{O}_2</math>-content)</i> | <i>Boiler size<br/>(MWh)</i> | <i>Flue gas treatment<br/>technique</i> |
|--|------------------|--|------------------------------|---|
| Federico II – Brindisi, Italy                  | hard coal        | 0.69   | 1,700                        | ESP+SCR+wFGD                            |
| Torrevaldaliga Nord, Italy                     | hard coal        | 0.99   | 1,420                        | FF+SCR+wFGD                             |
| Impianto termoelettrico di Fusina, Italy       | hard coal        | 0.8  | 431                          | FF+SCR+wFGD                             |
| Heyden, Germany                                | hard coal        | 0.5  | 2,150                        | ESP+SCR+wFGD                            |
| FHKW Mellach, Austria                          | hard coal        | 0.5  | 543                          | FF+SCR+wFGD                             |
| Brindisi BR III & BR II, Italy                 | hard coal        | 0.5  | 857                          | ESP+SCR                                 |
| Krefeld, Currenta , Germany(Industrial boiler) | hard coal        | 0.2  | 105                          | FF                                      |
| Salem Harbour, USA                             | hard coal        | 0.2-0.4  | 300                          | ESP                                     |
| Power plant Tusimice, Czech                    | lignite          | 2.6  | 890                          | ESP+wFGD                                |
| Neurath, A and F, Germany                      | lignite          | 3.0  | 855                          | ESP+wFGD                                |
| Teplarna Tabor, Czech                          | lignite          | 3.3  | 199                          | ESP                                     |

Note: all values are based on periodic samples except for Salem Harbour, which is based on continuous emissions monitoring. Data are for the year 2010.

### 3.2.1 Particulate matter control devices

Two major types of PM control devices include ESPs and FFs. Wet PM scrubbers are also used at coal-fired boilers.

#### 3.2.1.1 Electrostatic precipitators (ESPs)

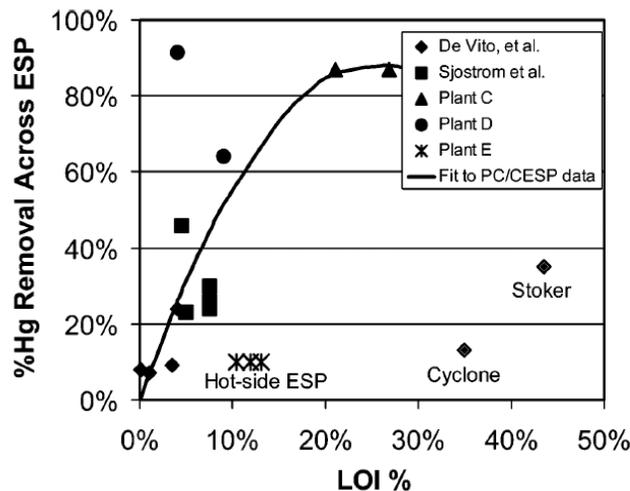
ESPs are typically designed to achieve greater than 99 per cent PM collection efficiencies, subject to various factors presented in the introductory section. The PM collection efficiency of an ESP is also a function of the sulfur content of coal, which affects the resistivity of fly ash. Coal that contains a moderate-to-high amount of sulfur produces an easily collected fly ash. Lower sulfur coal produces a higher resistivity fly ash that is more difficult to collect. Resistivity of the fly ash can be changed by decreasing the temperature in the ESP or by conditioning the particles upstream of the ESP with sulfur trioxide ( $\text{SO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), water, sodium, or ammonia ( $\text{NH}_3$ ).

For a given coal fly ash, the effectiveness of PM collection efficiency by an ESP is a function of particle size. Particles larger than about  $1\ \mu\text{m}$ – $8\ \mu\text{m}$  are typically collected with efficiencies from 95 to 99.9 per cent. However, particles near the  $0.3\ \mu\text{m}$  size are in a poor charging region that reduces collection efficiency to 80–95 per cent (Lawless, 1996).

An ESP can be used at one of two locations in a boiler system: the so-called “cold-side” ESP (ESPC) and “hot-side” ESP (ESPh). An ESPC is installed downstream of the air heater (flue gas temperature between  $130\ ^\circ\text{C}$  and  $180\ ^\circ\text{C}$ ). An ESPh is installed upstream of the air heater (flue gas temperature between  $300\ ^\circ\text{C}$  and  $400\ ^\circ\text{C}$ ) and makes it possible to take advantage of the lower fly-ash resistivity at higher temperatures. This is particularly important for units burning low-sulfur coal, resulting in fly ash with higher electrical resistivity. The wet ESP is a new type of ESP, which has higher removal efficiency for fine particles (Altman et al., 2001; Staehle et al., 2003). However, on-site measurements have not yet been conducted for mercury removal inside a wet ESP.

Varying levels of mercury removal have been observed for ESPs. The level of mercury removal depends on whether it is an ESPc or ESPh installation, the type of coal burned, the type of boiler, and other factors such as sulfur content in coal and the level of unburned carbon in the fly ash. An ESPh is generally much less effective than an ESPc at removing mercury. For example, while the average reported mercury removal for an ESP operating on bituminous coal was about 30 per cent, the range of measured removals varied from 0 to about 60 per cent (US EPA, 2001). The range of measured mercury removals, especially for the ESP, may be an indicator of the potential for improvement of mercury capture resulting from the increased efficiency of a PM collector. It is important to understand the PM collection performance of a device since this in turn affects the device's capability to reduce mercury emissions.

Fundamental modelling of mercury removal in ESPs indicates that mass-transfer limitations, even under idealized conditions, may restrict the potential for mercury capture by PM collected on electrodes in an ESP (Clack, 2006 and Clack, 2009). ESPs remove only  $Hg_p$  in the process of collecting PM.  $Hg_p$  is preferentially bound to unburned carbon (UBC). The mercury adsorption capacity of inorganic fractions (fly ash) is typically low compared to the UBC present in fly ash. A relationship between the amount of UBC and mercury removal across ESPc has been observed for bituminous coal fly ash (Senior and Johnson, 2008). This behaviour is shown in Figure 5, which shows the percentage capture (percentage of mercury incoming to the ESP) as a function of the amount of UBC. In figure 5, UBC is expressed as the measured loss on ignition (LOI). As can be seen, mercury capture of between 20 and 40 per cent was found in an ESP capturing fly ash containing about 5 per cent UBC. With higher UBC content, mercury capture of as much as 80 per cent could be seen; likely a function of the halogens present (Vosteen et al., 2003).



**Figure 5. Mercury removal by ESP as a function of the amount of unburned carbon (LOI%) in fly ash (Senior and Johnson, 2008)**

In addition to the amount of UBC, the properties of UBC such as surface area, particle size, porosity, and chemical composition may also affect the amount of mercury captured in an ESP (Lu et al., 2007). This study found that while UBC content in fly ash decreased with decreasing particle size, the mercury content of UBC generally increased with decreasing particle size. In addition, the particle size of UBC was found to be the major factor affecting mercury adsorption. Thus, increased efficiency of an ESP and the resultant increase in the capture of fine fly ash and fine UBC will likely cause a decrease in mercury emissions. It should be noted, however, that most of the mass of UBC is in very large particles.

Other important factors governing the amount of mercury that is captured in fly ash (and subsequently removed from the flue gas) are the type of ESP used (e.g. ESPc or ESPh), the use of  $SO_3$  as a flue gas conditioning agent, and the type of coal. Typically, higher mercury capture is observed in ESPs installed on boilers burning coals with higher halogen contents and producing higher levels of UBC in the flue gas. Both of these parameters promote the formation of oxidized mercury and PM-bound mercury, which are easier to capture in the ESP than elemental mercury. It follows that, if the performance of the ESP can be improved, an additional amount of mercury could be removed from the flue gas. The amount of this additionally removed mercury would be a function of the amount of additional PM removed by the ESP. Low-cost approaches such as accurate alignment of plates, adjustment of rapping pattern, elimination of in-leakages, among other approaches, can be used to improve the PM collection efficiency of ESPs (Zykov et al., 2004; Deye and Layman, 2008). Low temperatures

in the control device system (below 150 °C) also enhance mercury control and LLT-ESP has been practiced in Japan to achieve higher removal efficiency of dust and mercury (CRIEPI and FEPC, 2012).

It should be noted that the positive effects of SO<sub>3</sub> on particulate capture may be partially offset by the competition of SO<sub>3</sub> with mercury for adsorption on the fly ash.

### **3.2.1.2 Fabric filters (FFs)**

FFs provide higher removal efficiency of fine particles in comparison to ESPs, in particular submicron particles.

Higher removals of mercury are generally observed in FFs than in ESPs. FFs are more effective in removing fine PM (most importantly, submicron PM) than ESPs, and they tend to remove more of the gas-phase mercury than ESPs. In addition to longer contact time, better contact is provided in a FF (gas penetrates through the filter cake) than in an ESP (gas passes over the surface of the cake). The result is that gaseous elemental mercury is more likely to be oxidized and transformed into a form that can be captured when a FF is used. For example, a study comparing the capture of mercury in ESPs and FFs in coal-fired power plants in China revealed between 1 and 83 per cent capture in ESPs and between 9 and 92 per cent capture in FFs (Zhang et al., 2015). The average mercury removal efficiencies for ESPs and FFs in Chinese coal-fired power plants are 29 per cent and 67 per cent, respectively (Zhang et al., 2015).

FFs can also be integrated with ESPs to become ESP-FFs, which are employed in China to an extent comparable to FFs. The mercury removal efficiency of ESP-FFs is between that of ESPs and FFs. An average of 43 per cent of mercury removal can be achieved with ESP-FFs (Zhang, 2015).

### **3.2.1.3 Wet PM scrubbers**

Most of the small and medium-scale industrial boilers in China are equipped with wet PM scrubbers to reduce PM emissions. A wet PM scrubber system has chemistry similar to that of wet FGD. However, conventional wet PM scrubbers simply use water as the absorbent, so the re-emission of elemental mercury is significant. On-site measurements showed an average mercury removal efficiency of 23 per cent (between 7 and 59 per cent) for wet PM scrubbers at Chinese coal-fired industrial boilers.

The integrated marble scrubber (IMS) is a special type of wet PM scrubber for concurrent PM and SO<sub>2</sub> removal, and these are more and more widely used by coal-fired power plants in China owing to their technological economy. The IMS uses alkali liquor as the absorbent, which is more effective in capturing oxidized mercury, similar to wet FGD. The efficiency of IMSs in mercury removal could be higher than that of conventional wet PM scrubbers as a consequence of its SO<sub>2</sub> control capacity, but no on-site measurements have yet been conducted.

#### *Cross-media effects for PM control devices*

There are potential cross-media effects that apply to PM control devices. Mercury in the fly ash can be re-emitted if the fly ash collected by PM control devices is heated during reuse. For example, the mercury in fly ash may be released to the air if used as the raw material in a cement kiln. There is also potential for mercury from fly ash to leach into groundwater. Sound management of fly ash collected by PM control devices is needed.

### **3.2.2 SO<sub>2</sub> control devices**

There are two main techniques used for SO<sub>2</sub> emission reduction and dealt with below: first, wet FGD, and second, dry FGD, or dry scrubber.

#### **3.2.2.1 Wet flue gas desulfurization (wet FGD)**

In plants equipped with wet FGD, the amount of the co-benefit removal may be augmented by the increase of the fraction of oxidized mercury in the total mercury flue gas content or by the improvement of PM control effectiveness (Sloss, 2009). The increase of the fraction of oxidized mercury can be accomplished by the addition of chemical compounds (oxidizing agents) or by the oxidation of mercury over catalysts (Amar et al., 2010). The catalyst may be placed in the flue gas for the sole purpose of mercury oxidation or may be installed for another purpose (e.g., for the control of NO<sub>x</sub> emissions) and thus provide the co-benefit. The operation of a wet FGD requires that a PM control device be installed upstream of the wet FGD scrubber (Srivastava and Jozewicz, 2001).

As mentioned before, gaseous compounds of oxidized mercury are generally water-soluble, and thus wet FGD systems are expected to capture them efficiently (Reddinger et al., 1997; DeVito and Rossenhover 1999). Gaseous elemental mercury, however, is insoluble in water and therefore does not absorb in FGD slurries. Data from actual facilities have shown that the capture of oxidized mercury averaging 75 per cent (between 67 and 93

per cent) can be expected in calcium-based wet FGD systems (Chen et al., 2007; Kim et al. 2009; Wang et al., 2010; Sloss, 2015), although there are cases where significantly less capture has been measured as a result of unfavourable scrubber equilibrium chemistry (Niksa and Fujiwara, 2004).

It has also been shown that, under some conditions, oxidized mercury may be reduced in wet FGD scrubbers to elemental mercury, which could then be re-emitted (Nolan et al., 2003). Thus, in the case of wet FGD, the optimization of the co-benefit strategy sometimes means preserving the amount of oxidized mercury in the system in order to prevent the re-emission of mercury. Mercury re-emission may take place when oxidized mercury is absorbed by the wet FGD slurry, converted to elemental mercury, and then transferred to gas phase to exit the scrubber.

The net effect of re-emission is the limitation of mercury removal by a wet FGD. The occurrence and the extent of mercury re-emission from wet FGD depend on FGD chemistry (Renninger et al., 2004). There also appears to be increased potential for the re-emission of mercury in wet FGD with appreciable mercury concentrations in the liquid phase (Chang et al., 2008). In some cases chemical agents or activated carbon needs to be added to the FGD liquor to control re-emission.

### **3.2.2.2 Dry FGD**

Spray dryers are typically used for the control of SO<sub>2</sub> emissions for sources that burn low-to-medium-sulfur coal, or for smaller coal-fired combustion plants. Up to approximately 95 per cent mercury may be removed by SDA-FF combinations when used on bituminous coal-fired boilers. Much lower mercury capture, however, (about 25 per cent) is observed in SDA-FF units on boilers firing lignite or other low-rank coals with low chlorine content (Senior, 2000). Scrubbing of halogen species in the spray dryer absorber may make oxidation and subsequent capture of mercury (mostly in the form of elemental mercury for these coals) in the downstream FF less effective. Sometimes, the mercury capture for low rank coal accomplished by FFs alone is higher than that by SDA-FFs (Srivastava et al., 2006).

A dry desulfurization scrubber technology, in recent times increasingly used in coal combustion plants, is the circulating dry scrubber, CDS. Like the SDA scrubber, the CDS scrubber has a reaction chamber and a fabric filter for by-product and ash capture. A differentiating feature of the CDS is that reaction materials enter the reaction chamber dry and are fluidized in the reaction chamber before passing on to the fabric filter. A water spray is applied to the bottom of the reaction chamber to control the reactor temperature. The reaction materials are hydrated lime and recycled solids from the fabric filter. The CDS has a higher solids concentration than the SDA, which allows it to achieve SO<sub>2</sub> reductions of up to 98 per cent, as compared to a maximum of 95 per cent reduction by SDA scrubbers. In addition, the CDS can treat flue gas from higher sulfur coal than the SDA because SO<sub>2</sub> capture is not limited by the stoichiometry of a slurry (Ake, 2009).

Mercury capture in CDS as a co-benefit is similar in magnitude to SDA scrubbers where significant capture of oxidized mercury has been achieved. Accordingly, much higher co-benefit mercury capture can be achieved with higher chlorine coals than with low chlorine coals (Babcock Power, 2012).

#### *Cross-media effects for SO<sub>2</sub> control devices*

For the wet FGD system, retention of mercury through the FGD system requires high quality wastewater and sludge treatment to ensure that the mercury is not simply being transferred from air to water.

When the FGD gypsum is used for wallboard production, mercury contained in gypsum has the potential to be re-emitted. With an SDA-FF system, there is potential for mercury from fly ash collected by FF to leach into groundwater. Accordingly, there is a need for the sound management of fly ash collected by FFs.

#### *Cross-media effects for SO<sub>2</sub> control devices (non-mercury related)*

The operation of an FGD system generally increases energy consumption, typically by as much as 5 per cent.

### **3.2.3 Selective catalytic reduction for NO<sub>x</sub> control**

SCR technology has been designed to reduce NO<sub>x</sub> through a catalytically enhanced reaction of NO<sub>x</sub> with NH<sub>3</sub>, reducing NO<sub>x</sub> to water and nitrogen. This reaction takes place on the surface of a catalyst, which is placed in a reactor vessel. Under certain conditions, SCR catalysts have been shown to change mercury speciation by promoting the oxidation of elemental mercury to oxidized mercury, particularly for high chlorine coal. It should be noted that the SCR itself does not remove mercury. Instead, by increasing the amount of oxidized mercury the SCR improves mercury capture in PM control devices and wet FGD systems, resulting in the enhanced removal of mercury (Chu, 2004; Favale et al., 2013).

Since the operational parameters of the SCR (e.g., temperature, concentration of NH<sub>3</sub> in the flue gas, catalyst bed size, and catalyst age) will generally be dictated by the NO<sub>x</sub> control strategy, the parameter that shows the

most promise for the optimization of mercury removal is the chlorine content of the coal. As discussed in the section on coal blending below which is based on United States data, oxidation of elemental mercury to oxidized mercury is greater for bituminous coals than for subbituminous coals. Thus, the maximum co-benefit of the existing SCR may be achieved by an appropriate coal-blending or by bromide addition (Vostene et al., 2006). SCR catalysts are being designed to optimize both the NO<sub>x</sub> removal and mercury oxidation.

Use of SCR increases the extent of mercury oxidation and capture, in particular with increases of the fraction of bituminous coal in a subbituminous and bituminous coal blend. A field study at a large utility plant firing a 60 per cent subbituminous and 40 per cent bituminous blend at two identical boilers (one with SCR and the other without SCR) demonstrated an increase in the oxidized mercury fraction from 63 per cent without SCR to 97 per cent with SCR. Generally, in systems with SCR, mercury oxidation across the SCR system rises with an increasing percentage of bituminous coal in a subbituminous-bituminous coal blend. For example, for a 65:35 subbituminous-bituminous coal blend, the increase was 49 percentage points (from 13 to 62 per cent). For the 79:21 blend, however, the increase was only 14 percentage points (from 6 to 20 per cent) (Serre et al., 2008).

The unblended subbituminous coal in a unit without SCR would have achieved between 0 and 40 per cent oxidized mercury (ICAC, 2010). In another field study, tests conducted in three bituminous coal-fired plants showed mercury oxidation across the SCR of up to 90 per cent and more. The resultant mercury removal in downstream wet scrubbers was from 84 to 92 per cent with SCR operation compared to 43–51 per cent without SCR operation. Plants firing subbituminous coals, however, showed little change in mercury speciation across the SCR reactors (Laudal, 2002).

On-site measurements from four Chinese coal-fired power plants showed that the elemental mercury oxidation rate inside SCR was in the range of 34–85 per cent, affected by the total mercury and chlorine content in coal and the NH<sub>3</sub> injection rate of SCR (Zhang et al., 2013).

#### *Cross-media effects for NO<sub>x</sub> control devices*

With the mercury oxidation by SCR, there is possibility of increasing the mercury content of fly ashes and FGD gypsum. The used SCR catalyst might be hazardous in nature. The used SCR catalyst should be either regenerated or disposed of in an environmentally sound manner.

#### *Cross-media effects for NO<sub>x</sub> control devices (non-mercury-related)*

The operation of an SCR system generally increases energy consumption, typically up to 3 per cent.

### **3.3 Co-benefit enhancement techniques**

Co-benefit enhancement may be achieved by coal blending, coal additives, or by a number of other techniques described below.

#### **3.3.1 Coal blending**

Coal blending (or switching) at power plants is used as part of a strategy to meet SO<sub>2</sub> emission limits in a cost-effective manner, provided coal blending is compatible with the power plant design. Typically, high sulfur bituminous coals are blended with low sulfur subbituminous coals to lower SO<sub>2</sub> emissions. As an undesired side effect of this SO<sub>2</sub> emission control strategy, mercury speciation may be altered, reducing the amount of oxidized mercury and increasing the amount of elemental mercury, thus compromising mercury capture in a downstream FGD system. Blending of coals may also be used, however, to increase the amount of oxidized mercury in flue gas. In addition to mercury content, certain coal characteristics such as chlorine and bromine content or alkalinity content are important for mercury removal and should be known. Bituminous coals typically produce a higher fraction of oxidized mercury in the flue gas than do subbituminous coals. Since oxidized mercury is water-soluble, it is more readily captured in wet FGD systems. Consequently, the mercury capture efficiency of FGD systems depends largely on the fraction of oxidized mercury at the FGD inlet (Miller et al., 2006).

An example of coal blending that is used to improve mercury removal in downstream air pollution control equipment is discussed below. Table (UNEP, 2010) shows data on properties of typical subbituminous coal (from Wyoming, United States) and bituminous coal (from Illinois, United States). It should be noted that the properties given in Table 5 are for illustration only and will vary depending on the origin of the coal.

**Table 5**

Comparison of properties of subbituminous and bituminous coals

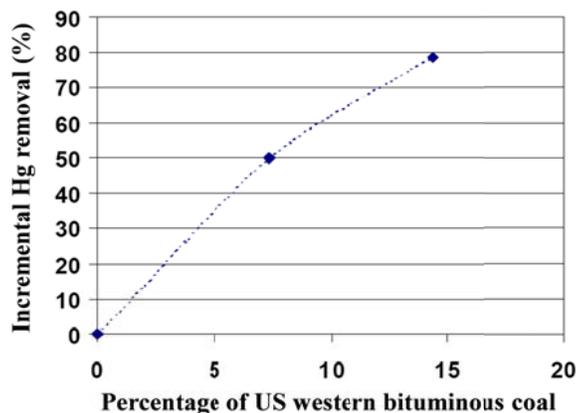
| <i>Content</i> | <i>Subbituminous coal,<br/>wt%</i> | <i>Bituminous coal,<br/>wt%</i> |
|----------------|------------------------------------|---------------------------------|
|----------------|------------------------------------|---------------------------------|

|                       |        |       |
|-----------------------|--------|-------|
| Bromine <sup>a</sup>  | 0.0006 | 0.02  |
| Chlorine <sup>a</sup> | 0.003  | 0.100 |
| Sulfur <sup>a</sup>   | 0.37   | 4.00  |
| CaO                   | 26.67  | 3.43  |
| MgO                   | 5.30   | 3.07  |
| Na <sub>2</sub> O     | 1.68   | 0.60  |
| Hg, ppm               | 0.1    | 0.1   |

<sup>a</sup> ultimate analysis, as received, wt %

It should be noted from Table 5 that, even though in these averaged data, mercury content is the same at 0.1 ppm for both types of coals, chlorine content varies significantly, from 0.003 per cent by weight for subbituminous coal to 0.1 per cent for bituminous coal. In addition, alkaline material (such as CaO) content varies from 3.43 per cent for subbituminous coal to 26.67 per cent for bituminous coal by weight. This illustrates that lower chlorine content in subbituminous coals may result in lower mercury oxidation and hence a higher percentage of elemental mercury. Blending bituminous coal with subbituminous coal provides the double benefit of higher chlorine concentration and lower alkalinity. In the context of mercury control, the objective of coal blending would be to increase halogen concentration by mixing relatively high halogen content coal with low halogen coal that might be used at the plant.

Figure below shows the trend of increasing mercury capture in a dry FGD system (dry FGD plus FF) with an increasing fraction of bituminous coal in a bituminous-subbituminous coal mixture (UNEP, 2011). As can be seen, coal blending has the potential of increasing the mercury capture by up to almost 80 per cent. Again, it should be noted that incremental mercury removal values are of an illustrative nature and that actual incremental mercury removal values may vary depending on sources of the coals used for blending.



**Figure 6. Possible effect of coal blending on mercury capture in dry FGD**

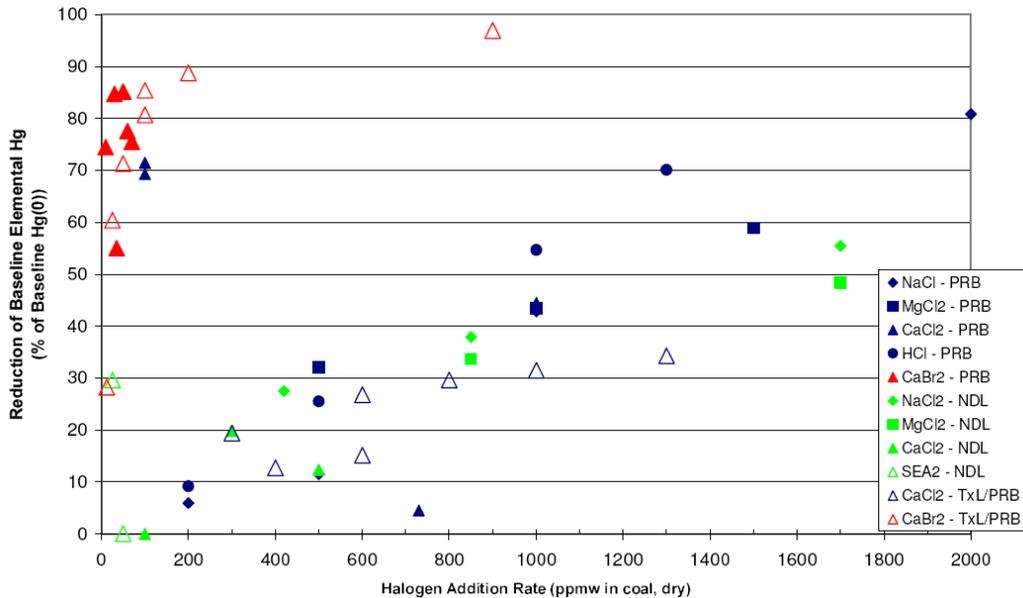
Thus, blending of coal may potentially increase mercury oxidation for plants firing low chlorine, high calcium coal. The characteristics of different coal types play a major role in determining the speciation of mercury. This, in turn, can dramatically affect the amount of mercury captured in existing pollution control devices like FGD systems. The effect may be more pronounced in plants equipped with SCR systems, as will be discussed later.

### 3.3.2 Mercury oxidation additives

The amount of mercury captured generally increases as the amount of halogens in coal increases. Consequently, to promote increased capture for coals that have low halogen concentrations, additional halogens such as bromine or chlorine salts are often added. Alternatively, HCl or ammonium chloride (NH<sub>4</sub>Cl) may be added. Halogen additives promote formation of oxidized and particulate-bound mercury, which is more easily captured in downstream devices. Halogen additives may be particularly useful in improving mercury removal for units firing low-halogen coals. The additives may be sprayed on coal or added as solids to a coal stream either upstream of the coal pulverizer or injected into the boiler.

Bromine is thought to have an advantage over chlorine in that it interacts more actively with mercury than chlorine does (Vosteen et al., 2002; Vosteen et al., 2003; Vosteen et al., 2003b; Vosteen et al., 2003c; Buschmann et al., 2005). A heterogeneous oxidation pathway is thought to be important under coal-fired flue

gas conditions despite the fact that chlorine content in coal is typically much higher than that of bromine (Vosteen et al., 2006b, Rini and Vosteen, 2008, Senior et al., 2008, Vosteen et al., 2010). Full-scale tests were conducted using a 52 weight percentage water solution of calcium bromide as a pre-combustion additive at a concentration of 25 part per million (ppm) in coal equivalent level, and mercury emission reduction was increased from 55 to 97 per cent in a 600 MW unit firing subbituminous coal and equipped with an SCR system and wet FGD (Rini and Vosteen, 2009). Full-scale tests conducted by the Electric Power Research Institute of the United States at 14 units firing low chlorine coals demonstrated more than 90 per cent flue gas mercury oxidation for bromide additions, equivalent to 25–300 ppm in coal (Chang et al., 2008).



**Figure 7. Performance of bromine-based and chlorine-based additives with different coals (PRB-subbituminous coal; TxL-lignite coal; NDl-lignite coal)**

A comparison of the performance of bromine-based and chlorine-based additives at coal-fired boilers firing different coals is shown in Figure ; this comparison gives the per cent reduction of baseline elemental mercury as a function of halogen addition rate (EPRI, 2006; Vosteen and Lindau, 2006; Chang et al., 2008). As can be seen in fFigure , for any amount of halogen addition, bromine was much more effective in decreasing the amount of baseline elemental mercury than chlorine. Baseline elemental mercury reduction of 80 per cent could be achieved by adding less than 200 ppm of bromine-based additive. Much more chlorine-based additive (by approximately an order of magnitude) was needed to achieve the same level of baseline elemental mercury reduction.

*Cross-media effects for mercury oxidation additives*

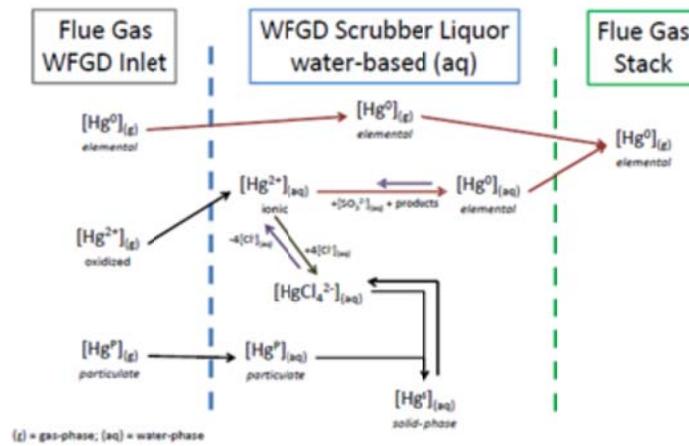
The use of mercury oxidation additives has potential impacts on the boiler, APCs, emissions and emission measurement. It increases corrosion potential in air preheaters and wet FGD (Srinivasan and Dehne, 2013). Bromine additive or brominated activated carbon results in an increase in bromine in fly ash (Dombrowski et al., 2008). Halogens added in coal may be emitted from the stack (ICR, 2010). Mercury measurements can be very difficult in the presence of bromine in the flue gas. There is also potential for bromine FGD discharges to form disinfection

by-products at drinking water plants downstream from coal-fired power plants and potential for impacts on other pollutants such as Se (McTigue et al, 2014; Richardson, et al., 2007; BREF, 2013). The full range of scientific uncertainties associated with pollutant releases from bromine addition is still unclear.

**3.3.3 Wet scrubber additives for mercury reemission control**

The absorption of oxidized mercury, followed by its retention in an aqueous phase, is the basis of the co-benefit contribution provided by wet SO<sub>2</sub> scrubbers. That said, however, there are many documented cases where scrubbers are not able to retain all of the aqueous phase mercury which has been absorbed. This condition is measured as a greater concentration of elemental mercury exiting the scrubber than entering the scrubber and has been labelled as “mercury re-emission” (Keiser et al., 2014).

In the re-emission of mercury from a wet scrubber, soluble ionic mercury is reduced to the insoluble, elemental form, resulting in its release back to the flue gas. Figure below shows the chemical path through which absorption and re-emission can occur.



**Figure 8. Illustration of flue gas mercury absorption/desorption across WFGD (Keiser et al., 2014)**

Much effort has been put into the development of techniques and products to avoid mercury re-emission and a number of these have been commercialized. In principle, all these techniques are based on a method of reducing the soluble mercury content in the scrubber liquor. This is accomplished by either absorption of the ionic mercury into a particle or the precipitation of ionic mercury out of the liquor (Chethan et al., 2014).

In the absorption technique, ionic mercury is absorbed by activated carbon. The activated carbon is added to the scrubber liquor either directly into the scrubber liquor lines or injected into the flue gas upstream of the scrubber. The activated carbon is removed from the scrubber via the dewatering step.

A number of precipitation agents have been identified and these can be grouped into five categories: first, inorganic sulfides; second, organic sulfides; third, organic compounds containing nitrogen and sulfur; fourth, organic compounds containing oxygen and sulfur; and, fifth, low molecular weight sulfur-containing polymers (Keiser et al., 2014).

#### *Cross-media effects for wet scrubber additives*

Depending on the scrubber additive, the captured mercury exits the scrubber either in the liquid or solid phases.

#### **3.3.4 Selective mercury oxidation catalyst**

It is well known that SCR catalysts can oxidize elemental mercury emitted from coal-fired boilers in a gaseous state and particulate form (Laudal et al., 2002). However, the mercury oxidation rate on the SCR catalyst correlates to the SO<sub>2</sub> oxidation and conversion rate which forms SO<sub>3</sub>, which can cause air heater fouling, stack corrosion, and visible stack plumes.

A special type of SCR catalyst achieving high mercury oxidation and high NO<sub>x</sub> removal with simultaneous low SO<sub>2</sub>-to-SO<sub>3</sub> conversion (known as the selective mercury oxidation catalyst) has therefore been developed. The basis for this approach is to oxidize as much elemental mercury as possible to then allow the downstream APCS to remove the oxidized mercury (Favale et al., 2013).

A selective mercury oxidation SCR catalyst that increases the mercury oxidation rate while maintaining its original SCR capability enhances the mercury removal in a co-benefit technique (Bertole, C., 2013). In some existing plants in North America, SCR catalysts have already been replaced by high mercury oxidation SCR catalysts. It has been confirmed that partial replacement can also lower mercury concentration in the stack gas (Favale et al., 2013).

#### *Cross-media effects for selective mercury oxidation catalyst*

Use of a selective mercury oxidation catalyst possibly increases the mercury content of fly ashes and FGD gypsum. The used catalyst should either be regenerated or disposed of in an environmentally sound manner.

### 3.4 Activated carbon injection for dedicated mercury control

Sorbents with or without chemical treatment may be used for injection in order to accomplish mercury removal. Injection of sorbents into the flue gas of coal-fired boilers for mercury control has been applied at boilers in Germany since the 1990s (Wirling, 2000) and has been implemented in the United States on over 100 full-scale systems (GAO, 2009; Amar et al., 2010). Since about 2005, activated carbon injection technology has been commercially applied in the United States (ICAC, 2010a, Amar et.al, 2010). In addition, it has been demonstrated at a Russian power plant burning Russian coal (USEPA, 2014). Since 2007, in a number of states in the United States, such as Massachusetts, New Jersey and Connecticut, for many existing coal-fired boilers using bituminous or subbituminous coals, activated carbon injection has been routinely used in order to meet regulatory emission limit values (ELVs) in the range of 1.1–3.3 grams per Gigawatt-hr (representing 85–95 per cent control). Regulatory compliance with these ELVs has been shown through measurements with mercury continuous emissions monitoring (CEM) systems or sorbent trap methods (Massachusetts Department of Environmental Protection, 2015; with similar reports from the New Jersey and Connecticut state environmental departments). ACI requires a downstream PM control device.

Table 6 below shows the emission values of four coal-fired power plants with dedicated mercury abatement techniques in the United States.

**Table 6**

Emission levels of coal-fired power plants with activated carbon injection

| <i>Name</i>  | <i>Coal type</i> | <i>Emission level normalized (<math>\mu\text{g}/\text{Nm}^3</math>) (normalized to 6 % <math>\text{O}_2</math> content)</i> | <i>Averaging period</i>          | <i>Boiler size (MWth)</i> | <i>Flue gas treatment technique</i> |
|--|------------------|---|----------------------------------|---------------------------|-------------------------------------|
| Oak Grove, Boiler 1 USA                                  | lignite          | <0.80 in 2012   | monthly/cont.                    | 870                       | FF+SCR+FGD + ACI                    |
| PPI Montana Corette (USA)                                | sub-bituminous   | 0.9   | Cont.                            | 163                       | ACI with C-PAC + ESP                |
| Brayton Point, Units 1,2,3 (combined), Massachusetts,USA | bituminous       | 0.2   | Annual, 12-month rolling average | 1350                      | ACI+ SCR+ESP+SDA                    |
| Bridgeport Harbor, Unit # 3, Connecticut, USA            | bituminous       | 0.2-0.5   | periodic                         | 400                       | ACI + ESP                           |

Note: C-PAC: Cement-friendly pulverized activated carbon; data are for year 2010 except for Oak Grove.

#### 3.4.1 Injection of sorbent without chemical treatment

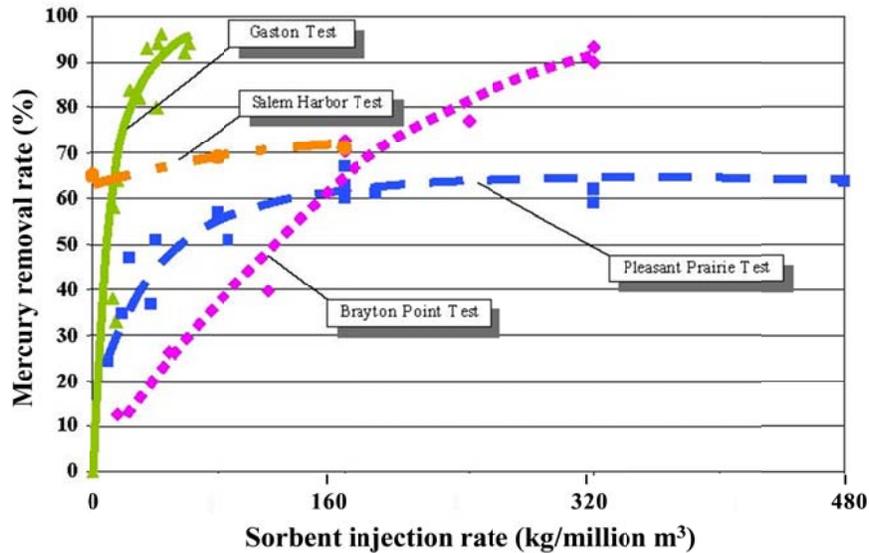
Some of the factors that affect the performance of any particular sorbent with regard to mercury capture include the physical and chemical properties of the sorbent, the injection rate of the sorbent, flue gas parameters (such as temperature, concentrations of halogen species, concentration of  $\text{SO}_3$ ) and existing APCS configuration (Pavlish et al., 2003; Srivastava et al., 2006; Martin, 2009).

Figure 9 provides a summary of a number of tests conducted more than ten years ago with untreated activated carbon injection at four power plants (Pleasant Prairie, Gaston, Salem Harbour, Brayton Point). Mercury removal efficiency by injection of untreated activated carbon depends strongly on the rank of coal and the type of PM control used in the plant. The Pleasant Prairie power plant used low-sulfur, Powder River Basin (PRB) coal and was equipped with an ESPc. PRB coal is a low rank subbituminous coal which contains low chlorine and high calcium, making it difficult for the elemental mercury to be oxidized by chlorine in the flue gas. Activated carbon injection was not effective for mercury control for this plant with mercury emissions consisting predominantly of elemental mercury, as untreated activated carbon is not effective for capturing the unreactive elemental mercury. As a strong contrast, the Gaston power plant demonstrated that activated carbon injection was extremely effective for controlling mercury emissions from this plant that burned low-sulfur bituminous coal and was equipped with an ESPh followed by a small, specially designed FF called a compact hybrid particulate collector (COHPAC). The injection of untreated activated carbon took place at the outlet of the ESPh because the temperature at the inlet was too high. The COHPAC was used for removing the injected

carbon. Application of a COHPAC as an effective means of mercury control was demonstrated in the Gaston power plant.

In some cases low mercury removal by untreated activated carbon is the result of a combination of lower levels of chlorine in subbituminous coal in the United States and the neutralization of halogen species by high levels of sodium and calcium in the subbituminous coal fly ash. As a result, there is little free chlorine in the flue gas stream for mercury oxidation. Mercury oxidation (with chlorination of the surface as the initial step) is necessary for the capture of elemental mercury by untreated activated carbon and, in general, the efficiency of mercury capture with untreated activated carbon increases with the amount of oxidized mercury in the flue gas (US DOE, 2005).

Thus, mercury capture with untreated activated carbon may be limited in plants firing low-rank coals, such as lignite and subbituminous.



**Figure 9. Testing of mercury removal efficiency as a function of untreated ACI rate**

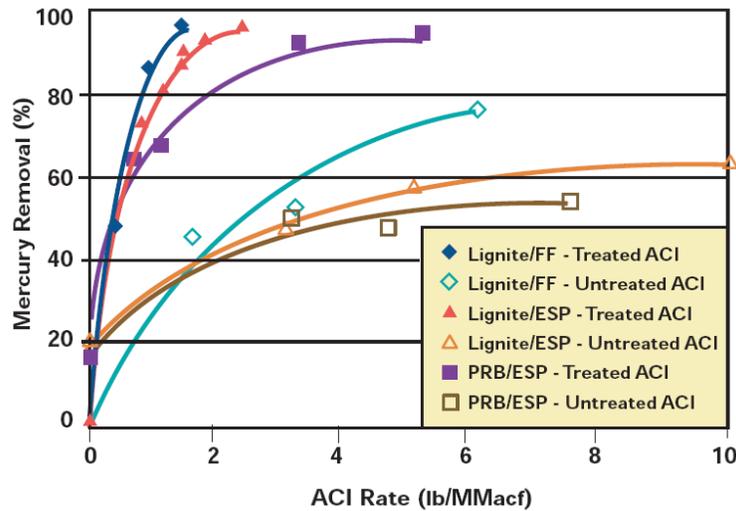
### 3.4.2 Injection of chemically treated sorbent

To overcome limitations described above and associated with the use of untreated activated carbon for mercury control in power plants, treated activated carbon sorbents have been developed (Nelson, 2004 and Nelson et al., 2004). The treatment most often used and that has been demonstrated as the most effective in enhancing the performance of activated carbon was bromination.

Relative to untreated activated carbon, brominated activated carbon:

- (a) Expands the usefulness of sorbent injection to situations where untreated activated carbon may not be effective;
- (b) In general, can be operated at lower injection rates, which leads to fewer plant impacts and a lower carbon content in the captured fly ash;
- (c) Results in better performance with low chlorine coals.

Improvement in the performance of mercury control was observed during full-scale field tests of chemically treated activated carbon injected upstream of the existing PM device (Feeley et al., 2008) and is shown in Figure . As may be seen in Figure , improved mercury capture efficiency was achieved using relatively low injection rates of treated activated carbon at power plants burning low-chlorine coals. The treated activated carbon achieved in excess of 90 per cent mercury capture at an injection rate of about 50 mg/m<sup>3</sup> (Feeley et al., 2008). Higher injection rates were required to achieve high mercury removal efficiency when untreated activated carbon was used, and in some cases, it was not possible to achieve 75 per cent capture.



**Figure 10. Comparison of untreated activated carbon and treated activated carbon performance for mercury removal**

### 3.4.3 Activated carbon injection applicability restrictions

Despite the activated carbon injection method being commercially implemented in multiple and diverse applications, some issues remain, including the marketability of fly ash for concrete manufacturers and the effect of  $SO_3$  on the performance of activated carbon injection systems.

A typical activated carbon injection system is located upstream of a PM control device, which leads to mixing of the sorbent and fly ash. While this is not a concern in cases where fly ash is not sold for concrete production, this mixing can negatively affect the use of fly ash in concrete production. Concrete quality is particularly sensitive to carbon content, and also affected by the surface area of the carbon present in the fly ash.

An effective method of eliminating fly ash contamination is to add an additional FF downstream of the existing ESP or to inject the activated carbon after the PM device and into a wet FGD, which may affect the quality of the gypsum produced by the FGD (Miller et al., 2014; Mimna et al., 2014). In addition, in some plants which burn low mercury coal and use FFs for PM control, the amount of treated activated carbon required for a mercury reduction greater than 85 per cent is as low as  $8 \text{ mg/m}^3$ . In such cases, the presence of activated carbon in the fly ash may not affect the sale of fly ash for concrete.

Concrete-compatible carbon sorbents have been developed that allow some coal-fired power plants to continue marketing fly ash for concrete production (Nelson et al., 2006; Landreth et al., 2012). These are commercially used in the United States.

Tests have also been carried out on other non-carbon sorbents designed to preserve fly ash quality while still allowing sorbent injection rates capable of delivering up to about 85 per cent mercury removal (Kang et al., 2007). Likewise, techniques for the post-treatment of fly ash to remove UBC and activated carbon have been developed. These include thermal treatment of fly ash and electrostatic separation of carbon from fly ash.

Testing has shown that  $SO_3$  in the flue gas, even at low concentrations, can interfere with the performance of activated carbon injection systems. It appears that  $SO_3$  competes with mercury for adsorption sites on the sorbent surface, thereby limiting its performance. This phenomenon may be particularly relevant to activated carbon injection applications at plants firing high-sulfur coal. One possible solution to the  $SO_3$  interference issue is the combined injection of mercury sorbents and alkaline materials. Some alkaline materials are being used as suggested in Feeley and Jones (2009) These include calcium hydroxide ( $Ca(OH)_2$ ), sodium bicarbonate ( $NaHCO_3$ ), and sodium sesquicarbonate (trona).

#### *Cross-media effects for activated carbon injection*

The use of non-concrete-compatible activated carbon injection methods can result in the loss of the use of fly ash in concrete, and therefore may increase the quantities of fly ash sent to landfill. Tests on two commercial activated carbons indicate that the mercury captured by activated carbon is sufficiently stable to provide permanent sequestration of mercury in activated carbon sorbents after disposal (Graydon et al., 2009; US EPA, 2006; US EPA, 2009a).

Activated carbon injection located upstream of a PM control device affects the quality of fly ash as a consequence of mixing of the activated carbon and the fly ash. There is the potential of secondary mercury release from fly ash when exposed to elevated temperatures during reuse of fly ash, for example, the use of fly ash for cement manufacture or brick-making (Pflughoeft-Haassett et al, 2007).

### 3.5 Cost of mercury control technologies

Mercury emission control can be accomplished as a co-benefit removal by the equipment already in place, which might have been installed for a different purpose. Defining the cost of mercury removal accomplished as a co-benefit is complex because cost apportionment needs to be considered between the costs of mercury control and those of controlling other pollutants such as PM, SO<sub>2</sub> or NO<sub>x</sub> (Sloss, 2008). Usually mercury reduction through co-benefit effects (the installation of technologies such as FGD and SCR which also reduce mercury emissions) can be regarded as minimal in cost or even cost-free. This is because high capital cost technologies like SCR and FGD are generally added for the purpose of NO<sub>x</sub> or SO<sub>x</sub> control, respectively, and would not be added solely for mercury control. Alternatively, mercury control may be accomplished by dedicated technology such as activated carbon injection at a much lower cost provided that there is an existing PM control device. Assigning costs for the latter is more straightforward.

There are three cost components resulting from the application of dedicated mercury emission control technology: capital cost, fixed operating and maintenance cost, and variable operating and maintenance cost. For activated carbon injection, the variable operating and maintenance cost is estimated to be small even though it is a major component of the total cost (EPA, 2005; Amar et al., 2010) because capital costs are relatively low. This depends on the application. Sorbent requirements can vary significantly between different sites. The major components of the variable operating and maintenance costs are sorbent costs and disposal costs. There may also be lost revenue from fly ash sales due to the contamination of fly ash by activated carbon. To overcome this, so-called “concrete-friendly” activated carbons have been developed, along with technologies to separate activated carbon from fly ash.

#### 3.5.1 Costs for co-benefit mercury control technologies

The actual capital costs of air pollution control at a particular facility are often proprietary and agreed to during direct negotiations between technology vendors and their clients. A substantial amount of cost information is publicly available, however, and this is presented below. Some general guidelines should be adhered to when evaluating these data:

- Capital costs for a new installation may vary depending on redundancy factors used for design and on locally prevailing financing options (e.g., capital charge rates);
- Capital costs for a retrofit installation may vary depending on the on-site conditions such as availability of space, and the so-called “retrofit difficulty factor”;
- Levelized cost of control equipment varies with the capacity factor of plant, with the levelized cost generally decreasing as the capacity factor increases (Celebi, 2014).

The costs of control technologies vary significantly when applied to different countries. Table 7 and 8 show the costs of co-benefit technology in China and United States. It can be seen that the capital cost of a wet FGD installed in a 600 MW unit may be 20 times lower in China than in the United States. It should be noted that, when considering nationwide or even region-wide deployment of BAT, a range of costs should be considered for any given BAT rather than an exact figure. In this context, the values in Table 7 and 8 should be considered to be indicative only, and reference should also be made to the other cost data (e.g., UK Department of Trade and Industry (2000); Sargent and Lundy (2007)).

The conventional APCs are not dedicated to mercury emission control, however, and therefore the total costs of co-benefit mercury control technologies need to be apportioned to different air pollutants. A Chinese study (Ancora et al., 2015) used a pollutant equivalent apportionment method based on the health and environmental impact of each pollutant and distributed the total annual cost to mercury, PM<sub>10</sub>, SO<sub>2</sub> and NO<sub>x</sub> (see Table 99).

**Table 7**

Costs of air pollution control devices in power plants (CNY/kQ, 2010 Yuan), China (Ancora et al., 2015)

| <i>APCD</i> | <i>Capacity (MW)</i> | <i>Capital cost (CNY/kW)</i> | <i>O&amp;M cost (CNY/kW/yr)</i> |
|-------------|----------------------|------------------------------|---------------------------------|
| ESP         | <100                 | 108±8                        | 7±2                             |

|      |      |         |       |
|------|------|---------|-------|
| ESP  | <300 | 100±7   | 6±2   |
| ESP  | >300 | 94±7    | 5±2   |
| FF   | <100 | 91±8    | 10±4  |
| FF   | <300 | 80±7    | 9±3   |
| FF   | >300 | 71±6    | 9±3   |
| WFGD | <100 | 736±178 | 74±29 |
| WFGD | <300 | 410±99  | 56±22 |
| WFGD | >300 | 151±37  | 36±14 |
| SCR  | <100 | 123±29  | 43±18 |
| SCR  | <300 | 99±23   | 31±13 |
| SCR  | >300 | 75±18   | 20±8  |

Key: APCD – air pollution control device; CNY – yuan renminbi; O&M – operating and maintenance

**Table 8**

Capital cost of co-benefit technology in the United States (\$/kW, 2012 dollars) (US EPA, 2013)

| <i>Technology</i> | <i>Unit size, MW</i> | <i>Coal type</i> | <i>Total capital cost (US\$/kW)</i> | <i>Total O&amp;M costs, fixed and variable (US\$/MWh)</i> |
|-------------------|----------------------|------------------|-------------------------------------|---|
| Wet FGD           | 500                  | Bituminous       | 531                                 | 11.52   |
| SDA FGD           | 500                  | Sub-Bituminous   | 470                                 | 10.45   |
| SCR               | 500                  | Bituminous       | 274                                 | 1.85  |
| FF                | 500                  | Bituminous       | 195                                 | 1.02  |

**Table 9**

Costs of APCS combinations apportioned to different pollutants for a 600MW unit, China (million CNY, 2010 Yuan)(Ancora et al, 2015)

| <i>APCS combination</i> | <i>Total annual costs</i> | <i>Costs apportioned to Hg removal</i> | <i>Costs apportioned to PM<sub>10</sub> removal</i> | <i>Costs apportioned to SO<sub>2</sub> removal</i> | <i>Costs apportioned to NO<sub>x</sub> removal</i> |
|-------------------------|---------------------------|--|---|--|--|
| ESP                     | 8.324                     | 0.479                                  | 7.845   | -  | -  |
| FF                      | 9.241                     | 1.167                                  | 8.075   | -  | -  |
| ESP+WFGD                | 39.871                    | 1.613                                  | 11.571  | 26.687   | -  |
| SCR+ESP+WFGD            | 56.992                    | 2.200                                  | 14.636  | 33.759   | 6.396  |
| FF+WFGD                 | 40.789                    | 2.181                                  | 11.759  | 26.849   | -  |
| SCR+FF+WFGD             | 57.909                    | 2.874                                  | 14.811  | 33.817   | 6.407  |

### 3.5.2 Costs for co-benefit enhancement techniques and ACI

The costs for activated carbon injection comprise of two components: first, capital costs for the sorbent storage and injection equipment; and, second, fixed and variable operating and maintenance costs (associated with the expendable sorbent). To assess the cost of mercury removal via the co-benefit route, a distinction must be drawn between the investment and operating and maintenance cost of the APCSSs, such as FGD and SCR, which are well defined, and the cost of enhancing or optimizing the mercury removal in those APCSSs.

In general, the cost of co-benefit enhancement techniques is difficult to assess since it is dependent on multiple variables such as coal origin and quality, the extent of refurbishment required for the existing PM controls (in the case of ESP), or site-specific operating regimes of wet FGD. As a result, relative costs were first arrived at for approaches discussed in this document; these approaches are shown in Table 10, which were, among other things, based on information presented in the process optimization guidance document (UNEP, 2010). The relative capital and incremental operating and maintenance costs shown in Table 10 should only be treated as trend indications, and should not be construed as universally applicable guidelines to the selection of cost-effective approaches to mercury emission control from coal-fired power plants or industrial boilers that might be located in different countries. Locally prevalent economic conditions (e.g., cost of supplies and materials,

efficiency and cost of labour, transportation cost, etc.) should always be considered during the selection of a mercury control option, while acknowledging the fact that many markets for emission control equipment and engineering construction companies are also global (Pacyna et al., 2010).

**Table 10**

Relative cost of mercury removal for various methods

| <i>Approach</i>                      | <i>Capital cost</i> | <i>O&amp;M cost</i> | <i>Comments</i>   |
|--------------------------------------|---------------------|---------------------|---|
| Coal washing                         | Moderate            | Low                 | Washing less expensive than chemical treatment.   |
| Coal blending                        | Very low            | Very low            | May require adjustment and/or refurbishment of pulverizers                                      |
| Hg oxidation additives               | Very low            | Low                 | Halogenated additives significantly increase Hg oxidation and capture                           |
| Re-emission control additives        | Very low            | Low                 | Potential for re-emission of Hg should be mitigated   |
| Selective Hg-oxidation SCR catalyst* | Low                 | Low                 | Only referring to Hg-specific catalyst, may require coal blending                               |
| Activated carbon injection (ACI)     | Low                 | Low to Moderate     | Preservation of ash quality an issue. Higher incremental costs for “concrete-friendly” sorbents |

\* with downstream wet FGD

**Table 11**

Capital cost of ACI in United States (\$/kW, 2007 dollars)

| <i>Technology</i> | <i>Unit size, MW</i> |            |            |            |
|-------------------|----------------------|------------|------------|------------|
|                   | <i>100</i>           | <i>300</i> | <i>500</i> | <i>700</i> |
| ACI               | 3–8                  | 2–6        | 2–5        | 2–5        |

Notes:

Data in table 11 from tables 5–16 in USEPA, 2010

Cost ranges are for modified pulverized activated carbon injection with FF or cold-side ESP

Case considered is for bituminous coal and other assumptions in EPA Base Case v.4.10

Relatively low sensitivity of capital cost of ACI to unit size, as shown in Table 11, may be interpreted as resulting in comparable cost effectiveness of mercury removal via activated carbon injection (cost of removing a unit mass of mercury) for small and large units (e.g., small industrial boiler vs. large utility boiler at a power plant). In-depth analysis of activated carbon injection costs for control of mercury emissions (USEPA, 2010), from which Table 11 was derived, gave capital costs in 2007 ranging from 2 to 8 \$/kW depending on configuration, activated carbon type (standard or modified), and unit size (from 100 to 700 MW). It should be noted that the cost values in Table 11 do not include the capital cost of FFs or ESPs. The cost of installing a new FF or baghouse is 55–70 \$/kW regardless of plant size. For the same range of variables, the study arrived at a fixed operating and maintenance cost varying from 0.03 to 0.1 \$/kW/year.

The actual cost of mercury control with activated carbon will also depend on the particulate control system used. Table 12 shows the operating costs for ESP and COHPAC (advanced hybrid particle collector) fabric filters. The estimates are for a 250 MW plant with an 80 per cent capacity for firing bituminous coal and assumed the cost of the COHPAC system would be around 50 \$/kW (\$12.5 million).

**Table 12**

Operating costs for activated carbon injection systems (on a 250 MW plant) followed by either ESP or FF for bituminous coals (IJC, 2005)

|                             | <i>ESP</i> | <i>COHPAC</i> |
|-----------------------------|------------|---------------|
| Mercury removal, %          | 70         | 90            |
| PAC injection rate, kg/Macm | 160        | 48            |
| PAC injection cost, \$      | 790 000    | 790 000       |
| Activated carbon cost, \$   | 2 562 000  | 796 000       |

The sorbent costs depend upon the coal characteristics, type of existing APCs at the plant, and the level of mercury capture required. Jones and others (2007) listed the costs of carbons from several different suppliers and they ranged from 0.87 \$/kg to 2.11 \$/kg.

The type of activated carbon affects both the injection rate and the operating cost. The unit price of brominated activated carbon can be 30 per cent higher than that of the untreated activated carbon. The performance of brominated activated carbon, however, can be significantly better than that of untreated activated carbon for certain types of coal (Chang et al., 2008).

## **4 BAT and BEP for coal combustion**

General principles for the choice of BAT for the point source categories listed in Annex D are described in the introductory chapter of this guidance document. Here we focus on the choice of mercury controls in the coal combustion sector.

### **4.1 Best available techniques**

There are four main types of control measures for atmospheric emissions of mercury from coal-fired power plants and industrial boilers.

#### **4.1.1 Primary measures to reduce the mercury content of coal**

The first type involves the removal of mercury prior to combustion. Coal washing, selection or blending are effective technologies for improving efficiency in the use of coal and for reducing the emission of air pollutants. The extent to which coal washing has been applied in coal-fired power plants and in industrial coal-fired boilers has been quite low, however, and the proportion of coal washing has grown slowly, because by itself it does not constitute BAT. Yet, when combined with other control measures described below, it can provide reasonable reductions in mercury emissions.

#### **4.1.2 Measures to reduce mercury emissions during combustion**

The second type of control measures involves the removal of mercury during combustion. The use of a fluidized bed boiler plays an important role in mercury removal downstream. Particularly important are the much higher percentages of particulate mercury in flue gas from fluidized bed compared with pulverized coal firing. This high percentage of mercury present as particulates leads to high mercury removal efficiency of downstream FFs or ESPs. It should be noted, however, that the use of a fluidized bed boiler itself does not constitute BAT.

#### **4.1.3 Mercury removal by co-benefit of conventional APCSS**

The third type of control measures for mercury removal involves the use of APCSS which are mainly used for the removal of PM (ESP, FF or a combination of both), SO<sub>2</sub> (dry or wet FGD), and NO<sub>x</sub> (SCR), but can result in substantial reductions in mercury emissions as a co-benefit. In some countries, the co-benefit removal of mercury is the first measure considered for the reduction of mercury emissions from coal-fired power plants or industrial boilers.

Emission levels and removal efficiencies achieved through the application of APCSS were shown in section 3.2 above. This demonstrates that the combination of SCR, ESP and FGD, which is widely used in the coal-fired power plants in Europe, the United States, China and Japan, can accomplish mercury removal efficiencies of up to 95 per cent and a concentration of less than 1 µg/Nm<sup>3</sup> of mercury in the flue gas from plants burning hard coal.

The combination of SCR, FF and FGD can achieve mercury removal efficiencies of up to 99 per cent and a concentration of less than 0.5 µg/Nm<sup>3</sup> of mercury in the flue gas from plants burning lignite.

#### **4.1.4 Dedicated mercury control technologies**

The fourth type of control measures involves dedicated technologies for the reduction of atmospheric mercury emissions, including activated carbon injection technology or the use of additives. Currently, activated carbon injection technology has been widely commercialized and adopted for coal-fired power plants in the United States and has successfully complied with regulatory emission limit values representing 85–95 per cent control over more than five years (Massachusetts Department of Environmental Protection, 2015). The operations of activated carbon injection technology in the United States show that the mercury concentration in flue gas after activated carbon injection and fabric filters may be lower than 1 µg/Nm<sup>3</sup>.

## **4.2 Best environmental practices**

Effective pollution control management strategies, well-maintained facilities, well-trained operators, and constant attention to the process are all important factors in controlling and, where feasible, reducing the emissions of mercury from coal combustion. As such, these practices, applicable to existing and new sources, are considered to be BEP and should be performed in a manner which is consistent with the application of BAT.

### **4.2.1 Key process parameters**

The first step in determining BEP for the coal combustion process is to identify the key process parameters (including mercury input control in coal and related monitoring), either from site-specific investigations or from testing undertaken on similar facilities elsewhere. Based on the investigations and testing, measures that enable control of key process parameters should be introduced into the management system.

#### **4.2.2 Consideration of energy efficiency for whole plant**

Energy efficiency of a coal-fired power plant is defined as the ratio between the output (net electricity, net heat, or both) from the plant and the amount of source energy (in coal) supplied to the plant over the same period. The efficiency of the steam turbine (based on lower heating value of coal) in a new pulverized coal-fired plant varies from 39 to 47 per cent, depending on steam conditions (Eurelectric, 2003). Newly constructed plants designed for subcritical steam conditions operate at the lower end, whereas plants designed for supercritical and ultra-supercritical steam conditions operate at the higher end of this efficiency range. Circulating fluidized bed combustion (CFBC) boilers typically operate above 40 per cent efficiency. As recently as 2011, only about half of all new coal-fired power plants were designed for high efficiency low emission operation (IEA, 2012).

As plants age their efficiency decreases, requiring more coal to generate the same amount of output. For any given coal-fired power plant or industrial boiler, the amount of uncontrolled mercury emissions from the plant or the boiler is directly related to the amount of coal burned. It follows that, if the amount of coal burned could be reduced, then the overall mercury emissions from a given power plant or industrial boiler would also decrease. This reduction in the amount of coal burned could be accomplished by measures undertaken to improve the energy efficiency of an existing power plant or industrial boiler.

Energy-efficient design, equipment maintenance, and improved efficiency also provide for the reduction of all emitted pollutants from the same volume of coal used, including greenhouse gases such as CO<sub>2</sub>, in addition to a reduction of mercury emissions. Should the upgrading of a plant be implemented for business or economic reasons, it would result in more energy and less emissions being produced from the same volume of coal used (Sloss, 2009).

Examples of measures to improve energy efficiency in coal-fired power plants or coal-fired industrial boilers can include detailed measurements to identify thermal losses, fixing leakages in flue-gas ducts, upgrading air heaters, new blading for turbine, overhauling or upgrading of the condenser, new packing for the cooling tower, or improving the electrical efficiency of the plant.

High efficiency combustion is facilitated by establishing a monitoring regime of key operating parameters, such as carbon monoxide (CO), volumetric flow rate, temperature and oxygen content. Low CO is associated with higher combustion efficiency in terms of the burnout of the feeding coal. Combustion efficiency depends on several factors, including steam conditions, type of coal, local climate at location, age of plant, capacity, and operation mode (IPPC, 2013).

#### **4.2.3 APCS maintenance and removal efficiency**

Beyond better energy efficiency, improving the efficiency of APCSs offers the opportunity to maximize the removal of mercury. The incremental amount of mercury removal is achieved as a result of operating APCS equipment originally designed to limit non-mercury emissions such as PM, SO<sub>2</sub>, or NO<sub>x</sub>, which is already in place at the power plant or an industrial boiler. Depending on the available APCS equipment, these approaches could include decreasing the parasitic power requirements of APCSs, modernization or upgrades of ESPs or FFs, alteration of SCR design and operation, or a combination of the above (Sloss, 2006).

#### **4.2.4 Environmentally sound management of the plant**

To improve the prevention and control of mercury emissions, an environmental management system that clearly defines responsibilities at all levels is needed for a coal-fired power plant or a coal-fired industrial boiler. Some of the most commonly applicable measures are dedicated to the improved operation of the boiler, such as implementing appropriate inspection and maintenance cycles. Operating and maintenance practices have the potential to improve plant performance, including its efficiency and reliability, and also to decrease the overall operating and maintenance costs themselves. Deterioration of plant equipment is unavoidable; however, the rate at which this deterioration occurs depends greatly on the operating and maintenance practices. Some of the good operating and maintenance practices include for example, steam line maintenance, water treatment, and a reliable protocol for monitoring and reporting. In addition, process improvements may be necessary to reduce bottlenecks and delays.

Adequate resources should be allocated to implement and continue the application of BEP, and staff should be appropriately trained relevant to their duties. Independent third-party field-based and remote auditing protocols are also important to ensure that BEP are actually being followed.

#### **4.2.5 Environmentally sound management of coal combustion residues**

Environmentally sound management of coal combustion residues (CCRs) is important to minimize the potential for increasing the risk of mercury re-emission and other potential problems.

Throughout the process of mercury emission control from coal-fired sources, mercury is removed from flue gas and transferred to CCRs, including boiler bottom ash, fly ash, and sludge from wet FGD. Sludge from wet FGD and other CCRs are either stored at the site or reused, including through further processing into gypsum wallboard. In the latter case, after FGD gypsum has been filtered out of the sludge, mercury may need to be extracted from the FGD wastewater effluent depending on the levels present. This may be accomplished via chemical treatment, ion exchange, or with membrane filtration. In the processes of gypsum wallboard production, other use of CCRs, including during storage of CCRs at the site, mercury contained within them may have the potential of being re-released.

In the process of gypsum wallboard production, a fraction of mercury may be re-released because the production processes often include high-temperature units. In one study, total mercury loss across the wallboard plant represented about 5 per cent of the incoming FGD gypsum mercury content (Marshall, 2005). Another study by Liu et al. (2013) indicated, however, that 12–55 per cent of total mercury in the FGD gypsum would be emitted during wallboard production and a third study found releases ranging from 2 to 66 per cent of the mercury in the incoming FGD gypsum (Sanderson et al, 2008). Given the potential variability in release rates, wallboard production using FGD gypsum is not regarded as BEP unless the mercury re-emissions are shown to be minimal or are captured during the wallboard production.

In the case of on-site storage of CCRs, there may be a potential for cross-media impacts (e.g., for leaching of mercury into groundwater). A multi-year study of leaching characteristics of CCRs concluded that any potential release of metals from CCRs to the environment is affected by leaching conditions (USEPA, 2006; USEPA, 2008; USEPA, 2009a).<sup>1</sup> Leaching conditions are affected by the pH and by the amount of water contact (ratio of liquid-to-solids). When evaluated over the pH range from 5.4 to 12.4 (plausible range for management of CCRs), the mercury leach results did not exceed existing standards for the concentration of mercury in well-water in the United States. In these same studies, some leach results for some other heavy metals, such as arsenic, were found to exceed existing standards for concentration in well-water in the United States. It should be noted that the data presented do not include any attempt to estimate the amount of constituent that may reach an aquifer or drinking water well. Groundwater transport and fate modelling, including the consideration of many additional factors – including how the fly ash is managed – would be needed to assess the potential risk. The storage of CCRs with impervious surfaces at the site can be considered as one aspect of environmentally sound management.

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<sup>1</sup> The leach testing methods used in these studies have been developed into standard tests, known as the “LEAF” methods, by the USEPA. The methods are numbered 1313–1316, and can be found at: [http://epa.gov/wastes/hazard/testmethods/sw846/new\\_meth\\_meth.htm](http://epa.gov/wastes/hazard/testmethods/sw846/new_meth_meth.htm).

## **5 Mercury emissions monitoring**

General and cross-cutting aspects of testing, monitoring and reporting are discussed in the introductory chapter of this document. The present section is limited to specific aspects of mercury emissions monitoring for coal-fired power plants and industrial boilers.

### **5.1 Continuous emissions monitoring**

Mercury monitoring using continuous emissions monitoring (CEM) instruments is effective for coal combustion flue gas streams (Sarunac, 2007). For emission compliance purposes, CEM instruments are located in the stack and measure a gas stream of low particulate concentration.

For mercury process optimization purposes, CEM instruments are sometimes used to sample the particulate-laden gas stream before a particulate control device. A commonly used filter probe technology for this purpose is the inertial filter. It uses a technique of sample gas acceleration and relies on the inertial forces of the particulate and a sintered filter to separate the gas and particulates.

CEM monitoring of sample gas saturated with water by a wet scrubber is commonly practised although it requires more elaborate procedures. A special fixed filter probe is used to avoid blockage from the condensation of water and typically employs a frequent filter media cleaning cycle using compressed air. All applications of CEM monitoring use heated sample lines with careful regulation of sample gas temperature to avoid the condensation of water and the resulting absorption of oxidized mercury into this water.

A CEM instrument provides the coal combustion operator with real time mercury analysis which can be used in a feedback loop with the sorbent injection or coal additive feed equipment. This feature allows tight control over the concentration of mercury emissions, despite changes of mercury concentration in the fuel.

The CEM also provides the advantages of sensitivity to low concentrations of mercury, down to  $0.5 \mu\text{g}/\text{m}^3$ , speciated mercury measurements, and high repeatability of results when calibrated with a dynamic mercury spiking methodology.

### **5.2 Sorbent trap monitoring**

Sorbent traps for mercury monitoring in coal combustion gas streams have been shown to provide accurate and replicable data, even at very low mercury emission concentrations (Sarunac, 2007). It is possible to monitor using one set of traps over a sampling period lasting several days in coal combustion plants.

### **5.3 Impinger sampling**

The use of impinger methods for mercury monitoring in coal combustion plants has historically been the prominent method. Impinger methods are not appropriate for long sampling periods and in practice are limited to several hours in length (Sarunac, 2007).

Many impinger methods separately collect particulate, oxidized, and elemental mercury and are therefore useful in coal combustion plants for determining the mercury speciation.

The impinger methods use multiple impingers in series to allow a certain measure of quality control.

### **5.4 Mass balance**

Mass balance measurements in coal combustion plants are not a direct monitoring method for mercury air emissions and it can be expected that the accuracy of air emissions calculated from mass balance will be low.

The data required to perform a mass balance measurement of mercury in coal combustion plants are readily available in some regions because the mercury content of solid and liquid waste streams from the plant is regulated. Waste streams include bottom ash, fly ash, scrubber wastewater, scrubber products such as gypsum, and scrubber waste solids. Mercury measurement of the coal burned is also regularly measured in certain regions and is necessary for the mass balance calculation.

Mass balance accuracy is heavily dependent on representative sampling of the coal and waste streams and of proper sample stabilization. Special procedures must be followed to avoid loss of mercury from collected samples. Greater accuracy of the mass balance results can be achieved with a greater number of samples collected and analysed. A significant variation in the mercury content of the coal may be expected, so frequent coal analysis is required for an accurate mercury input value. Periodic mercury air emissions monitoring must be practised to validate the mass balance calculations.

Considering the number of material streams which require monitoring and the frequency of sampling to achieve an accurate mass balance, it may be more difficult to use a mass balance method for the monitoring of mercury air emission in coal combustion plants than a direct flue gas monitoring method.

### **5.5 Predictive emissions monitoring systems (PEMS)**

Predictive emissions monitoring is a good screening tool for coal combustion plants but, owing to the wide mercury content variation of coal, it is not an accurate means of monitoring mercury air emissions.

The predictive monitoring systems are useful for estimating the mercury air emissions in preparation for sorbent trap or other monitoring activities. A good estimate of the air emission range will allow for a more efficient sorbent trap test.

### **5.6 Emission factors**

Emission factors are not an accurate means of monitoring mercury air emission for coal combustion gas streams. This is due to the variation of mercury content in coal and the wide variation in mercury capture within a coal combustion plant's emission control equipment. This latter point makes emission factors very difficult to accurately apply across the fleet of coal combustion plants.

### **5.7 Engineering estimates**

Engineering estimates are not an accurate method of monitoring mercury air emission for coal combustion plants.

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