Guidance on best available techniques and best environmental practices

Emerging Techniques

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**Emerging techniques**

The technical experts developing the guidance on BAT and BEP identified several techniques that, although they may still be at the bench or pilot stage, have already shown promising mercury control effectiveness. The emerging techniques are either dedicated to mercury emission control or designed for multi-pollutant emission control. Information on some of these techniques is provided below. It is recognized that these techniques may not yet be widely available and that some parties will require capacity building and training to tnable them to keep such techniques under review and to evaluate their suitability.

# Emerging techniques for coal combustion

There are plenty of emerging techniques for mercury emission control in coal-fired power plants. Although they may still at the bench or pilot stage, some of the techniques have already shown promising mercury control effectiveness and low cost. The emerging techniques are either dedicated to mercury emission control or designed for multi-pollutant emission control. Information on some of these techniques is provided below.

Non-carbon sorbents

Metal oxides, such as TiO2, are non-carbon sorbents for flue gas mercury. Laboratory and pilot-scale studies in the United States (Suriyawong et al., 2009) showed high mercury capture efficiency of up to 94 per cent using TiO2 with UV irradiation. Copper-based sorbents are also used to control mercury emissions in coal-fired flue gas. CuOX impregnated on neutral Al2O3 (CuOX-Al2O3) sorbents were found to enhance the 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 CuOX-Al2O3 and activated carbon can remove more than 90 per cent elemental mercury with a lower cost for industrial applications (Du et al., 2015).

Non-thermal plasma

The use of non-thermal plasma (NTP) offers 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 pulsed corona discharge, induce the oxidation of Hg0. HCl can promote the oxidation of mercury due to chlorine atoms produced in the plasma process (Ko et al., 2008). The rate of elemental mercury oxidation by the dielectric barrier discharges (DBD) system, averages at around 59 per cent (Jia et al., 2013). Another study showed that the NO, SO2 and elemental mercury oxidation rates by the pulsed corona discharge (PCD) system reached 40, 98 and 55 per cent respectively (Xu et al., 2009).

Cerium-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, when loaded 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).

Sorbent polymer composite module

This technique uses a sorbent and polymer composite (SPC) which is mounted in modules and placed downstream of the existing APCS. The SPC media can adsorb both elemental and oxidized mercury. The modules are stackable and each module has a given mercury capture potential. The amount of mercury removal therefore depends on the number of modules used.

The SPC technique can be applied in combinations with other APCSs. The optimal mercury adsorption temperature of the SPC is 85 °C and where the flue gas temperature is higher, an evaporative cooler can be installed upstream of the SPC modules.

Series of SPC modules have the capability to reduce mercury emissions by 90 per cent or more. One feature of SPC technique is that its collected mercury is separated from coal combustion residues such as scrubber water, gypsum and fly ash.

At this time the SPC technique has been installed on approximately 1,000 MW of coal-fired power plants (ZMWG, 2015).

# Emerging and other processes for smelting and roasting processes used in the production of non-ferrous metals (lead, zinc, copper and industrial gold as specified in Annex D to the Convention)

In this section, mercury removal processes which are emerging or not widely in application are considered.

Selenium scrubber

The selenium scrubber ([Sundström 1975](#_ENREF_11); [Reimers et al. 1976](#_ENREF_9); [Coleman 1978](#_ENREF_4); [Habashi 1978](#_ENREF_5)) is a wet scrubber which uses the reaction between mercury and amorphous solid selenium in sulfuric acid. It is mainly used to remove high concentrations of mercury vapour. The acid concentration is maintained between 20 and 40 per cent. The acid concentration must be kept within these limits because complex and highly soluble selenium sulfur compounds are formed at low acid concentrations, making it ineffective in reacting with the mercury in the gas. At higher acid concentrations, the oxidizing power of the acid will result in the formation of selenium dioxide or selenite.

If the gas being treated contains sufficient selenium, there may not be a requirement to add selenium to the scrubber solution. The mercury reduction efficiency of a selenium scrubber is about 90–95 per cent, resulting in mercury concentrations of about 0.2 mg/m³. At low incoming mercury concentrations, however, the removal efficiency may be less than 90 per cent.

Removal by reaction with sulfuric acid

### Description

A number of techniques for controlling mercury emissions from smelting and roasting have been developed based on their reaction with sulfuric acid. The Bolkem process is located in the acid plant, and the removal is achieved by 99 per cent sulfuric acid. This acid comes from the absorption part of the acid plant and oxidizes the mercury at ambient temperature. The resulting acid that contains mercury is diluted to 80 per cent and the mercury is precipitated as sulfide with thiosulfate. After filtering off the mercury sulfide, the acid is returned to the absorption stage. No acid is therefore consumed in the process.

Mercury may also be removed before the washing step in the acid plant.[[1]](#footnote-2) Gas at temperatures of about 350 °C is washed countercurrently with 90 per cent sulfuric acid at about 190 °C in a packed bed tower. The acid is formed in situ from the SO3 in the gas. The process is based on converting the elemental mercury in the gas into a sulfate. The acid is recirculated until the solution becomes saturated with HgSO4 and precipitation begins. The crystals of HgSO4 are then separated in a thickener. In addition to removing mercury, other contaminants in the gas will be removed in the scrubber. Mercury can be recovered by mixing the solids with calcium oxide, and then heating to distil away the mercury, which can then be dealt with in accordance with the Convention.

Alternatively, mercury may be precipitated and the mercury sludge removed from the cooled acid, filtered and washed. Part of the acid is then recycled to the scrubbing step. In a revision to this process, mercury is removed from the gases by washing with a solution of selenium ions, and selenium metal is produced along with mercury(II) selenide.

A thiosulfate process has also been described by Schulze ([2009](#_ENREF_10)). In this process the absorption efficiency of mercury depends on the acid strength and acid temperature. The lower the acid temperature and the higher the acid concentration, the higher is the absorption efficiency. To avoid an accumulation of mercury in the product acid it is essential to absorb the mercury vapour in a two-stage drying tower unit running with different acid concentrations in which the acid concentration in the second drying tower is higher than the acid concentration of the downstream absorption units.

The mercury-containing acid of the drying towers has to be cleaned before discharging into the absorption circuits. The acid streams are therefore gathered and treated in reaction units with sodium thiosulfate (Na2S2O3∙5H2O).

The total amount of acid of both drying towers is stripped with air in a stripping tower to remove the dissolved sulfur dioxide. The stripped acid is discharged to a reaction tank in which a solution of 40 per cent sodium thiosulfate and a filter aid medium are added. Sulfur is formed according to the reaction:

H2SO4 + Na2S2O3 => S + SO2 + Na2SO4 + H2O

The sulfur reacts with the mercury in the acid to form mercury(II) sulfide, which precipitates. The temperature at this stage is about 50 °C and the acid concentration is about 80 weight per cent. The treated acid overflows to a maturing tank in which the reaction is completed.

These processes have been included in this section. It is not clear, however, how many smelters or roasters are currently using these processes.

# Emerging techniques for waste incineration facilities

* 1. **High efficiency activated carbon adsorber**

A high efficiency activated carbon adsorber, trade-named “JFE-Gas-Clean-DX,” has been developed, in which activated carbon is packed in an activated carbon cartridge with a fixed bed and lateral flow-type structure, thereby realizing efficient contact between the flue gas and the activated carbon.

**Error! Reference source not found.**7 provides a schematic illustration of the appearance of the device and Figure 8 the activated carbon cartridge. The device consists of an activated carbon cartridge, of a compact size, which can be easily detached and installed in the device housing. High efficiency contact between the flue gas and activated carbon is realized by adopting a fixed bed and lateral flow type structure.



**Figure 7 Activated carbon adsorber**



**Figure 8 Cartridge packed with activated carbon**

As shown in Figure 8, flue gas is uniformly dispersed as it passes through the multiple thin packed layers of activated carbon installed in the activated carbon cartridge. As a result, contact efficiency between the activated carbon and trace harmful substances in the flue gas is high and a large decrease in activated carbon use is necessary. As an additional advantage, because thin layers of activated carbon are used, pressure loss is low in comparison with the conventional moving bed-type activated carbon adsorber, which has pressure loss of approximately 2–3 kPa. Because the pressure loss is no more than 0.5 kPa per activated carbon cartridge stage, electric power consumption can be kept to a low level. To prevent dust from clogging the packed bed of activated carbon, the basic method when applying this device is installation after the bag filter. For this reason, activated carbon with high ignition prevention performance should be used, enabling treatment up to a maximum service temperature of 200 °C, which is the temperature of general bag filters.

Trials at a waste incineration plant have shown mercury concentrations below the detection limit of 5 µg/m3 in the clean gas during an inlet concentration of 65 µg/m3. The Hg concentrations under the minimum determination limit were being maintained after six months at the waste incineration plant.

*Co-benefits*

Co-benefits include the reduction of other harmful substances such as dioxins and other heavy metals.

* 1. **Coconut char as an alternative to coal-based activated carbon**

As an alternative to activated carbon, char from coconut fibres and from coconut pith has been developed. Coconut husk is a waste from coconut processing that is widely found in the tropical region.

Trials showed that the elemental mercury adsorption capacity of coconut pith is better than that of coconut fibres under the conditions of the trial. The adsorption capacity for elemental mercury of coconut pith char (3,142 µg/g) in these trials was much higher than of coal-based activated carbon (119 µg/g). This may indicate that activated char coals from CP may be a future potential source of adsorbents, which would replace the existing adsorbents, e.g., AC (Khairiraihanna et al. 2015).

*Co-benefits*

The use of waste such as coconut husk could provide economic benefits, in addition to reducing waste disposal problems due to reduced amounts of additives. Coconut char contaminated with mercury will still need to be disposed of properly.

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## Coal

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## Smelting and roasting processes used in the production of non-ferrous metals (lead, zinc, copper and industrial gold as specified in Annex D to the Convention)

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1. <http://www.sulphuric-acid.com/techmanual/GasCleaning/gcl_hg.htm>; accessed 16 April 2015. [↑](#footnote-ref-2)