

**BEST AVAILABLE TECHNIQUES –
COMPILATION OF RELEVANT INFORMATION IN THE EU BREFS**

1. COAL-FIRED POWER PLANTS AND INDUSTRIAL BOILERS

Relevant documents: http://eippcb.jrc.ec.europa.eu/reference/BREF/lcp_bref_0706.pdf;
http://eippcb.jrc.ec.europa.eu/reference/BREF/LCP_D1_June2013_online.pdf

- 1. LCP (Large Combustion Plants) BREF 2006 ..- adopted*
- 2. Draft 1 of revised LCP BREF – version XX 2013 – under consideration by Technical Working Group*

Scope: *LCP BREF covers the combustion of fuels in installations with a total rated thermal input of 50 MW or more (Annex I IED, point 1.1)*

1.1 Background information

Source: Large Combustion Plants (LCP) BREF (adopted by the Commission in 2006)

Chapter 3: Common processes and techniques

3.6.1 Control of mercury (Hg) emissions

3.6.1.1 Primary measures to reduce the Hg content of solid fuel

Fuel cleaning (mainly the cleaning of coal) is one option for removing mercury from the fuel prior to combustion. There are many types of cleaning processes, all based on the principle that coal is less dense than the pyritic sulphur, rock, clay, or other ash-producing impurities that are mixed or embedded in it. Mechanical devices using pulsating water or air currents can physically stratify and remove impurities. Centrifugal force is sometimes combined with water and air currents to aid in a further separation of coal from impurities. Another method is dense media washing, which uses heavy liquid solutions usually consisting of magnetite (finely ground particles of iron oxide) to separate coal from impurities. Smaller sized coal is sometimes cleaned using froth flotation. This technique differs from the others because it focuses less on gravity and more on chemical separation.

3.6.1.2 Flue-gas treatment technologies to reduce mercury emissions

Most metals have sufficiently low vapour pressures at typical air pollution control device operating temperatures that condensation onto particulate matter is possible. Mercury, on the other hand, has a high vapour pressure at typical control device operating temperatures, and collection by particulate matter control devices is highly variable. The most important factors affecting mercury control on utility boilers include the flue-gas volume, flue-gas temperature and chloride content, the mercury concentration and the chemical form of the mercury being emitted. The chemical species of mercury emitted from utility boilers vary significantly from one plant to another. Removal effectiveness depends on the species of mercury present.

Factors that enhance mercury control are low temperatures in the control device system (less than 150 °C), the presence of an effective mercury sorbent and the application of a method to collect the sorbent. In general, high levels of carbon in the fly ash enhance mercury sorption onto particulate matter, which is subsequently removed by the particulate matter control device.

Additionally, the presence of hydrogen chloride (HCl) in the flue-gas stream can result in the formation of mercury chloride, which is readily adsorbed onto carbon-containing particulate matter. Conversely, sulphur dioxide (SO₂) in flue-gas can act as a reducing agent to convert oxidised mercury to elemental mercury, which is more difficult to collect.

Control technologies designed for controlling pollutants other than mercury (e.g. acid gases and particulate matter) vary in their mercury-removal capability, but generally can achieve reductions no greater than 50 % (except for high removal efficiencies for mercury chloride by wet scrubbers).

Carbon filter beds have been used successfully in Germany for mercury control on utility boilers and municipal waste incinerators. Injection of activated carbon into the flue-gas has been applied for a LCP co-combusting sewage sludge where mercury reductions of at least 85 per cent have been achieved. The addition of activated carbon to utility flue-gas for mercury control increase the amount of particulate matter requiring disposal

3.6.2 Reduction of metal emissions in particulate control systems

Electrostatic precipitators and fabric filters are commonly used to remove particulate matter from flue-gases generated by combustion plants burning solid or liquid fuels. These systems can operate with an overall efficiency of >99.9 %. However, the removal efficiency is generally lower in the smaller particle size range, i.e. the size range in which particles enriched with metal elements might be found.

Fabric filters have a similar overall particulate removal efficiency to ESPs (i.e. greater than 99.9 %) but are better at controlling fine particulate matter and less sensitive to particulate

loading and fly ash characteristics. The collection efficiency may be increased further still by using flue-gas conditioning with small amounts of additives added to the gas flow upstream of the filters.

Some elements may remain in the gas phase until the flue-gases have cooled sufficiently for condensation to occur. By the time flue-gases encounter the fabric filter, they have cooled

sufficiently to allow also some condensation of Hg, similar to cold-side ESP. Some estimates report that an average Hg removal efficiency of about 40 % can be achieved for power stations fitted with fabric filter systems. The Hg removal efficiency depends strongly on the fuel properties (e.g. Cl).

3.6.3 Reduction of metal emissions in FGD systems

Wet scrubber FGD systems are an effective method for reducing emissions of certain metals. This is mostly because the flue-gas temperature is reduced to about 50 – 60 °C by passing through the absorber, which allows many of the more volatile metals to condense from the vapour phase, and allows them to be removed from the flue-gas. The condensed metals are then mainly transferred to the waste water from the wet FGD system. Various studies have given removal efficiencies from the flue-gas of 30 – 50 % for Hg and 60 - 75 % for Se. However, the lime used in some systems may be an important source of As, Cd, Pb, and Zn, and so the concentrations of these elements can even increase downstream of the FGD. Emissions from the scrubber depend on the specific process and operating conditions. An average Hg removal efficiency of 96.6 % was achieved for instance by adding sodium hypochlorite additives to the flue-gas from a waste incinerator in Japan. Sodium hypochlorite stabilises Hg in the flue-gas, allowing it to be captured in the scrubber water. The Hg can then be removed from the waste water stream using reduction, volatilisation, condensation and Hg separation processes.

The overall removal of Hg in various **spray dry systems** varies from about 35 – 85 %. Those systems configured with a particulate removal system before a spray dry scrubber, have high metal retention because a large proportion of these elements (including volatile species) are removed before the FGD unit. Highest particulate removal efficiencies, especially for fine particles, are achieved by spray dry systems fitted with downstream fabric filters. These systems may also be expected to achieve the highest metal removal efficiencies. Those plants fitted with particulate removal systems before the spray dry scrubber had Hg removal efficiencies up to 70 % already before entering the FGD unit. Activated carbon technology has been applied in the US to increase Hg removal in spray dry scrubber/ESP systems. Tests indicate an increase in Hg removal efficiency from 27 to 78 % at an outlet temperature of 140 °C, and from 66 to 86 % at an outlet temperature of 110 °C. Similar improvements were also noted for spray dry scrubber/fabric filter systems, with an improvement in Hg removal from 69 % without additives to 91 – 95 % with additives. This technology is currently being used at a waste incinerator in Switzerland.

It is also possible to reduce Hg emissions using additives in other FGD systems, such as dry injection systems. With regard to the additive, Sorbalit may be added for instance. This is a sorbent that is composed of calcium hydroxide and various other organic and inorganic constituents.

3.6.4 Reduction of metal emissions in NOx control systems

Low NOx burners do not appear to influence the behaviour of metals during combustion. Metal emissions may increase in selective catalytic cleaning systems (SCR) which involve the addition of chemicals to flue-gases. However, most NOx control systems appear to neither reduce nor increase metal emissions.

3.6.5 Reduction of metal emissions by systems designed for metal Removal

Some systems have been developed expressly for the purpose of reducing certain metals from flue-gas streams, mostly to reduce emissions of Hg and other toxic metals (such as As, Cd, and Pb) from waste incinerators. These systems include selenium filters, activated carbon filters and various sorbents. They are only briefly discussed in this section.

Different sorbents such as silica, bauxite (alumina), kaolinite, emathlite, and lime have been investigated for their ability to remove metals from flue-gas. A detailed list of them and other possible sorbents can be found in [33, Ciemat, 2000] but note that some of the processes are of limited practical use for large power stations because of the low operating temperatures, harmful secondary effects and the high cost of some of the sorbents.

Activated carbon or coke filter systems have been developed which can be used to remove metals such as Cd, Hg, and Pb from flue-gases. Information can be found in [33, Ciemat, 2000] regarding a lignite coke filter and catalyst system which, in addition to acid gas removal, adsorbs metal elements. Tests carried out at a pilot scale system, fitted to a municipal waste incinerator, indicate that virtually all the Hg is removed from the flue-gases by the lignite coke material. Experimental tests show that a reduction in the concentration of metallic Hg is obtained when activated carbon is added to the flue-gas stream. The carbon collected downstream in a fabric filter contained 40 – 60 ppm Hg, which corresponded to between 13 and 20 % of the Hg in the flue-gas.

The removal of Hg vapour from flue-gases using **sulphur-impregnated adsorbents** has been studied using packed beds. The experimental results have shown that the impregnation of active alumina and zeolite by sulphur increases the adsorption capacity, by several orders of magnitude. Although the sorbents have a high Hg adsorption capacity, they are unable to remove all the Hg (as they already have an outlet concentration greater than zero for gases passing through the filters, even at the beginning of gas breakthrough). Very low Hg concentrations in the flue-gases may be achieved using a bed of sulphur-impregnated active alumina and zeolite adsorbents followed by a second bed of sulphur-impregnated active carbon adsorbents.

A system is available for Hg removal that uses a **selenium impregnated filter** which may be retrofitted to existing exhaust ducting after scrubbers. The filter relies on the strong affinity of Hg to Se, with which it combines to form mercury selenide (HgSe), a highly stable compound. Spent filters are returned to the manufacturer for recharging.

In future, these new systems for removing metal elements could be an important method of reducing metal emissions. However, at present most processes are not at a commercial stage or seem more appropriate for controlling emissions from waste incinerators. Additional research is required to assess the application of such systems to large combustion plants.

4.1.9.1.4 Abatement of mercury (Hg) emission

In general, no dedicated systems for Hg removal are currently applied at thermal power plants burning coal or lignite only. FF and ESP or wet scrubbers are designed for dust and SO₂, HCl and HF removal, respectively. The removal of Hg by these systems is an additional positive side effect. The abatement of Hg by flue-gas cleaning devices depends on the Hg specification. Both gaseous elemental mercury (Hg₀) and gaseous oxidised mercury (Hg₂₊) are in the vapour phase at flue-gas cleaning temperatures. Hg₀ is insoluble in water and cannot be captured in wet scrubbers. The predominant Hg₂₊ compounds of coal flue-gas are weakly to strongly soluble, and the more soluble species can generally be captured in wet FGD scrubbers. Both Hg₀ and Hg₂₊ are adsorbed onto porous solids such as fly ash, in principle powdered activated carbon which is relative costly, or calcium-based acid gas sorbents for subsequent collection in a dust control device. Hg₂₊ is generally easier to capture by adsorption than Hg₀. Particle-bound mercury Hg_p is attached to solids that can be readily captured in an ESP or fabric filter [171, UN ECE, 2002]. The removal efficiency in an ESP depends on the following factors:

- temperature of the ESP
- Cl-content in the coal
- unburned carbon in the ash
- calcium compounds in the ash.

Flue-gas cleaning techniques applied in combustion installations use three basic methods to capture Hg:

- capture of Hg in the dust of particulate matter control devices, such as an ESP or FF as a side effect
- adsorption of Hg₀ and Hg₂₊ onto entrained sorbents (injection of activated carbon) for subsequent capture in an ESP or FF. Alternatively, Hg may be captured in a packed carbon bed
- solvation of Hg₂₊ in wet scrubbers.

Chapter 4: Combustion techniques for coal and lignite

4.5.7 Heavy metals

The mineral content of the fuel includes different substances depending on its origin. All solid fuels such as coal and lignite have a certain concentration of trace elements, such as heavy metals. The behaviour of heavy metals in the combustion process involves complex physicochemical processes. Basically most of the heavy metals evaporate in the combustion process and condensate later in the process onto the surfaces of the particulate matter (i.e. fly ash). Most metals have sufficiently low vapour pressures at the operating temperatures that exist at typical air pollution control devices that condensation onto particulate matter is possible. Therefore, BAT to reduce the emissions of heavy metals from flue-gases of coal- and lignite-fired combustion plants is to use a high performance ESP (reduction rate >99.5 %) or a fabric filter (reduction rate >99.95 %). Mercury has a high vapour pressure at the typical control device operating temperatures, and its collection by particulate matter control devices is highly variable. Taking into account that spray dryer FGD scrubbers and wet lime/limestone scrubbers are regarded as BAT for the reduction of SO₂ for larger combustion plants, low Hg emission levels are achieved. For the reduction and limitation of Hg emissions, it can be stated, that coals of

good quality have comparably low Hg contents and that the best levels of control are generally obtained by emission control systems that use FFs and ESPs, where high efficiency ESPs show good removal of Hg (bituminous coal) at temperatures of less than 130 °C. In addition, some combinations of flue-gas cleaning systems can remove oxidised and particle bound Hg to some extent. For FFs or ESPs operated in combination with FGD techniques, such as wet limestone scrubbers, spray dryer scrubbers or dry sorbent injection, an average removal rate of 75 % (50 % in ESP and 50 % in FGD) or 90 % in the additional presence of SCR can be obtained. The reduction rate when firing sub-bituminous coal or lignite is considerably lower and ranges from 30 – 70 %. The lower levels of Hg capture in plants firing sub-bituminous coal and lignite are attributed to the low fly ash carbon content and the higher relative amounts of gaseous Hg in the flue-gas from the combustion of these fuels. Periodic monitoring of Hg is BAT. A frequency of every year up to every third year, depending on the coal used, is recommended. Total Hg emissions need to be monitored and not only Hg present as part of the particle matter.

1.2 Techniques to consider for the prevention and control of mercury emissions

Source: LCP Revision – DRAFT (as of June 2013)

Table 1.1: General techniques to consider for the prevention and control of mercury emissions

Technique	Technical description	Achieved environmental benefits	Environmental performance and operational data	Cross-media effects	Technical considerations relevant to applicability		Economics	Driving force for implementation	Example plant	Reference literature Remarks
					New plants	Existing plants				
ESP - see Section 3.3	Co-benefit of dust emissions reduction by capture of particle-bound mercury	Reduction of mercury emissions	<ul style="list-style-type: none"> • High operational experience • See also graphs and info below the table 	None	Generally applicable	Generally applicable				
Fabric Filter (FF) - see Section 3.3	Co-benefit of dust emissions reduction by capture of particle-bound mercury	Reduction of mercury emissions	<ul style="list-style-type: none"> • High operational experience • See also graphs and info below the table 	The efficiency of the power plant will be reduced by 0.1 percentage points	Generally applicable	Generally applicable	Operating and maintenance costs are higher than for an ESP			
SCR - see Section 3.3	Co-benefit of NO _x emissions reduction by enhancing the mercury oxidation before capture in a subsequent FGD unit	Improvement of mercury emissions reduction								

Technique	Technical description	Achieved environmental benefits	Environmental performance and operational data	Cross-media effects	Technical considerations relevant to applicability		Economics	Driving force for implementation	Example plant	Reference literature
					New plants	Existing plants				Remarks
FGD - see Section 3.3	Co-benefice of SO _x emissions reduction by solubilising and capturing the oxidised mercury	Reduction of mercury emissions								

Environmental performance and operational data for mercury emissions based on collected data at European level for 2011:

- Reported mercury emissions from coal-fired plants sized 15 - 300 MW_{th} (3 plants reported) are between 0.5 and 20 µg/Nm³, as yearly average based on 1 to 3 periodic measurements/year. The corresponding plants are fitted with ESPs and were commissioned between 1974 and 2008. It should be noted that, their NO_x and SO_x emissions being quite high (respectively above 320 mg/Nm³ and 690 mg/Nm³), these plants may have to implement additional techniques for reducing such pollutants; this will also have a positive side-effect on mercury emissions reduction.
- **Error! Reference source not found.** shows mercury emissions from coal-fired plants sized between 380 and 2800 MW_{th}, operated between 3000 and 8760 h/yr, with equivalent load factors in general above 65 %, for power generation and district heating. They burn anthracite or bituminous coal, with a Hg content between 0.05 and 0.1 mg/kg, and a chlorine content between 45 and 560 mg/kg. They were commissioned between 1968 and 2008. The last commissioned plant (plant 253V – 2008) has Hg yearly-averaged emission concentrations about 1µg/Nm³ and is fitted with SCR, wet FGD and a bag filter. Most of these plants are carrying out Hg emission periodic monitoring (with 2 to 9 periodic measurement/year), and 4 of them monitor continuously this pollutant.
- shows mercury emissions from low-rank coal-fired plants sized between 74 and 2300 MW_{th}, operated between 3000 and 8000 h/yr, with equivalent load factors in general above 65%, for power generation and district heating. They burn sub-bituminous coal or lignite, with a chlorine content between 100 and 150 mg/kg. Only one Hg fuel content has been reported (0.23 mg/kg for Plant 23V). These plants were commissioned between 1972 and 2010. The plants recently built (23V and 19V) have Hg yearly-averaged emission concentrations lower than 3.5 µg/Nm³. Reported emission values are the result of estimation or of few periodic measurements (1 or 2 times/year), except for Plants 127-2V and 128-1V, where they are the average of 9 periodic measurements.

Specific techniques for the prevention and control of mercury emissions

US-EPA data suggest that about a quarter of US installations may be achieving > 90% Hg reductions simply as a co-benefit of using other pollution abatement devices, such as flue-gas desulphurisation, selective catalytic reduction and a fabric filter. This technology control configuration is largely implemented in Europe at coal-fired plants for controlling dust and acid gases air emissions. However, these abatement techniques may not be enough or appropriate for always reaching this performance level, due to the coal-lignite characteristics, and may require additional/alternative solutions as described below, for mercury control.

Fuel pretreatment

Description

Pretreating the fuel before combustion by cleaning or blending with another fuel or with additives are options to consider that can enable achieving good levels of mercury reduction in emissions to air, without implementing, or in combination with, additional end-of-pipe or specific techniques.

Technical description

Coal cleaning:

There are many types of cleaning processes, all based on the principle that coal is less dense than the pyritic sulphur, rock, clay, or other ash-producing impurities that are mixed or embedded in it. Mechanical devices using pulsating water or air currents can physically stratify and remove impurities. Centrifugal force is sometimes combined with water and air currents to aid in a further separation of coal from impurities. Another method is dense media washing, which uses heavy liquid solutions usually consisting of magnetite (finely ground particles of iron oxide) to separate coal from impurities. Smaller sized coal is sometimes cleaned using froth flotation. This technique differs from the others because it focuses less on gravity and more on chemical separation [168, US EPA, 1997].

These processes remove some of the mercury associated with the incombustible mineral materials; however, they will not typically remove the mercury associated with the organic carbon structure of the coal.

Furthermore, the effectiveness of mercury removal from coal during conventional coal cleaning varies widely depending on the source of the coal and on the nature of the mercury within it.

Generally, mercury reduction in lower rank coals could be expected to be lower than in bituminous coals, because in lower rank coals a greater fraction of mercury is likely to be bound to the organic carbon structure and so will not be removed.

Coal blending/switching:

In the context of mercury control, there are 2 objectives of coal blending:

- to increase the halogen concentrations, thereby increasing the proportion of oxidised mercury, which is water-soluble and can therefore be more easily captured by the flue-gas desulphurisation scrubber;
- to reduce the amount of mercury to be removed by blending with or switching to low mercury coals.

Coal additives:

The amount of mercury capture generally increases as the amount of halogens in coal and unburnt carbon increases. Therefore, mercury capture in coals with low halogen content can be increased by adding halogens such as bromine or chlorine salts. Alternatively, hydrogen chloride or ammonium chloride may be added. Bromine is thought to have an advantage over chlorine as its Deacon-type reactions are more favourable and it is consumed by SO₂ to a lower degree than chlorine, thus requiring the use of fewer additives.

Achieved environmental benefit

Reduction of mercury in emissions to air.

Environmental performance and operational data

Two studies concerning 50 US bituminous coal samples show mercury removal efficiencies varying from 0 % to 78 %, with an average between 21 % and 37 %.

Coal blending has the potential to achieve 80 % mercury capture in some cases.

Mercury reduction of 80 % can also be achieved by using additives.

Cross-media effects

None.

Technical considerations relevant to applicability

Given the variability in the source of the coal and the nature of the mercury in it, the testing of coal pretreatment techniques is needed to understand quantitatively how much mercury could be removed from a given coal.

Carbon sorbent injection in the flue-gas

Description

Mercury absorption by carbon sorbents, such as activated carbon.

Technical description

This is the most mature mercury-specific control technology, in which mercury is absorbed by carbon sorbents, with or without chemical treatment. The sorbent injection system can be enhanced by the addition of a supplementary fabric filter. Untreated carbon sorbents are not effective for lignite and sub-bituminous coals. However, chemically treated sorbents (e.g. with halogens such as chlorine or bromine) can help to convert the more difficult-to-capture mercury common in lignite and sub-bituminous coals to a more easily captured form, thereby achieving high mercury reduction across all coal types.

Sorbent enhancement additives have been also used at some plants to considerably reduce the rate of sorbent injection and to preserve the quality of its fly ash for reuse. These objectives are being further enhanced by refining sorbents through milling and changing the sorbent injection sites. In addition, some applications have found that injecting sorbents on the hot side of air pre-heaters can decrease the amount of sorbent needed to achieve the desired levels of mercury control.

Achieved environmental benefit

Reduction of mercury emissions.

Positive side effect on the removal of SO_x and NO_x, thereby increasing the cost-effectiveness of the application.

Environmental performance and operational data

Commercial deployments and 50 US Department of Energy (DoE) industry tests of sorbent injection systems achieved on average 90 % reductions in mercury emissions. These systems are being used on 25 boilers at 14 US coal-fired plants. The effectiveness of the sorbent injection is largely affected by the coal type and boiler configuration. A US-Environmental Protection Agency (EPA) analysis of the best performers showed an average mercury emission reduction of nearly 96 % across all three primary coal ranks i.e. bituminous, sub-bituminous and lignite.

Mercury removal increases with the amount of sorbent injected into the flue gases. Among the plants studied by the US DoE, the average sorbent injection rate was 6.5 % vol., with rates ranging from 0.8 to 17.5 %.

The removal efficiency of the carbon sorbents increases if a fabric filter is used instead of an ESP, due to the longer residence time allowing more contact between the sorbent and the mercury-laden flue gas. As a result, only one third of the sorbent is needed to capture the same amount of mercury compared to an ESP.

However, substantial reductions are not achievable at all plants as:

- Sulphur trioxide – which can form under certain operating conditions or from using high-sulphur bituminous coals – may limit mercury reductions by preventing mercury from binding to carbon solvents.
- Hot-sided electrostatic precipitators can reduce the effectiveness of sorbent injection systems, because the high operating temperatures reduce the ability of mercury to bind to sorbents and to be collected in the devices. However, high temperature mercury sorbents have now been developed for use in hot-sided ESPs at temperatures up to 427 °C.
- Lignite has relatively high levels of elemental mercury, the most difficult form to capture, e.g. a share of Hg^0 to total Hg in flue gas of 80 % for lignite-firing boilers against a similar share of 30 % for coal-firing boiler according to a study performed at 6 power plants in China

Other strategies, such as blending coals or using other technologies, may be needed to achieve substantial reductions at some plants with these issues, e.g.:

Sulphur trioxide:

- Using an alkali injection system in conjunction with sorbent injection can effectively lessen the sulphur trioxide interference.
- Mercury control vendors are working to develop alternative flue-gas conditioning agents that could be used instead of sulphur trioxide in the conditioning system to improve the performance of the electrostatic precipitators without jeopardising mercury reductions using sorbent injection.
- Although selective catalytic reduction NO_x abatement systems often improve mercury capture, in some cases they may lead to sulphur trioxide interference when sulphur in the coal is converted to sulphur trioxide gas. Newer selective catalytic reduction systems often have improved catalytic controls that can minimise the conversion of sulphur to sulphur trioxide gas.
- High sulphur bituminous coal (i.e. with a sulphur content of at least 1.7 % by weight) may also lead to the formation of sulphur trioxide interference in some cases, although the number of plants using these high sulphur coals is likely to decline with increasingly stringent sulphur controls. However, there are two ways of addressing this problem:
 - using alkali-base sorbents to adsorb sulphur trioxide gas before it can interfere with the performance of the sorbent injection system;
 - blending the fuel to include some low sulphur coal.

Hot-side ESP

- Using a heat resistant sorbent. Non-brominated ACI has very little mercury capture above 149 °C. Brominated ACI can provide both stable and high levels of mercury reduction, up to temperatures of about 289 °C, and heat resistant sorbents operate up to 427 °C.
- Installing a fabric filter in addition to the sorbent injection system.

Lignite

- Using a higher sorbent injection rate.
- Blending with sub-bituminous coal.

Finally, according to a 2009 US-EPA study at 2 plants equipped with a cold-side or hot side ESP, with different coal chlorine contents (150 ppm in one case and 1400 ppm in the other case), with brominated activated carbon injection upstream of these devices, no increase in air emissions of total and Toxic Equivalent (TEQ) chlorinated and brominated dioxin compounds were noted when compared to the content without activated carbon injection.

Cross media effects

Possibility of raising the mercury content of the gypsum.

Effects on coal combustion residues

Both chemically and non-chemically treated carbon sorbents impact on coal combustion residues (CCRs), in particular the fly ash and FGD sludge. This results in CCRs with an increased content of mercury and other co-collected metals (e.g. arsenic and selenium) and the presence of injected sorbent and other chemical modifiers. Tests undertaken by the US EPA show that the mercury is strongly retained in the CCRs, and is unlikely to be leached at levels of environmental concern. In some facilities, arsenic and selenium may be leached at levels of potential concern, but this can occur both with and without enhanced mercury control technologies. However, in many cases, the amount of mercury, arsenic and selenium released from CCRs is estimated to be a small fraction (< 0.1% - 5%) of the total content.

Excess bromine that has not reacted with mercury, and which is converted to bromide, can leach to some degree if stored in wet ponds, depending on the contact time and the amount of water to which it is exposed. Apart from that, Br will not leach because it is chemically reacted onto the activated carbon in the gas phase bromination process. There is also no Br leaching when the fly ash containing the sorbents is used in concrete.

The carbon in sorbents can render fly ash unusable for some purposes, thus increasing the need for storage and disposal. However, advances in sorbent technologies that have reduced sorbent costs at some plants also offer the potential to preserve the market value of fly ash, and therefore its reuse as a product e.g. at least one manufacturer offers a concrete-friendly sorbent to help preserve fly ash sales. Alternatively, the fly ash could be segregated with a supplementary fabric filter.

Calculations by a company providing brominated ACI (Activated carbon injection) have shown that the mercury content of the concrete is 0.00001%. However, some discolouration of the concrete can occur with the use of ACI.

There is an increase in PM loading of < 4%, due to sorbent injection, and this is even lower when halogenated sorbents are injected. Calculations suggest that the increase in PM_{2.5} would be < 0.2 %. When ESPs are used, this increase is offset by the brominated ACI improving the operation of the ESP, by the sorbent changing the resistivity of the fly ash, resulting in the change of the electric field of the ESP.

Technical considerations relevant to applicability

Generally applicable for new and existing plants.

Mercury removal is more effective with the use of fabric filters. 80-90 % reductions were achieved with all 3 main types of coal (bituminous, sub-bituminous and lignite) and on boiler types that exist at three-quarters of US coal-fired plants.

In the US DoE R&D programme, the costs of purchasing and installing sorbent injection systems and monitoring equipment averaged USD 3.6 million, ranging from USD 1.2 million to USD 6.2 million. Where fabric filters have also been installed, primarily to assist the sorbent injection system in Hg reduction, the average cost is USD 16 million, ranging from USD 12.7 million to USD 24.5 million. The apportioning of these average capital costs is set out in Table 1.2

Table 1.2: Example of capital cost for implementing a sorbent injection system for mercury reduction

Component costs	Sorbent injection system	Sorbent injection system + fabric filter to assist in mercury removal
Number of boilers	14	5
Sorbent injection system	USD 2 723 277	USD 1,334,971
Mercury emissions monitoring system	USD 559 592	USD 119,544
Consulting and engineering	USD 381 535	USD 1,444,179
Fabric filter		USD 19 009 986
TOTAL	USD 3 594 023 ⁽¹⁾	USD 15 785 997 ⁽¹⁾
⁽¹⁾ Numbers do not add up to total. Total cost was provided for all of the boilers, but individual cost category data was only provided for some of them		

The average annualised operating costs of sorbent injection systems in the US are USD 640,000 – almost entirely sorbent costs. These costs are now being reduced in some applications by the use of sorbent enhancement additives.

Eight boilers in the DoE study reported actual or estimated fly ash related costs of an average net cost of USD 1.1 million per year.

For those plants that installed a sorbent injection system alone to meet mercury emission requirements, the cost to purchase, install and operate sorbent injection and monitoring systems represented an additional cost of USD 0.12 cents per kilowatt hour.

Driving force for implementation

The driver for implementing mercury control techniques is the prospect or fact of legislation.

Example plant

The US EPA undertook a detailed study of 25 boilers at 14 coal-fired plants in the United States where sorbents have been commercially applied. Thirteen of these have been identified by the US authorities – BI England, New Jersey; Brayton Point, Massachusetts; Bridgeport Harbor, Connecticut; Crawford, Illinois; Fisk, Illinois; Indian River Generating Station, Delaware; Mercer Generating Station, New Jersey; Presque Isle, Michigan; TS Power Plant, Nevada; Vermillion Power Station, Illinois;²⁸ Walter Scott junior Energy Centre, Iowa; Waukegan, Illinois; Weston, Wisconsin. All met the emissions reductions required by their State, and averaged 90 % reductions. For example:

- A 164 megawatt bituminous-fired boiler, built in the 1960s and operating a cold-side electrostatic precipitator and wet scrubber, exceeded its 90 % reduction requirement, achieving more than 95 % mercury emission reductions using chemically treated carbon sorbent.
- A 400 megawatt sub-bituminous-fired boiler, built in the 1960s and operating a cold-side electrostatic precipitator and a fabric filter, achieved a 99 % mercury reduction using untreated carbon sorbent, exceeding its 90 % reduction regulatory requirement.
- A recently constructed 600 megawatt sub-bituminous-fired boiler operating a fabric filter, dry scrubber, and selective catalytic reduction system achieved an 85 % mercury emission reduction using chemically treated carbon sorbent, exceeding its 83 % reduction regulatory requirement.

Beyond this, the [US] Institute of Clean Air Companies reported that power plants had 121 sorbent injection systems on order as of February 2009, in order to meet State requirements. Most are for retrofit installations at units burning sub-bituminous coal, but several are also listed

for lignite and bituminous-fired units. Further examples include Joliet 29, Comanche, Edge Moor, Brandon Shores, ED Edwards, Meredosia, Kincaid Generation LLC, Powerton, Will County, Joppa Steam, Baldwin Energy Complex, Havana, Hennepin Power Station, Wood River, Boswell Energy centre, JE Corette Plant, Merrimack Station, San Juan, AES Greenidge, CR Huntley Generating Station, Dunkirk Generating Plant, Shawville, Big Brown, Edgewater, Pulliam, Genoa, Newton, John P Madgett, Iatan, Colstrip, Lewis and Clark, Charles P Crane.

Boiler bromide addition (BBA)

Description

Addition of halogens into the furnace to oxidise the flue-gas mercury into a soluble species, thereby enhancing mercury removal in downstream control devices.

Technical description

The addition rates range from <40 to 440 ppm Br per tonne of coal, dry basis, the more common addition rate being 52 ppm.

Another option for halogen addition is to add halogen additives to the fuel or to use brominated activated carbon injection (brominated-ACI) into the flue gas.

Achieved environmental benefit

Reduced mercury emissions.

Environmental performance and operational data

For units equipped with an SCR and WFGD: stack emissions reduced to <0.5 kg NO_x/GJ.

For units without SCR: Higher bromide addition rates are required to achieve the same mercury oxidation than units with an SCR.

For units without an FGD: BBA alone does not reduce Hg emissions significantly, but it improves the effectiveness of ACI for these units. High levels of SO₃ in the flue-gas may limit the efficiency of such combination BBA/ACI and may require an additional SO₃ mitigation technology.

Cross-media effects

Flue-gas mercury measurements are very difficult to make in the presence of bromine in the flue-gas.

Potential for bromide-induced corrosion in the ductwork, air heater and in FGD systems.

Increase in bromide and mercury in the fly ash. A decrease in Se in the fly ash is offset by an increase in Se in the FGD liquor.

Economics

For plants without SCR (with and without FGD), the use of ACI in conjunction with BBA may be more cost effective than either ACI or BBA alone to achieve the same level of performance.

Example plants

In the past few years, dozens of US coal-fired units have begun to operate furnace calcium bromide addition systems to achieve mercury air emissions limits set by local regulations. 50 of them took part in a survey (see reference for the survey findings).

Table 1.3: Other specific techniques to consider for the prevention and control of gaseous mercury emissions

Technique	Technical description	Achieved environmental benefits	Environmental performance and operational data	Cross-media effects	Technical considerations relevant to applicability		Economics	Driving force for implementation	Example plants	Reference literature
					New plants	Retrofitable				Remarks
Addition of bromide compounds to fuel		Increased share of HgCl ₂ in raw gas and hence capture in filter and/or scrubber	Several full scale tests	More bromide in waste water than from coal only	Generally applicable in systems with or without wet scrubbing	Generally applicable in systems with or without wet scrubbing	Low investment. Operating costs seem to be low			
Optimisation of SCR-catalysts for oxidation of Hg ⁰ to Hg ²⁺		Increased share of HgCl ₂ in raw gas and hence capture in filter and/or scrubber	R&D on optimised catalysts ongoing	None	Generally applicable	Generally applicable - co-benefit already exists in SCR upstream wet FGD	Could be high in case that existing catalysts would have to be replaced			
Addition of activated carbon in FGD		Reduction of Hg emissions	Limited	Reduction in gypsum quality (colour, Hg content)	Generally applicable	Generally applicable	Addition of activated carbon in FGD has low investment and operation costs			
Addition of organic or inorganic sulphides in FGD		Reduction of Hg emissions	Well known in waste incineration	Gypsum quality	Generally applicable	Generally applicable	Low investment			

Technique	Technical description	Achieved environmental benefits	Environmental performance and operational data	Cross-media effects	Technical considerations relevant to applicability		Economics	Driving force for implementation	Example plants	Reference literature
					New plants	Retrofitable				Remarks
Addition of strong ligands like bromide in FGD		Reduction of Hg emissions	Limited to lab-scale and a few full-scale tests	More bromide in waste water than from coal only	Generally applicable	Generally applicable				
Precipitate Hg separately from other metals in FGD waste water	Concentrates Hg to a low-mass sink and thus indirectly helps to keep Hg away from all other sinks, such as clean gas, gypsum etc.	Makes a small stream waste product the main sink for Hg	Tested in full scale	Reduces cross-media effects			Only small amount of waste to be disposed Low-Hg main share of sludge can be recycled to the furnace			

Additional information about the addition of bromide compounds to the fuel:

Elemental mercury is a large atom with 80 electrons moving around its nucleus. As a result, it is highly polarisable [Liu et al., 2007]. Bromine has 35 electrons compared to 17 electrons on Cl. It is expected that Br is more effective than Cl for Hg^0 oxidation. The bromine content of coal eventually determines the Hg^{2+} percentage in the flue-gas more than chlorine.

For a certain amount of adsorbent, more mercury leads to higher mercury partial pressure, and higher partial pressure leads to a larger amount of adsorption. In other words, the higher ratio of mercury content to ash content of coal (M/A ratio) contributes to a higher adsorption rate, i.e. Hg_p percentage in flue-gas.

1.3 BAT conclusions

Source: Draft LCP BREF 2013

Chapter 10: BAT conclusions

Mercury emissions to air

In order to reduce mercury emissions to air from the combustion of coal and lignite, BAT is to use an appropriate combination of the techniques given below.

Technique		Description	Applicability
Co-benefit from measures taken for other pollutants			
a	Bag Filter	See description in Section Error! Reference source not found.. See BAT Error! Reference source not found.	Generally applicable
b	ESP	See description in Section Error! Reference source not found.. See BAT Error! Reference source not found.. Better removal efficiency at flue-gas temperatures below 130°C	Generally applicable

c	SCR	See description in Section Error! Reference source not found.. See BAT Error! Reference source not found.. Only used in combination with other techniques to enhance the mercury oxidation before capture in a subsequent FGD unit	Generally applicable to plants > 300 MW _{th} Applicable to coal-fired PC boilers for plants < 300 MW _{th}
d	FGD technique (e.g. wet limestone scrubbers, spray dryer scrubbers or dry sorbent injection)	See descriptions in Section Error! Reference source not found.. See BAT Error! Reference source not found.	Generally applicable when there is a need to reduce SO _x content in emissions to air
Specific measures for mercury reduction			
e	Fuel choice	Select coal and lignite with Hg content < 25 µg/kg	Applicable within the constraints associated with the availability of different types of fuel, which may be impacted by the energy policy of the Member State
f	Carbon sorbent (e.g. activated carbon) injection in the flue-gas	See description in Section Error! Reference source not found.. Generally used in combination with ESP/bag filter	Generally applicable
g	Use of halogenated additive to the fuel or injected in the furnace	Addition of halogens into the furnace to oxidise the flue-gas mercury into a soluble species, thereby enhancing mercury removal in downstream control devices	Applicable in the case of a low halogen content in the fuel, within the constraints associated with the control of halogen emissions to air
h	Fuel pretreatment	Fuel washing, blending and mixing in order to limit / reduce the Hg content	Applicability is subject to a previous survey for characterising the fuel and for estimating the potential effectiveness of the technique

BAT-associated emission levels

The BAT-associated emission levels for mercury are given in Table 1.4 and Table 1.5.

Table 1.4: BAT-associated emission levels for mercury emissions to air from the combustion of coal (anthracite and bituminous)

Combustion plant rated thermal input (MW _{th})	BAT-AEL (µg/Nm ³)		Averaging period	Monitoring frequency
	New plants	Existing plants		
<300	0.5 – 5	1 – 10	Average of samples obtained during one year	Periodic measurement: 4 times/yr
>300	0.2 – 2	0.2 – 6	Yearly average	Continuous measurement

Table 1.5: BAT-associated emission levels for mercury emissions to air from the combustion of sub-bituminous coal and lignite

Combustion plant rated thermal input (MW _{th})	BAT-AEL (µg/Nm ³)		Averaging period	Monitoring frequency
	New plants	Existing plants		
<300	1 – 10	2 – 20	Average of samples obtained during one year	Periodic measurement: 4 times/yr
> 300	0.5 – 5	0.5 – 10	Yearly average	Continuous measurement

2. SMELTING AND ROASTING PROCESSES USED IN THE PRODUCTION OF NON-FERROUS METALS

Relevant documents: http://eippcb.jrc.ec.europa.eu/reference/BREF/nfm_bref_1201.pdf,
http://eippcb.jrc.ec.europa.eu/reference/BREF/NFMbw_17_04-03-2013.pdf

1. NFM (non-ferrous metal industries) BREF 2001 .- adopted

2. Draft 3 of revised LCP BREF – version February 2013 – under consideration by Technical Working Group

Scope: *NFM BREF covers the Processing of non-ferrous metals:*

(a) production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes;

(b) melting, including the alloyage, of non-ferrous metals, including recovered products and operation of non-ferrous metal foundries, with a melting capacity exceeding 4 tonnes per day for lead and cadmium or 20 tonnes per day for all other metals. (Annex I IED, point 2.5)

2.1 Background information

Source: Non-ferrous Metals Industries (NFM) BREF (adopted 2001)

General information – chapter 1.7 Mercury

2.1.1. General

Mercury is the only metal that is liquid at room temperature and has the lowest fusion and boiling points of all metals. It also has a high electrical conductivity and these features are used in a variety of applications such as electrical switch-gear and battery production. Mercury forms alloys easily with a number of other metals and these are known as Amalgams, which are extensively used in dentistry. The major use of mercury is as a flowing cathode in the Chlor-Alkali process. This process exploits mercury's high conductivity and the formation of an amalgam with sodium.

Mercury is characterised by the toxicity of the metal and its' vapour and the extreme toxicity of some of its' compounds. The result is that mercury is being replaced by alternative materials in many of its' uses and so the demand and production of mercury has declined rapidly. There are implications in the future as it is likely that some existing inventories of mercury will come on the market or may even become wastes.

2.1.2. Sources of materials

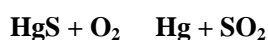
Mercury appears in nature in the form of cinnabar (sulphide of mercury), which is associated with very hard gangues such as the quartzite and the basalts. It is also present in the form of other

compounds such as oxides, sulphates, chlorides or selenides. These are rare and are always associated with the cinnabar and generally have a low relevance. There are exceptions such as livinstonite (HgSbS), which has been used in Mexico. The quality of primary ores varies considerably from 0.1% mercury to more than 3%.

Other sources of mercury are the ores and concentrates of other metals such as copper, lead and zinc etc. Mercury is produced from the purification of gases emitted during the production of these metals. Mercury is also recovered from secondary materials such as dental amalgam and batteries and it is also obtained from the refining of oil.

2.1.3. Production and consumption

The decomposition of the cinnabar is complete at temperatures of 600° C shown by the formula below. Mercury metal is condensed at room temperature. The heating can be carried out in either “Herreschoff”, “Muffle” or rotating furnaces. The last two are not frequently used.



Source	Mercury content in the ore [%]	Production [t/a]
Almaden, Spain	> 3	390
Mc Dermitt, USA	0.5	
Nikitovska, Ukraine	0.1	

Table 2.1: Sources of mercury

In the case of rich ores, above 2% mercury, pre-treatment by crushing and grading is only required and the crushed ore can then be fed directly into the furnace. In the case of poor ores with 0.5% mercury, differential flotation is used to separate the silica rock to obtain concentrates with an average mercury content of 70%. For minerals below 0.1% of mercury, the ore is roasted after crushing. Furnaces of large capacity (1000 t/day) are used.

Mercury production from the production of other non-ferrous metals in Europe for 1997 is estimated at 350 tonnes. These processes generally produce mercury or calomel in the range 0.02 to 0.8 kg of mercury per tonne of metal produced depending on the mercury content of the concentrate.

The decline in mercury production can be seen in the European production for 1960, 1970 and 1980.

Year	Production [t/a]

1960	4250
1970	3700
1980	1100

Table 2.2: Production of mercury in Western Europe

2.1.4. Environmental issues

The toxicity of mercury and its compounds is a significant factor. Mercury in the environment can interact with various organic compounds to produce very toxic organo-mercury compounds. Current legislation is therefore imposing more stringent standards on the industry to prevent emissions, to curtail its' use in various processes and to remove mercury from the environment.

Mercury is a List 1 Substance under the 76/464 Directive on Pollution covered by the section Dangerous Substances Discharged to the Aquatic Environment of the Community. Directive 84/156 set EU wide discharge limit values for mercury.

Best available techniques -chapter2.17.6 Removal of mercury

Mercury removal is necessary when using some raw materials that contain the metal. Specific instances are referred to in the metal specific chapters and in these cases the following techniques are considered to be BAT.

- The Boliden/Norzink process with the recovery of the scrubbing solution and production of mercury metal.
- Bolchem process with the filtering off the mercury sulphide to allow the acid to be returned to the absorption stage.
- Outokumpu process.
- Sodium thiocyanate process.
- Activated Carbon Filter. An adsorption filter using activated carbon is used to remove mercury vapour from the gas stream as well as dioxins.

For processes where mercury removal from the gases is not practicable the two processes to reduce the mercury content in sulphuric acid produced during the production of non-ferrous metals are considered to be BAT.

- Superlig Ion Exchange process.
- Potassium iodide process.

The emissions associated with the above processes are related to any residual mercury that will be present in the acid that is produced, the product specification is normally < 0.1 ppm (mg/l) and is equivalent to ~ 0.02 mg/Nm³ in the cleaned gas.

Source: NFM Revision – DRAFT BREF (as of February 2013)

Chapter 2.12.5.5 Techniques to reduce mercury emissions

Description

Set of techniques to reduce mercury emissions to air.

Technical description

Mercury is volatile at the temperatures encountered in most abatement processes, and hence other techniques may be needed to remove it. In the case of mercury removal before a sulphuric acid plant, any residual mercury will be present in the acid that is produced, the product specification is normally <0.1 to 0.5 ppm and is equivalent to ~ 0.02 mg/Nm³ in the cleaned gas. All processes listed below are reported to achieve this:

- **Boliden-Norzink process:** this process is based on a wet scrubber using the reaction between mercuric chloride and mercury to form mercurous chloride (calomel), which precipitates from the liquor. The process is placed after the washing and cooling step in the acid plant, so the gas is dust and SO₃ free and the temperature is about 30 °C. The gas is scrubbed in a packed bed tower with a solution of HgCl₂. This reacts with the metallic mercury in the gas and precipitates it as calomel, Hg₂Cl₂. The calomel is removed from the circulating scrubbing solution and partly regenerated by chlorine gas to HgCl₂, which is then recycled back to the washing stage. The mercury product bleed is either used for mercury production or stored. Mercury chloride is a very toxic compound of mercury and great care should be taken when operating this process.
- **Bolchem process:** this process step is located in the acid plant, as in the Boliden-Norzink process, but the removal is effected by 99 % sulphuric acid. This acid comes from the absorption part of the acid plant and it oxidises the mercury at ambient temperature. The resulting acid that contains mercury is diluted to 80 % and the mercury is precipitated as sulphide with thiosulphate. After filtering off the mercury sulphide, the acid is returned to the absorption stage. No acid is therefore consumed in the process.
- **Outotec process:** in this process the mercury is removed before the washing step in the acid plant. The gas at about 350 °C, is led through a packed bed tower where it is washed countercurrently with 90 % sulphuric acid at about 190 °C. The acid is formed *in situ* from the SO₃ in the gas. The mercury is precipitated as a selenium chloride compound. The mercury sludge is removed from the cooled acid, filtered and washed and sent to the production of metallic mercury. 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 selenide.
- **Sodium thiocyanate process:** this process is used at a zinc roaster. The SO₂ gas is washed with a solution of sodium thiocyanate and the mercury is removed as sulphide. Sodium thiocyanate is regenerated, the reaction is shown in the following formula.
$$3\text{Hg} + 8\text{SCN}^- + 4\text{H}^+ + \text{SO}_2 \Rightarrow 2(\text{Hg}(\text{SCN})_4)^{2-} + \text{HgS} + 2\text{H}_2\text{O}$$
- **Activated carbon filter (Lurgi process):** this is an adsorption filter using activated carbon to remove mercury vapour from the gas stream.

The Boliden-Norzink and Outotec processes detailed above are most commonly used, but other processes have been reported elsewhere.

- **Selenium scrubber:** this is also based on a wet scrubber and uses the reaction between amorphous selenium in sulphuric acid and mercury to remove high concentrations of mercury vapour.
- **Selenium filter:** a dry scrubbing process which uses amorphous selenium to react with mercury vapour to form mercury selenide.
- **Lead sulphide process:** a dry scrubbing process using lead sulphide nodules to remove mercury from the gas stream.
- **Tinfos/Miltec process:** a mercury cleaning process, which is based on the oxidation of mercury in the off-gas using sodium hypochlorite. After oxidation in a washing tower, the mercury is precipitated as mercury sulphide (HgS) by the addition of disodium sulphide.

The mercury sulphide is removed from the process in a press filter. The sludge that contains mercury is treated as hazardous waste and disposed of in a sealed disposal site. Mercury emissions are reduced by approximately 94 %. The mercury cleaning plant at Tinfos is thoroughly described by Haaland et. al. at Infacon 9.

- Lurgi mercury cleaning process: the Lurgi mercury removal unit consists of an electrostatic precipitator to remove residual dust and tars, a gas heater, a packed bed absorber, a fan-damper system to control the gas flow through the unit, and extensive gas analysis nitrogen purge equipment to maintain low oxygen levels in the gas. The heater is required to warm the gases to the optimum temperature of 60 - 85 °C; lower gas temperatures result in lower reaction rates and moisture condensation in the packed bed, higher temperatures can result in sulphur being lost from the absorbent. Eramet commissioned a mercury removal unit in 2001 and reports trouble free operation since. Gas flowrates through the unit are around 15 000 Nm³/hour. The mercury absorption efficiency is 98 %. After allowing for plant start-ups, etc, 94 % of the total mercury in the raw gases is captured. The absorber mass is changed after about 8 months of operation and is disposed of in a secure disposal. Only trace amounts of mercury report to the scrubber water.
- Boliden-Contech process: selenium coated spheres are used in a packed bed. The method works but experience in the Scandinavian ferro-alloy industry is limited for this technique.
- The Dowa process: mercury is adsorbed onto pumice stones coated with lead sulphide.

Two other processes are available to reduce the mercury content in sulphuric acid produced during the production of non-ferrous metals, but their use is based on a need to improve the quality of the acid rather than on environmental effects:

- Superlig ion exchange process: this process uses ion exchange to remove mercury from the product acid and achieves a concentration of mercury of <0.5 ppm.
- Potassium iodide addition to the acid: this should be at least 93 % strength, at a temperature of about 0 °C. Mercury iodide, HgI₂, is then precipitated.

Achieved environmental benefits

- Reduction of Hg emissions.

Environmental performance and operational data

The product specification is normally <0.1 to 0.5 ppm in sulphuric acid and is equivalent to <0.02 mg/Nm³ in the cleaned gas. The aims are for the reduction of emissions and recovery of mercury, and the production of mercury-free sulphuric acid. In compliance with regulation EC 1102/2008, metallic mercury gained from non-ferrous mining, smelting operations and extracted from cinnabar ore in the European Union shall be considered as waste as from 15 March 2011.

Data reported in the metal-specific chapters range between 0.02 and 0.05 mg/Nm³.

Cross-media effects

- Increase in energy use. A solid or liquid waste is produced that will require disposal.

Technical considerations relevant to applicability

Applicable to pyrometallurgical processes using raw materials with Hg content.

Economics

The processes are known to be operating economically and costs, where they are available, are reported in Annex of this document.

2.2 BAT Conclusions

Source: NFM Revision – DRAFT BREF (as of February 2013)

14.10.1.5 Hg emissions

Technique	Description
Boliden-Norzink process	This process is based on a wet scrubber using the reaction between mercuric chloride and mercury to form mercurous chloride (calomel), which precipitates from the liquor. The process is placed after the washing and cooling step in the acid plant
Bolchem process and filtering off mercury sulphide	This process is based in the use of sulphuric acid (from the absorption part of the acid plant) to oxidise mercury at ambient temperature. The resulting acid that contains mercury is diluted to 80 % and the mercury is precipitated as sulphide with thiosulphate
Outotec process	In this process the mercury is removed before the washing step in the acid plant. The gas at about 350 °C, is led through a packed bed tower where it is washed countercurrently with 90 % sulphuric acid at about 190 °C. The acid is formed <i>in situ</i> from the SO ₃ in the gas. The mercury is precipitated as a selenium chloride compound. The mercury sludge is removed from the cooled acid, filtered and washed and sent to the production of metallic mercury. 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 when selenium metal is produced along with mercury selenide
Sodium thiocyanate process	In this process, the SO ₂ gas is washed with a solution of sodium thiocyanate and the mercury is removed as sulphide
Use of an activated carbon filter	This process is based in the adsorption of mercury molecules in the activated carbon. When the surface has adsorbed as much as it can, the adsorbed content is desorbed as part of the regeneration of the adsorbent
Tynfos-Miltec application	This process is based on the oxidation of mercury in the off-gas using sodium hypochlorite
Lurgi process	This process consists of an electrostatic precipitator to remove residual dust and tars, a gas heater, a packed bed absorber, a fan-damper system to control the gas flow through the unit and extensive gas analysis nitrogen purge equipment to maintain low oxygen levels in the gas

Boliden/Contec process	This process is based in the use of selenium coated spheres in a packed bed
DOWA adsorption process	This process is based on the adsorption onto pumice stones coated with lead sulphide

3. WASTE INCINERATION FACILITIES

Relevant document: http://eippcb.jrc.ec.europa.eu/reference/BREF/wi_bref_0806.pdf

WI (waste incineration) BREF 2006 .- adopted

Scope: WI BREF covers Disposal or recovery of waste in waste incineration plants or in waste co-incineration plants:

(a)for non-hazardous waste with a capacity exceeding 3 tonnes per hour;

(b)for hazardous waste with a capacity exceeding 10 tonnes per day

(Annex I point 5.2 IED)

3.1 Background information

Source: Waste Incineration (WI) BREF (adopted 2006)

Chapter 2.5.6 Techniques for the reduction of mercury emissions

2.5.6.1 Primary techniques

Mercury is highly volatile and therefore almost exclusively passes into the flue-gas stream. The limit value set in the waste incineration directive is 0.05 mg/m³. Limit values as low as 0.03 mg/m³ as a daily average value (with continuous monitoring) have been set in some European Member States [1, UBA, 2001]. Continuous measurement is also prescribed in some national waste incineration legislation (e.g. Austria, Germany). The majority of installations cannot meet these limit values, particularly for peak loads, without the addition of special gas cleaning measures for Hg.

The only relevant primary techniques for preventing emissions of mercury to air are those which prevent or control, if possible, the inclusion of mercury in the waste:

- efficient separate collection of waste that may contain heavy metals e.g. cells, batteries, dental amalgams, etc.
- notification of waste producers of the need to segregate mercury
- identification and/or restriction of receipt of potential mercury contaminated wastes
 - by sampling and analysis of wastes where this is possible
 - by targeted sampling/testing campaigns
- where such wastes are known to be received - controlled addition to avoid overload of abatement system capacity.

2.5.6.2 Secondary techniques

Mercury vaporises completely at a temperature of 357 °C and remains gaseous in the flue-gas after passing through furnace and boiler. Inorganic mercury (mainly Hg²⁺ as a chloride) and elemental mercury are affected differently by FGT systems and detailed consideration of the fate of both is required.

The selection of a process for mercury abatement depends upon the load fed in and upon the chlorine content of the burning material. At higher chlorine contents, mercury in the crude flue-

gas will be increasingly in the ionic form which can be deposited in wet scrubbers. This is a particular consideration at sewage sludge incineration plants where raw gas chlorine levels may be quite low. If, however, the chlorine content in the (dry) sewage sludge is 0.3 % by mass or higher, only 10 % of the mercury in the clean gas is elemental; and the elimination of only the ionic mercury may achieve a total Hg emission level of 0.03 mg/Nm³.

Metallic mercury can be removed from the flue-gas stream by:

- transformation into ionic mercury by adding oxidants and then deposited in the scrubber - the effluent can then be fed to waste water treatment plants with heavy metal deposition, where the mercury can be converted to a more stable form (e.g. HgS), thus more suitable for final disposal or
- direct deposition on sulphur doped activated carbon, hearth furnace coke, or zeolites.

Tests have shown that sulphur dioxide neutralisation in the furnace by adding limestone, can reduce the proportion of metallic mercury, making overall Hg removal from the gas stream more efficient.

In incineration plants for municipal and hazardous wastes, the chlorine content in the average waste is usually high enough, in normal operating states, to ensure that Hg is present mainly in the ionic form. However, specific inputs of certain waste may change the situation and metallic mercury may need to be deposited, as mentioned above.

High Hg wastes:

For the incineration of waste with a high mercury content in hazardous waste incineration plants Hg deposition degrees of 99.9 % can only be ensured when highly chlorinated waste is also incinerated in an appropriate proportion to the Hg load. Multistage wet scrubbing processes are typical of this type of plant. High proportions of ionic Hg (e.g. >99.9 %) in the boiler crude flue-gas before wet gas cleaning are caused by including highly chlorinated waste. This assists total Hg removal from the flue-gas.

High chlorine total loads (approx. 4 % w/w input) and a therefore high interim Cl₂ supply lead to high Hg chlorination levels and Hg deposition of close to 100 %. With lower chlorine loads the Hg deposition degree reduces rapidly.

Mercury emissions

The data include results from continuous measurement (used in Germany for over two years and Austria for over one year) and from discontinuous measurements (minimum twice a year). Therefore, comparability of data between these two types of measurement may be not very high. Continuous measurements will also include events with elevated emissions due to higher loads in the waste feed, which have been reported by some plants.

Level of annual averages	Number of plants/lines
>200 µg/Nm ³	0
>100 <200 µg/Nm ³	1
>50 <100 µg/Nm ³	3
>30 <50 µg/Nm ³	7

<30 µg/Nm ³	83
------------------------	----

Table 3.1: Mercury emissions survey of European MSWIs

For several plants in France, mercury measurements are not given alone but in combination with Cd (the ELV being given as a sum of the two). As the distribution of the two is not necessarily predictable, these results are presented in the following additional table:

Level of annual averages	Number of plants/lines
>200 µg/Nm ³	0
>100 <200 µg/Nm ³	1
>50 <100 µg/Nm ³	5
>30 <50 µg/Nm ³	8
<30 µg/Nm ³	18

Table 3.2: Combined Cd and Hg emissions of selected MSWIs in France

Chapter 4.4.6 Reduction of mercury emissions

4.4.6.1 Low pH wet scrubbing and additive addition

Description

The use of wet scrubbers for acid gas removal causes the pH of the scrubber to reduce. Most wet scrubbers have at least two stages. The first removes mainly HCl, HF and some SO₂. A second stage, maintained at a pH of 6 - 8 serves to remove SO₂.

If the first stage is kept at a pH of below 1, the removal efficiency of ionic Hg as HgCl₂, which is generally the main compound of mercury after waste combustion, is over 95 %. However, the removal rates of metallic Hg are only in the order of 0 – 10 %, mainly as a result of condensation at the scrubber operational temperature of around 60 to 70 °C.

Metallic mercury adsorption can be improved up to a maximum of 20 – 30 % by the:

- addition of sulphur compounds to the scrubber liquor
- addition of activated carbon to the scrubber liquor
- addition of oxidants, e.g. hydrogen peroxide to scrubber liquor. This technique converts metallic mercury to the ionic form as HgCl₂ to facilitate its precipitation, and has the most significant effect.

The overall Hg removal (both metallic and ionic) efficiency is around 85 %.

It is reported that a removal efficiency higher than 90 % can also be achieved with a technique adding bromine containing wastes or by injection of bromine containing chemicals into the combustion chamber.

At the inlet concentrations usually found with many waste types, and with the additional uncertainty over composition of most wastes, the removal efficiencies of this type of scrubbing is

not generally sufficient to reach an emission level below 50 µg/Nm³. In one Member State an ELV of 30µg/Nm³ has been set. In either case, the addition of further Hg abatement capacity may be required, depending on the inlet concentration, such as:

- carbon injection before a bag filter system
- static coke bed filter.

(see Sections 0 and 0)

Achieved environmental benefits

Percentage reduction efficiencies are given in the description above.

The impact of the concentration of Hg in the incinerated waste and the content of Cl are decisive in the determination of the final emission levels achieved.

Cross-media effects

Cross-media effects of the use of wet scrubbing are given in Section **Error! Reference source not found..**

Consumption of any reagents added.

Operational data

For MSW with an average concentration of 3 - 4 mg Hg/kg of MSW, emission concentrations to air of 50 – 80 µg/Nm³ are achieved.

The variation of Hg input to MSW can be very large and, therefore, can result in significant variations in emission levels. Values measured at an Austrian MWI gave values between 0.6 and 4 mg/kg. This variation can be much greater in other waste types, e.g. some hazardous wastes.

Achieved levels just with a wet scrubbing system are approx. 36 µg/Nm³, with a wet scrubber and an activated coke filter <2 µg/Nm³ and with a combination of the flow injection process and a wet scrubber 4 µg/Nm³.

Applicability

The use of acid wet scrubbers for mercury emission reduction can only meet the emission limits set in Directive EC/2000/76 where:

- the pH is well controlled below 1
- chloride concentrations are high enough for the crude flue-gas Hg content to be almost entirely ionic (and hence removable as the chloride)
- additives are added to the low pH scrubber in some cases.

The applicability of this technique is assessed in the table below:

Criteria	Evaluation/comment
Waste type	
Plant size range	<ul style="list-style-type: none"> • any
New/existing	<ul style="list-style-type: none"> • not generally applied on its own at new installations

Inter-process compatibility	<ul style="list-style-type: none"> • see comments for wet scrubbers • additional Hg removal may be required to comply with EC/2000/76 (depending on the Hg inlet content)
Key location factors	<ul style="list-style-type: none"> • none

Table 3.3: Assessment of the applicability of wet scrubbing for Hg control

The technique is only applicable to Hg air emission control as an Hg pretreatment step, or where input waste concentrations are low enough (e.g. below 4 mg/kg). Otherwise emissions to air of above 50 µg/Nm³ may result.

Economics

Information not supplied.

Driving force for implementation

This technique has been implemented as an adaptation to wet scrubbing for acid gas removal in order to reduce Hg emissions.

Example plants

Wet scrubbing is widely used in Europe.

4.4.6.2 Activated carbon injection for Hg adsorption

Description

This technique involves the injection of activated carbon upstream of a bag filter (see also Section **Error! Reference source not found.**, bag filters are described in Section **Error! Reference source not found.**), or other de-dusting device. Mercury metal is adsorbed in the stream and where barrier filters such as bag filter are used, also on the reagent that is retained on the bag surface.

Achieved environmental benefits

Metallic mercury is adsorbed (usually at about 95 % removal efficiency) to result in emissions to air of below 30 µg/Nm³. Ionic mercury is also removed by chemi-adsorption arising from the sulphur content in the flue-gases or from sulphur impregnated in some types of activated carbon.

In some systems where removal of mercury is carried out in wet acid scrubbers (pH<1) to reduce the inlet concentration, final emission levels below 1µg/Nm³ are seen.

The carbon also adsorbs dioxins . Bag filters also provide a means of particulate and heavy metal removal.. It is normal for alkaline reagents to be added with the carbon, this then also allows the reduction of acid gases in the same process step as a multifunctional device.

Cross-media effects

The cross-media effects are similar to those for other situations where bag filters are used. The energy consumption of bag filters is a significant aspect.

In addition, for this technique the most significant cross-media effect is the production of residues contaminated with removed pollutant (Hg).

In cases where the solid reagent is re-burned (for PCDD/F destruction) in the incinerator it is important that:

- the installation has an outlet for Hg that prevents internal pollutant build up (and eventual breakthrough release)
- the alternative outlet removes the pollutant at a sufficient rate
- where wet scrubbers are used, the Hg can pass into the effluent stream (although it can then be precipitated to the solid residue using treatment techniques).

Operational data

Operational aspects are similar to other situations where bag filters are used. Effective bag filter and reagent injection system maintenance are particularly critical to achieving low emission levels.

Different types of activated carbon have different adsorption capacities. Another possibility to improve mercury removal is sulphur impregnation of the adsorbent.

In experiments carried out at an HWI, various types of activated carbon were used, and the consumption rate per hour required to obtain a particular Hg emission level was as follows:

- coke from coconut shells 8 - 9 kg/h
- coke from peat 5.5 - 6 kg/h
- brown coal 8 - 8.5 kg/h
- peat coal 4 - 4.5 kg/h.

The carbon consumption rate is similar as the mentioned for PCDD/F, as the adsorbent is generally used for both Hg and PCDD/F removal. Carbon consumption rates of 3 kg/t of waste are typical for MSWI. Levels from 0.3 to 20 kg/t of hazardous waste have been reported. The adsorption capacity of the reagent, the Hg inlet concentrations and the required emission level determine the required reagent-dosing rate.

The fire risk is significant with activated carbon. The adsorbent may be mixed with other reagents to reduce the fire risk. 90 % lime and 10 % carbon is used in some cases. The proportion of carbon is generally higher where there are additional process stages that perform acid gas removal (e.g. wet scrubbers).

Applicability

The table below details the specific aspects that relate to the use of activated carbon injection:

Criteria	Evaluation/comment
Waste type	<ul style="list-style-type: none">• provides effective emission reductions across a range of waste types
Plant size range	<ul style="list-style-type: none">• any
New/existing	<ul style="list-style-type: none">• applicable to new installations and as a retrofit
Inter-process compatibility	<ul style="list-style-type: none">• no specific issues
Key location factors	<ul style="list-style-type: none">• none

Table 3.4: Assessment of the applicability of carbon injection for Hg removal

Economics

Additional capital costs of the technique at processes that already have, or intend to use, reagent injection and bag filters are minimal.

Additional operational costs are from:

- reagent consumption
- disposal of residues.

The cost of operations (carbon cost) is approx EUR 125000/yr for a facility treating 65000 tonnes of hazardous waste per year.

Driving force for implementation

The technique has been applied to both new and existing systems as a means of reducing Hg emissions to air.

Example plants

Widely used throughout Europe.

4.4.6.3 Use of condensing scrubbers for flue-gas polishing

Description

This technique has already been described in Sections **Error! Reference source not found.** and **Error! Reference source not found.**, where they are presented primarily from the energy recovery point of view. In addition to the potential benefits of the use of such systems for energy recovery, the condensing effect of the use of a cold scrubber can condense some pollutants. This may reduce releases of pollutants to air, but only to a significant degree where the scrubber is operated at a particularly low temperature e.g. 40 °C.

Achieved environmental benefits

The condensation of pollutants from the flue-gas provides an additional reduction of emissions to air. For mercury this technique cannot generally be relied upon, on its own, to achieve emission levels below 50 µg/Nm³. It is therefore, only be considered as an additional polishing stage.

The condensation of the water from the flue-gas can, when used with downstream flue-gas heating, greatly reduce plume visibility and reduce scrubber water consumption.

Cross-media effects

The condensed water will contain pollutants that require treatment in a water treatment facility prior to discharge. Where an upstream wet scrubbing system is applied the effluent from the condensing scrubber can be treated in the same facility.

The technique is generally only applied where there is a readily available cooling source. For example, a particularly cold (40 °C) district heating water return, which is generally only encountered in colder climates. The application of this technique in other circumstances (it is not reported in other circumstances) would lead to high energy costs for the cooling required.

The low temperature of the stack discharge will reduce the thermal buoyancy of the plume and hence reduce dispersion. This can be overcome by using a taller and/or reduced diameter stack.

Operational data

The temperature of the scrubber effluent is critical for some pollutants, e.g. to ensure mercury is condensed and does not pass through the scrubber to be released to air. The supply of a sufficiently cold cooling medium is, therefore, critical. To be effective for metallic Hg removal, scrubber outlet temperatures of below 40 °C may be required (note: even lower temperatures still are reported in some cases - see below).

Cooling the gas using a gas cooler (i.e. no liquid injection) until the temperature is as low as 5 °C has been reported not to give sufficient results for Hg abatement (ref. Bayer AG Dormagen, DE - HWI).

The low temperature of the flue-gases can result in condensation and, hence, corrosion in the chimney unless lined.

Applicability

The technique is applied primarily as an energy recovery technique and where additional pollutant removal steps have already been incorporated in the installation (e.g. carbon absorption, low pH wet scrubbing).

The technique is not generally applied on its own as a means for pollution control but can be effective as a polishing stage in combination with other systems.

Waste types: Because the technique is applied after the flue-gas cleaning stages, in principle the technique could be applied to any waste type.

Plant size: The technique has been applied at municipal plants of 175000 and 400000 tonnes per year throughput.

New/existing: The technique is applied at/near the end of the FGT system and could therefore be applied to new and existing processes alike.

The technique is only likely to be applicable where energy is not required to provide the additional scrubber cooling necessary to achieve the low temperatures. It is, therefore, only likely to be applicable in colder northern climates, where colder district heating returns provide the energetic driving force.

Economics

The total additional investment for a condensation scrubber is roughly estimated to EUR 3 million.

Driving force for implementation

Additional heat sales are the main driver for using the technique. The additional pollutant removal is a secondary benefit.

Example plants

Several examples of MWI in Sweden, and a SSI in the Netherlands.

4.4.6.4 *Separation of mercury using a resin filter*

Description

After dust separation and the first acidic wet rinse, the raw acids in the ionically bound heavy metal are carried off through an Hg ion exchanger. Mercury is separated off in a resin filter. Then the acid is neutralised using lime milk.

If, after washing, there is still residual mercury in the exhaust air, it is retained by a downstream oven coke filter.

Achieved environmental benefits

High reliability abatement of Hg.

Cross-media effects

The resin filter will require regeneration which results in the transfer of the abated Hg.

Operational data

Information not supplied.

Applicability

The technique is reported to not be widely applied in the sector.

Economics

The technique is indicated by the TWG to be expensive in relation to alternatives.

Driving force for implementation

Information not supplied.

Example plants

RMVA Köln, Germany

4.4.6.5 *Chlorite injection for elemental Hg control*

Description

While oxidised mercury is readily soluble in water and can be removed using a wet scrubber, elemental mercury is not. Therefore, it is difficult to achieve a significant abatement of the elemental mercury in a wet scrubber, unless activated carbon is also used.

The injection of a strong oxidising agent will convert the elemental mercury into oxidised mercury and make its scrubbing possible in the wet scrubber. To avoid that, this agent is used up by reaction with other compounds (e.g. sulphur dioxide) and it is introduced just before the spray nozzles of the first acidic scrubber. The pH of the scrubber is kept between 0.5 and 2.

When the sprayed liquid comes into contact with the acidic fumes containing hydrogen chloride, chlorite is transformed into chlorine dioxide, which is the actual active species. It is to be noted that, unlike other oxidants such as hypochlorite (bleach), the chlorite or chlorine dioxide lacks the ability to introduce a chlorine atom into an aromatic ring, and therefore cannot alter the dioxin balance.

Achieved environmental benefits

Reduced mercury emissions.

Side benefit: NO_x reduction.

Cross-media effects

The use of oxidants favours removal of NO in the scrubber (by changing it into NO₂ which is more soluble). This can lead to problem of high nitrogen content in the waste water. There is no ELV for NH₃ in the WI Directive, but local regulation often sets a limit, as it is a great concern for the aquatic environment.

Operational data

Information not supplied.

Applicability

Incineration of waste; mercury abatement of flue-gas containing at least 400 mg/Nm³ of hydrogen chloride.

Compatible only with wet scrubbing systems.

Economics

The cost of the reagent is the limiting factor.

Driving force for implementation

Information not supplied.

Example plants

Bottrop & Ludwigshafen waste incineration plants in Germany

4.4.6.6 Addition of hydrogen peroxide to wet scrubbers

Description

The purpose of the system is to separate Hg, HCl and SO₂ from flue-gas. In the process all elemental mercury is oxidised to water soluble Hg.

The first step is a quench situated downstream from a baghouse filter (with carbon injection – which will absorb much of the Hg). In the quench the flue-gas is cooled so that it is saturated. After the quench the flue-gas comes into contact with the scrubber fluid which contains hydrogen peroxide and an additive. The scrubber fluid reacts with the flue-gas and an acidic waste water is transferred to neutralisation and precipitation of mercury.

Achieved environmental benefits

Additional reduction of concentration of all types of mercury in flue-gas (together with activated carbon usually at about 99.5 % removal efficiency) as well as reduction of HCl and SO₂.

Cross-media effects

Consumption of reagents added H₂O₂ (35 %wt) 4 - 5 kg/t hazardous waste. The consumption can increase as H₂O₂ reacts not only with Hg but also with all other oxidisable compounds like Fe or heavy metals.

Operational data

Similar to those described for other wet scrubbers.

Applicability

This method is applicable to all types of waste incinerators using wet scrubbing. The best effect is reached if the scrubber is situated downstream from a baghouse filter with carbon injection.

Economics

The cost of an installation is approx EUR 4 million for a capacity of 200000 tonnes of waste.

This is the cost of the wet scrubber including the specific technique mentioned here, but not the additional cost of applying this technique.

H₂O₂ is reported to be costly and its consumption may prove difficult to control.

Driving force for implementation

Technique can be used at both new and existing facilities that needs to cope with new and lower emission limits for Hg, HCl and SO₂.

Example plants

Sydskraft Sakab in Sweden.

4.4.6.7 Use of static activated carbon or coke filters

The use of these techniques, and their benefits for Hg reduction, cross-media effects and other issues has already been described in another Section.

Hg is adsorbed to give emissions to air typically below 30 µg/Nm³.

4. CEMENT CLINKER PRODUCTION FACILITIES

Relevant documents: http://eippcb.jrc.ec.europa.eu/reference/BREF/CLM_Published_def.pdf,

<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:100:FULL:EN:PDF>

1) CLM (production of cement, lime and magnesium oxide) BREF 2013 - adopted

2) Commission Implementing Decision 2013/163/EU of 26 March 2013 establishing the best available techniques (BAT) conclusions under Directive 2010/75/EU of the European Parliament and of the Council on industrial emissions for the production of cement, lime and magnesium oxide (OJ L 100, 9.4.2013, p.1)

Scope: *CLM BREF covers the production of cement, lime and magnesium oxide:*

(a) production of cement clinker in rotary kilns with a production capacity exceeding 500 tonnes per day or in other kilns with a production capacity exceeding 50 tonnes per day;

(b) production of lime in kilns with a production capacity exceeding 50 tonnes per day;

(c) production of magnesium oxide in kilns with a production capacity exceeding 50 tonnes per day.

(Annex I point 3.1 IED)

4.1 Background information

Source: Production of Cement, Lime and Magnesium Oxide (CLM) BREF (adopted 2013)

Chapter 1.3.4.7.1 Mercury

Mercury and its compounds are particularly easily volatilised (highly volatile metal). It is a toxic metallic element and pollution of mercury is understood to be global, diffuse and chronic, so atmospheric emissions from plants have to be reduced. Therefore, to control mercury emissions, it can be necessary to limit mercury input into the kiln system. Mercury and its compounds are not completely precipitated and retained in the kiln system and/or the preheater and therefore, they are not captured in the clinker. They are precipitated on the exhaust gas route due to the cooling of the gas and are partially adsorbed by the raw material particles, depending on the temperature of the waste gas. This portion is precipitated in the kiln exhaust gas filter. Therefore, mercury may only become enriched in the external cycle, where the concentration level and the emissions are mainly determined by the exhaust gas conditions. To prevent a long-cycle increase in mercury emissions, it may become necessary to limit the concentration of the external cycle, e.g. by continuously or intermittently extracting part of the dust collected in the filter system. Furthermore, precipitation and hence, mercury removal increases with decreasing exhaust gas temperature. Indications from measurements performed on cyclone preheater kiln systems show that more than 90 % of mercury exists on particles which are formed at exhaust gas temperatures of below 130 °C. Mercury compounds are then completely removed from the dust collector of the

kiln system. Due to the high collection efficiency of the dust collector, mercury concentrations in the clean gas of rotary kiln systems are often below the detection limit.

The dust from the dust collector can be recirculated back to the cement mill. In the case of the use of waste fuels, the mercury input to the kiln can be limited regularly. Another possibility to reduce mercury emissions is to reduce the off-gas temperature after the conditioning tower to improve the precipitation of mercury and its compounds during dust filtration. Furthermore, in one German plant, activated carbon is injected as an adsorbent to the flue-gas.

Mercury emissions were collected from 306 spot Hg measurements in the clean gas of rotary kilns. In 2004, these measurements were all taken from different plants located in several EU-27 and EU-23+ countries. Six measurements are above the scale. Of these, one is of '0' substitution rate, one is '0–10', two are '10–20' and two measurements are 'above 40'. As explained, mercury is the most volatile heavy metal and has a poor trapping coefficient. Waste fuels undergo a rigorous acceptance and inspection procedure before being used.

Chapter 1.4.7 Reduction of metal emissions

Description and achieved environmental benefits

Feeding materials with a high content of volatile metals into the kiln system should be avoided. The use of materials with a high content of volatile metals such as Hg and Tl should especially be controlled as they will lead to higher emissions whereas other metals will be found within the clinker and the dust. Careful selection and guaranteed characteristics of substances entering the kiln can reduce emissions, e.g. using a quality assurance system to guarantee the characteristics of the waste materials used.

The accumulation of metals, especially thallium, in the internal and external cycles of a cement kiln system results in an increase of emissions with increasing kiln operating time. This can be reduced by partly or completely interrupting these cycles. However, the close interconnection between internal and external cycles means it is sufficient to interrupt only the external cycle. This can be done by discarding the dust collected in the dust collector, instead of returning it to the raw meal. When its chemical composition is suitable, this discarded cement kiln dust can be added directly to the cement milling stage.

As the emitted metals (except part of the mercury) are, to a large extent, bound to dust, abatement strategies for metals are covered by abatement strategies for dust. Effective dust removal reduces metal emissions. One way to minimise mercury emissions is to lower the exhaust temperature. Non-volatile elements remain within the process and exit the kiln as part of the cement clinker composition. When high concentrations of volatile metals (especially mercury) occur, the volatile metals content (especially mercury) in the materials has to be minimised and it can be necessary to limit the input of these substances into the kiln system.

Furthermore, absorption on activated carbon is an option. Semi-volatile metals condense as fine fumes and are captured but with a lower removal efficiency than for non-volatile metals. When non-volatile metals are introduced into the kiln system they are, to a large extent, captured within the clinker.

Cross-media effects

Effective dust removal also reduces metal emissions.

Operational data and applicability

By using powdered activated carbon injection, mercury is adsorbed by activated carbon. Removal efficiency for mercury (metallic and ionic) of about 85 - 95 % is reported for this measure/technique. This results in Hg emissions of 0.01–0.03 mg/Nm³. However, there is no industrial reference method for this measure/technique.

The static activated carbon or coke filter involves the adsorption of mercury with PCDD/F on the activated carbon filter that is a packed-bed with modular partition walls. The use of this measure/technique provides Hg emissions of below 0.03 mg/Nm³. The filter has to be periodically replaced when it is saturated. Wastes, such as used activated carbon with PCDD/F and other pollutants such as mercury, is hazardous waste and has to be managed as such.

However, there is only one activated carbon filter in use in EU-23+ countries, this being in Siggental in Switzerland.

Furthermore, mercury emissions of between <0.01–0.05 mg/Nm³ were also achieved without the injection of activated carbon.

When co-incinerating waste, the requirements of Chapter IV of and Annex VI to the Directive 2010/75/EU have to be met.

Economics

A required quality assurance system to guarantee the characteristics of materials fed to the kiln may result in additional costs.

Effective dust removal can avoid high costs for activated carbon filters.

For the Siggental plant in Switzerland, the City of Zurich financed about 30 % of the total investment cost of approximately EUR 15 million.

Driving force for implementation

Legal requirements.

Example plants

Siggental, Switzerland

4.2 BAT Conclusions

Source: Commission Decision 2013/163/EU (excerpt)

1.2.4 Use of waste

1.2.4.1 Waste quality control

11. In order to guarantee the characteristics of the wastes to be used as fuels and/or raw materials in a cement kiln and reduce emissions, BAT is to apply the following techniques:

A) Apply quality assurance systems to guarantee the characteristics of wastes and to analyse any waste that is to be used as raw material and/or fuel in a cement kiln for: I. constant quality II. physical criteria, e.g. emissions formation, coarseness, reactivity, burnability, calorific value III. chemical criteria, e.g. chlorine, sulphur, alkali and phosphate content and relevant metals content

B) Control the amount of relevant parameters for any waste that is to be used as raw material and/or fuel in a cement kiln, such as chlorine, relevant metals (e.g. cadmium, **mercury**, thallium), sulphur, total halogen content

C) Apply quality assurance systems for each waste load

1.2.8 Metal emissions

28. In order to minimise the **emissions of metals from the flue-gases of the kiln firing processes**, BAT is to use one or a combination of the following techniques:

A) Selecting materials with a low content of relevant metals and limiting the content of relevant metals in materials, especially mercury

B) Using a quality assurance system to guarantee the characteristics of the waste materials used

C) Using effective dust removal techniques as set out in BAT 17

1.3.5.1 Use of waste fuels

1.3.5.1.1 Waste quality control

37. In order to guarantee the **characteristics of waste to be used as fuel in a lime kiln**, BAT is to apply the following techniques:

A) Apply a quality assurance system to guarantee and control the characteristics of wastes and to analyse any waste that is to be used as fuel in the kiln for:

I. constant quality

II. physical criteria, e.g. emissions formation, coarseness, reactivity, burnability, calorific value

III. chemical criteria, e.g. total chlorine content, sulphur, alkali, and phosphate content and relevant metals content (e.g. total chromium, lead, cadmium, **mercury**, thallium)

B) Control the amount of relevant components for any waste that is to be used as fuel, such as total halogen content, metals (e.g. total chromium, lead, cadmium, **mercury**, thallium) and sulphur

1.3.9 Metal emissions

53. In order to minimise the emissions of metals from the **flue-gases of kiln firing processes**, BAT is to use one or a combination of the following techniques:

A) Selecting fuels with a low content of metals

B) Using a quality assurance system to guarantee the characteristics of the waste fuels used

C) Limiting the content of relevant metals in materials, **especially mercury**

D) Using one or a combination of dust removal techniques as set out in BAT 43

1.4.6 Use of wastes as fuels and/or raw materials

69. In order to guarantee the characteristics of **waste** to be used as fuels and/or raw materials in **magnesium oxide kilns**, BAT is to use the following techniques:

A) To select suitable wastes for the process and the burner

B) To apply quality assurance systems to guarantee and control the characteristics of wastes and to analyse any waste that is to be used for: I. availability II. constant quality III. physical criteria, e.g. emissions formation, coarseness, reactivity, burnability, calorific value IV. chemical criteria, e.g. chlorine, sulphur, alkali and phosphate content and relevant metals (e.g. total chromium, lead, cadmium, **mercury**, thallium) content

C) To control the amount of relevant parameters for any waste that is to be used, such as total halogen content, metals (e.g. total chromium, lead, cadmium, **mercury**, thallium) and sulphur.