

EPPSA Report

MERCURY REMOVAL

GUIDELINE FOR ASSESSMENT AND DESIGN RECOMMENDATIONS



European Power Plant Suppliers Association

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The European Power Plant Suppliers Association (EPPSA) is the voice, at European level, of companies supplying power plants, components and services.

EPPSA actively promotes awareness of the importance of flexible and efficient, state-of-the-art thermal power generation and its crucial contribution to ensuring a clean, secure, and affordable energy supply.

Virtually all thermal power plants in the EU are built by members of EPPSA or equipped with their components, and provide around 50 % of Europe's electricity.

EPPSA members provide the most advanced thermal power technologies in the world.

The aim of this paper is to outline technologically and economically feasible solutions for coal fired power plants in order to comply with regulations on mercury emissions in the European Union.

1. Introduction

On 24 November 2010, the Industrial Emissions Directive 2010/75/EU (IED) was adopted.

The IED is a recast of 7 previous directives (Integrated Pollution Prevention and Control Directive 2008/1/EC – Large Combustion Plants Directive 2001/80/EC – Waste Incineration Directive 2000/76/EC – etc.) and regulates different industrial activities in the EU with the aim of preventing/reducing “emissions into air, water and land and to prevent the generation of waste, in order to achieve a high level of protection of the environment as a whole” (IED, art.1).

It entered into force on 6 January 2011 and had to be transposed into national legislation by member states by 7 January 2013. The IED repeals the Integrated Pollution Prevention and Control (IPPC) Directive and the sectorial directives as of 7 January 2014, with the exception of the Large Combustion Plants (LCP) Directive, which will be repealed with effect from 1 January 2016.

The IED is based on several principles, namely an integrated approach, Best Available Techniques (BAT), flexibility, inspections and public participation.

The emission levels that are permitted are those consistent with Best Available Techniques (BAT). BAT

are those techniques which achieve a high general level of protection of the environment and are both economically and technically feasible; overall, they must be reasonably accessible to the operator. Finally, BAT refer not only to specific types of technology or to specific components, but also to the way that an entire installation is designed, maintained, and operated.

For large combustion plants, the permitting authorities in each Member State must ensure that permits are granted only to installations that are able to fulfil Europe’s strict emissions legislation, and this is guaranteed by requiring the application of BAT, which can be found in the BAT Reference documents (BREFs).

These technologies do not only capture mercury in order to reduce the emission to air but also to achieve a mercury content in flue gas desulphurisation (FGD) gypsum lower or equal to the actual FGD gypsum levels without mercury treatment.

This document explores the state-of-the-art mercury removal technologies as recommended by the European power plant suppliers.

2. Mercury – facts and figures

Mercury is the only metal that is a liquid at room temperature and has an appreciable vapour pressure. The lustrous silvery metal occurs naturally, but mostly as a sulphide (HgS, cinnabar), rarely as HgO, and also as an amalgam with noble metals.

Mercury is able to form alloys (amalgams) with many metals. In its pure form (elemental Hg; Hg{el}), it is virtually insoluble in water, although it is very soluble in its oxidised state [+2].

Mercury has been known to humankind since antiquity, if not earlier. In addition to its medicinal applications, it was also used for fire-gilding and later on for extracting noble metals [Lit. 1].

The associated health hazards, particularly those of organic mercury compounds, were recognised in the middle of the 20th century after large quantities of mercury compounds (methylmercury iodide) entered the sea near Minamata and Niigata, Japan, as a result of uncontrolled release of wastewater containing heavy metals from industrial factories. Its accumulation in foodstuffs (particularly fish) and drinking water led to slow poisoning of the population, mainly manifested by damage to the central nervous system.

Based on the insights from these tragedies in Japan, the use and transportation of mercury were severely restricted at the beginning of the 21st century.

The first binding agreement (ratified by 140 states) to limit the extraction and use of mercury was signed in Geneva in January 2013. This included a ban on new mercury mines and the phase-out of existing mines within 15 years [Lit. 1].

Anthropogenic release

The primary emission sources are the extraction of noble metals, the cement industry and chlorine production, but mainly from the generation of electricity from coal (~50 % of the total Hg emissions). Although coal contains only traces of mercury (on

average ~0.2 mg/kg dry solids, Lit. 2), the very large mass volumes lead to the release of a considerable quantity of mercury.

Legislation – limit values for mercury

Owing to the recognised environmental relevance, there has been a significant tightening of the limit values for mercury emissions in recent years. In the European Union, mercury, along with other pollutants, has been classified as a priority substance. This hazardous priority substance classification means that the individual member states are required to progressively reduce pollution by and to cease or phase-out emissions, discharge, and losses of this substance [Lit. 3].

In this respect, legislators are increasingly focussing on electricity generation from coal (see above). Whereas relatively moderate limit values apply in Europe, with the exception of The Netherlands (limit values of 3 µg/Nm³ and below), in the USA, mercury emissions from existing (bituminous coal) plants have already been limited to 1.2 lb/TBtu by the MATS (Mercury Air Toxics Standards)¹ and for new plants it is even lower. The emitted quantity of Hg is specified with respect to the heating value of the combusted coal. The limit value applies to hundreds of US power stations and is in force until 2016. Depending on the Hg content of the coals, this requires a removal efficiency of around 91 % with respect to the amount present in the coal [Lit. 4].

Coal fired (bituminous) power plants in Europe usually have the following air pollution control technologies: Boiler » Selective Catalytic Reduction » Air Heater » Electrostatic Precipitator » Wet Flue gas Desulphurisation (» Wastewater Treatment Plant).

Each facility offers potential for synergistic mercury manipulation/separation steps. Figure 1 below shows the most widespread power plant schema (in Europe) using a DeNO_x, Dedusting and Wet Scrubber System.

Instead of the system shown in Figure 1, dry/semi dry

¹ The value of 1.2 lb/TBtu is a 30-day rolling average and corresponds to about 1.5 µg/Nm³ (for 5 vol.-% O₂)

FGD systems have also become commonly used for desulphurisation. High efficiency dry FGD technologies are generally divided into two categories: Circulating Fluid Bed [Circulating Dry Scrubber, CDS] and Spray Dryer [SD] technologies. Especially the CDS technology is an excellent candidate for carbon-based separation technologies for mercury. The high contact time in the absorber and the high ash recirculation rates will provide significant time for the carbon particles

to contact the mercury in the flue gas resulting in lower consumption rates. Most of these plants use the activated lignite carbon [Hearth Furnace Coke, HOK] and/or activated carbon technologies [Lit. 22 & 23].

The following chapters identify the potentials of each step to manipulate mercury species/separate mercury from the flue gas.

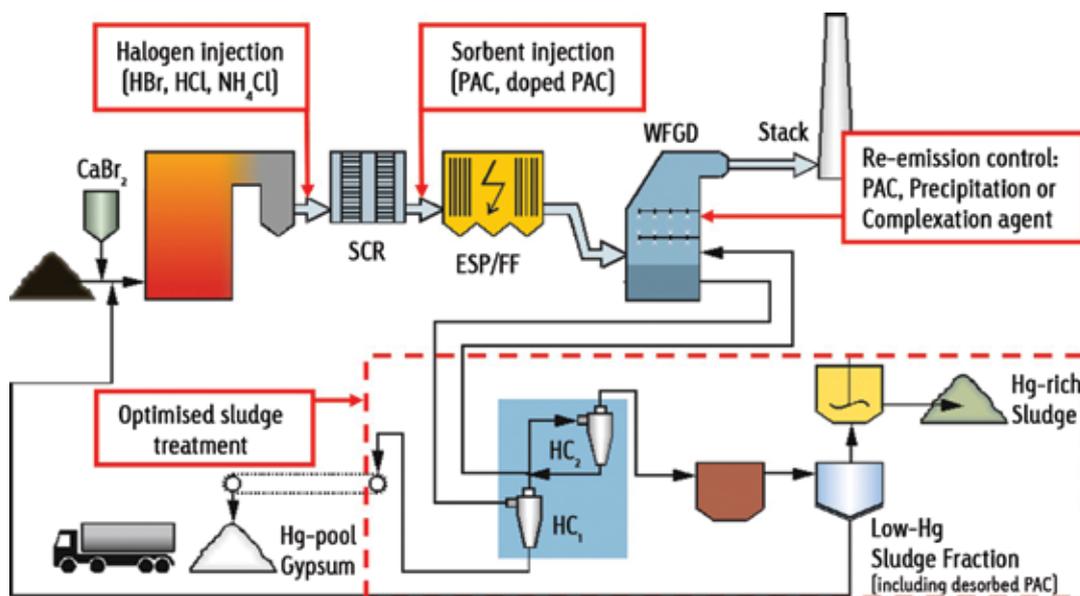


Figure 1: Typical power plant schema for a European facility

3. Relevant gas-phase reactions/mercury oxidation in the boiler

Mercury is liberated from its compounds during combustion. Elemental mercury is thus present as a gas in the high-temperature region ($T > 1,200\text{ }^{\circ}\text{C}$) of the boiler [Lit. 5].

As it passes through the downstream sections, it can be oxidised if the flue gas composition is favourable (usually to HgCl_2 or HgBr_2). This oxidation is important because the resulting mercury products are not only water-soluble, but they are also adsorbed more efficiently, e.g. by fly ash. Oxidation is promoted

by a sufficiently high concentration of halogens, particularly bromine [per unit of mass, it is ~ 10 x more effective than chlorine], which ensures that an oxidation partner is also available for the mercury. If the halogen concentrations are too low, oxidation can be enhanced by addition of halogen (e.g. as a 52 % solution of CaBr_2) to the boiler or to the coal feed. This means that the addition of a few mg bromine/kg coal can already achieve a high degree of mercury oxidation in the combustion chamber

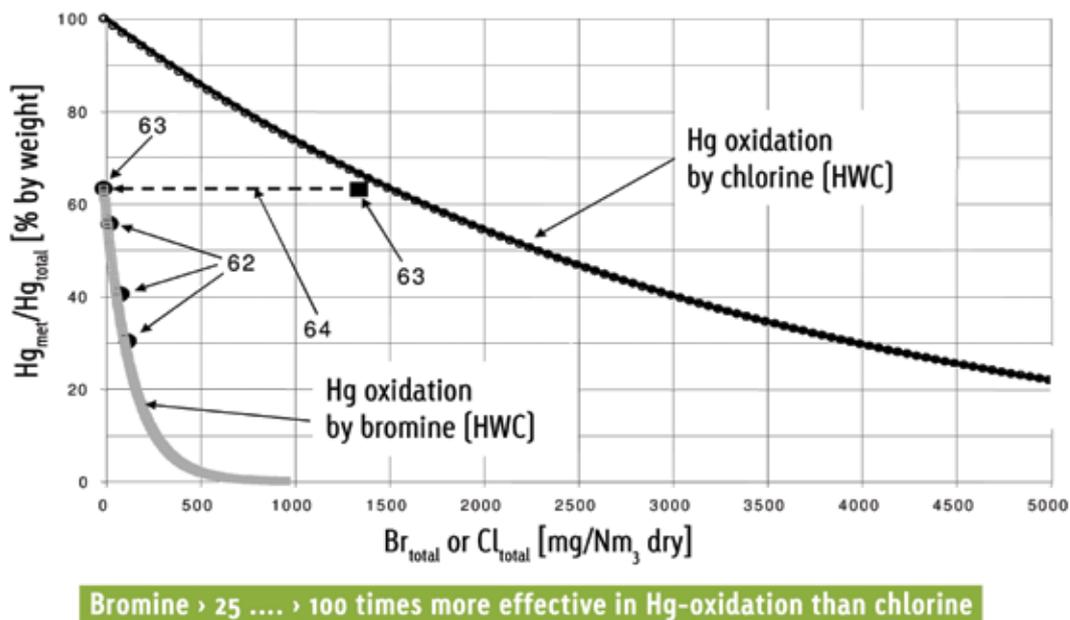


Figure 2: Bromine versus Chlorine oxidation potential [Source: Lit. 21]

Operational reliability

The very corrosive properties of bromine in a wet environment can lead to problems. A survey conducted by the Electric Power Research Institute (EPRI) summarises experience gained by 70 plant operators that have used bromine (added as CaBr_2 to the coal feed) as an oxidising reagent over a period of between several months and several years [Lit. 6].

Corrosion was found in 24 of the 52 plants with more than 1 year's experience of adding bromine reagents

in concentrations of 10 to ~ 450 ppm (with respect to dry coal). This corrosion mainly occurred at the cold ends of the air preheater panels. Minor corrosion was found in the boiler, electrostatic precipitator and coal mill, although the cause could not always be unambiguously assigned to the bromine additive.

There also seemed to be problems if the operating temperature of the air preheater was too low. Although

HBr from the boiler has a significantly lower dew point than SO_3 , if a $[\text{H}_2\text{SO}_4]$ film starts to form on the air preheater panels, HBr can dissolve in the aqueous phase, thus becoming corrosive.

Direct gas-phase corrosion reactions are rather unlikely because this would require 50 ppmv HBr in the flue gas, which is generally nowhere near the actual value [Lit. 6].

The corrosion found in a scrubber is attributed not only to a low-quality material, but also to exceeded service time of the scrubber itself [~25 years].

No damage was found in the majority of the plants. Damage to the air preheater should be avoidable by modifying the operating conditions (increasing the temperatures) or more cost-effectively, by adopting enamelled cold-end elements to resist corrosion. Indeed, the use of such elements is consistent with the approach commonly adopted to resist corrosion and deposition of air preheater elements in SCR applications.

Costs of adding halogen salt into boiler without considering SCR/DeNO_x system

The following estimate is based on an 800 MW power plant (mercury content in coal: 0,2 mg/kg).

- Costs for the additive feed system and integration into the DCS (distributed control system): ~€400,000.
- Quantity of additives for a coal feed rate of 300 t/h: required concentration is ~100 mg/kg dry coal, and thus ~30 kg/h bromine reagent. CaBr_2 solution (52 %) costs ~1.35 €/kg, which corresponds to ~ 3.3 €/kg Br reagent. This gives hourly costs of ~100 €/h. Thus the costs for 7500 operating hours per year are ~750,000 €/a.

Not included are any consequential costs due to the aforementioned corrosion problems as well as other possible effects on residual materials generated in the power plant.

Technological background

The oxidised form (with halogens Cl, Br, I) is only produced at temperatures of 600–700 °C and below. Conversion rates to HgCl_2 are only significant below 450 °C, without consideration of the kinetics and assuming sufficient quantities of acidic constituents are present in the raw gas [Lit. 5].

The goal is to produce an oxidised form of mercury; either HgCl_2 or HgBr_2 , as these species are water-soluble, can be removed in a downstream FGD unit or with conventional activated carbon, and have a more favourable adsorption efficiency on fly ash. By comparison, the removal of elemental mercury requires the use of doped grades of activated carbon, which are much more expensive [see Chapter 4].

Depending on the raw gas composition, only a small fraction of oxidised mercury usually forms in the boiler. This is due to the kinetic barrier associated with indirect oxidation ($\text{Hg} + 2 \text{HCl} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{HgCl}_2 + \text{H}_2\text{O}$), which assumes that the coal generally contains much more chlorine than bromine. Chlorine is mainly present in the boiler as HCl, which reacts according to the Deacon equilibrium for Cl_2 ($2 \text{HCl} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{Cl}_2 + \text{H}_2\text{O}$) only at temperatures below 600 °C to produce more chlorine gas (particularly in the presence of a catalytic surface), which then very efficiently converts elemental mercury into oxidation state +2 via direct oxidation [Lit. 7].

In contrast, the Deacon equilibrium for bromine lies much further to the right in the high-temperature range. This is probably why mercury is oxidised much more efficiently by bromine than by chlorine [Lit. 7].

The addition of halogen-containing salts can also provide an improvement at ambient conditions that are unfavourable for oxidation. A series of large-scale industrial tests have been carried out in the USA in recent years, in which particular attention was paid to the addition of bromine salts to the boiler [e.g. Lit. 7]. An important finding of these tests is that it can safely be assumed that the addition of bromine salts leads to a much higher mercury oxidation rate, both in the boiler itself and in a downstream SCR unit, if installed.

4. SCR unit

Oxidation of residual elemental mercury in the SCR unit is very efficient, provided there is an adequate halogen concentration in the raw gas. This requires catalyst beds with a good activity and the lowest possible stoichiometric excess of NH_3 [NH_3 slip].

Catalyst beds that have been specially developed for mercury oxidation achieve an even better ratio between the mercury oxidation efficiency and the halogen concentration. The advantage of this technology lies in the effective utilisation of the oxidation potential for a constant $\text{SO}_2 - \text{SO}_3$ conversion rate and constant NO_x decomposition rate [Lit. 8].

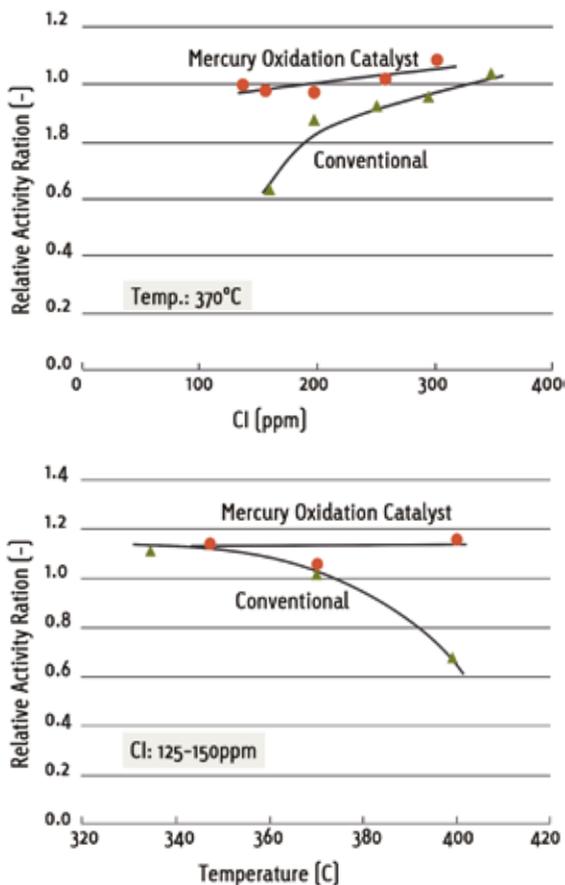


Figure 3: Behaviour of Oxidation Catalyst [Source Lit. 8]

Design values (boiler and catalyst unit):

- Oxidation rates of ~80 % and above can be achieved in the boiler with Hg/Cl ratios of >1:20000, a moderate S content [max. 3000 mg/Nm³] and a low proportion of basic ashes,
- The same values can be achieved with a mercury/bromine ratio of about one order of magnitude lower [Hg:Br ~ 1:2000],
- In the presence of a SCR catalyst, the necessary concentrations are reduced by a factor of ~10 for both oxidising agents. Oxidation takes place in the downstream catalyst beds, where the added ammonia has generally already been consumed.
- Special Hg oxidation catalysts appear to achieve even greater efficiencies. Sufficient conversion takes place even at a lower halogen concentration [Lit. 8].

Operational reliability

- Long-term suitability and susceptibility to poisoning [arsenic, alkali metals, etc.] of SCR catalysts used for mercury oxidation have not yet been resolved. As the service life increases, it can be assumed that unconsumed ammonia is able to reach the downstream catalyst beds so that it blocks the active sites required for Hg oxidation. This relationship applies to both conventional SCR catalysts as well as to the recently commercially launched special Hg oxidation catalysts (although possibly to a lesser extent). The latter catalysts have a modified metal doping that can achieve sufficient Hg oxidation with much lower halogen concentrations. See [Lit. 9, 12] and above.
- Depending on the gas composition, catalysts tend to accumulate increasing amounts of mercury. Changing the raw gas composition may result in a sudden desorption along with an Hg[ox] peak. Considering that Hg[el] adsorbs better than Hg[ox], changing the halogen content in the raw gas can lead to oxidation of the elementary Hg adsorbed on the catalyst so that a higher concentration of the oxidised form then leaves the catalyst. Hg also desorbs at higher temperatures, and a high SO_2 content in the raw gas generally decreases desorption [Lit. 11].

Costs of the catalyst technology

- Replacing the last [conventional] catalyst bed with a special mercury oxidation catalyst will increase the investment costs by approximately 15 % compared to a conventional catalyst.
 - Operating the SCR with a constant number of beds [exchange of the most downstream bed with an Hg oxidation catalyst] assumes a nearly constant pressure loss as a first approximation. Provided that the service time of the oxidation catalyst is comparable to that of a conventional catalyst bed, the operating costs are about the same as a conventional SCR catalyst unit. A positive feature is the much lower amount of halogen [e.g. CaBr_2] that is required to ensure sufficient oxidation. Savings of around 80 % for the halogen salts can be assumed for low-halogen coals. Furthermore, a negligible susceptibility to corrosion can be expected at lower halogen concentrations [see Chapter 1]. However, a financial assessment of this side-effect has not been carried out owing to the complexity.
- efficiency]; bromine is much less sensitive in this respect.
 - High contents of basic ashes consume the acidic constituents of the raw gas and thus lower Hg oxidation.
 - NH_3 slip and service time: tests have shown [Lit. 8] that mercury oxidation in the SCR catalyst is significantly lowered in the presence of NH_3 . Negative effects on the oxidation efficiency of the catalyst can also be expected with increasing service time.
 - Increasing temperatures have a negative effect, particularly on the oxidation potential of chlorine. Chlorine-based oxidation is significantly inhibited at temperatures above 400 °C.
 - Controlled addition of halogens can be used to increase the oxidation rate virtually independently of the raw material. They can be added to the boiler [see Chapter 1] or to the raw gas upstream of the oxidation catalyst [addition of HBr , HCl , NH_4Cl , etc.].

Technological background

There is usually a relatively small degree of mercury oxidation in the high-temperature zone of the boiler. This is due to indirect oxidation [see Chapter 3], which is kinetically inhibited for chlorine. As the temperature drops, the equilibrium shifts towards the oxidation side [formation of more Cl_2 , Br_2], and thus [theoretically] to higher conversion rates. Unfortunately, the residence time is usually insufficient to reach this condition; therefore, insufficient Hg oxidation can usually be assumed if no catalyst is present.

This can be remedied with a SCR catalyst that greatly accelerates the reaction and, for a suitable raw gas composition and operating conditions, can thus provide the largest contribution to Hg oxidation. Details on catalyst technology are given in [Lit. 8, 9, 10, 11].

The key parameters affecting the degree of oxidation downstream of the catalyst are:

- Halogen content of the raw gas [Br, Cl, I].
- Higher SO_2 content in the raw gas: consumes chlorine [and thus lowers the Hg oxidation

Recent attention has been focused on a catalyst specially tailored to Hg oxidation. A modified material concept was used to achieve much more selective Hg oxidation with significantly lower halogen concentrations. It also improved the temperature sensitivity of the reaction and lowered the negative effect of NH_3 [Lit. 8]. This catalyst bed is generally used in the most downstream position. Data from detailed long-term tests on catalyst poisoning and service time are not yet available.

5. Removal in an electrostatic precipitator/bag filter

Elemental mercury is insoluble in water and is already volatile at room temperature. In this state, it can only be removed on the industrial scale (dry) using adsorption (with adsorbents or fly ash).

Oxidised mercury (valence state +2) adsorbs considerably better than elemental Hg and is also very soluble in water. Carbon (unburned carbon, activated carbon) is very suitable, particularly for binding Hg(ox), whereas elemental mercury generally requires doped grades of activated carbon (doped with bromine/iodine/SO₃).

Key factors for its removal are the mass ratio between the adsorbent and the pollutant as well as the contact time and the spatial packing density of the adsorbent and the heavy metal. Very low concentrations per unit volume of both mercury and any adsorbents are present in the ESP. Achieving adequate removal efficiency with a bag filter is much less complicated than with an ESP. In a bag filter, the flow through the filter dust forces contact between the adsorbent and the pollutant, which is why the adsorption probability is much higher compared to an ESP. Common adsorbent addition rates for mercury removal are thus in the range of ~50–200 mg/Nm³ for an ESP and much lower for a bag filter (up to ~50 mg/Nm³).

Operational reliability

The controlled addition of adsorbents is a tried and tested process and is currently standard practice. Major risks with respect to plant availability are therefore not expected.

A few authors attribute corrosion of the air preheater to the use of activated carbon upstream of the air preheater, among other factors (Lit. 6).

If the filter ash is to be used in the cement industry, the elevated residual carbon content may cause problems. In particular, the high adsorption capacity of activated carbon may have a negative effect on the functionality of individual aggregates in the cement.

Costs

Installation costs of around 5\$/kW installed capacity have been reported (Lit. 12).

Depending on the particular grade, costs for consumables are about ~1.5\$/kg for conventional AC and up to 2\$/kg for doped AC (Lit. 13). Consumable concentrations of 50–200 mg/Nm³ are necessary for ESPs (which dominate in Europe). Thus, for an 800 MW power plant with ~2 million Nm³/h, the required mass flow rate of activated carbon is around 100 to 400 kg/h. For 7,500 operating hours per year, this leads to operating costs of ~€850,000–€3,400,000. This does not include the respective electricity and maintenance costs.

Using the aforementioned value of 5\$/kW gives an investment volume of ~€3,000,000 (currency conversion rate of 0.75 Euro/\$).

For an amortisation period of 10 years, the additional costs for the aforementioned example are ~20 to 80 eurocent/MWh (which does not include maintenance costs).

Technological background

In the usual operating window of a bituminous coal fired power station (temperature, moisture, dust load, etc.), the Hg removal efficiency in an ESP operating at cold temperatures (~120 °C) is ~10–50 % (without added adsorbent).

AC (pure or doped) grades are particularly effective adsorbents, lime-based materials and zeolites are slightly inferior. Removal efficiencies of more than 90 % can be achieved in combination with injection of a suitable adsorbent.

CaO: Can only be used below 150 °C; above 350 °C it has a reducing effect on Hg(ox) (Lit. 5). The achievable removal rates are moderate: up to ~40 %.

AC/HAC: Particularly suitable for the removal of oxidised Hg (chemisorption, see below). High elemental mercury contents significantly lower the removal efficiency. In contrast, the combination of bromine salt added to the boiler and injection of adsorbent (AC) upstream of the ESP is very effective.

Doped activated carbon: Binds elementary mercury, in particular, is using acidic groups on its surface. The formation/adsorption mechanism has not been elucidated in detail.

Physical adsorption

Physical adsorption is characterised by a strong temperature dependency. Efficient removal requires not only a high contact probability, but also sufficient residence time. It is also important that the adsorbent has a high specific surface area. This combination is commonly found in the presence of elemental mercury in the raw gas and in the presence of only small amounts of acidic gas constituents (such as HCl, HBr, SO₃, etc., otherwise, self-doping of the UBC can occur in the fly ash). Purely physical adsorption probably occurs during binding of elemental Hg to undoped AC and to inorganic (usually basic) minerals such as calcium oxide as well as fly ash in general. Removal efficiencies that can be achieved with physical adsorption tend to be in the lower range because binding to the adsorbent is hampered owing to the relatively high raw gas temperatures.

Chemisorption

In contrast to physical sorption, chemisorption involves a reaction of the substance adsorbed on the particle surface. Either doped activated carbons (with sulphur or with bromine/iodine) are used or the concentrations of acidic gases in the raw gas stream are so high that the AC undergoes self-doping (acidic constituents adsorb on the AC surface). Furthermore, chemisorption can also be assumed for oxidised mercury on conventional activated carbons.

The presence of large amounts of SO₃ is regarded as a negative factor because, under some conditions, this can lead to a blockade of the active sites and thus has an adverse effect on Hg removal. It is not clear why self-doping based on SO₃ does not appear to improve the removal efficiency. The influence of temperature on chemisorption is much less strongly pronounced and operating ranges up to 200 °C and above are feasible. Doped AC grades are particularly popular for the removal of elemental Hg from raw gas. Removal efficiencies of up to 90 % and more are possible if sufficient adsorbent is added [Lit. 14]. Alternatively, a combination of adding bromine salts to the coal in combination with injection of a sorbent (AC) upstream of the ESP is very effective. Particularly if an SCR is installed, very high mercury oxidation efficiencies can be achieved with effective binding to a conventional activated carbon [Lit. 15-16].

Factors affecting removal:

The primary parameters affecting Hg removal via chemisorption are temperature, residence time, amount of added adsorbent, particle size distribution of the adsorbent, moisture content of the raw gas, SO_x content, doping of the adsorbent, and mercury species.

Reference values for removal:

The following removal efficiencies can be assumed for electrostatic precipitators [Lit. 12].

90 % removal under favourable conditions. Controlled addition of doped activated carbon or ensuring a high oxidation efficiency if conventional AC is added. Addition rates of ~80 mg/Nm³ to 200 mg/Nm³, depending on the conditions. For bag filters under conditions similar to those above, reference consumption values are in the range from ~20 mg/Nm³ to 50 mg/Nm³.

6. Removal in scrubbers

Removal in scrubbers requires the presence of oxidised (Hg^{+2}) or particle-bound (Hg_p) mercury. Mercury must be removed from the raw gas using 2 process steps.

Step 1 comprises the actual capture from the raw gas. The removal efficiency of oxidised mercury in conventional scrubbers is > 90 % [higher with an increasing liquid/gas ratio]. Particle-bound Hg is removed during dedusting in the scrubber, for which removal efficiencies of 50 – 70 % can be assumed. However, particle-bound mercury does not usually play a significant role in a wet FGD unit.

Step 2 comprises stabilisation of the captured mercury

in the scrubber to prevent re-emissions, i.e. transfer of already captured mercury back into the clean gas, either due to the volatility of the captured [oxidised] mercury or to mercury that has been reduced in the scrubber and is thus elemental.

One method of stabilisation is to add sorbents to the scrubber circuit. The heavy metal dissolved in the gypsum suspension adsorbs on the added activated carbon and is thus effectively prevented from being transferred back into the clean gas. Other feasible mercury stabilisation options besides the addition of activated carbon include precipitation reactions and complexation.



Figure 4: Wet Limestone FGD plant Lünen [Source Trianel]

Operational reliability

Addition of activated carbon is already being carried out in a number of plants in the USA with the goal of minimising mercury emissions from the scrubber sump.

In the meantime, the efficiency of this technology operating in compliance with the necessary general conditions has been well documented and can be assumed to have been verified [Lit. 20].

The dark discolouration of the FGD gypsum can be a problem because, although it is very fine, the activated carbon is able to accumulate in the cyclone underflow. This results in discoloured gypsum as well as an elevated mercury content, which can be regarded as a quality deficiency if this material is to be used as a raw material in the construction industry.

A special hydrocyclone technology, which offers the possibility to reduce the fines concentration in the gypsum underflow, is mandatory to reduce this impact.

The mercury in the scrubber is influenced by a very complex interplay between a number of chemical parameters and has not been completely elucidated so far. However, it has been established that complexation with the help of [halogen] salts significantly lowers the volatility of the mercury halogen compound and converts it into halogen/mercury ions. Even concentrations of a few g/l chloride/bromide ions are sufficient for initial stabilisation. This also hampers a possible reduction to elemental mercury. Problems arise with sulphitic compounds in the scrubber that promote reduction of mercury into its elemental form, which is insoluble in water and can outgas from the scrubber. A very low redox potential can be regarded as an indicator for the presence of sulphite in the scrubber and can thus be regarded as a risk factor [Lit. 17-18]. It is therefore preferential to control the sulphite content and this can be achieved with newly-developed technologies that directly measure the sulphite content in the scrubbing liquid [Lit. 24].

Costs

The removal of mercury using a wet desulphurisation unit does not, in principle, lead to additional operating costs.

However, if it is assumed that re-emission of mercury from the scrubber must be prevented to guarantee the highest removal efficiencies, then it is necessary to intervene in the operating mode of the scrubber. The following exemplary calculation can be carried out based on stabilisation of the mercury dissolved in the scrubber liquor via adsorption on activated carbon.

Assumptions: 800 MW power plant, wastewater flow rate 8 m³/h, sump volume 3,500 m³, 7,500 operating hours per year.

Required quantity of activated carbon: 200 mg/l; costs for the activated carbon: ~1.5 \$/kg for an undoped grade.

This example requires a single large addition of ~700 kg. The demand caused by wastewater discharge and calculated for the entire year, gives losses of ~12,800 kg.

The resulting costs for sorbents are thus ~19,000\$ [currency conversion rate of 0.75 Euro/\$].

Installation costs for the implementation of an AC dosing station are estimated to be in a range of approximately < €500,000.

Not included are any licensing fees for the process or optional replacement of the existing cyclone by a special wash water cyclone.

Technological background

Efficient removal of mercury from the scrubber requires minimising re-emissions [discharge of captured mercury] out of the scrubber sump. Three methods of capturing Hg in the scrubbing liquor are feasible:

Hg_{ox} as dissolved molecules and NOT complexed:

In this state, mercury has a relatively low stability with respect to reduction ($\text{Hg}_{\text{ox}} \rightarrow \text{Hg}_{\text{el}}$). The resulting elemental Hg would immediately escape into the clean gas. This reduction can be brought about not only by divalent iron ions and sulphite, but also high pH values as well as organic acids and HADS [hydroxyl amine disulphonate, Lit. 19].

Moreover, divalent mercury-halogen compounds have very different volatilities [increasing in the sequence

chlorine » bromine » iodine), so that re-emission of the oxidised components themselves can be expected.

The Hg vapour pressure increases with its concentration in the scrubber (linearly), with the temperature (progressively) and with the pH value (above 7, also progressively). These effects are significantly weaker in systems that have been stabilised (by precipitation, complexation or adsorption).

Complexed Hg: Simple complexation reactions occur in the presence of halogen ions (salt, i.e. Cl, Br). Complexes containing one or two anions generally form with different proportions of Cl and Br. In this state, Hg no longer has a vapour pressure and is also much more stable with respect to reduction reactions. This requires halogen contents > 2,000 mg/l, for which more stable conditions can be expected as the concentration increases. However, higher salt concentrations are required as the Hg content in the scrubber increases. High pH values also increase re-emissions. Overall, owing to the aforementioned interfering factors, stabilisation in the scrubber based solely on dissolved salts seems to be too risky to guarantee Hg removal. There are currently no known alternative additives that provide sufficiently stable and economically viable complexation; however, this would be interesting on account of the gypsum problem (less Hg in the gypsum). It is always important to take into account of effects on the wastewater treatment plant and on the scrubber chemistry.

Adsorbed Hg: Stabilisation by adsorption ($\text{Hg}_{\text{ox}} \rightarrow \text{Hg}_{\text{p}}$) is another possible method of immobilising the dissolved mercury. Activated carbon is an excellent Hg_{ox} adsorbent. Addition of ~200 mg/l activated carbon is sufficient to convert the majority of the dissolved mercury into the adsorbed state. However, this is associated with the disadvantage that particle-bound mercury is enriched in the gypsum fraction (underflow) in the cyclone and thus leads to a grey discolouration. This means that a special type of cyclone (a so-called wash water cyclone) has to be used to purify the gypsum and remove the AC if it is intended for use as a raw material in the construction industry. It is also important that the added AC has the smallest possible particle size distribution to allow adequate removal by scrubbing in the underflow. Hg removal efficiencies of up to 95 % (with respect to Hg in the cyclone feed) have already been achieved with simultaneous brightening of the gypsum compared to a

conventional (cyclone) system.

Adsorption on the activated carbon is controlled via the redox potential and is very effective within the usual operating windows (up to 95 % adsorption efficiency and more). Adsorption on activated carbon is favoured at moderate redox potentials (~220 mV); however, the adsorbed Hg is released again at very high potentials (> 600 mV) [Lit. 19]. This reversibility enables production of 2 sludge grades in the downstream wastewater treatment plant that have high and low heavy-metal contents, respectively.

Reference values for design:

- Required quantity of added AC:
~200 mg/l (at least 1:50 for Hg/AC)
- Stabilisation effect:
~90 %
- Required operating window:
redox potential < 400 mV
- Interfering factors:
hydroxide sludges, bromide

7. Wastewater treatment unit

Wastewater treatment technology is not discussed in detail in this report. However, it should be mentioned that it is possible to use fractionated precipitation in order to deplete the mercury and thus produce an enriched sludge. The two-stage wastewater treatment process allows selective separation of mercury from wastewater filter cake by effectively separating it into two qualities.

Stage 1 involves conventional sulphate precipitation to eliminate most of the solids. Increasing the redox potential in this stage keeps the heavy-metal inventory in solution (or dissolves it), thus separating it from the sludge of Stage 1. The amount of quality 1 sludge counts for approximately 95 % of total production. This quality can be recycled to the coal feeder to be burned in the boiler.

Stage 2 uses sulphidic precipitation to remove the dissolved heavy-metal ions as a concentrate. This quality has to be stored as hazardous waste [Lit. 20].

8. Conclusions

To choose the right mercury control technology is mainly influenced by the type of fuel (high/low halogen content in coal) and the available plant configuration. Most mercury control projects are retrofit projects, where the necessary process steps for mercury control have to be fitted to the existing equipment in the most economical way.

In the following figure you can find an overview of the necessary process unit operations to be installed to reach a certain mercury emission target.

| Oxidation | Separation | Treatment |
|---|---|--|
| High Halogenic Content Fuel + SCR DeNO _x Catalyst | Absorption into Wet Scrubber + Additives to Minimise Re-Emission | Gypsum-, Wastewater- + Sludge Treatment |
| Low Halogenic Content Fuel + Oxidation Catalyst | Adsorption on PAC in Fabric Filter/ CDS/SDA Systems | |
| Low Halogenic Content Fuel + Bromine Addition to Fuel | | |

Figure 4: Main unit operation for mercury control

Every mercury control technology uses at least an oxidation process and a separation process, though an additional treatment process will be necessary for some. Depending on the existing flue gas treatment installation, individual solutions have to be developed.

In the following table it is shown in which way some of the most common flue gas treatment installations could be retrofitted to reach mercury removal efficiencies beyond 95 %. To take into consideration the influence of the fuel, two different fuel qualities – lignite coal with low halogen content (Cl- content < 0.03 % in coal) and bituminous with high halogen content (Cl- content > 0.1 % in coal) are considered. The mercury content in the coal was estimated to be in the range of 0.2 mg/kg.

The suggested Oxidation and Separation technologies are already used in a lot of plants all over the world (Lit. 23); the Treatment technologies have been demonstrated in large scale applications in the USA and in large scale demonstration projects in Germany (Lit. 20).

When there is a decision to go for a Hg reduction in a power plant, the best fit solution has to be developed taking into account all influencing boundary conditions.

This table is describing the typical technologies for large combustion plants. Note that for ≤50 MW, the first two techniques would be more commonly applied.

| Description of Technique | Fuel type | Oxidation | Separation | Treatment | Invest Costs for Hg control * [EUR/MW] | Operation Costs for Hg control * [EUR/MW/year] |
|--|------------------|-----------------|------------|------------|---|---|
| SNCR +DSI + FF | Low Cl- content | Br ₂ | ACI | None | 2,000 | 2250 |
| | High Cl- content | n.a. | ACI | None | 1,250 | 1500 |
| SCR +SDA/CDS + FF/ESP | Low Cl- content | Br ₂ | ACI | None | 1,500 | 1300 [FF]/3700 [ESP] |
| | Low Cl- content | OXI | ACI | None | 1,250 | 1100 [FF]/3500 [ESP] |
| | High Cl- content | n.a. | ACI | None | 1,000 | 1000 [FF]/3400 [ESP] |
| SCR +ESP + WFGD (with not sellable gypsum) | Low Cl- content | Br ₂ | ACIW / OSW | WTP | 1,000 | 300 |
| | Low Cl- content | OXI | ACIW / OSW | WTP | 850 | 150 |
| | High Cl- content | n.a. | ACIW / OSW | WTP | 500 | 50 |
| SCR +ESP + WFGD (with sellable gypsum) | Low Cl- content | Br ₂ | ACIW | GPT + WTPS | 2,000 | 275 |
| | Low Cl- content | OXI | ACIW | GPT + WTPS | 1,700 | 125 |
| | | n.a. | ACIW | GPT + WTPS | 1,400 | 30 |

* no license fees (operation licenses) are considered in the costs.

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Abbreviations

| | | | |
|-----------------|--|-------|--|
| AC | Activated Carbon | HOK | Hearth Furnace Coke/Activated Lignite Carbon |
| ACI | Active Carbon Injection | IED | Industrial Emissions Directive |
| ACIW | Active Carbon Injection into Wet Scrubber | IPPC | Integrated Pollution Prevention and Control |
| BAT | Best Available Technique | LCP | Large Combustion Plants |
| Br ₂ | Bromine Addition | MATS | Mercury Air Toxics Standards |
| BREF | Best Available Technique Reference Document | n.a. | not applicable |
| CDS | Circulating Dry Scrubber/Circulating Fluid Bed | OSW | Organosulfid Addition to Wet Scrubber |
| DSI | Duct Sorbent Injection | OXI | Oxidation Catalyst |
| EU | European Union | PAC | Powdered Activated Carbon |
| EPRI | Electric Power Research Institute | SCR | Selective Catalytic Reduction |
| ESP | Electrostatic Precipitator | SDA | Spray Drier Absorber |
| FF | Fabric Filter/Baghouse | SNCR | Selective Non Catalytic Reduction |
| FGD | Flue gas desulphurisation | UBC | Unburned Carbon |
| GPT | Gypsum Pretreatment | WFGD | Wet Flue Gas Desulphurisation |
| HAC | High Activated Carbon | WTP | Waterwater Treatment Plant |
| HWC | Hazardous Waste Combustor | WTPSC | Waterwater Treatment Plant with Sludge Concentration |

Authors: Harald Reissner, Stéphane Crèvecoeur, Michael Kramer, Nicolas Kraus, Reijo Kuivalainen, Markus Michel,
Frank Oberheid, Bernd Vollmer
Editor: Tom De Latte

EPPSA
European Power Plant Suppliers Association
Avenue Adolphe Lacomblé 59/8
B-1030 Brussels
phone +32 2 743 29 86
fax +32 2 743 29 90
www.eppsa.eu



www.eppsa.eu