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

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List of Acronyms and Abbreviations

APCS	Air Pollution Control System
BAT	Best Available Technique
BEP	Best Environmental Practice
СОР	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 (BATs) and Best Environmental Practices (BEPs) 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 supplying electricity to national electricity grids; some also supply heat (combined heat and power plants, district heating, etc.). Industrial boilers provide heat and/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 increased potential mercury emissions). However, the number of industrial boilers usually is 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 often are 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 a technical feasibility standpoint, 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. While 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 (so-called mercury co-benefit of APCS). 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 similar 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.

Comment [D[1]: David Lean, Lean Environmental: The focus is on coal fired power plants and other facilities that use coal but other forms of fossil fuels and even biomass including wood burning also release mercury. Natural gas has been thought to be 'clean' and low in mercury but that is because the producers often remove mercury before putting it into pipelines. The removal and storage of mercury from natural gas should also be reviewed. Activated carbon removal and storage in landfill is one method used but is likely not a permanent sink for mercury Another removal technique is the use of zinc amalgamation and then the zinc is sent to smelters where the mercury is released to the atmosphere. The reason for the removal of mercury from natural gas is not because of an environmental concern but to avoid having mercury in pipelines where it makes them brittle and they fail or rupture more often

Comment [KTA2]: Extraneous parentheses ...

2 Processes Used In The 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 deposit. The quality of a coal deposit 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", -bituminous and anthracite coals are termed "hard coal". The ASTM nomenclature will be used throughout this document.

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

Subbituminous coal typically contains 35 to 45per cent carbon (w/w) and has a heating value between 19.26 and 26.80 kJ/kg. It is widely used for electricity generation as well as in industrial boilers.

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

Anthracite contains a very large amount of carbon, as high as 86 to 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). However, it is the most difficult coal fuel to burn due to its low volatile content.

<u>Figure 1</u> presents typical use of different types of coals (WCA, 2014). As is shown in <u>Figure 1</u>, <u>Figure 1</u>, 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.



Comment [KTA3]: From these given values, I am presuming that these descriptions are in regards to "fixed carbon"...if so, I would suggest adding that detail herein for valuable clarity.

Comment [SC4]: In coal analysis distinction should be made between as received and dry basis values; the values presented here appear to be as received.

Comment [KTA5]: Our understanding of coal used in Canadian electricity generation is that this range is a little narrow. Observations in Canada would broaden this range to 15-30 kJ/kg

Figure 1. Use of different ranks of coal

Key parameter affecting the amount of uncontrolled mercury emission is the mercury content of coal. <u>Table 1</u>, 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 Subbituminous	0.20 0.3	0.04-0.81 (23) 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 Subbituminous	0.21 0.033	0.03-2.2 (19) 0.022-0.057 (4)	Tewalt et al., 2010
China	Bituminous/Subbituminou s	0.17	0.01-2.248 (482)	Zhang et al., 2012; UNEP, 2011
Colombia	Subbituminous	0.069	>0.02-0.17 (16)	Finkelman, 2004
	Lignite	0.338	< 0.03-0.79 (16)	Finkelman, 2003
Czech Rep.	Bituminous	0.126	0.03-0.38 (21)	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 Lignite	0.05	0.7-1.4 Max: 0.09	Pirrone et al., 2001 MUNLV 2005
Hungary	Bituminous Subbituminous Lignite	0.354 0.138 0.242	0.091-1.2 (5) 0.04-0.31 (19) 0.075-0.44 (12)	Tewalt et al., 2010
India	Bituminous Lignite	0.106 0.071	0.02-0.86 (99) 0.053-0.093 (8)	Tewalt et al., 2010;UNEP, 2014
·	Lignite	0.11	0.02-0.19 (8)	Finkelman, 2003; Tewalt et al., 2010
Indonesia	Subbituminous	0.03	0.01-0.05 (78)	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 Subbituminous	0.073 0.082	0.03-0.1 (5) 0.062-0.13 (9)	Tewalt et al., 2010
Mongolia	Bituminous	0.097	0.02-0.22 (36)	Tewalt et al., 2010
Peru	Anthract+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/ Subbituminous	0.12	<0.02-0.25 (23)	UNEP, 2013b Romanov et al., 2012
Slovak Rep.	Bituminous Lignite	0.08 0.057	0.03-0.13 (7) 0.032-0.14 (8)	Finkelman, 2004 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

Comment [SC6]: The list seems somewhat selective; e.g. no reference to coal type for Canada or to Australian brown coal, but does give a pretty good overview. Not clear whether the values are as received or dry.

Comment [KTA7]: This information does not well match information that ECD has on the concentration of mercury in Canadian coals. The given average and range is consistent with Canadian observations for bit coal. Mercury concentrations in Canadian sub-bit and lignite are significantly higher than those listed in Table 1. The significance of this difference is that most Canadian coal use, now and in the future, is in the sub-bit and lignite ranks, i.e., Table 1 biases the mercury input to coal plants downwards. It is understood that Table 1 is likely not easily changed since it is copied from another paper; however, I would suggest either modifying the range or adding a footnote to the table. If desired, ECD can contribute to such additional information.

United Kingdom	Bituminous	0.216	0.012-0.6 (84)	Tewalt et al., 2010	
United Kingdom USA Vietnam Zambia	Subbituminous	0.1	0.01-8.0 (640)	US EPA, 1997	
LIC A	Lignite	0.15	0.03-1.0 (183)	US EPA, 1997	
USA	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 given as to if Mercury concentrations reported are on the dry coal- or on the as-received coal-basis. This data may not be representative of coals as-burned.

2.2 Mercury transformations during combustion of coal

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

Physical and chemical transformations that mercury undergoes during coal combustion, and subsequently in the resulting flue gas, are shown schematically in Figure 2Figure 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 (FeS₂) and cinnabar (HgS) are the two dominant mineral hosts for mercury in coal. As the mineral (and possibly organo-mercuric) hosts of mercury decompose during combustion (>1400°C), mercury evolves as elemental mercury (Hg⁰). The mode of occurrence of mercury in coal does not affect this initial combustion transformation mechanism.



Coal Combustion Postcombustion

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 (Hg^0), gaseous oxidized mercury (Hg^{2+}), and particulate-bound mercury (Hg_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/chlorination is assumed to be the dominant mercury chemical transformation mechanism 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 as well as 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, 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 fourteen 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 to 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 (PC 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)

Most large steam generation at power plants is produced through the PC firing. In a PC boiler, finely grounded coal is pulverized to a fine powder and blown directly to individual burners where it is mixed with pre-heated 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 a lot among the tested PC 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 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 matters per unit of fuel fired, and coarser particulates compared with PC firing, because combustion takes place in a quiescent fuel bed without significant ash carryover 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 total solids inventory. The temperature in a fluidized-bed combustor is controllable in a narrow range. Onsite measurement of mercury concentrations from a circulating fluidized bed boiler shows that particulate mercury is of majority in flue gas of the boiler (Duan et al., 2010).

Comment [KTA8]: This range is not consistent with Canadian observations for lignite; SaskPower has reported oxidation levels in the range of ~20%. Would suggest that a footnote be added indicating that coals can be (significantly) outside of this range and use lignite as an example.

Comment [SC9]: Low rank western Canadian coals yield primarily elemental mercury in the flue gas outside the range cited here; e.g. at our SaskPower units oxidized mercury is commonly 10% or lower. This is consistent with the low chlorine contents of these coals (on the order of 10 ppm).

This could have implications on what levels of control can be expected from the various techniques discussed as oxidized mercury is much easier to control.

Comment [KTA10]: The meaning of this sentence is not clear to me; I would suggest that it be edited to provide extra clarity.

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). They include coal treatment, co-benefit Mercury removal, and dedicated Mercury removal technologies.

3.1 Coal washing

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 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 O&M 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).

Coal washing reduces ash content and improves its heating value, thus increasing boiler efficiency (Satyamurty, 2007). Coal washing can lower the ash content from around 40 per cent to around 20 to 30 per cent or better, depending on the coal mineralogy. Some coals may be very difficult or even unsuitable for conventional coal washing. Conventional coal washing methods separate the organic fraction of the as-mined coal from the mineral materials according to the differences in either the density-based or surface-based characteristics of the different materials.

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) that 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 utilized. However, the effectiveness of mercury removal from coal during conventional coal washing varies widely depending on the source of coal and on the nature of mercury in coal.

Cross-media effects of coal washing

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

3.2 Contributions of APCSs in terms of mercury removal

The APCSs installed primarily for control of SO₂, NO_x, or particulate matter (PM) remove mercury from the flue gas. This is called the co-benefit mercury removal. Co-benefit mercury removal by nonmercury air pollution control equipment is most often accomplished in two fundamental modes: removal of oxidized mercury in a wet FGD scrubber and removal of PM-bound mercury in a PM control device (ESP or 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 **Comment [D[11]**: David Lean, Lean Environmental: This is done to lower ash levels and improve the coal burning efficiency of heat generated per unit coal burned. We are left with the impression that this also reduces mercury and it does in the emission to the atmosphere but where does the water go. There is likely local mercury pollution as a consequence that may be even more severe.

Releases to water are as important as releases to air even for long range transport. My students have lead in this aspect and their models for release from water to air are internationally recognized. When mercury is released to water, most of it will be in the atmosphere within a few days.

Comment [KTA12]: This document has already defined brown coal as lignite and sub-bit, so the sentence as written seems to place extra emphasis on lignite. I would suggest either using "brown coal" or "lignite and sub-bituminous coals"

Comment [D[13]: Government of Manitoba: these 2 paragraphs deal with the same issue i.e., coal washing and resulting benefits. Can be combined and re-written to reflect the main purpose. mercury removal could be accomplished. The overview of the magnitude of co-benefit mercury removal for different configurations of existing APCSs are shown in Table 2 Table 2 (Srivastava et al., 2006; EIPPCB, 2013). It should be noted that the co-benefit removal as shown in Table 2Table 2 will vary depending on coal properties and operational parameters of the APCSs.

Table 2.	Overview	of co-benefit	mercury remova	l in APCSs
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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		Comment [SC14]: We do not see this in
ESPc + wet FGD	Generally, good capture for high chlorine coals due 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 <u>unless the appropriate scrubber additives are used</u> .		our lignite coals; we have seen some mercury oxidation across a FF, but without any mercury capture
ESPh + wet FGD	Generally, good capture for high chlorine coals due 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 <u>unless the appropriate scrubber additives are used</u> .		
SDA + FF	Generally good capture for high chlorine coals; less co-benefit capture expected for low rank	·	Comment [SC15]: The low rank coal
FF + Wet FGD	Generally, good capture for high chlorine coals due 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 <u>unless the appropriate scrubber additives are used</u> . Elemental mercury may be oxidized across the FF and captured in the wet scrubber.		comment is consistent with our observation of no mercury capture across a FF
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 due to increased amount of soluble oxidized mercury in the flue gas which is promoted by the SCR. Improved capture for low rank coals due to greater amount of soluble oxidized mercury in the flue gas. Elemental mercury re-emission may decrease the amount of co-benefit unless the appropriate scrubber additives are used. Good capture of particulate-bound mercury.		Comment [SC16]: Mercury oxidation across an SCR does not always occur, especially for low rank coals which have low chlorine contents. Note: ammonia,
SCR + HEX + LLT-ESP + wet FGD	Very high capture for high chlorine coals due to increased amount of soluble oxidized mercury in the flue gas which is promoted by the SCR. Improved capture for low rank coals		which is used in SCR for NO _x control is a reducing agent and can result in increased elemental mercury.
	due to greater amount of soluble oxidized mercury in the flue gas. Elemental mercury re- emission may decrease the amount of co-benefit <u>unless the appropriate scrubber additives are</u> <u>used</u> . Combination of heat exchanger and low-low temperature ESP enhances capture of particulate and vapor phase mercury.		Comment [SC17]: Mercury oxidation across an SCR does not always occur, especially for low rank coals which have low chlorine contents.
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.	'	Comment [SC18]: Again, mercury oxidation across an SCR does not always
SCR + ESPh + wet FGD	Good capture for high chlorine coals due to increased amount of soluble oxidized mercury in the flue gas which is promoted by the SCR. Improved capture for low rank coals due to greater amount of soluble oxidized mercury in the flue gas. Elemental mercury re-emission		occur, especially for low rank coals which have low chlorine contents.
SCD + EE + wet ECD	may decrease the amount of co-benefit <u>unless the appropriate scrubber additives are used</u> . Good capture for high chlorine coals due to increased amount of soluble oxidized mercury in the flue gas which is promoted by the <u>SCR</u> . Improved capture for low rank coals due to grader amount of soluble oxidized mercury in the flue gas. Elemental mercury is a minimum of the flue gas which is promoted by the <u>SCR</u> .		Comment [SC19]: Again, mercury oxidation across an SCR does not always occur, especially for low rank coals which have low chlorine contents.
50K + FF + WELFUD	may decrease the amount of co-benefit <u>unless the appropriate scrubber additives are used</u> . Good capture of particulate-bound mercury;		Comment [SC20]: Again, mercury oxidation across an SCR does not always
Note:			occur, especially for low rank coals which have low chlorine contents.

Note:

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 APCS configurations presented in <u>Table 2Table 2</u> (SCR+ESPc+FGD) is shown schematically in <u>Figure 3Figure 3</u> below (Ito et al., 2006). For example, such a combination in Japan achieved an average mercury removal efficiency of 73 per cent (Ito et al., 2006). Therefore, co-benefit techniques, which can control air pollutants emission and moreover remove mercury, <u>is-may be</u>quite effective as a comprehensive air pollution control.



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

High level co-benefit removal of mercury can be achieved by combining these techniques. The combination of SCR, ESP and FGD is quite typical at advanced coal-fired power plants and is widely used, for example in Japan, as shown in Figure 4Figure 4 and Figure 5Figure 5. The combination of SCR, ESP and FGD can achieve removal efficiencies of 50 to 90 per cent for NO_X, more than 99 per cent for PM, and 76.0 to 98.0 per cent for SO₂, as well as high level mercury removal efficiency as averagely 74.4 per cent, which results in 1.2 μ g/m³ of mercury concentration in the flue gas. Furthermore, the combination of SCR, Low Low Temperature ESP (LLT-ESP), and wet FGD, can achieve quite high level mercury removal efficiency as averagely 86.5 per cent, which results in 0.88 μ g/m³ of mercury concentration in the flue gas for this specific case. The mercury concentrations in Figure 5 show wide ranges because these include older and/or smaller units which provide the higher concentration. On the other hand, two units with the 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).

Comment [D[21]: SaskPower: This is true for cases where this works, but this does not work in all cases.

Comment [SC22]: This is not always the case. SCR is still not compatible with all kinds of coal; e.g. lignites found in Saskatchewan and North Dakota and wet FGD is not always the technology of choice to achieve high degrees of removal of SO₂; e.g. for western Canadian coal plants.

Comment [SC23]: This clearly depends on how much mercury is in the coal and will vary significantly as a result of this.

Comment [SC24]: In the process diagram they refer to dry FGD as a moving bed of coke. The cojke would be expected to remove significant amounts of mercury, but this kind of dry FGD is largely limited to Japan and more conventional dry FGD technologies do not have this effect.



Figure 4. Mercury reduction efficiency of coal-fired power plants with SCR+ESP+FGD and SCR+LLT-ESP+FGD



Figure 5. Mercury concentrations in flue gas from coal-fired power plants with SCR+ESP+FGD and SCR+LLT-ESP+FGD

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. The effectiveness of an ESP depends largely on the electrical resistivity of the particles being collected.

Above and below an optimum value that exists for a given ash, particles become less effectively charged and collected. The PM collection efficiency of an ESP is also a function of 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 (SO₃), sulfuric acid (H₂SO₄), water, sodium, or ammonia (NH₃). 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 to 8 μ m are typically collected with efficiencies from 95 to 99.9 per cent. However, particles near the 0.3 μ m size are in a poor charging region that reduces collection efficiency to 80 to 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 and 180 °C). An ESPh is installed upstream of the air heater (flue gas temperature between 300 to 400 °C) and allows taking 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. 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 wet ESP.

Varying levels of mercury removal has been observed for ESPs. The level of mercury removal depends on whether it is a ESPc or ESPh installation, the type of coal burned, the type of boiler, and other factors. For example, while the average reported mercury removal for an ESP operating on a 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 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 modeling of mercury removal in ESPs indicate 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 generally remove only Hg_P in the process of collecting PM. Hg_P is preferentially bound to unburned carbon (UBC). 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 behavior is shown in Figure 6Figure 6, which shows the percentage capture (percentage of mercury incoming to the ESP) as a function of the amount of UBC. In Figure 6Figure 6, UBC is expressed as the measured loss on ignition (LOI). As can be seen, between 20 and 40 per cent mercury capture 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 halogens presents (Vosteen et al., 2003).





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). The 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 impacting mercury adsorption. Thus, an 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. However, it should be noted that most of the mass of UBC is in very large particles.

Other important factors governing the amount of mercury that is captured on fly ash (and subsequently removed from the flue gas) are type of ESP used (e.g. ESPc or ESPh), the use of SO₃ 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 content and producing higher levels of UBC in the flue gas. Both of these parameters promote 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 (less than 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).

3.2.1.2 Fabric filters (FFs)

FFs provide higher removal efficiency of fine particles in comparison to ESPs, especially 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 an ESP, 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). For example, a study comparing the capture of mercury in ESPs and FFs in coal-fired power plants in

Comment [SC25]: Lower flue gas temperatures do tend to result in greater mercury retention. However, there are practical low temperature limits (with 150°C being typical) for ESP operation in order to avoid corrosion due the condensation of acidic flue gas constituents. China revealed between 4 and 20 per cent capture in ESPs and between 20 and 80 per cent capture in FFs (Wang et al., 2008). The average mercury removal efficiencies for ESP and FF in Chinese coal-fired power plants are 29 per cent and 65 per cent, respectively (Wang et al., 2010).

FF can also be integrated with ESP to become ESP-FF, which has comparative application rate as FF in China. The mercury removal efficiency of ESP-FF is between ESP and FF. Averagely 43 per cent or mercury removal can be achieved by ESP-FF (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 (7-59 per cent) for wet PM scrubber at Chinese coal-fired industrial boilers.

Integrated marble scrubber (IMS) is a special type of wet PM scrubber for concurrent PM and SO_2 removal, which is more and more widely adopted by coal-fired power plants in China due to its technological economy. IMS uses alkali liquor as the absorbent, which is more effective in capturing oxidized mercury, similar to wet FGD. The efficiency of IMS on mercury removal could be higher than that of conventional wet PM scrubber due to its effect of SO_2 control, but no onsite measurements have been conducted yet.

3.2.1.4 Influence of flue gas cooling

Flue gas cooling is one of the options to enhance the mercury removal across the existing ESP (or FF). Flue gas cooling has been employed at commercial coal-fired power plants and the recovered heat is used to re-heat scrubbed flue gas in order to eliminate visible plumes. Figure 7Figure 7 shows an example of technology application for both reheating scrubbed flue gas (a) and recovering power from the waste heat (b) (Nakayama et al., 2006, Iwatsuki et al., 2008).



(a) Application for Reheating Scrubbed Flue Gas

Comment [SC26]: This is very much application dependent. Again, we see very little mercury removal across a FF or an ESP with our flue gases, likely related to very low levels of chlorine and UBC present.



Figure 7. Flow schematic for flue gas cooling

Flue gas cooling results in the reduction of temperature from 135 to 90 °C of the flue gas exiting the air heater. This is accomplished by using a cooling medium. This heat exchange process realizes the following benefits: 50 per cent reduction in water evaporated from the FGD system, reduction of SO₃ emissions by condensation on fly ash, improved particulate control through reduced gas volume and lower ash resistivity due to SO₃ conditioning and moisture adsorption to fly ash, increased mercury removal by fly ash due to lower flue gas temperature and reduced SO₃, and avoided costs with flue gas reheat or wet stack retrofits. In cases where re-heating wet-FGD exhaust is not as appealing, the recovered heat can be used in the boiler/steam turbine to improve the efficiency of the unit, thus increasing net output.

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 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 SO₂ control devices

There are two main techniques used for SO₂ emission reduction and dealt with below: (i) wet FGD, (ii) dry FGD, sometimes termed Spray Dryer Absorber, 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 oxidation of mercury over catalysts (Amar et al., 2010). The catalyst may be placed in the flue gas for

Comment [SC27]: SaskPower uses flue gas cooling to reach 85^oC at its Boundary Dam Unit 3 where a carbon capture system was recently installed. The recovered heat is used for feed water heating. There may be mercury co-benefits from this, but the new system has not been operating consistently enough to determine this. the sole purpose of mercury oxidation or may be installed for another purpose (e.g., for the control of NO_x 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 Rossenhoover 1999). However, gaseous elemental mercury is insoluble in water and therefore does not absorb in FGD slurries. Data from actual facilities has shown that capture of oxidized mercury averaging 75 per cent (67-93 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), though there are cases where significantly less capture has been measured as a result of unfavorable scrubber equilibrium chemistry (Niksa and Fujiwara, 2004).

It has also been shown that under some conditions, oxidized mercury may be reduced in wet FGD 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 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 Spray dryer absorber (SDA)

Spray dryers are typically used for the control of SO₂ emissions for sources that burn low- to mediumsulfur coal, or for smaller coal-fired combustion plants. Some issues that limit the use of spray dryers with high-sulfur coals include the ability of the existing PM control device (most often a FF) to handle the increased loading and achieve the required efficiency. Up to approximately 95 per cent mercury may be removed by SDA-FF combinations when used on bituminous coal-fired boilers. However, much lower mercury capture (about 25 per cent) is observed in SDA-FF units on boilers firing lignite or other low-rank coals with low Cl 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, higher mercury capture is accomplished by FF alone for low rank coal than mercury capture by SDA-FF (Srivastava et al., 2006).

Cross-media effects for SO₂ 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 for being re-emitted. For SDA-FF system, there is potential for mercury from fly ash collected by FF to leach into groundwater. Sound management of fly ash collected by FF is needed.

Cross-media effects for SO₂ control devices (non-mercury related)

The operation of FGD system generally increases energy consumption, typically up to 5 per cent.

Comment [SC28]: Circulating dry scrubbing (CDS) has become more widely deployed recently. CDS can achieve higher SO₂ removal than SDA-FF and is less capital intensive than wet FGD. It appears well suited for relatively small units that burn lower sulfur coal, as is the case in western Canada. The potential for mercury removal should, be similar to SDA-FF, but I don't know how much information there is on this.

3.2.3 NO_x control devices

SCR technology has been designed to reduce NO_X through a catalytically enhanced reaction of NO_X with NH_3 , reducing NO_X 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 pointed out that the SCR itself does not remove mercury. Instead, by increasing the amount of oxidized mercury upstream of the wet FGD, the SCR improves mercury capture in the 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_3 in the flue gas, catalyst bed size, and catalyst age) will generally be dictated by the NO_X 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 coal blending section below, 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 (Vosteen et al., 2006). SCR catalysts are being designed to optimize both the NO_X removal and mercury oxidation.

The extent of mercury oxidation and capture by increasing the fraction of bituminous coal in a subbituminous/bituminous coal blend, may be augmented by an SCR. 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 SCRs, mercury oxidation across the SCR increases with an increasing percentage of bituminous/bituminous coal blend. For example, for the 65/35 subbituminous/bituminous coal blend, the amount of increase was 49 percentage points (from 13 to 62 per cent). However, the increase was only 14 percentage points (from 6 to 20 per cent) for the 79/21 blend (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 over 90 per cent. The resultant mercury removal in downstream wet scrubbers was 84 to 92 per cent with SCR operation compared to 43 to 51 per cent without SCR operation. However, plants firing subbituminous coals 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 is in the range of 34 to 85 per cent, affected by the total mercury and Cl content in coal and the NH₃ injection rate of SCR (Zhang et al., 2013).

Cross-media effects for NO_X control devices

With the mercury oxidation by SCR, there is possibility to increase 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 environmentally sound disposed.

Cross-media effects for NO_X control devices (non-mercury related)

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

 $\label{eq:comment_scale} \begin{array}{l} \mbox{Comment_scale} \end{tabular} \end{tabular} \\ \mbox{discussion of low NO}_x \mbox{combustion would} \\ \mbox{be useful. Low NO}_x \mbox{combustion is} \\ \mbox{frequently associated with higher amounts} \\ \mbox{on UBC, which can result in greater} \\ \mbox{mercury capture. However, extra UBC} \\ \mbox{results in efficiency penalties and low NO}_x \\ \mbox{combustion systems are often designed to} \\ \mbox{mitigate this, resulting in reduced NO}_x \\ \mbox{emissions, but limited additional mercury} \\ \mbox{capture.} \end{array}$

Comment [SC30]: See comments on Table 2.

Comment [SC31]: Care needs to be taken here as incidents of corrosion, especially in the air heaters have been attributed to bromide addition.

3.3 Co-benefit enhancement techniques

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

3.3.1 Coal blending

Coal blending (and/or switching) at power plants is used as part of a strategy to meet SO₂ emission limits cost-effectively. Typically, high sulfur bituminous coals are blended with low sulfur subbituminous coals to lower SO₂ emissions. As an undesired side effect of this SO₂ 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. However, blending of coals may also be used 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 used to improve mercury removal in downstream air pollution control equipment is discussed below. <u>Table 3 Table 3</u> (UNEP, 2010) gives typical subbituminous coal (from Wyoming, USA) and bituminous coal (from Illinois, USA). It should be noted that properties given in <u>Table 3 Table 3</u> are only for illustration and will vary depending on coal origin.

Subbituminous Coal, wt%	Bituminous Coal, wt%
0.0006	0.02
0.003	0.100
0.37	4.00
26.67	3.43
5.30	3.07
1.68	0.60
0.1	0.1
	Subbituminous Coal, wt% 0.0006 0.003 0.37 26.67 5.30 1.68 0.1

Table 3. Comparison of properties of subbituminous and bituminous coals

^a ultimate analysis, as received, wt %

It should be noted from <u>Table 3</u> that even though 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 to 26.67 per cent by weight, respectively. This illustrates that lower chlorine content in subbituminous coals may result in lower mercury oxidation and hence higher elemental mercury percentage. 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 8 Figure 8 below shows the trend of increasing mercury capture in a dry FGD system (dry FGD plus FF) with increasing fraction of bituminous coal in a bituminous/subbituminous coal mixture

Comment [SC32]: Coal blending is generally more of an option for plants that obtain their coals from multiple sources. Western Canadian plants are usually mine mouth in nature and are designed to burn that particular coal. Using an alternate fuel source for these plants usually results in fuel cost penalty and sub-optimal operation. (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 illustrative nature and that actual incremental mercury removal values may vary depending on sources of coals used for blending.



Figure 8. 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 increase. 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_4Cl) may be added. Halogen additives promote formation of oxidized and particulate-bound mercury, which are 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 bromine is more active than chlorine for interaction with mercury (Vosteen et al., 2002; Vosteen et al., 2003; 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 ppm in coal equivalent level, and mercury emission reduction was increased from 55 to 92-97 per cent in a 600 MW unit firing subbituminous coal and equipped with an SCR 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 to 300 ppm in coal (Chang et al., 2008).

Comment [SC33]: See comment on 3.3.2 above. In addition, emissions of the added halogens could be an environmental concern.



Figure 9. Performance of bromine- 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 9Figure 9; 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 Figure 9Figure 9, 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. An order of magnitude more of chlorine-based additive was needed to achieve the same level of baseline elemental mercury reduction.

Cross-media effects for mercury oxidation additives

Use of mercury oxidation additives has potential impacts on the boiler, APCSs, 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 increase in bromine in fly ash (Dombrowski et al., 2008). Halogens added in coal can be potentially emitted from 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 byproducts 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).

3.3.3 Wet scrubber additives for mercury reemission control

The absorption of oxidized mercury followed by the retention of it in an aqueous phase is the basis of the co-benefit contribution provided by scrubbers. 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 labeled 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 10-Figure 10 below shows the chemical path through which absorption and re-emission can occur.



Figure 10. Illustration is provided of flue gas mercury absorption/desorption across WFGD (Keiser et al., 2014)

Much study has been put into the development of techniques and products to avoid mercury reemission and a number of these have been commercialized. In principle, all these techniques are based on a method to reduce 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 from 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: 1) inorganic sulfides; 2) organic sulfides; 3) organic compounds containing nitrogen and sulfur; 4) organic compounds containing oxygen and sulfur; and 5) 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_2 oxidation/conversion rate which forms SO_3 , 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_x removal with simultaneous low SO_2 to SO_3 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).

Selective mercury oxidation SCR catalyst that increases 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 catalyst has been already replaced by high mercury oxidation SCR catalyst. 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 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 (ACI) for dedicated mercury control

Sorbents without chemical treatment or chemically treated 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 one hundred full-scale systems (GAO, 2009; Amar et al., 2008). Since about 2005, activated carbon injection (ACI) has been commercially applied technology in the United States (ICAC, 2010a). Furthermore, it has been demonstrated at a Russian power plant burning Russian coal (USEPA, 2014). In a number of individual states in the U.S. (for example, Massachusetts, New Jersey, and Connecticut), for many existing coal-fired boilers, regulatory emission limit values (ELVs) in the range of 0.0025 to 0.0075 pounds per Gigawatt-hr (representing 85 to 95 per cent control) have been met with routine use of ACI for about seven years starting 2007. Regulatory compliance with these ELVs has been shown through measurements with mercury CEMs or sorbent trap methods (Massachusetts Department of Environmental Protection, 2015; similar reports from New Jersey DEP and Connecticut DEP). ACI requires a downstream PM control device.

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 physical and chemical properties of the sorbent, injection rate of the sorbent, flue gas parameters (such as temperature, concentrations of halogen species, concentration of SO₃) and existing APCS configuration (Pavlish et al., 2003; Srivastava et al., 2006; Martin, 2009).

Figure 11 Figure 11 is a summary of a number of tests conducted more than ten years ago with untreated ACI at four power plants. As can be seen in Figure 11 Figure 11, mercury removal efficiency by injection of untreated activated carbon (AC) depends strongly on the rank of coal and the type of PM control used in the plant. The plant in the Pleasant Prairie Test used low-sulfur 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. ACI was not effective for mercury control for this plant with mercury emissions predominantly elemental mercury, as untreated AC is not effective for capturing the unreactive elemental mercury. As a strong contrast, the Gaston Test demonstrated that ACI was extremely effective for control mercury emissions from this plant that burned low-sulfur bituminous coal and was equipped an ESPh followed by a small specially designed FF. Injection of untreated AC was at the outlet of the ESPh because temperature at the inlet was too high for ACI. A specially designed FF, Compact Hybrid Particulate Collector (COHPAC) located downstream of ACI, was used for

Comment [SC34]: The extent of mercury removal achieved this way is very much application dependent and is a key reason what the US MATS rule has adopted separate sets of limits for low rank and higher rank coal. removing the injected carbon. The application of COHPAC as an effective mercury control was demonstrated in the Gaston test.

In some cases low mercury removal by untreated activated carbon is the result of a combination of lower levels of chlorine in subbituminous coal 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 capture of elemental mercury by untreated ACI and, in general, the efficiency of mercury capture with untreated ACI increases with the amount of oxidized mercury in the flue gas (US DOE, 2005).

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



Figure 11. Testing of mercury removal efficiency as a function of untreated ACI rate

3.4.2 Injection of chemically treated sorbent

To overcome this set of limiting conditions associated with untreated ACI for mercury control in power plant applications, treated ACI sorbents have been developed (Nelson, 2004 and Nelson et al., 2004). The most often used and most thoroughly demonstrated treatment to enhance the performance of ACI was bromination.

Relative to untreated activated carbon, brominated activated carbon:

1) expands the usefulness of sorbent injection to situations where untreated activated carbon may not be effective;

2) 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;

3) results in better performance with subbituminous and lignite coals.

Improvement in performance of mercury control was observed during full-scale field tests of chemically-treated ACI injected upstream of the existing PM device (Feeley et al., 2008) and is shown in Figure 12Figure 12. As can be seen in Figure 12Figure 12, improved mercury capture efficiency was achieved using relatively low injection rates of treated ACI at power plants burning low-chlorine coals. The treated ACI achieved in excess of 90 per cent mercury capture at an injection rate of about

50 mg/m³) (Feeley et al., 2008). Higher injection rates were required to achieve high mercury removal efficiency when untreated ACI was used, and in some cases, it was not possible to achieve 75per cent capture.



Figure 12. Comparison of untreated ACI and treated ACI performance for mercury removal

3.4.3 ACI applicability restrictions

Despite the ACI being commercially implemented in multiple and diverse applications, there are some remaining potential issues that include fly ash marketability for concrete manufactures and the effect of SO_3 on the performance of ACI.

A typical ACI system is located upstream of a PM control device, which leads to mixing of the sorbent and fly ash. This is not a concern where fly ash is not sold for concrete production₁₅ however this mixing can negatively affect the use of fly ash in concrete production. Concrete quality is particularly sensitive to carbon content as well as the surface area of the carbon present in the fly ash.

Another effective way to eliminate 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). Additionally, in some plants which burn low mercury coal and utilize FF for PM control, the amount of treated activated carbon required for a mercury reduction greater than 85 per cent is as low as 8 mg/m³. In such cases, the presence of activated carbon in the fly ash may not affect the sale of fly ash for concrete.

Carbon sorbents were developed that allow some coal-fired power plants to continue marketing fly ash for concrete production (Nelson et al., 2006; Landreth at al., 2012). These are commercially used in the U.S.

Other non-carbon sorbents were also tested that were 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 post treatment of fly ash to remove UBC and AC have been developed. These include thermal treatment of fly ash and electrostatic separation of carbon from fly ash.

Testing has shown that SO₃ in the flue gas, even at low concentrations, can interfere with the performance of ACI. It appears that SO₃ competes with mercury for adsorption sites on the sorbent surface thereby limiting its performance. This phenomenon may be particularly relevant to ACI

applications at plants firing high-sulfur coal. One possible solution to address the SO₃ interference issue is combined injection of mercury sorbents and alkaline materials. Alkaline materials that have been considered and tested for this application include magnesium oxide (MgO), calcium hydroxide (Ca(OH)₂), sodium bicarbonate (NaHCO₃), and sodium sesquicarbonate (trona) (Feeley and Jones, 2009).

Cross-media effects for ACI

The ACI increases the quantities to landfill. Tests on two commercial activated carbons indicate that the mercury captured by AC is sufficiently stable to provide permanent sequestration of mercury in activated carbon sorbents after disposal (Graydon et al., 2009).

AC injection located upstream of a PM control device affects the quality of fly ash due to mixing of the AC and fly ash. There is potential of secondary mercury release from thermal treatment of fly ash and electrostatic separation of carbon from fly ash.

3.5 Cost of mercury control technologies

Mercury emission control can be accomplished as a co-benefit removal by the equipment already in place, that 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 mercury control cost and the cost of controlling other pollutants such as SO_2 or NO_X (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 or even 'free'. Alternatively, mercury control may be accomplished by dedicated technology such as ACI. 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 (O&M) cost, and variable O&M cost. For ACI, the variable O&M cost is estimated to be small even though it is a major component of the total cost (EPA, 2005; Amar et al., 2010). The major components of the variable O&M costs are sorbent costs and disposal costs. There may also be lost revenue from fly ash sales due to contamination of fly ash by activated carbon. To overcome this, "concrete-friendly" activated carbons have been developed, as well as technologies to separate activated carbon from fly ash.

3.5.1 Costs for co-benefit mercury control technologies

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. However, there is a substantial amount of cost information publicly available, which is presented below. Some general guidelines should be adhered to when evaluating these data:

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

The costs of control technologies vary significantly when applied to different countries. <u>Table 4</u> and <u>Table 5</u> show the costs of co-benefit technology in China and United States. It can be

Comment [KTA35]: Some of these materials have recently begun to be used as a direct form of SO₂ control and have been found to impair the reduction efficiency of mercury control systems using AC. As this is fairly common knowledge within the power sector, I would suggest that this section be expanded to 1) acknowledge these facts, and 2) discuss how such issues can be addressed. As it reads now, this section seems outdated and thus could lower perceptions of the entire document's relevancy.

Comment [SC36]: This is very much application dependent. Sorbent requirements can vary dramatically to achieve similar mercury removals at different sites. Sorbent is the major cost component for our mercury-control systems. seen that the capital cost of a wet FGD installed in a 600 MW unit can be 20 times lower in China than that in the United States. Therefore, the BAT chosen for mercury capture can be different in different countries. It should be pointed out 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, values in <u>Table 4Table 4</u> and <u>Table 5Table 5</u> should be considered to be indicative only and also the other cost data should be referred (e.g., UK Department of Trade and Industry (2000); Sargent & Lundy (2007)).

However, the conventional APCSs are not dedicated to mercury emission control, 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 (PEA) method based on the health and environmental impact of each pollutant and distribute the total annual cost to mercury, PM_{10} , SO_2 and NO_X (see <u>Table 6Table 6</u>).

APCD	Capacity (MW)	Capital cost (CNY/kW)	O&M cost (CNY/kW/yr)
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

 Table 4.
 Costs of air pollution control devices in power plants, China (Ancora et al., 2015)

Table 5.Capital cost of co-benefit technology in United States (\$/kW, 2012 dollars) (USEPA, 2013)

75±18

SCR

>300

Technology	Unit size, MW	Coal type	Total capital cost (US\$/kW)	Total O&M coats , fixed and variable (US\$/MWh)
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 6.Costs of APCS combinations apportioned to different pollutants for a 600MWunit, China (million CNY)

APCS combination	Total annual costs	Costs apportioned to Hg removal	Costs apportioned to PM ₁₀ removal	Costs apportioned to SO ₂ removal	Costs apportioned to NO _X removal
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 20 ± 8

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 consist of two components: 1) capital costs for the sorbent storage and injection equipment and 2) fixed and variable operating and maintenance costs (associated with the expendable sorbent). For assessing the cost of mercury removal via the co-benefit route, one needs to distinguish the investment and O&M cost of the APCSs, such as FGD and SCR, which are well defined and the cost for enhancing or optimizing the mercury removal in those APCSs.

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 regime of wet FGD. Therefore, relative costs were first arrived at for approaches discussed in this document; these approaches are shown in Table <u>7Table 7</u> (UNEP, 2010). The relative capital and incremental O&M costs shown in Table <u>7Table 7</u> 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 labor, transportation cost, etc.) should always be considered during the selection of a mercury control option, while acknowledging the fact that many markets are also global for emission control equipment and engineering construction companies (Pacyna et al., 2010).

Table 7. Relative cost of mercury removal for various methods (UNEP, 2010)

Approach	Capital Cost	O&M Cost	Comments
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

a = a = a = a = a = a = a = a = a = a =	Table 8.	Capital cost of ACI in United States (\$/kW, 2007 dollars)
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Technology		Unit si	ze, MW	
	100	300	500	700

29

Comment [SC37]: What are the criteria

for very low, low, moderate?

ACI	3-8	2-6	2-5	2-5	 Comment [SC38]: These values are
					low.

Notes:

Data in Table 8 from Table 5-16 in US EPA, 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 <u>Table 8</u> Table 8, may be interpreted as resulting in comparable cost effectiveness of mercury removal via ACI (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 ACI costs for control of mercury emissions
 (USEPA, 2010) from which <u>Table 8</u> Table 8 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 <u>Table 8Table 8</u> does not include the capital cost of FF or ESP. Installing a new fabric filter/baghouse is 55-70 \$/kW regardless of plant size. For the same range of variables, the study arrived at fixed O&M 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 9 shows the operating costs for ESP and COHPAC (advanced hybrid particle collection) 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 9.	Operating costs for activated carbon injection systems (on a 250 MW plant) followed
by either E	CSP or fabric filter for bituminous coals (IJC, 2005)

	ESP	COHPAC
Mercury removal, %	70	90
PAC injection rate, kg/Macm	160	48
PAC injection cost, \$	790000	790000
Activated carbon cost, \$	2562000	796000

The sorbent costs depend upon the coal characteristics, type of existing APCSs 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. However, the performance of brominated ACI canb be significantly better than that of untreated activated carbon for certain type of coal (Chang et al., 2008).

4 Emerging technologies

There are plenty of emerging technologies for mercury emission control in coal-fired power plants. Although they are still at bench- or pilot-scale stage, some of the technologies have already shown promising mercury control effectiveness and low cost. The emerging technologies are either dedicated to mercury emission control or designed for multi-pollutant emission control. Two of the major methods are: 1) providing oxidants or catalysts for elemental mercury oxidation to enhance mercury capture in downstream wet FGD; and 2) using sorbent other than activated carbon by injection with downstream PM control devices or fixed-bed reactor for mercury adsorption.

4.1 Non-carbon sorbents

Metal oxides, such as TiO_2 , are non-carbon sorbents for flue gas mercury. Laboratory- and pilot-scale studies in the US (Suriyawong et al., 2009) showed high mercury capture efficiency of up to 94 per cent using TiO_2 with UV irradiation. Copper based sorbents are also used to control mercury emissions in coal-fired flue gas. CuO_X impregnated on neutral Al_2O_3 ($CuO_X-Al_2O_3$) sorbents were found to enhance catalytic oxidation of elemental mercury in the presence of HCl and the mercury adsorption rate was over 75 per cent in the early stage of the mercury removal process (Du et al., 2015). Non-carbon sorbent can also be mixed with activated carbon to enhance the performance. A mixture of $CuO_X-Al_2O_3$ and activated carbon can remove more than 90 per cent elemental mercury with a lower cost for industrial applications (Du et al., 2015).

4.2 Non-thermal plasma

The non-thermal plasma (NTP) is a promising technology for elemental mercury oxidation. NTP is recognized as a potential process for the simultaneous removal of NO, SO₂ and elemental mercury. Chemically active species such as O, OH, HO₂ and O₃ formed from the electrical discharge induce the oxidation of Hg⁰ (Jia et al., 2013). HCl can promote the oxidation of mercury due to chlorine atoms produced in the plasma process (Ko et al., 2008). The elemental mercury oxidation rate by the dielectric barrier discharges (DBD) system averages at around 59 per cent (Byun et al., 2008). Another study showed that the NO, SO₂ and elemental mercury oxidation rates by the pulsed corona discharge (PCD) system reached to 40, 98 and 55 per cent respectively (Xu et al., 2009).

4.3 Treated activated coke

Activated coke is a regenerative sorbent for multi-pollutant (NO, SO₂ and elemental mercury) control. Virgin activated coke can remove 30-40 per cent of elemental mercury, while loading with 5 per cent CeO₂, the performance of activated coke can achieve a stable elemental mercury removal efficiency of over 60 per cent (Hua et al., 2010).

5 Best Available Technique and Best environmental practices (BEPs) 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. Here we focus on the choice of mercury controls in the coal combustion sector.

5.1 Best Available Techniques

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

5.1.1 Primary measures to reduce the mercury content of coal

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

5.1.2 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 percentage of particulate mercury in flue gas from fluidized bed compared with PC firing, which leads to high mercury removal efficiency of downstream FF or ESP. However, it should be noted that fluidized bed boiler itself does not constitute BAT.

5.1.3 Mercury removal by co-benefit of conventional APCSs

The third type of control measures for mercury removal involves the use of conventional post combustion APCSs. Existing flue gas cleaning devices are mainly used for the removal of PM, SO_2 , and NO_X . The mainstream PM removal technologies include ESP, FF, and a combination of these two technologies. The most commonly used desulfurization technology is the wet FGD scrubber, while the most common denitrification technology is SCR.

All of the three abovementioned control measures for SO₂, NO_X, and PM can result in substantial reductions in mercury emissions as a "co-benefit". In some industrialized 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. The combination of SCR, ESP and FGD, which is widely used in the coal-fired power plants in China and Japan, is a quite efficient mercury removal technique, since it can accomplish high level mercury removal along with the emission control of the other air pollutants. The combination of SCR, ESP and wet FGD can achieve mercury removal efficiencies up to 74 per cent and 0.0012 mg Hg/Nm³ of mercury concentration in the flue gas. Moreover usually the cost of controlling mercury as a "co-benefit" is small because it is mainly for other pollutants such as PM, SO₂ or NO_X.

5.1.4 Dedicated mercury control technologies

The fourth type of control measures involves dedicated technologies for the reduction of atmospheric mercury emissions, including ACI technology or use of additives. Currently, the ACI technology has been widely commercialized and adopted for coal-fired power plants in the U.S. and has successfully complied with regulatory emission limit values representing 85 to 95 per cent control over more than five years (Massachusetts Department of Environmental Protection, 2015). The operations of ACI technology in the United States show that mercury concentration in flue gas after ACI and fabric filters are lower than 0.001 mg Hg/ Nm³.

5.2 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 the BEPs.

5.2.1 Key process parameters

The first step to determine BEPs for the coal combustion process is to identify key process parameters (including mercury input control in coal and related monitoring), either from site-specific investigations or 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.

5.2.2 Consideration of energy efficiency for whole plant

Energy efficiency of coal-fired power plant is defined as the ratio between 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 of time. The efficiency of steam turbine (based on lower heating value of coal) in new PC-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 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 new coal-fired power plants were designed for high efficiency low emission operation (IEA, 2012).

As plants age, their efficiency decreases causing the need for 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 improvement of the efficiency also provide for reduction of all emitted pollutants from the same volume of coal used including greenhouse gases such as CO₂, in addition to a reduction of mercury emissions. Should plant upgrading 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,

Comment [SC39]: In some cases

upgrading air heaters, new blading for turbine, overhaul/upgrade of condenser, new packing for cooling tower, or improving electrical efficiency in 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).

5.2.3 APCS maintenance and removal efficiency

Beyond energy efficiency improvement, improving the efficiency of APCSs offers the opportunity to maximize the removal of mercury. This incremental amount of mercury removal that is realized as a result of operating APCS equipment originally designed to limit non-mercury emissions such as PM, SO₂, or NO_x, 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/upgrades of electrostatic precipitators (ESPs) or fabric filters (FF), alteration of selective catalytic reduction (SCR) design and operation, or a combination of these (Sloss, 2006).

5.2.4 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. Operation and Maintenance (O&M) practices have the potential to improve plant performance, including its efficiency and reliability, as well as to decrease the overall O&M costs themselves. Deterioration of plant equipment is unavoidable; however, the rate at which this deterioration occurs depends greatly on the O&M practices. Some of the good O&M practices include, for example, steam line maintenance, water treatment, and a reliable monitoring and reporting protocol. In addition, process improvements may be necessary to reduce bottlenecks and delays.

Adequate resources should be allocated to implement and continue application of BEPs 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 BEPs are actually being followed.

5.2.5 Environmentally sound management of coal combustion residues

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

Throughout the process of <u>mM</u>ercury 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 flue gas desulfurization (FGD). Sludge from wet FGD and other CCRs are either stored at the site or further processed into gypsum wallboard. In the latter case, after FGD gypsum has been filtered out of the sludge, mercury must be extracted from FGD wastewater effluent. This may be accomplished via chemical treatment, ion exchange, or with membrane filtration. In the processes of gypsum wallboard production, other utilization of CCRs, as well as during storage of CCRs at the site, mercury contained in CCRs may have potential for being re-released. In the processes offen 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). However, another study by Liu et al. (2013) indicated that 12-55 per cent of total mercury in the FGD gypsum would be emitted

during wallboard production. Therefore the wallboard production using FGD gypsum is not regarded as BEPs unless the mercury re-emissions 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 multiyear 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)¹. 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), mercury leach results did not exceed existing standards for concentration of Mercury in well water in the United States. In these same studies, the 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. Note, 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 modeling, including consideration of many additional factors, including how the fly ash is managed, would be needed to assess the potential risk. The storage of CCRs at the site with impervious surfaces can be considered as one aspect of ESM.-

¹ 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.htm

6 Mercury emission monitoring

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

6.1 Continuous Emissions Monitoring

Mercury monitoring using 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 low particulate concentration gas stream.

For mercury control purposes, CEMs 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 practiced although it requires special considerations. A special fixed filter probe is used to avoid blockage from condensation of *water* and typically employs a frequent filter media cleaning cycle using compressed air. Heated sample lines are used with careful regulation of sample gas temperature to avoid condensation of water and the resulting absorption of oxidized mercury into this water.

A CEM 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 mercury emission concentration 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 ug/m^3 , speciated mercury measurements, and high repeatability of results when calibrated with a dynamic mercury spiking methodology.

Semi-continuous emission monitors (SCEM), which are often labeled as CEM, are commonly used to overcome interference from other gases in the sample stream. These instruments provide mercury concentration averages over a short sample periods, which are typically less than 5 minutes. The short sample period averages provide adequate data in almost all situations.

6.2 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). In the US, these advantages have resulted in many coal combustion facilities performing their own monitoring using sorbent traps. It is possible to monitor using one set of traps over a sampling period lasting several days in coal combustion plants.

6.3 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 therefore these are useful in coal combustion plants for determining the mercury speciation.

Comment [SC40]: Inertial filters have contributed significantly to the high maintenance requirements of mercury CEMs and are being replaced by simpler systems

Comment [SC41]: A mercury CEMS is very complex compared to a CEMS for other flue gas constituents and subject to more maintenance than other CEMSs. Depending on the sampling environment the maintenance can become challenging to the point of being impractical. Some mercury CEMSs can determine speciated mercury, but this makes them more complex and challenging than a mercury CEMS that just does total gas phase mercury. The impinger methods use multiple impingers in series to allow some QC evaluation.

6.4 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 will be low of air emissions calculated from mass balance.

The data to perform a mass balance measurement of mercury in coal combustion plants is readily available in some regions due to regulations of the mercury content of solid and liquid waste streams from the plant. 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 analyzed. It is expected that there is a significant variation in the mercury content of the coal, so frequent coal analysis is required for an accurate mercury input value. Periodic mercury air emission monitoring must be practiced 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, a mass balance method for mercury air emission monitoring in coal combustion plants may be more difficult than a direct flue gas monitoring method.

6.5 Predictive Emissions Monitoring Systems (PEMS)

Predictive emission monitoring is a good screening tool for coal combustion plants but due 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 monitoring activities. A good estimate of the air emission range will allow for a more efficient sorbent trap test.

6.6 Emission Factors

Emission factors are not an accurate means of mercury air emission monitoring for coal combustion gas streams. This is due to the mercury content variation 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.

6.7 Engineering Estimates

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

Comment [SC42]: Again this is application specific. Mass balance monitoring can be very effective in cases where other monitoring is problematic and vice versa

Comment [SC43]: Mercury concentrations can be very consistent in mine mouth operations and these could be good candidates for PEMS. PEMS may also be useful to complement CEMS where high maintenance requirements result in lower desired availability.

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