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### Economic Commission for Europe

Executive Body for the Convention on Long-range  
Transboundary Air Pollution

### **Guidance document on best available techniques for controlling emissions of heavy metals and their compounds from the source categories listed in annex II to the Protocol on Heavy Metals**

#### *Summary*

At its thirty-first session, the Executive Body to the Convention on Long-range Transboundary Air Pollution adopted decisions amending the Protocol on Heavy Metals and its annexes (ECE/EB.AIR/113/Add.1, decisions 2012/5 and 2012/6), and adopted a guidance document on best available techniques for controlling emissions of heavy metals and their compounds from the source categories listed in annex II to the Protocol (*ibid.*, decision 2012/7). The present document contains the final version of the guidance document, as adopted.

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## List of abbreviations and acronyms

ACI	Activated carbon injection
As	Arsenic
BAT	Best available techniques
BOF	Basic oxygen furnace
BREF <sup>1</sup>	Best available techniques reference document
Ca.	Circa
CaBr <sub>2</sub>	Calcium bromide
Cd	Cadmium
CEN	European Committee for Standardization
CFA	Circulating fluidized-bed absorber
Cl <sub>2</sub>	Chlorine
Co	Cobalt
Cr	Chromium
Cu	Copper
Cu <sub>2</sub> HgI <sub>4</sub>	Copper(I) tetraiodomercurate(II)
cts/kWh	Cents per kilowatt hour
EAF	Electric arc furnace
ECE	United Nations Economic Commission for Europe
ELV	Emission limit value
EPA	Environmental Protection Agency
ESP	Electrostatic precipitator
FF	Fabric filter
FGD	Flue gas desulphurization
HEPA	High efficiency particulate air filter
H <sub>2</sub> O	Water
H <sub>2</sub> SeO <sub>3</sub>	Selenious acid
Hg	Mercury
HgCl <sub>2</sub>	Mercuric chloride
Hg <sub>2</sub> Cl <sub>2</sub>	Mercury(I) chloride

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<sup>1</sup> For latest reference documents giving information on all relevant sectors, techniques and processes used, current emission and consumption levels, BAT and emerging techniques, see <http://eippcb.jrc.es/reference/>.

Hg <sup>+</sup>	Mercury ion
HgO	Mercury oxid
HgSO <sub>4</sub>	Mercury(II) sulphate
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
IGCC	Integrated gasification combined-cycle
K	Kelvin
kPa	Kilopascal
kWel	Kilowatt electric
mg/l	Milligram per litre
mg/m <sup>3</sup>	Milligram per cubic metre
mg/Nm <sup>3</sup>	Milligram per normal cubic metre
mg/t	Milligram per ton
Mg	Megagram, metric ton
Mn	Manganese
MRU	Mercury removal units
MRT	Molecular Recognition Technology
µg/Nm <sup>3</sup>	Microgram per normal cubic metre
Ni	Nickel
NO <sub>x</sub>	Nitrogen oxide
O <sub>2</sub>	Oxygen
Pb	Lead
PARCOM	Commission for the Prevention of Marine Pollution from Land-based Sources
PCDD/F	Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran
PM	Particulate matter
ppm	Parts per million
Sb	Antimony
SCR	Selective Catalytic Reduction
Se	Selenium
Sn	Tin
SO <sub>2</sub>	Sulphur dioxide
SO <sub>3</sub>	Sulphur trioxide
SO <sub>x</sub>	Sulphur oxide
TOC	Total organic carbon
UNEP	United Nations Environment Programme
V	Vanadium

## I. Introduction

1. This guidance document addresses the control options for the heavy metals cadmium, lead and mercury. It aims to provide Parties to the Protocol on Heavy Metals to the Convention on Long-range Transboundary Air Pollution with guidance on identifying best available techniques for stationary sources to enable them to meet their Protocol obligations.
2. In this guidance document the definition of best available techniques (BAT) is identical to the definition of BAT in annex III to the Protocol on Heavy Metals.

### **Definition of best available techniques in annex III to the Protocol on Heavy Metals (paras. 2 and 3)**

2. The expression “best available techniques” (BAT) means the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing the basis for emission limit values (and other permit conditions) designed to prevent and, where that is not practicable, to reduce emissions and their impact on the environment as a whole:

(a) “Techniques” includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

(b) “Available” techniques means those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the territory of the Party in question, as long as they are reasonably accessible to the operator;

(c) “Best” means most effective in achieving a high general level of protection of the environment as a whole.

3. Criteria for determining BAT are as follows:

(a) The use of low-waste technology;

(b) The use of less hazardous substances;

(c) The furthering of recovery and recycling of substances generated and used in the process and of waste, where appropriate;

(d) Comparable processes, facilities or methods of operation which have been tried with success on an industrial scale;

(e) Technological advances and changes in scientific knowledge and understanding;

(f) The nature, effects and volume of the emissions concerned;

(g) The commissioning dates for new or existing installations;

(h) The length of time needed to introduce the best available technique;

(i) The consumption and nature of raw materials (including water) used in the process and energy efficiency;

(j) The need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risks to it;

(k) The need to prevent accidents and to minimize their consequences for the environment;

(l) Information published by national and international organizations.

The concept of BAT is not aimed at the prescription of any specific technique or technology, but at taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions.

3. The information regarding emission control performance and costs is based on official documentation of the Executive Body and its subsidiary bodies, in particular documents received and reviewed by the Task Force on Heavy Metals. Other relevant international information, such as BAT reference documents (BREFs) from the European Integrated Pollution Prevention and Control Bureau, the United Nations Environment Programme (UNEP) 2002 and 2008 Global Mercury Assessments and various technical reports from the United States Environmental Protection Agency (EPA), Environment Canada and the European Commission, as well as information provided directly by experts, has also been taken into consideration.

4. Experience with new products and new plants incorporating low-emission techniques, as well as with the retrofitting of existing plants, is growing continuously; this guidance document may, therefore, need updating.

5. Although this guidance document lists a number of measures spanning a range of costs and efficiencies, it cannot be considered as an exhaustive statement of control options. The choice of measures for any particular case will depend on, and may be limited by, a number of factors, such as economic circumstances, technological infrastructure, any existing emission control device, safety, energy consumption and whether the source is a new or existing one.

6. This guidance document takes into account emissions of cadmium (Cd), lead (Pb) and mercury (Hg) and their compounds, in solid (particle-bound) and/or gaseous form. Speciation of these compounds is, in general, not considered here. Nevertheless, the efficiency of emission control devices with regard to the physical properties of the heavy metal, especially in the case of mercury, has been taken into account.

7. Emission values expressed as milligram per cubic metre ( $\text{mg}/\text{m}^3$ ) refer to standard conditions (volume at 273.15 Kelvin (K), 101.3 kilopascal (kPa), dry gas) not corrected for oxygen content unless otherwise specified, and are calculated in accordance with the draft European Committee for Standardization (CEN) standard and, in some cases, national sampling and monitoring techniques.

8. The content of heavy metals in dust varies widely, e.g., between sectors, raw material and fuels. To obtain information on actual emissions and to derive emission factors, monitoring of heavy metals is necessary.

## II. General options for reducing emissions of heavy metals and their compounds

9. There are several possibilities for controlling or preventing heavy metal emissions. Emission reduction measures focus on add-on technologies and process modifications (including maintenance and operating control). The following measures, which may be implemented depending on the wider technical and/or economic conditions, are available:

- (a) Application of low-emission process technologies, in particular in new installations;
- (b) Off-gas cleaning (secondary reduction measures) with filters, scrubbers, absorbers, etc.;
- (c) Change or preparation of raw materials, fuels and/or other feed materials (e.g., use of raw materials with low heavy metal content);
- (d) Best management practices such as good housekeeping, preventive maintenance programmes, or primary measures such as the enclosure of dust-creating units;
- (e) Appropriate environmental management techniques for the use and disposal of certain products containing Cd, Pb and/or Hg.

10. It is necessary to monitor abatement procedures to ensure that appropriate control measures and practices are properly implemented and achieve an effective emission reduction. Monitoring abatement procedures will include:

- (a) Developing an inventory of those reduction measures identified above that have already been implemented;
- (b) Comparing actual reductions in Cd, Pb and Hg emissions with the objectives of the Protocol;
- (c) Characterizing quantified emissions of Cd, Pb and Hg from relevant sources with appropriate techniques;
- (d) Regulatory authorities periodically auditing abatement measures to ensure their continued efficient operation.

11. Emission reduction measures should be cost-efficient. Cost-efficient strategy considerations should be based on total costs per year per unit abated (including capital and operating costs). Emission reduction costs should also be considered with respect to the overall process.

## III. Control techniques

12. The major categories of available control techniques for Cd, Pb and Hg emission abatement are primary measures, such as raw material and/or fuel substitution and low-emission process technologies, and secondary measures, such as fugitive emissions control and off-gas cleaning. Sector-specific techniques are specified in chapter IV.

13. The data on efficiency are derived from operating experience and are considered to reflect the capabilities of current installations. The overall efficiency of flue gas and diffuse emission reductions depends to a great extent on the evacuation performance of the gas and

dust<sup>2</sup> collectors (e.g., suction hoods). Capture/collection efficiencies of over 99% have been demonstrated. In particular cases experience has shown that control measures are able to reduce overall emissions by 90% or more.

14. In the case of particle-bound emissions of Cd, Pb and Hg, the metals can be captured by dust-cleaning devices. Typical dust concentrations after gas cleaning with selected techniques are given in table 1. Most of these measures have generally been applied across sectors. The minimum expected performance of selected techniques for capturing gaseous mercury is outlined in table 2. The degree of mercury control shown in this table is largely dependent on the chemical state and form of the mercury (e.g., oxidized, elemental or particle bound). The application of these measures depends on the specific processes and is most relevant if concentrations of mercury in the flue gas are high.

Table 1  
**Performance of dust-cleaning devices expressed as hourly average dust concentrations**

<i>Dust-cleaning devices</i>	<i>Dust concentrations after cleaning (mg/m<sup>3</sup>)</i>
Fabric filters	< 1–5
Fabric filters, membrane type	< 1
Dry electrostatic precipitators	< 5–15
Wet electrostatic precipitators	< 1–5
High-efficiency scrubbers	< 20
Ceramic filters	0.1–1

*Source:* “Assessments of technological developments: Best available techniques (BAT) and limit values” report submitted to the fourth meeting of the Task Force on Heavy Metals (Vienna, 6–8 June 2007). Available from <http://www.unece.org/fileadmin/DAM/env/lrtap/TaskForce/tfhm/Post-Ottawa.htm>.

*Note:* Medium- and low-pressure scrubbers and cyclones generally show lower dust removal efficiencies and are not considered to be BAT on their own.

Table 2  
**Minimum expected performance of mercury separators expressed as hourly average mercury concentrations**

<i>Mercury separator</i>	<i>Mercury content after cleaning (mg/m<sup>3</sup>)</i>
Selenium filter	< 0.01
Selenium scrubber	< 0.2
Carbon filter	< 0.01
Sulphur impregnated carbon filter	< 0.01
Carbon injection plus dust separator	< 0.05
Odda Norzink chloride process	< 0.1
Lead sulphide process	< 0.05
Bolkem (thiosulphate) process	< 0.1
Injection of brominated activated carbon plus dust separator	0.001

<sup>2</sup> The terms “dust” and “particulate matter” are used interchangeably throughout this document.



15. Care should be taken to ensure that these control techniques do not create other environmental problems, e.g., due to more water pollution from liquid effluents. The fate of captured dust as well as of mercury-charged activated carbon resulting from improved gas cleaning must also be taken into consideration. A negative environmental impact from the handling of such wastes will reduce the gain from lower emissions of process dust and fume into the air. Studies by the United States Environmental Protection Agency show that the mercury is well-captured on the activated carbon and does not leach, e.g., from landfills.

16. Emission reduction measures can focus on process techniques as well as on off-gas cleaning. The two are not independent of each other; the choice of a specific process might exclude some gas-cleaning methods.

17. The choice of a control technique will depend on such parameters as the pollutant concentration and/or speciation in the raw gas, the gas volume flow, the gas temperature, and others. Therefore, the fields of application may overlap; in that case, the most appropriate technique must be selected according to case-specific conditions.

18. Adequate measures to reduce stack gas emissions in various sectors are described below. Fugitive emissions have to be taken into account. Dust emission control associated with the discharging, handling and stockpiling of raw materials or by-products, although not relevant to long-range transport, may be important for the local environment. The emissions can be reduced by moving these activities to completely enclosed buildings, which may be equipped with ventilation and dedusting facilities, spray systems or other suitable controls. When stockpiling in unroofed areas, the material surface should be otherwise protected against wind entrainment. Stockpiling areas and roads should be kept clean.

19. The investment/cost figures listed in the tables have been collected from various sources and are highly case-specific. They depend on such factors as plant capacity, removal efficiency and raw gas concentration, type of technology and the choice of new installations as opposed to retrofitting.

## **IV. Sectors**

20. This chapter contains a table per relevant sector with the main emission sources, control measures based on the best available techniques, their specific reduction efficiency and the related costs, where available. Unless stated otherwise, the reduction efficiencies in the tables refer to direct stack gas emissions.

### **A. Combustion of fossil fuels in utility and industrial boilers (annex II, category 1)**

21. The combustion of coal in utility and industrial boilers is a major source of anthropogenic mercury emissions. The heavy metal content is normally several orders of magnitude higher in coal than in oil or natural gas. Fuel switching is sometimes an option if fuels with a lower mercury content are available (e.g., natural gas or specific types of coal with lower mercury content).

22. Improved energy conversion efficiency and energy conservation measures will result in a decline in the emissions of heavy metals because of reduced fuel requirements. Combusting natural gas or alternative fuels with lower heavy metal content instead of coal would also result in a significant reduction in heavy metal emissions such as mercury and can be regarded as one form of BAT. Integrated gasification combined-cycle (IGCC) power

plant technology is a high efficiency technology that can have reduced emissions compared to large scale power production based on solid fuels that do not use IGCC.

23. With the exception of mercury, heavy metals are mostly emitted in solid form in association with fly-ash particles. Therefore, BAT to reduce the emissions of heavy metals is generally the application of high performance dedusting devices such as electrostatic precipitators (ESP) or fabric filters (FF).

24. Beneficiation, e.g., “washing” or “bio-treatment”, of coal reduces the heavy metal content associated with the inorganic matter in the coal, but is connected with emissions of heavy metals to water. However, the degree of heavy metal removal with this technology varies widely. Furthermore, the addition of halogens (especially bromides) to the fuel can promote the oxidation to less volatile mercury compounds, which can be removed in the ESP and flue gas desulphurization (FGD).

25. With regard to BAT for dust, for the combustion of coal and lignite and of liquid fuels a total dust removal of more than 99.5% can be obtained with ESP (dust reduction rate > 99.5%) or FF (dust reduction rate > 99.95%). ESP and FF are both considered as BAT with daily average values for the concentration of dust in the range of below 5 mg/m<sup>3</sup> to up to 20 mg/m<sup>3</sup> (given a flue gas oxygen content of 6% for solid fuels and 3% for liquid fuels).<sup>3</sup> When operated with well and continuously maintained equipment, large coal-fired power plants fitted with ESP or FF can achieve yearly average values of < 5 mg/m<sup>3</sup>. With the exception of mercury, heavy metal emissions can be reduced by at least 90% to 99% using an ESP or FF, the lower figure for the more easily volatilized elements.

26. Mercury is at least partly and up to 90% present in the vapour phase and its collection by dust control devices is highly variable. Low filter temperature helps to reduce the gaseous mercury off-gas content. By injecting chemically treated activated carbon, e.g., brominated activated carbon, into the flue gas stream prior to the ESP or FF, mercury and mercury salts can be abated by more than 90% (Hg concentration < 1 microgram per normal cubic metre (µg/Nm<sup>3</sup>)) and taken out with the fly ash.

27. The application of techniques to reduce emissions of nitrogen oxides by selective catalytic reduction (SCR) in combination with removal of sulphur dioxide from the flue gas can also remove heavy metals. For ESP or FF operated in combination with wet FGD techniques, an average removal rate of 75% for Hg can be obtained, for certain coals, and/or if an adequate amount of oxidizing agent (e.g., halogens) are present in the flue gas. If a high dust SCR device is added upstream of the FGD an average removal rate of 90% can be obtained for Hg, as long as adequate amounts of halogens are present in the flue gas (e.g., naturally present chlorine or added bromine). The best levels of mercury control are generally achieved by emission control systems (e.g., SCR, FGD plus particulate control device) that use FF. The capture of mercury can be enhanced by injecting (chemically treated) activated carbon or adding other oxidizing compounds into the flue gas upstream of the ESP or FF or by distributing the flue gas throughout a carbon filter bed, except for high-volume combustion sources.

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<sup>3</sup> In the guidance document on control techniques for emissions of sulphur, nitrogen oxides, volatile organic compounds and particulate matter (including PM<sub>10</sub>, PM<sub>2.5</sub> and black carbon) from stationary sources of the Gothenburg Protocol (ECE/EB.AIR/117, forthcoming), adopted by the Executive Body in 2012, the emissions of dust for existing installations of 50MWth–100 MWth in the range of 5 mg/m<sup>3</sup>–30 mg/m<sup>3</sup> are identified as BAT. For existing installations, in the range of 100 MWth–300 MWth, dust emissions in the range of 5 mg/m<sup>3</sup>–25 mg/m<sup>3</sup> are identified as BAT.

28. The least costly retrofit options for the control of Hg emissions from units with ESP or FF are believed to include:

- (a) Modification of dry FGD systems by the use of appropriate sorbents for the capture of Hg;
- (b) Injection of a sorbent upstream of the ESP or FF;
- (c) Injection of a sorbent between the ESP and a pulse-jet FF retrofitted downstream of the ESP;
- (d) Installation of a semi-dry circulating fluidized-bed absorber (CFA) upstream of an existing ESP used in conjunction with sorbent injection.

29. The wet scrubber efficiency for mercury removal can be increased by:

- (a) Improving the liquid-to-gas ratio;
- (b) Wet FGD tower design. Research has shown that tray tower or open spray tower designs are effective in removing oxidized mercury from boiler flue gas;
- (c) Injection of activated carbon impregnated with additives (e.g., sulphur, bromine) increasing adsorption capacity;
- (d) Increasing the ratio of oxidized mercury by:
  - (i) Addition of SCR device upstream of the wet scrubber;
  - (ii) Pre-treating coal (e.g., calcium bromide (CaBr<sub>2</sub>)).

30. The most cost-effective approach to control mercury emission from large combustion plants is an integrated multi-pollutant (sulphur dioxide (SO<sub>2</sub>), nitrogen oxide (NO<sub>x</sub>), particulate matter (PM) and Hg) control technology. By applying a combination of SCR, FGD and ESP or FF, the concentration of mercury (gaseous and solid) in the flue gases can be reduced to levels below 0.003 mg/m<sup>3</sup> as daily average at 6% oxygen (O<sub>2</sub>). A gas-phase oxidation process to simultaneously capture sulphur oxide (SO<sub>x</sub>), NO<sub>x</sub> and Hg is under demonstration.

Table 3

**Control measures, reduction efficiencies and costs for solid and liquid fossil-fuel combustion emissions**

<i>Control measure(s)</i>	<i>Reduction efficiency (%)</i>	<i>Indicative abatement costs (total costs US\$)</i>
Switch to fuels with lower heavy metals emissions	Dust 70–100 <sup>a</sup>	Highly case-specific
Coal cleaning	Cd, Pb: up to 80 <sup>b</sup> Hg: <sup>c</sup> 10–50	
ESP (cold-side)	Cd, Pb: > 90 <sup>a</sup> Hg: <sup>c</sup> 10–40 <sup>a</sup> PM: > 99.5–99.8 <sup>b</sup>	Specific investment US\$ 5/m <sup>3</sup> –US\$ 10/m <sup>3</sup> waste gas per hour (> 200,000 m <sup>3</sup> /h) <sup>a</sup>
(Wet) flue gas desulphurization (FGD) <sup>d</sup>	Cd, Pb: > 90 <sup>a</sup> Hg: <sup>e</sup> 30–70 <sup>i,b</sup>	15/Mg–30/Mg waste gas <sup>a</sup>
FF	Cd: > 95 <sup>a</sup> Pb: > 99 <sup>a</sup> Hg: <sup>e</sup> 10–60 <sup>a</sup> PM > 99.95 <sup>b</sup>	Specific investment US\$ 8/m <sup>3</sup> –US\$15/m <sup>3</sup> waste gas per hour (> 200,000 m <sup>3</sup> /h) <sup>a</sup>

<i>Control measure(s)</i>	<i>Reduction efficiency (%)</i>	<i>Indicative abatement costs (total costs US\$)</i>
ESP or FF, and FGD	Hg: <sup>e</sup> 75 (average) <sup>g</sup>	US\$ 0.03– US\$ 0.15/kWh <sup>h</sup>
ESP or FF, and sorbent injection	Hg: 50– > 95	90% control: US\$ 35,000–US\$ 70,000 per pound <sup>f</sup> Hg removed (US\$ 0.0003–US\$ 0.002/kWh) <sup>b</sup>
Injection of (brominated) activated carbon (ACI)	Hg: > 90	US\$ 15,000 per pound Hg removed/US\$ 0.0012/kWh (ACI only)/ €6 million–€30 million per installation or €0.0001 per kWh); US\$ 1 million–US\$ 2 million per installation; <sup>j</sup> US\$ 0.0005–US\$0.003/kWh <sup>k</sup>
ESP or FF, and carbon filter bed	Hg: 80–90 <sup>b</sup>	US\$ 33,000–US\$ 38,000 per pound Hg removed <sup>b</sup>
ESP or FF, and FGD and SCR (multi-pollutant approach)	Hg: 90 (average) <sup>b</sup> Hg: 30–70 for sub-bituminous coal and lignite <sup>h</sup>	No additional costs for Hg reduction based on the multi-pollutant approach for SO <sub>2</sub> and NO <sub>x</sub> <sup>l</sup>

<sup>a</sup> See Protocol on Heavy Metals, annex III.

<sup>b</sup> See “Assessments of technological developments: Best Available Techniques (BAT) and limit values,” draft background document for the third meeting of the Task Force Heavy Metals, April 2006; available from <http://www.unece.org/env/lrtap/taskforce/tfhm/3rdmeeting.html>.

<sup>c</sup> Dependent on the type of coal used.

<sup>d</sup> Hg removal efficiencies increase with the proportion of ionic mercury. High-dust SCR installations facilitate Hg(II) formation. Removal can be facilitated by having adequate halogens present in the flue gas.

<sup>e</sup> Dependent upon the form of mercury present (HgO, Hg<sup>+</sup>).

<sup>f</sup> This efficiency is primarily for SO<sub>2</sub> reduction. Reduction in heavy metal emissions is a side benefit. (Specific investment US\$ 60– US\$250/kW<sub>e</sub>). Wet scrubbers installed primarily for mercury cost between US\$ 76,000 and US\$ 174,000 per pound of mercury removed.

<sup>g</sup> See O. Rentz et al., “Erstellung eines wissenschaftlichen Gutachtens zur Unterstuetzung des ‘Review der Technischen Anhaenge des UNECE Schwermetallprotokolls’” (Karlsruhe, French-German Institute for Environmental Research, November 2006).

<sup>h</sup> See European Union, *Integrated Pollution Prevention and Control: Reference Document on Best Available Techniques for Large Combustion Plants* (2006); available from [http://eippcb.jrc.es/reference/BREF/lcp\\_bref\\_0706.pdf](http://eippcb.jrc.es/reference/BREF/lcp_bref_0706.pdf).

<sup>i</sup> The international pound equals 0.45359237 kilograms.

<sup>j</sup> Information provided by the Albemarle chemical company (<http://albemarle.com/Albemarle/Home-3.html>).

<sup>k</sup> See *IPM Model — Revisions to Cost and Performance for APC Technologies: Mercury Control Cost Development Methodology* (Chicago, United States, Sargent & Lundy, March 2011); available from [http://www.epa.gov/airmarkets/progsregs/epa-ipm/docs/append5\\_3.pdf](http://www.epa.gov/airmarkets/progsregs/epa-ipm/docs/append5_3.pdf).

<sup>l</sup> See “Reduction of mercury emissions from coal fired power plants”, Informal document No. 3, forty-eighth session of the Working Group on Strategies and Review (2011); available from <http://www.unece.org/env/lrtap/workinggroups/wgs/docs48thsession.html>.

## B. Primary iron and steel industry (annex II, categories 2 and 3)

31. This section deals with emissions from sinter plants, pellet plants, blast furnaces, and steelworks with a basic oxygen furnace (BOF) with subsequent casting. In integrated steelworks, sinter plants and steelworks dominate the overall emissions for most atmospheric pollutants including heavy metals. Emissions of Cd, Pb and Hg occur in association with dust. The content of the heavy metals of concern in the emitted dust

depends on the composition of the raw materials, and the types of alloying metals. The most relevant emission reduction measures are outlined in table 4. FFs should be used whenever possible; if conditions make this impossible, ESPs and/or high-efficiency scrubbers may be used.

32. The following techniques are considered as BAT:

(a) **For sinter plants**, BAT for dedusting of primary waste gas is to reduce dust emissions from sinter strand waste gas by means of a bag filter. For existing plants, if bag filters are not applicable, an advanced ESP should be used. BAT for primary emissions from sinter strands is to prevent or reduce mercury emissions by selecting raw material with low mercury content or to treat waste gases in combination with activated carbon or activated lignite coke injection. A part of the waste gas should be recirculated if applicable in order to reduce the waste gas as well as some other pollutants (e.g., NO<sub>x</sub> or polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/F)). Please note that waste gas recycling does not affect the specific emissions of heavy metals per ton of sinter. BAT for secondary emissions from sinter strand discharge, sinter crushing, cooling, screening and conveyer transfer points is to prevent dust emissions and/or to achieve an efficient extraction of dust emissions by using a combination of the following techniques:

- (i) Hooding and/or enclosure;
- (ii) ESP or a bag filter.

The emissions level for mercury from sinter plants is < 0.03 mg/Nm<sup>3</sup>–0.05 mg/Nm<sup>3</sup>;

(b) **For pelletization plants**, BAT is to reduce the dust emissions in the waste gases from the raw materials' pre-treatment, drying, grinding, wetting, mixing and balling; from the induration strand and from the pellet handling and screening, by using one or a combination of the following techniques:

- (i) ESP;
- (ii) Bag filter;
- (iii) Wet scrubber;

(c) **For blast furnaces:**

(i) BAT for casting houses (tap holes, runners, torpedo ladles charging points, skimmers) is to prevent or reduce diffuse emissions by using the following techniques:

- a. Covering the runners;
- b. Optimizing the capture efficiency for diffuse dust emissions and fumes with subsequent off-gas cleaning by means of an electrostatic precipitator or bag filter;
- c. Fume suppression using nitrogen while tapping, where applicable and where no collecting and dedusting system for tapping emissions is installed;

(ii) BAT is to minimize the release of blast furnace gas during charging by using one or a combination of the following techniques:

- a. Bell-less top with primary and secondary equalizing;
- b. Gas or ventilation recovery system.

(iii) For blast furnace gas cleaning BAT is to reduce dust emissions by using one or a combination of the following techniques:

- a. Dry pre-dedusting devices (such as deflectors, dust catchers, cyclones and ESP);
- b. Subsequent dust abatement (such as hurdle-type scrubbers, venture scrubbers, annular gap scrubbers, wet electrostatic precipitators and disintegrators);
- (d) **For BOF plants:**
  - (i) BAT for BOF gas recovery by suppressed combustion is to extract the BOF gas during blowing as much as possible and to clean it by using the following techniques in combination:
    - a. Suppressed combustion process;
    - b. Pre-dedusting to remove coarse dust by means of dry separation techniques (e.g., deflector, cyclone) or wet separators;
    - c. Dust abatement by means of:
      - i. Dry dedusting (e.g., ESP) for new and existing plants;
      - ii. Wet dedusting (e.g., wet electrostatic precipitators or scrubber) for existing plants;
  - (ii) BAT for BOF gas recovery during oxygen blowing in the case of full combustion is to reduce dust emissions by using one of the following techniques:
    - a. Dry dedusting (e.g., ESP or bag filter) for new and existing plants;
    - b. Wet dedusting (e.g., wet ESP or scrubber) for existing plants.

33. BAT for secondary dedusting is to minimize dust emissions by means of process integrated techniques, such as general techniques to prevent or control diffuse or fugitive emissions, and by using appropriate enclosure and hoods with efficient extraction and a subsequent off-gas cleaning by means of a bag filter or an ESP or any other technique with the same removal efficiency. This applies also for the emissions from the following processes:

- (a) Reladling of hot metal from the torpedo ladle (or hot metal mixer) to the charging ladle;
- (b) Hot metal pre-treatment (i.e., preheating of vessels, desulphurization, dephosphorization, deslagging, hot metal transfer processes and weighing);
- (c) BOF-related processes like the preheating of vessels, slopping during oxygen blowing, hot metal and scrap charging, tapping of liquid steel and slag from BOF;
- (d) Secondary metallurgy and continuous casting.

For BOF plants the overall average dust collection efficiency using BAT is well above 90%.

Table 4

**Emission sources, control measures, dust reduction efficiencies and costs for the primary iron and steel industry**

<i>Emission source</i>	<i>Control measure(s)</i>	<i>Dust reduction efficiency (%)</i>	<i>Dust emission levels (mg/Nm<sup>3</sup>)</i>	<i>Abatement costs</i>
Sinter plants:	Emission optimized sintering	ca. 50	–	–

<i>Emission source</i>	<i>Control measure(s)</i>	<i>Dust reduction efficiency (%)</i>	<i>Dust emission levels (mg/Nm<sup>3</sup>)</i>	<i>Abatement costs</i>
primary emissions				€3,000–€16,000/annum <sup>a</sup>
	Bag filters	> 99	1–15	
			20–40	
			Hg:	
			< 0.03	
	Advanced ESP (Moving Electrode ESP, ESP pulse system, high voltage ESP, etc.)	–	0.05 mg/Nm <sup>3</sup>	–
Sinter plants: secondary emissions	Bag filters	–	< 10	–
	ESP	–	< 30	–
Pellet plants	ESP + lime reactor + fabric filters	> 99	–	–
	Scrubbers or semi-dry desulphurization and subsequent dedusting	> 95	< 10	–
	Crushing, grinding, drying	–	< 20	–
	Other process steps	–	< 10–15	–
Blast furnaces: gas cleaning				ESP: US\$ 0.24–US\$ 1/Mg pig iron
	ESP	> 99	< 10	–
	Wet scrubbers	> 99	< 10	–
	Wet ESP	> 99	< 10	–
Blast furnace	Capture of diffuse emissions from the casting bay/cast house and subsequent dedusting by FF or ESP			
	Diffuse emissions from casting bay/ cast house	–	1–15	–
BOF	Primary dedusting:			
	– dry ESP or FF	> 99	10–30	Dry ESP: US\$ 2.25/Mg steel
	– wet ESP (existing plants)		< 50	
	Secondary dedusting (including hot metal treatment and secondary metallurgy):			
	– dry ESP		< 20	FF: US\$ 0.26/Mg steel
	– FF	> 97	1–10	
Fugitive emissions	Closed conveyor belts, enclosure, wetting stored feedstock, cleaning of roads	80–99	–	–

<sup>a</sup> See “Assessments of technological developments: Best Available Techniques (BAT) and limit values,” draft background document for the third meeting of the Task Force Heavy Metals, April 2006; available from <http://www.unece.org/env/lrtap/taskforce/tfhm/3rdmeeting.html>.

34. Direct reduction and smelting reduction are proven alternative iron-making processes to the coke oven/blast furnace route that may reduce the need for sinter plants and

blast furnaces in the future. The application of these technologies depends on the ore characteristics and requires the resulting product to be processed in an electric arc furnace, which should be equipped with appropriate controls. As the heavy metals originate from the raw material, their emission levels are determined by the level of emission control (not by the choice of process steps).

### C. Secondary iron and steel industry (annex II, category 3)

35. The secondary production of iron and steel is mainly based on the use of Electric Arc Furnaces (EAF). BAT for EAF primary and secondary dedusting (including scrap preheating, charging, melting, tapping, ladle furnace and secondary metallurgy) is to achieve an efficient extraction of dust emissions from all emission sources by using one of the techniques listed below and to use subsequent dedusting by means of an FF:

- (a) A combination of direct off-gas extraction and hood systems;
- (b) Direct gas extraction and doghouse systems;
- (c) Direct gas extraction and total building evacuation.

Ninety-eight per cent and more collection efficiency of primary and secondary emissions from EAF are achievable and considered as BAT. The captured off-gases can be treated with activated carbon injection and subsequent dedusting by means of a fabric filter, which reduces the dust content to less than 5 mg/Nm<sup>3</sup> and can achieve emission levels for mercury of < 0.05 mg/Nm<sup>3</sup>. The specific dust emissions (including diffuse emissions directly related to the process) range between 0.06 and 0.35 kg/Mg steel.

36. Mercury emissions can vary strongly from charge to charge depending on scrap composition/quality. Mercury emissions in the sector are expected to decline due to the progressive phasing out of mercury following the full implementation of several directives and regulations in place, such as the End-of-Life Vehicles Directive,<sup>4</sup> the Waste Electrical and Electronic Equipment Directive<sup>5</sup> and the Batteries Directive<sup>6</sup> in the European Union. For the melting of scrap, open-hearth furnaces are still in use, but are about to be phased out because of their inefficiency.

37. The content of the heavy metals of concern in the emitted dust depends on the composition of the iron and steel scrap and the types of alloying metals added in steelmaking. Mercury emissions can strongly vary from charge to charge. Measurements at EAF have shown that 95% of emitted mercury and 25% of cadmium emissions occur as vapour, which makes them difficult to capture. Exceedances of mercury emission limit values (ELVs) have been observed, indicating that mercury-bearing components still occur in scrap sources; emissions factors for mercury of 170 mg/t liquid steel could be detected.<sup>7</sup> It is recommended as a best environmental practice to implement operating practices to prevent and minimize the presence of mercury and other heavy metals in the scrap, e.g., to remove mercury-bearing components prior to recycling in secondary iron and steel

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<sup>4</sup> Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of-life vehicles.

<sup>5</sup> Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment.

<sup>6</sup> Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC.

<sup>7</sup> Reported by a Norwegian member of the technical working group on iron and steel of the European Union, 2008.



facilities. The most relevant dust emission reduction measures are outlined in table 5. Dust abatement techniques also provide for significant reductions of emissions of heavy metals. Gaseous lead and cadmium and its compounds as well as mercury that pass the dust filter can be abated by carbon adsorption, e.g., leading to 95% reduced emissions of mercury.

38. In recent years a number of new furnace types have been introduced, that might show advantages with regard to heavy metals and dust emissions, like the Comelt EAF and the Contiarc furnace which are seen by some experts as emerging techniques.

Table 5

**Emission sources, control measures, dust reduction efficiencies and costs for the secondary iron and steel industry**

<i>Emission source</i>	<i>Control measure(s)</i>	<i>Dust Reduction efficiency (%)</i>	<i>Emission levels (mg/Nm<sup>3</sup>)</i>	<i>Abatement costs (total costs US\$)</i>
EAF	ESP	> 99	–	–
	FF	> 99.5	Dust < 5	24/Mg steel
	Activated carbon + FF	Hg: > 98%	Hg: < 0.05	–

#### **D. Iron and steel foundries (annex II, category 4)**

39. In the foundry process, emissions to air will typically not be limited to one (or several) fixed point(s). The process involves various emission sources (e.g., from melting and pouring processes). It is very important to capture all the emissions efficiently. That is possible by installing doghouses or movable hoods or by total building evacuation. The captured emissions must be cleaned. In iron foundries, cupola furnaces, electric arc furnaces, induction furnaces, hearth type furnaces and rotary furnaces are operated. Direct particulate and gaseous heavy metal emissions are in particular associated with melting and sometimes, to a small extent, with pouring. Diffuse emissions arise from raw material handling, melting, pouring and fettling. The most relevant emission reduction measures are outlined in table 6 with their achievable reduction efficiencies. The BAT associated emission level for dust, after collecting and dedusting exhaust gases, for all types of furnaces (cupola, induction, and rotary furnace) and mouldings (lost mould and permanent mould), as well as finishing operations, is 5 mg/m<sup>3</sup>–20 mg/m<sup>3</sup>.

40. The following techniques are considered as BAT:

(a) For cupola furnace melting, use divided blast operation for cold blast cupolas, use oxygen enrichment of the blast air with oxygen levels between 22% and 25%, minimize the blast-off periods for hot blast cupolas, use coke with known properties and of a controlled quality, and clean furnace off-gas using a bag filter or wet scrubber;

(b) For induction furnace melting, increase furnace efficiency, maximize off-gas collection during the full working cycle, and use dry flue-gas cleaning keeping dust emissions below 0.2 kg/ton molten iron;

(c) For rotary furnace melting, optimize furnace operation and increase the melting efficiency. To collect the off-gas close to the furnace exit, apply post combustion, cool it using a heat exchanger and to apply dry dedusting;

(d) For electric arc furnaces a shortening of meltdown times can be achieved by a close control of the composition (e.g., total content of phosphorus, sulphur and carbon), temperature control and efficient methods of deslagging. The foamy slag practice reduces the energy consumption and therefore the amount of exhaust gases;

(e) For hearth type furnaces the use of oxyburners can reduce the amount of energy necessary (e.g., gas or oil) for smelting of iron and therefore the total flow of exhaust gases;

(f) For moulding, enclose all the unit operations and dedust the exhaust gas, if necessary, post combustion;

(g) For finishing operations, collect and treat the finishing off-gas using a dry system.

Table 6

**Emission sources, control measures, dust reduction efficiencies and costs for iron foundries**

<i>Emission source /furnace</i>	<i>Control measure(s)</i>	<i>Dust reduction efficiency (%)</i>	<i>Emission levels (mg/Nm<sup>3</sup>)</i>
Induction furnace	FF/dry absorption + FF	> 99	< 5
Cold blast cupola	Below-the-door take-off: FF	> 98	< 5
	Above-the-door take-off: FF + pre-dedusting	> 97	< 5
	FF + chemisorption	> 99	< 5
Hot blast cupola	FF + pre-dedusting	> 99	< 5
	Disintegrator/venturi scrubber	> 97	< 5
Electric Arc Furnace	ESP	> 99	< 5
	FF	> 99.5	< 10 for existing plants

**E. Primary and secondary non-ferrous metal industry (annex II, categories 2, 5 and 6)**

41. Smelting processes to obtain non-ferrous metals are known to be large sources of heavy metals released into the atmosphere.<sup>8</sup>

42. This section deals with emissions and emission control of cadmium, lead and mercury in the primary and secondary production of non-ferrous metals like lead, copper, zinc, gold, silver, tin, nickel, and silico- and ferro-manganese alloys. Due to the large number of different raw materials used and the various processes applied, nearly all kinds of heavy metals and heavy metal compounds might be emitted from this sector. Given the heavy metals of concern in this guidance document, the production of copper, lead, zinc, gold and production of silico- and ferro-manganese alloys are particularly relevant.

43. Environmental issues for the production of most non-ferrous metals from primary raw materials, e.g., ores and concentrates, include the emission to air of dust containing heavy metals and metals/metal compounds. Emissions of dust and metals occur from roasters, furnaces, reactors and the transfer of molten metal. Environmental issues for the production of non-ferrous metals from secondary raw materials, e.g., scrap, residues etc., is

<sup>8</sup> N. Pirrone et al., "Global mercury emissions to the atmosphere from anthropogenic and natural sources", in *Atmospheric Chemistry and Physics*, vol. 10, No. 13, (July 2010), pp. 5951–5964.

also related to the off-gases from the various furnaces and transfers that contain dust and metals.

44. In the majority of cases process gases are cleaned in FFs. Gas cleaning using wet scrubbers and wet electrostatic precipitators (wet ESP) is particularly effective for process gases that undergo sulphur recovery in a sulphuric acid plant. In some cases where dust is abrasive or difficult to filter, wet scrubbers are also effective. The use of furnace sealing and enclosed transfers and storage is important in preventing diffuse emissions. The significance of diffuse emissions in many processes is very high, and diffuse emissions can be much greater than those that are captured and abated. In these cases it is possible to reduce environmental impact by implementing the following measures:

- (a) Process optimization and minimization of emissions;
- (b) Sealed reactors and furnaces;
- (c) Targeted fume collection;
- (d) Use of (mobile) evacuated hood systems above charging, discharging or tapping areas;
- (e) Closed conveyor routes;
- (f) Unloading and storage of raw materials in closed buildings (or sealed packaging);
- (g) Sprinkling systems to avoid emissions from vehicle movements.

45. Where prerequisites are given, dusts should be recycled internally or externally. BAT for gas collection and abatement for the various process stages regarding particulate matter (PM) and heavy metals are summarized in table 7 (a) below.

Table 7 (a)

**PM emission control measures for different process stages**

<i>Process stage</i>	<i>Control measures</i>
Materials handling and storage	Correct storage, handling and transfer. Dust collection and fabric filter if necessary.
Grinding, drying	Dust collection and fabric filter.
Sintering/roasting, smelting, converting	Gas collection and fabric filter, heat recovery, combination of ESP/wet ESP and/or scrubbers.
Slag treatment	Dust collection, cooling and fabric filter.
Thermal refining	Gas collection and fabric filter, combination of ESP/wet ESP and/or scrubbers.
Metal powder production	Gas collection and fabric filter.
Melting and casting	Gas collection and fabric filter.

46. In general, processes should be combined with effective PM collecting devices and abatement for both primary gases and diffuse emissions. The BAT associated emission levels for PM are  $< 1 \text{ mg/Nm}^3$ – $5 \text{ mg/Nm}^3$  using high performance fabric filters or combinations of ESP/wet ESP and scrubbers. In the United States of America, there are at least 30 control devices at secondary lead smelters that are followed by secondary high efficiency particulate air filter (HEPA) filtration. Many of these 30 HEPA-controlled

sources are used for controlling building ventilation and process fugitive emissions, but some control devices treating furnace exhaust are currently controlled with secondary HEPA filters. PM levels well below 1 mg/Nm<sup>3</sup> can be achieved with the combination of certain controls such as an FF plus HEPA filter or an FF plus wet ESP.<sup>9</sup>

47. In general, emission reduction measures for Pb and Cd are limited to PM abatement, while emission reduction of Hg requires specific control measures. Table 7 (b) below gives examples of PM control costs and Hg reduction efficiencies.

48. The non-ferrous metals copper, zinc and lead are mainly produced from sulphidic ores. For technical and product quality reasons, the off-gas typically must go through a thorough dedusting (< 3 mg/Nm<sup>3</sup>) and could also require additional Hg removal before being fed to an sulphur trioxide (SO<sub>3</sub>) contact plant, thereby also minimizing heavy metal emissions.

Table 7 (b)

**Examples of PM control costs and Hg reduction efficiencies**

Sector	Specific activity indicator (SAI)	Emission control technology	Hg red (%)	Annual cost <sup>a</sup> (US\$ 2008/SAI)		Total costs
				Investment costs	Operation and maintenance costs	
Primary lead	Metric ton primary lead	Dry ESP	5	0.1	0.04	<b>0.1</b>
	Metric ton primary lead	FF	10	0.1	1.1	<b>1.2</b>
	Metric ton primary lead	Activated carbon injection +FF+FGD	90	2.5	1.3	<b>3.8</b>
Primary zinc	Metric ton primary zinc	Dry ESP	5	0.1	0.06	<b>0.2</b>
	Metric ton primary zinc	FF	10	4.5	1.1	<b>5.6</b>
Primary copper	Metric ton primary copper	FF	5	1.8	13.8	<b>15.6</b>
	Metric ton primary copper	FF state-of-the-art	10	3.9	25.7	<b>29.5</b>
Secondary lead	Metric ton secondary lead	Dry ESP	5	0.1	0.06	<b>0.2</b>
	Metric ton secondary lead	FF	10	6.8	1.1	<b>7.9</b>
Secondary zinc	Metric ton secondary zinc	Dry ESP	5	0.1	0.06	<b>0.2</b>
	Metric ton secondary zinc	FF	10	0.1	1.4	<b>1.5</b>
Secondary copper	Metric ton secondary copper	Dry ESP	5	10.9	15.9	<b>26.8</b>
	Metric ton secondary copper	FF	10	6.6	44.0	<b>50.6</b>

Source: UNEP(DTIE)/Hg/INC.2/4, Study on mercury sources and emissions and analysis of the costs and effectiveness of control measures, November 2010. Available from

<sup>9</sup> Information provided by representative of United States EPA in 2010 and 2012.

<http://www.unep.org/hazardoussubstances/Mercury/Negotiations/INC2/INC2MeetingDocuments/tabid/3484/language/en-US/Default.aspx>.

<sup>a</sup> The accuracy of cost estimates in the table is within  $\pm 50\%$ .

49. A typical combination of abatement techniques in primary non-ferrous metals production is the use of Dry (Hot) ESP followed by the process steps in the following order: water scrubber, Wet ESP, mercury removal, Sulphuric acid plant. In the case of an acid plant, it is desirable to remove the mercury before it enters the acid plant to minimize the possibility of mercury entering the final acid product (normally the quality requirement for Hg in sulphuric acid is  $< 0.1$  ppm (mg/l) which is equivalent to  $< 0.02$  mg/Nm<sup>3</sup> in the cleaned gas).<sup>10</sup> Mercury can be treated during both phases — the off-gas and the liquid phase (acid plant). Different processes are available. The basic principle is the reaction of mercury with a reagent to form a product which can be precipitated out of the gas or liquid.

50. Several technologies for removing mercury vapour from the gas stream are available. The removal efficiency depends on the specific conditions of the gas, e.g., mercury concentration, but can be  $> 99\%$ . Removal efficiencies for some techniques are given in table 7 (c) below. The following techniques are considered to be BAT:

(a) The **Boliden Norzink process**<sup>11</sup> is based on the oxidation of mercury vapour by mercuric chloride to form mercurous chloride (calomel) according to the reaction:  $\text{HgCl}_2 + \text{Hg} \rightarrow \text{Hg}_2\text{Cl}_2$ . A product acid containing less than 0.5 ppm mercury can be produced from a gas containing 150 ppm mercury (99.7% removal efficiency). The acid produced typically contains 0.3 ppm–0.5 ppm of mercury.<sup>12</sup> Mercury can be reduced to 0.05 ppm by adding on a polishing stage with selenium filter.<sup>11</sup> The process is also known as the Outotec chloride scrubber process, the Outotec BN Process and the Odda chloride process. Moderate investment costs and low operating costs, which are practically independent of the mercury level;<sup>11</sup>

(b) The **Outokumpu process**<sup>10</sup> is based on converting the elemental mercury in the gas into a sulphate according to the reaction:  $\text{Hg} + \text{H}_2\text{SO}_4 \rightarrow 1/2 \text{O}_2 + \text{HgSO}_4 + \text{H}_2\text{O}$ ;

(c) The **Bolkem process**<sup>10</sup> is based on mercury being reacted with sulphuric acid and treated with sodium thiosulphate to precipitate the mercury as mercuric sulphide;

(d) The **selenium filter**<sup>10</sup> is especially suited for low mercury concentrations in the gas and consists of a porous inert material soaked with selenious acid which is then dried to precipitate red amorphous selenium according to the reaction:  $\text{H}_2\text{SeO}_3 + \text{H}_2\text{O} + 2 \text{SO}_2 \rightarrow \text{Se} + 2 \text{H}_2\text{SO}_4$ . The filter will remove approximately 90% of the incoming mercury. The investment cost is proportional to the gas flow rate;<sup>8</sup>

(e) The **selenium scrubber**<sup>10</sup> like the selenium filter, relies on the presence of amorphous elemental selenium to react with the elemental mercury in the gas. The selenium scrubber is suitable for removing relative large quantities of mercury in the gas and has a removal efficiency of approximately 90%;

(f) The **activated carbon filter**<sup>10</sup> is well known for its adsorption properties. For the adsorption of mercury, activated carbon can normally adsorb 10%–12% of its own weight. The operating temperature of the carbon filter is limited to 50°C. The method is

<sup>10</sup> See “Assessments of technological developments: Best available techniques (BAT) and limit values” report submitted to the fourth meeting of the Task Force on Heavy Metals (Vienna, 6–8 June 2007). Available from <http://www.unece.org/fileadmin/DAM/env/lrtap/TaskForce/tfhm/Post-Ottawa.htm>.

<sup>11</sup> For more information, see [http://www.sulphuric-acid.com/techmanual/GasCleaning/gcl\\_hg.htm](http://www.sulphuric-acid.com/techmanual/GasCleaning/gcl_hg.htm).

<sup>12</sup> See <http://www.outotec.com/en/About-us/Our-technologies/Gas-cleaning/Mercury-removal/>.

especially suitable for low mercury concentrations in the gas. A 90% removal efficiency is normally achievable;

(g) The **Lurgi application**<sup>13</sup> is a kind of activated carbon filter. Lurgi consists of mercury removal units (MRU) which uses wet ESP and a packed bed absorber using sulphur-impregnated coal to remove mercury from the off-gas. The wet ESP removes dust and tars before the mercury contaminated off-gas is heated to 60°C–85°C and is absorbed in a series of packed bed absorbers. In order to control the gas flow through the unit, the MRU is equipped with a system for pressure control. The MRU has a removal efficiency of 95%;

(h) The **Tinfos Miltec process**<sup>14</sup> removes mercury from the off-gas by washing it concurrently with seawater containing sodium hypochlorite which oxidizes the mercury. In addition, the wash water collects dust, and reduces SO<sub>2</sub> emissions to air. The wash water after gas cleaning contains the mercury as mercury salts, which is added disodium sulphide (Na<sub>2</sub>S). This leads to the formation of mercury sulphide (HgS) and other metal sulphide precipitate, which can be removed from the process using a press filter. The Miltec process removes 95% of the mercury from the off-gas;

(i) The **DOWA filter** process (lead (II) sulphide covered pumice filter) captures metallic, oxidized and particulate mercury.

Table 7 (c)

**Mercury reduction efficiencies in gas phase for some techniques**

Mercury removal techniques		Total mercury concentration (Hg-tot)		
		Before ( $\mu\text{g}/\text{Nm}^3$ )	After ( $\mu\text{g}/\text{Nm}^3$ )	Reduction efficiency (%)
<b>Boliden</b>				
<b>Norzink</b>				
<b>Process</b>				
30,000 Nm <sup>3</sup> /h	High concentration	9 879	30	99.7
	Low concentration	51	13	74
<b>Dowa filter</b>				
170,000 Nm <sup>3</sup> /h	High concentration	50	1.4	97
	Low concentration	10.5	1.2	88
<b>Selenium</b>				
<b>filter</b>				
80,000 Nm <sup>3</sup> /h	High concentration	1 008	48	95
	Low concentration	42	12	71
<b>Active carbon</b>				
<b>filter</b>				
80,000 Nm <sup>3</sup> /h	High concentration	1 206	32	97
	Low concentration	37.2	2.7	93

Source: Ahmadzai, H; Borell, M.; and Svedberg, A.: Information Exchange on Boliden AB Non-ferrous Smelter at Rönnskär; Arctic Council Action Programme (ACAP) Mercury Steering Group, Copenhagen, March 10, 2006.

Notes: The Rönnskär smelter is a copper-lead-zinc smelter.

<sup>13</sup> Information provided by the Norwegian Climate and Pollution Agency regarding practice at the Eramet plant in Porsgrunn, Norway.

<sup>14</sup> Information provided by the Norwegian Climate and Pollution Agency regarding practice at the Eramet plant in Kvinesdal, Norway.

51. For processes where mercury removal from the gases is not practicable there are techniques for mercury removal in the liquid phase. These techniques are primarily used to improve the quality of the sulphuric acid. The following techniques to reduce the mercury content in sulphuric acid produced during the production of non-ferrous metals are available:

(a) **Molecular Recognition Technology**<sup>10</sup> (MRT) consists of highly selective, often non-ion exchange systems using specifically designed ligands or macrocycles. These ligands can be chemically bonded to solid supports, such as silica gel or polymers, or used free in a solution to form a complex with selected ions. The solid phase system consists of the bound ligand material, called SuperLig, packed into fixed bed columns or filter cartridge elements. The MRT process can be used as the primary method of mercury removal or it can be used as a polishing stage where the plant has an existing mercury removal system;

(b) The **Toho Process**<sup>10</sup> is based on the addition of potassium iodide and precipitating mercury as mercuric iodide. The addition of cuprous iodide in addition to potassium iodide will form the more stable precipitate  $\text{Cu}_2\text{HgI}_4$ . The precipitated mercury is separated by filtration;

(c) **Sulphide Precipitation**.<sup>10</sup> Colloidal sulphur can be created in the acid by the addition of sodium thiosulphate. The sulphur will react with the mercury to form crystalline mercury sulphide ( $\text{HgS}$ ).

52. In the **primary copper** industry the  $\text{SO}_2$ -rich primary off-gases from the roasting and converting process are commonly treated in a multi-stage abatement plant upstream to the sulphuric acid plant. In order to produce a high quality sulphuric acid, heavy metals need to be reduced (see paras. 48–49). Diffuse emissions occur during charging, discharging, transport and storage processes and from the anode furnace and anode casting process. To avoid these emissions, a sufficient capturing is necessary (see para. 44). After capturing, the loaded off-gas is commonly cleaned in fabric filter systems. If the fabric filter system is well operated and maintained, dust emission concentrations of  $< 1 \text{ mg/Nm}^3$ – $5 \text{ mg/Nm}^3$  are achievable. For specific heavy metals, the following emission concentrations are achievable:<sup>15</sup>

- (a) Lead:  $0.01 \text{ mg/Nm}^3$ – $0.60 \text{ mg/Nm}^3$ ;
- (b) Cadmium:  $0.01 \text{ mg/Nm}^3$ – $0.05 \text{ mg/Nm}^3$ ;
- (c) Mercury:  $< 0.01 \text{ mg/Nm}^3$ .

53. In the **secondary copper** industry heavy metals emissions occur during smelting, converting and fire refining processes. As in the primary copper industry, the capturing and sufficient treatment of diffuse emissions is crucial (see para. 44). Captured emissions are commonly treated in fabric filter systems. Additionally adsorbent injection, wet scrubbers and/or thermal or regenerative afterburners are used to reduce other pollutants (e.g.,  $\text{SO}_2$ , total organic carbon (TOC) or PCDD/F). If the FF system is well operated and maintained dust emission concentrations of  $< 1 \text{ mg/Nm}^3$ – $3 \text{ mg/Nm}^3$  are achievable. For specific heavy metals the following emission concentrations are achievable:<sup>15</sup>

- (a) Lead:  $0.01 \text{ mg/Nm}^3$ – $0.50 \text{ mg/Nm}^3$ ;
- (b) Cadmium:  $0.01 \text{ mg/Nm}^3$ – $0.02 \text{ mg/Nm}^3$ ;

<sup>15</sup> German Federal Environment Agency, 2012, emission values derived from measurements in different German plants. Data provided by German permitting authorities.

- (c) Mercury: < 0.03 mg/Nm<sup>3</sup>.

54. In the **primary lead** industry the SO<sub>2</sub>-rich primary off-gases from the ore oxidation process are commonly treated in a multi-stage abatement plant upstream to the sulphuric acid plant. In order to produce a high quality sulphuric acid, heavy metals need to be reduced (see paras. 48–49). Diffuse emissions occur during charging, discharging, transport and storage processes and from refining and casting process. To avoid these emissions a sufficient capturing is necessary (see para. 44). After capturing, the loaded off-gas is commonly cleaned in fabric filter systems or in a combination of cyclones and fabric filters. If the fabric filter system is well operated and maintained, dust emission concentrations of < 1 mg/Nm<sup>3</sup>–2 mg/Nm<sup>3</sup> are achievable. For specific heavy metals the following emission concentrations are achievable:<sup>15</sup>

- (a) Lead: 0.01 mg/Nm<sup>3</sup>–0.90 mg/Nm<sup>3</sup>;  
 (b) Cadmium: 0.01 mg/Nm<sup>3</sup>–0.02 mg/Nm<sup>3</sup>;  
 (c) Mercury: < 0.01 mg/Nm<sup>3</sup>.

55. In the **secondary lead** industry lead acid batteries, residues from batteries and other lead-bearing materials are processed. Therefore mercury occurs dependent on the scrapped material. As in the primary lead industry, the capturing and sufficient treatment of diffuse emissions is crucial (see para. 44). After pre-treatment the raw materials are processed in a range of different furnaces. Currently in Europe, Rotary, Blast Drum and Reverberatory furnaces are used for secondary lead production. Captured emissions are commonly treated in fabric filter systems. By using this technique, dust emission concentrations of 0.5 mg/Nm<sup>3</sup>–2 mg/Nm<sup>3</sup> are achievable. For specific heavy metals the following emission concentrations are achievable:<sup>15</sup>

- (a) Lead: < 0.5 mg/Nm<sup>3</sup>;  
 (b) Cadmium: < 0.05 mg/Nm<sup>3</sup>;  
 (c) Mercury: 0.025 mg/Nm<sup>3</sup>.<sup>16</sup>

56. In the **primary zinc** industry one has to distinguish between the pyrometallurgical Imperial Smelting Process and the mainly hydrometallurgical process. Only the first process step (roasting) of the hydrometallurgical process creates considerably heavy metals dust in the off-gas. The SO<sub>2</sub>-rich off-gases from the roasting are commonly treated in a multi-stage abatement plant upstream to a sulphuric acid plant. In order to produce a high quality sulphuric acid, heavy metals need to be reduced (see paras. 48–49). During the leaching and leach purification steps scrubbers are commonly used to clean the occurring off-gases. By using these techniques, dust emission concentrations of 0.3 mg/Nm<sup>3</sup>–1 mg/Nm<sup>3</sup> are achievable. For specific heavy metals the following emission concentrations are achievable:<sup>15</sup>

- (a) Lead: < 0.01 mg/Nm<sup>3</sup>;  
 (b) Cadmium: < 0.01 mg/Nm<sup>3</sup>;  
 (c) Mercury: mainly removed in wet process steps, measured after wastewater treatment plant: < 0.005 mg/l.

<sup>16</sup> Information provided by the Austrian Environment Agency (2003); emission value derived from measurement in an Austrian plant.



57. Cadmium is a by-product in the primary zinc industry. It is produced in a separate four-stage process:

- (a) Smelting of cadmium briquettes from leach cleaning process;
- (b) Dezincification with caustic soda;
- (c) Vacuum distillation to separate cadmium from other metals like copper (Cu), nickel (Ni) and Pb;
- (d) Condensation in fine-cadmium furnace and casting. The off-gases from furnaces are commonly captured and treated in an advanced ESP. By using this technique, dust emission concentrations of 0.3 mg/Nm<sup>3</sup>–1 mg/Nm<sup>3</sup> are achievable. For specific heavy metals the following emission concentrations are achievable:<sup>15</sup>
  - (e) Lead: < 0.01 mg/Nm<sup>3</sup>;
  - (f) Cadmium: < 0.01 mg/Nm<sup>3</sup>.

To avoid diffuse emissions sufficient capturing and treatment is necessary (see para. 44).

58. **Secondary zinc** can be produced from EAF-dust and other zinc-bearing materials. These materials can be refined in rotary furnaces (Waelz process) to separate the zinc from other elements. In this process, heavy metals occur as dusty emissions which are mainly captured and treated in multi-stage fabric filter systems. To reduce gaseous mercury emissions, it is common to inject an adsorbent (lime, activated coke, etc.) into the off-gas stream before the last fabric filter step. By using these techniques, dust emission concentrations of 0.5 mg/Nm<sup>3</sup>–5 mg/Nm<sup>3</sup> are achievable. For specific heavy metals the following emission concentrations are achievable:<sup>15</sup>

- (a) Lead: < 0.02 mg/Nm<sup>3</sup>;
- (b) Cadmium: < 0.01 mg/Nm<sup>3</sup>;
- (c) Mercury: < 0.01 mg/Nm<sup>3</sup>–0.05 mg/Nm<sup>3</sup>.

To avoid diffuse emissions, a sufficient capturing and treatment is necessary (see para. 44).

59. For **large-scale gold production** various alternative processes to amalgamation have been developed. In cases where mercury levels in various ores are elevated (e.g., dome gold mine ores) activated carbon adsorber beds can be used to capture most of the mercury emissions from various processes (e.g., kilns, refinery furnaces). By applying pollution prevention measures, including mercury condensers, carbon adsorption units (e.g., single fixed carbon beds, multiple beds or columns or other designs), mercurous chloride scrubbers, venturi scrubbers and chemical additives to improve mercury capture, mercury emissions from gold production have been reduced by about 97%.<sup>17</sup>

60. Production of silico- and ferro-manganese alloys from ore with a high mercury content is a significant source of mercury emissions. Using activated carbon adsorption of mercury in waste gas from a furnace can give reductions of 95%.

<sup>17</sup> United States, EPA, National Emission Standards for Hazardous Air Pollutants: Gold Mine Ore Processing and Production Area Source Category; and Addition to Source Category List for Standards; Final Rule, 40 CFR Parts 9 and 63, Federal Register, Vol. 76, No. 33 (17 February 2011).

## F. Cement industry (annex II, category 7)

61. Cement kilns may use secondary fuels and materials (waste co-processing), such as waste oil or waste tyres. The co-incineration of waste in cement kilns is treated within the waste incineration category. Mercury emissions can be reduced by controlling the amount of mercury in the input of the kiln, reducing the off-gas temperature to improve mercury precipitation during first filtration or by abating mercury through activated carbon injection as an adsorbent to the flue gas. Quality control of fuels and content of mercury of raw materials should be checked in order to reduce and limit mercury emissions.

62. Mercury and its compounds are not completely precipitated and retained in the kiln system and/or the pre-heater due to the high temperatures existent there and the mercury high volatility. 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 exhausted 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. The dust from the dust collector can be recirculated back to the cement mill. Furthermore, precipitation and, hence, mercury removal, increases with decreasing exhaust gas temperature. Therefore, 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.

63. Dust is emitted at all stages of the cement production process, consisting of material handling, raw material preparation (crushers, dryers), clinker production and cement preparation. Mercury is predominantly introduced into the kiln with raw materials, with generally a minor amount coming from the fuels. There is a constant increase in the use of waste fuels in the clinker production, which can be a source of heavy metals. It is generally the raw material input and not the process type which has the greater effect on heavy metal emissions.

64. For clinker production the following kiln types are available: rotary kiln with cyclone pre-heater and precalciner; rotary kiln with cyclone pre-heater; rotary kiln with grate pre-heater; long wet rotary kiln; long dry rotary kiln; and shaft furnace. The selected process has a major impact on the energy use and air emissions from the manufacture of cement clinker. For new plants and major upgrades, BAT for the production of cement clinker is considered to be a dry process kiln with multi-stage preheating and precalcination.

65. For heat recovery purposes, rotary kiln off-gases are conducted through the preheating system and the mill dryers (where installed) before being dedusted. The collected dust is returned to the feed material. Excess heat from the kiln off-gases, as well as from the clinker cooler, can be used for electricity generation (cogeneration) or externally, e.g., for district heating.

66. Less than 0.5% of lead and cadmium entering the kiln is released in exhaust gases. The high alkali content and the scrubbing action in the kiln favour metal retention in the clinker or kiln dust.

67. The emissions of heavy metals into the air can be reduced by, for instance, taking off a bleed stream and stockpiling the collected dust instead of returning it to the raw feed. However, in each case these considerations should be weighed against the consequences of releasing the heavy metals into the waste stockpile. The collected dust can be recirculated also to the cement mill. If the exhaust gas of the kiln is filtered by ESPs, an important measure is to have a very well-controlled, steady operation of the kiln in order to avoid

emergency shut-offs of the ESPs. These may be caused by excessive carbon monoxide concentrations. It is important to avoid high peaks of heavy metal emissions in the event of such an emergency shut-off.

68. BAT for the manufacturing of cement with regard to dust and heavy metals emissions requires the combination of the following general primary measures:

(a) A smooth and stable kiln process. Therefore monitoring and measurement of process parameters and emissions on a regular basis is important;

(b) Careful selection and control of substances entering the kiln; if available selection of raw materials and fuels with low contents of sulphur, nitrogen, chlorine, metals (especially mercury) and volatile organic compounds should be preferred;

(c) Use of a quality assurance system to control the characteristics of wastes to be used as raw material and/or fuel for constant quality and other physical and chemical criteria. Relevant parameters for any waste to be used as raw material and/or fuel should be controlled;

(d) Use of effective dust removal measures/techniques like fabric filters (with multiple compartments and “burst bag detectors”) or ESP (with fast measuring and control equipment to minimize the number of carbon monoxide trips).

(e) Minimization or reduction of dust emissions from diffuse sources,<sup>18</sup> through the use of the following measures and techniques:

(i) Minimization/prevention of dust emissions from diffuse sources;

(ii) Measure techniques for dusty operations;

(iii) Bulk storage area measures/techniques.

69. The most relevant emission reduction measures are outlined in table 8. To reduce direct dust emissions from crushers, mills and dryers, FF are mainly used, whereas kiln and clinker cooler waste gases are controlled by ESP or FF. Dust emissions from kiln firing, cooling and milling processes can be reduced to concentrations < 10 mg/Nm<sup>3</sup>–20 mg/Nm<sup>3</sup> (daily mean value, 10 vol% O<sub>2</sub>), from other processes to concentrations < 10 mg/Nm<sup>3</sup>.

Table 8

**Emission sources, control measures, reduction efficiencies and costs for the cement industry**

<i>Emission source</i>	<i>Control measure(s)</i>	<i>Reduction efficiency (%)</i>	<i>Reported emissions (mg/Nm<sup>3</sup>)</i>
Direct emissions from kiln firing, cooling and milling processes	Primary measures plus FF or ESP	Cd, Pb: > 95	Dust: < 10–20
Direct emissions from dusty operations <sup>a</sup>	Primary measures plus FF or ESP		Dust: < 10
Direct emissions from rotary kilns	Activated carbon adsorption	Hg: > 95	Hg: 0.001–0.003

<sup>a</sup> Dusty operations: e.g., crushing of raw material, conveyers and elevators, storage of fuels and raw material.

<sup>18</sup> For a detailed description of measures for diffuse sources, see chapters 1.4.4.1 and 1.4.4.3 of the European Commission’s BREF for Cement, Lime and Magnesium Oxide Manufacturing Industries (May 2010); available from [http://eippcb.jrc.ec.europa.eu/reference/BREF/clm\\_bref\\_0510.pdf](http://eippcb.jrc.ec.europa.eu/reference/BREF/clm_bref_0510.pdf).

70. A way to minimize mercury emissions is to lower the exhaust temperature. When high concentrations of volatile metals (especially mercury) occur, adsorption on activated carbon is an option; an increased efficiency of ESP could be shown when additionally using halogenides (especially bromides).

### **G. Glass industry (annex II, category 8)**

71. In the glass industry, lead emissions are particularly relevant given the various types of glass in which lead is introduced as raw material. Lead is used in fluxes and colouring agents in the frit industry, in some special glasses (e.g., coloured glasses, cathode ray tube funnels) and domestic glass products (lead crystal glasses). In the case of soda-lime container glass, lead emissions depend on the quality of the recycled glass used in the process. External cullet is an important source of metal contamination particularly for lead. The lead content in dusts from crystal glass melting is usually about 20%–80%.

72. Dust emissions stem mainly from batch mixing, furnaces, diffuse leakages from furnace openings and finishing and blasting of glass products. They depend notably on the type of fuel used, the furnace type and the type of glass produced. Oxy-fuel burners can reduce waste gas volume and flue dust production by 60%. The lead emissions from electrical heating are considerably lower than from oil/gas-firing systems. In general and where it is economically viable, predominantly electrical melting is considered BAT for lead crystal, crystal glass and opal glass production, since this technique allows efficient control of potential emissions of volatile elements. Where crystal glass is produced with a less volatile formulation, other techniques may be considered when determining BAT for a particular installation.

73. The batch is melted in continuous tanks or day tanks. During the melting cycle using discontinuous furnaces, the dust emission varies greatly. The dust emissions from crystal glass tanks (< 5 kg/Mg melted glass) are higher than from other tanks (< 1 kg/Mg melted soda and potash glass). BAT for lead from the melting furnace in the domestic glass sector when used for manufacturing lead crystal glass is < 0.5 mg/Nm<sup>3</sup>–1 mg/Nm<sup>3</sup> (< 0.001 kg/t–0.003 kg/t melted glass).

74. Some measures to reduce direct metal-containing dust emissions are:

- (a) Pelleting the glass batch;
- (b) Changing the heating system from oil/gas firing to electrical heating;
- (c) Charging a larger share of glass returns (cullet) in the batch;
- (d) Applying a better selection of raw materials (size distribution) and recycled glass (avoiding lead-containing fractions).

In general, BAT for controlling dust emissions from furnaces in the glass industry is the use of either an ESP or FF system, operating where appropriate, in conjunction with a dry or semi-dry acid gas scrubbing system. The BAT emission level for dust associated with these techniques is generally < 10 mg/Nm<sup>3</sup>–20 mg/Nm<sup>3</sup>; for some glass types, such as domestic glass or special glass, generally < 10 mg/Nm<sup>3</sup>–20 mg/Nm<sup>3</sup>; and 1 mg/Nm<sup>3</sup>–10 mg/Nm<sup>3</sup> when significant amounts of dangerous substances are applied, which generally equates to less than 0.1 kg/ton of glass melted. In some cases, the application of BAT for metals emissions may result in lower emission levels for dust. The emission level associated with BAT for the sum of the concentrations of heavy metals including lead (arsenic (As), cobalt (Co), Ni, Cd, selenium (Se), chromium (Cr), antimony (Sb), Pb, Cu, manganese (Mn), vanadium (V) and Tin (Sn)) is generally < 1 mg/Nm<sup>3</sup>–5 mg/Nm<sup>3</sup>. Secondary dust abatement represents BAT for most glass furnaces, unless equivalent emissions can be

achieved with primary measures. The corresponding emission reduction efficiencies are given in table 9.

75. The development of crystal glass without lead compounds is in progress. The Plasma Melter makes use of the electrical conductivity of molten glass and operates with negligible dust emissions. It is, however, not expected to be a viable technique for melting within the foreseeable future.

76. For potentially dusty downstream activities, BAT is considered to be dust minimization, e.g., by cutting, grinding or polishing under liquid or by extraction of off-gases to a bag filter system. The emission level for these activities is  $< 1 \text{ mg/Nm}^3$ – $10 \text{ mg/Nm}^3$  (up to  $20 \text{ mg/Nm}^3$  for flat glass and up to  $50 \text{ mg/Nm}^3$  only for mineral wool downstream processes).

Table 9

**Emission sources, control measures, dust reduction efficiencies and costs for the glass industry**

<i>Emission source</i>	<i>Control measure(s)</i>	<i>Dust reduction efficiency (%)</i>
Direct emissions	FF	> 99
	ESP	> ~ 95

## H. Chlor-alkali industry (annex II, category 9)

77. In the chlor-alkali industry, chlorine gas ( $\text{Cl}_2$ ), alkali hydroxides and hydrogen are produced through electrolysis of a salt solution. Commonly used in existing plants are the mercury process, the diaphragm process and the membrane process. All these processes need the introduction of good practices to reduce environmental problems. The selected process technology has a major impact on the energy use and emissions from the manufacture of chlor-alkali. BAT for the production of chlor-alkali is considered to be membrane technology. Non-asbestos diaphragm technology can also be considered as BAT. The use of mercury-cell technology has been declining in Europe and North America over the past few decades, as many such plants have shut down or been converted to non-mercury processes. Moreover, European and North American producers are committed to not building any new mercury-cell facilities. The last chlor-alkali mercury cell plant in Canada closed in 2008. European regulations do not allow the construction of these facilities.

78. Mercury releases from chlor-alkali operations can be entirely eliminated only by converting to a non-mercury process such as the membrane cell process. Conversion to membrane cell technology is considered as BAT. Decision 90/3 of 14 June 1990 of the Commission for the Prevention of Marine Pollution from Land-based Sources (PARCOM) recommends that existing mercury cell chlor-alkali plants should be phased out as soon as practicable with the objective of phasing them out completely by 2010. Decision 90/3 was reviewed in 1999–2001 without any changes. Among countries of the successor to PARCOM, the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention), and in the European Union there has been considerable discussion about the possible impacts the remarketing of the mercury from decommissioned chlor-alkali facilities will have on the global mercury market. In 1999, all West European chlor-alkali producers presented the authorities with a voluntary commitment to shut down their chlor-alkali plants by 2020 at the latest. Another clause of PARCOM decision 90/3 commits them not to sell or transfer mercury cells after plant shutdown to any third party for reuse. In February 2009, the Governing Council of UNEP agreed on the need to develop

a global legally binding instrument on mercury and started negotiations on a global mercury convention. Key elements of these negotiations are, for example, reducing the supply of mercury onto the market, reducing mercury demand for products and processes, reducing atmospheric emissions of mercury, addressing mercury containing waste and remediation of contaminated sites. The negotiations will be concluded by 2013.<sup>19</sup>

79. The specific investment for replacing mercury cells by the membrane process is reported to be in the region of US\$ 700–US\$ 1,000/Mg Cl<sub>2</sub> capacity. Although additional costs may result from, inter alia, higher utility costs and brine purification cost, the operating cost will in most cases decrease. This is due to savings mainly from lower energy consumption, and lower wastewater treatment and waste-disposal costs.

80. The sources of mercury emissions into the environment in the mercury process are: cell room ventilation, end box ventilation air and by-product hydrogen. With regard to emissions into air, Hg diffusely emitted from the cells to the cell room is particularly relevant. Preventive measures and control are of great importance and should be prioritized according to the relative importance of each source at a particular installation. In any case, specific control measures are required when mercury is recovered from sludges resulting from the process.

81. During the remaining life of mercury cell plants, all possible measures should be taken to protect the environment as a whole, including minimizing mercury losses to air by:

- (a) Use of equipment and materials and, when possible, a lay-out of the plant that minimizes losses of mercury due to evaporation and/or spillage;
- (b) Good housekeeping practices and good maintenance routines;
- (c) Collection and treatment of mercury-containing gas streams from all possible sources, including hydrogen gas. Typical devices for removal of mercury air emissions are shown in table 10 (a);
- (d) Reduction of mercury levels in caustic soda;
- (e) Minimizing current and future mercury emissions from handling, storage, treatment and disposal of mercury-contaminated wastes;
- (f) Decommissioning carried out in a way that prevents environmental impact during and after the shutdown process, as well as safeguarding human health.

Table 10 (a)

**Control measures, reduction efficiencies and costs for chlor-alkali plant emissions**

<i>Emission source</i>	<i>Control measure</i>	<i>Reduction efficiency (%)</i>
Chlor-alkali production	Gas stream cooling to remove mercury from hydrogen stream; mist eliminators; scrubbers; adsorption on activated carbon and molecular sieves	> 90

82. These measures can cut mercury emissions to values well below 2.0 g/Mg of Cl<sub>2</sub> production capacity, expressed as an annual average. All plants comply with the limit value of 2 g Hg/Mg Cl<sub>2</sub> for air emissions in PARCOM decision 90/3, and it is clear that in many

<sup>19</sup> Editor's note: since the time of writing the negotiations have concluded. The text of the Minamata Convention on Mercury will be open for signature from 9 to 11 October 2013.

plants air emissions continue to fall. However, for reported emissions a wide range in actual values from 0.14 g Hg/Mg Cl<sub>2</sub>–1.57 g Hg/Mg Cl<sub>2</sub> is shown. The best performing mercury cell plants are achieving total mercury losses to air, water and with products in the range of 0.2 g Hg/Mg Cl<sub>2</sub>–0.5 g Hg/Mg Cl<sub>2</sub> as a yearly average, and with regard to air emissions 0.21 g Hg/Mg Cl<sub>2</sub>–0.32 g Hg/Mg Cl<sub>2</sub>, as shown in table 10 (b). Since emissions depend to a large extent on good operating practices, the average should depend on and include maintenance periods of one year or less.

Table 10 (b)

**Mercury losses to air from best performing mercury cell plants**

	<i>g Hg/Mg Cl<sub>2</sub><sup>a</sup></i>
Cell room	0.2–0.3
Process exhausts, including Hg distillation unit	0.0003–0.01
Untreated cooling air from Hg distillation unit	0.006–0.1
Hydrogen gas	< 0.003

<sup>a</sup> Total grams of mercury per megagram of chlorine production.

## I. Municipal, medical and hazardous waste incineration (annex II, categories 10 and 11)

83. There are wastes that are neither classified as hazardous, municipal nor medical waste, depending on national legislation (e.g., non-hazardous industrial wastes, sludge, etc.), that may be incinerated as well as co-incinerated in other industries, therefore potentially constituting a relevant source of heavy metal emissions. Furthermore, there are other thermal waste treatment methods (e.g., pyrolysis) that may be a relevant source of heavy metal emissions. For BAT, no differentiation is made between municipal, hazardous and medical waste in terms of applied techniques or achievable emission limits, as all types of waste are often incinerated in the same installation. Emissions of cadmium, lead and mercury result from the incineration of municipal, medical and hazardous waste. Mercury, a substantial part of cadmium and minor parts of lead are volatilized in the process. Particular actions should be taken both before and after incineration to reduce these emissions. The only relevant primary techniques for preventing emissions of mercury into the air before incinerating are those that prevent or control, if possible, the inclusion of mercury in waste. In some countries mercury-containing components are separated out of the solid waste stream and managed or recycled properly. Removing mercury from the waste stream before it enters the incinerator is much more cost-effective than capturing mercury later from flue gases using emissions control devices. Lower emissions of mercury from municipal waste combustors and medical waste incinerators can be achieved through product substitution. Although this is potentially applicable to a wide range of components, batteries have received the greatest attention because of their significant contribution to total mercury content in municipal and medical wastes. The applicability of the product substitution to other areas should be based on technical and economic feasibility.

84. BAT for dedusting and reducing heavy metals emissions is considered to be FFs in combination with dry or wet methods for controlling volatiles. ESPs in combination with wet systems can also be designed to reach low dust emissions, but they offer fewer opportunities than FFs especially with pre-coating for adsorption of volatile pollutants. Between 30% and 60% of mercury is retained by high efficiency ESPs or FFs and FGD systems capture a further 10% to 20%. When using a dry system, the additional injection of activated carbon (impregnated with sorbents like sulphur, bromine or others), sodium

hydrogen carbonate or calcium hydroxide upstream of a fabric filter or use of lignite coke or zeolite can reduce the mercury emissions by more than 90%. When using a wet scrubber system with ESP or FF, to improve the mercury removal different chemicals can be added to the wet scrubber solution, e.g., hydrogen peroxide, liquid chelating reagents with copper or manganese salts or sodium hypochlorite (NaClO).

85. When BAT is used for cleaning the flue gases, the concentration of dust can be reduced to 1 mg/m<sup>3</sup>–5 mg/m<sup>3</sup>. In general, the use of fabric filters gives the lower levels within these emission ranges. Effective maintenance of dust control systems is very important. Controlling dust levels generally reduces metal emissions too. The concentration of mercury can be reduced to a range of 0.001 mg/m<sup>3</sup>–0.02 mg/m<sup>3</sup> (daily average, normalized to 11% O<sub>2</sub>). Adsorption using carbon based reagents is generally required to achieve these emission levels with many wastes. Some waste streams have very highly variable Hg concentrations and waste pre-treatment may be required in such cases to prevent peak overloading of the flue gas treatment system capacity.

86. The most relevant secondary emission reduction measures are outlined in table 10. It is difficult to provide generally valid data because the relative costs in US\$/ton depend on a particularly wide range of site-specific variables, such as waste composition.

87. If re-burn of flue gas treatment residues is applied, then suitable measures should be taken to avoid the recirculation and accumulation of Hg in the installation.

88. Metallic mercury can be adsorbed (usually at about 95% removal efficiency) to result in emissions to air of below 30 µg/Nm<sup>3</sup> if an activated carbon injection in combination with a dedusting device is used. Ionic mercury is also removed by chemi-adsorption due to the sulphur content in the flue gases or from sulphur impregnated carbon in some types of activated carbon. There is a significant fire risk when using activated carbon. The adsorbent may be mixed with other reagents to reduce the fire risk. In some cases, 90% lime and 10% carbon is used. The proportion of carbon is generally higher where there are additional process stages that perform acid gas removal (e.g., wet scrubbers). 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 1 µg/Nm<sup>3</sup> are seen.

89. SCR for control of nitrogen oxides also reduces mercury emissions as a co-benefit by changing it into a form that can be collected by FF or precipitated by wet scrubbers.

90. Most Parties require discontinuous monitoring of mercury emissions only, while some consider continuous monitoring as BAT; proven systems for continuous measurements of mercury emissions are available on the market.

91. For the co-incineration of waste and recovered fuel in cement kilns, in general, BAT for cement kilns apply.

92. For the co-incineration of waste and recovered fuel in combustion installations, in general, BAT for combustion installations apply.

93. The Peck process is a promising technique with negligible heavy metals emissions in the flue gas. It has been developed for municipal solid waste treatment but could in principle be applied to other wastes. Other options to reduce heavy metals emissions may be the heavy metal evaporation process and the hydro-metallurgical treatment plus vitrification.

94. If the first stage of a high efficiency scrubber is kept at a pH of below 1, the removal efficiency of ionic Hg as Hg<sub>2</sub>Cl<sub>2</sub>, which is generally the main compound of mercury after waste combustion, is over 95%. Metallic mercury adsorption can be improved by addition of sulphur compounds, activated carbon or oxidants, e.g. hydrogen peroxide, to the scrubber liquor. The overall Hg removal (both metallic and ionic) efficiency is around 85%.



Levels achieved with just a wet scrubbing system are approximately  $36 \mu\text{g}/\text{Nm}^3$ ; with a wet scrubber and an activated coke filter,  $< 2 \mu\text{g}/\text{Nm}^3$ ; and with a combination of the flow injection process and a wet scrubber,  $4 \mu\text{g}/\text{Nm}^3$ .

Table 11

**Control measures, dust reduction efficiencies and costs for municipal, medical and hazardous waste incineration for stack gases**

<i>Control measure(s)</i>	<i>Reduction efficiency (%)</i>	<i>Abatement costs (total costs US\$)</i>
High-efficiency scrubbers	Pb, Cd: $> 98$ ; Hg: ca. 50	–
ESP (3 fields) with activated carbon or equivalent adsorptive reagents	Pb, Cd: 80–90	10–20/Mg waste
Wet ESP (1 field) with additives, in combination with activated carbon injection, or activated carbon or coke filters	Pb, Cd: 95–99 Hg: $> 90$ ( $1 \mu\text{g}/\text{Nm}^3$ )	1,600–4,000 per pound Hg removed
Fabric filters	Pb, Cd: 95–99	15–30/Mg waste
Activated Carbon injection + FF or ESP	Hg: 50–95 ( $< 1 \mu\text{g}/\text{Nm}^3$ )	Operating costs: ca. 2–3/Mg waste; municipal waste combustors, 211–870; medical waste incinerators, 2,000–4,000 per pound Hg removed. Operating cost (carbon cost): €125,000 annually for a facility treating 65,000 tons of hazardous waste <sup>a</sup>
Carbon bed filtration	Hg: $> 99$	Operating costs: ca. 50/Mg waste; 513–1,083 per pound Hg removed
Selenium filters (inlet mercury concentrations of up to $9 \text{ mg}/\text{m}^3$ )	–	–

<sup>a</sup> See BREF on Waste Incineration, chapter 4.4.6.2 (2006), available from <http://eippcb.jrc.es/reference/wi.html>.