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Background information for negotiating Annex V of the revised Heavy Metals Protocol

Prepared by the Chair of the Task Force on Heavy Metals

Why this paper?

This paper is intended to assist negotiations of emission limit values (ELV) for Annex V of a new or revised HM Protocol (HMP). It l give a quick review of each category by comparing the 1998 HM Protocol with the proposed options for the revised Gothenburg Protocol (GP) and the new/revised HMP. Technical information is given (links to used documents are available on the internet) at the end of a category from up-to-date versions for the GP, the HMP and technical papers discussed at the Task Force meetings. Further technical information is included if it adds value to certain categories.

What is the added value to limit heavy metals additionally to dust?

A very good explanation is given already in paragraph 2 of this document (see below). Additionally, it can be stated that the aim of the protocol is a significant reduction of heavy metals as air pollutants and that this can be done most effectively by limiting the pollutants themselves. ELVs are derived by taking into account their toxicity, which is why the lowest values are proposed for mercury. Using separate ELVs, the quantities emitted into the environment can be calculated and determined much easier and more precisely.

The content of heavy metals in dust can vary if parameters of the process change, e.g. temperature, charge or raw material. Often dust can be seen as a “black box”; it is unknown which heavy metals are contained at what concentrations. Theoretically it is possible that when the amount of dust is reduced the amount of emitted heavy metals is increased, particularly when processes or process steps and raw material are changed. For some important sources the percentage of heavy metals in dust can be a very high, for example >40%.

The advantage of dust ELVs is that these are easier to monitor even when this is carried out continuously. To reduce dust is a ‘multi pollutant control strategy’ in that all heavy metals will be reduced simultaneously. Controlling single heavy metals and dust is a complementary process.

When only dust emissions are controlled, it is possible that the reduction of heavy metals to the desired level will not be achieved.

Many countries within the EU apply limit values for these categories. The proposed limit values are linked to Option 2 for dust. When Option 1 is chosen the limit values for HM can often be lowered accordingly.

Is there always an overlap with the GP?

No; not for all categories. Some important categories for dust don't emit heavy metals and some emitters of heavy metals are not important dust emitters (e.g. in the chlor-alkali-industry). Areas where there is overlap between the HMP and GP are highlighted in yellow in the Tables below. If a category or ELV for an option of the HMP does not correspond with the same option of the GP it is highlighted in green. Relevant HM emissions stem from liquid and solid fuels, therefore gaseous fuels and biomass were not taken into account as they were addressed in the GP.

Sources of information used are referenced below the tables. Because the large amounts of technical information contained in the references they are not included as full documents, as was originally planned.

Information regarding emission control performance and costs is based on official documentation from the Executive Body and its subsidiary bodies. In particular, the following have been taken into consideration.

- Documents received and reviewed by The Task Force on Heavy Metals
- BAT reference documents from the European Integrated Pollution Prevention and Control Bureau (EIPPCB)
- The United Nations Environment Program (UNEP) 2002 Global Mercury Assessment,
- Various technical reports from United States Environmental Protection Agency (U.S. EPA), Environment Canada and the European Commission, and
- Information provided directly by experts, e.g. the background document for technical information: http://www.unece.org/env/lrtap/TaskForce/tfhm/third%20meetingdocs/Background_BAT-ELV_060407.doc which was elaborated/discussed at the TF meeting in Ottawa, 2006.

I. Introduction

1. Two types of limit value are important for heavy metal emission control:

- Values for specific heavy metals or groups of heavy metals; and
- Values for emissions of particulate matter in general.

2. In principle, limit values for particulate matter cannot replace specific limit values for cadmium, lead and mercury, because the quantity of metals associated with particulate emissions differs from one process to another. However, compliance with these limits contributes significantly to reducing heavy metal emissions in general. Moreover, monitoring particulate emissions is generally less expensive than monitoring individual species. Therefore, particulate limit values are of great practical importance and are also laid down in this annex in most cases to complement or replace specific limit values for cadmium or lead or mercury.

3. Limit value means the quantity of a substance contained in the waste gases from an installation that is not to be exceeded. Limit values for particulate matter refer to the solid substance in the waste gases. Limit values for heavy metals include the solid, gaseous and vapour form of the metal and its compounds, expressed as the metal. Unless otherwise specified, it shall be calculated in terms of mass of pollutant per volume of the waste gases (expressed as mg/m3), assuming standard conditions for temperature and pressure for dry gas (volume at 273.15 K, 101.3 kPa). With regard to the oxygen content of exhaust gas, the values given in the tables below for each source category shall apply. Dilution for the purpose of lowering concentrations of pollutants in waste gases is not permitted. Start-up, shutdown and maintenance of equipment are excluded.

4. Emissions shall be monitored in all cases. Compliance with limit values shall be verified. The methods of verification can include continuous or discontinuous measurements, type approval, or any other technically sound method1. In case of continuous measurement, compliance with the emission standards is achieved if the validated [daily/monthly] emission average does not exceed the limit values. In case of discontinuous measurement or other appropriate determination procedures, compliance with the emissions standards is achieved if the mean value based on an appropriate number of measurements under representative conditions does not exceed the value of the emission standard. The inaccuracy of the continuous and discontinuous measurement methods may be taken into account for verification purposes.

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[1] Indirect monitoring of substances is also possible via sum parameters/ cumulative parameter (e.g. dust as sum parameter for heavy metals). In some cases using a certain technique to treat emissions can assure a value/limit value is maintained or met.

5. Sampling and analysis of relevant polluting substances and measurements of process parameters, as well as the quality assurance of automated measuring systems and the reference measurement methods to calibrate those systems shall be carried out in accordance with CEN standards. If CEN standards are not available, ISO standards, national or international standards which will ensure the provision of data of an equivalent scientific quality shall apply.

6. The following emission limit values can be achieved by applying BAT:

II. Specific limit values for selected major stationary sources by source categories

I. Combustion of fuels in utility and industrial boilers (annex II, category 1)

<table>
<tr><td>HM Protocol 1998</td><td>Draft revised HM protocol</td></tr>
<tr><td>6. Limit values refer to 6% O2 in flue gas for solid fuels and to 3% O2 for liquid fuels</td><td>7. Combustion plants (boilers and process heaters) with a rated thermal input exceeding 50 MWth or combustion plants when combined to a common stack with a total rated input exceeding 50 MWth.[2] Limit values refer to 6% O_2 in flue gas for solid fuels and to 3% O_2 for liquid fuels. These values do not apply to combustion plants running less than 500 hours a year. The competent authorities may grant derogations from the obligation to comply with the emission limit value for combustion plants not operated more than [XXX] operating hours, starting from [DATE] and ending no later than [DATE].</td></tr>
<tr><td>7.Limit values for particulate emissions for solid and liquid fuels: 50 mg/m3</td><td>8. Limit value for particulate emissions for <u>solid and liquid fuels</u> (if not stated different):
<table>
<tr><td>Thermal input[MWth]</td><td>Option 1</td><td>Option 2</td><td>Option 3</td></tr>
<tr><td>New installations 50 to 100</td><td>[10]</td><td>[20]</td><td>[50]</td></tr>
<tr><td>Existing installations 50 to 100</td><td>[15]</td><td>[30]</td><td>[50]</td></tr>
</table>
</td></tr>
</table>

[2] Individual combustion plants below 15 MWth shall not be considered to calculate the total rated input.

New installations 100 - 300	[10]	[20]	[30]
Existing installations 100 - 300	[15]	[25]	[50]
New installations > 300	solid fuel [10] liquid fuel [5]	[10]	[30]
Existing installations > 300	[10]	[20]	[50]

9. Special provision for combustion plants:

(a) For combustion plants larger than 50 MWth, the competent authority may grant derogation from the obligation to comply with the emission limit values provided for in paragraph [X] in the following cases:

(i) For combustion plants using [only/mainly] gaseous fuel who have to resort exceptionally to the use of other fuels because of a sudden interruption in the supply of gas and for this reason would need to be equipped with a waste gas purification facility];

(ii) [For combustion plants not operated more than XXX operating hours, starting from DATE and ending no later than DATE].

(b) Where a combustion plant is extended by at least 50MW, the emission limit value specified in paragraph [X] for new installation shall apply to the extensional part and to the plant affected by the change.

(c) Parties shall ensure that provisions are made in the permits for procedures relating to malfunction or breakdown of the abatement equipment.

(d) In the case of a multi-fuel firing combustion plant involving the simultaneous use of two or more fuels, the competent authority shall provide rules for setting the emission limit values.

(e) In particular the, the limit values shall not apply to:

(i) Plants where the combustion process is an integrated part of a specific production, i.e. the coke oven used in the iron and steel industry and glass and ceramic production

	plants; (ii) Plants in which the products of combustion are used for direct heating, drying, or any other treatment of objects or materials; (iii) Post combustion plants designed to purify the waste gases by combustion which are not operated as independent combustion plants; (iv) Facilities for the regeneration of catalytic cracking catalysts; (v) Facilities for the conversion of hydrogen sulphide into sulphur; (vi) Reactors used in the chemical industry; (vii) Coke battery furnaces; (viii) Cowpers; (ix) Waste incinerators; and, (x) Plants powered by diesel or petrol or combustion turbines, irrespective of the fuel used.
No values	**10.** Limit value for cadmium emissions: [0.05] mg/m³. **11.** Limit value for lead emissions: [0.5] mg/m³. **12.** Limit value for mercury emissions: [0.03] mg/m³.

Yellow underlined / overlap with Gothenburg Protocol

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 20 to 28 and table 3 http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust for http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf
- informal document No3 by the Netherlands, 48th session of WGSR http://www.unece.org/env/documents/2011/eb/wg5/WGSR48/Informal%20docs/Info.doc.3_Reduction_of_mercury_emissions_from_coal_fired_power_plants.pdf
- Best results achieved using techniques with injection of activated carbon, or injection of bromine or chloride (below 1µg/m3) http://www.vdi-nachrichten.com/vdi-nachrichten/aktuelle_ausgabe/akt_ausg_detail.asp?cat=2&id=51772&source=rubrik

II. Primary Iron and Steel Industry (annex II, category 2)

So far the following categories were regulated by the HM Protocol

HM Protcol 1998	New proposal
Sinter plants	Sinter plants
Pellet plants	Pellet plants
	Blast and oxygen furnaces including continuous casting (note: in HM Protocol 98 these installations belonged to category 3)

13. Limit values for sinter plants for particulate emissions

	HM Protocol 1998	Option 1	Option 2	Option 3
Limit value for particulate emissions	8.) 50 mg/m^3	[10] GP [15]	new installations [20] existing installations [50] 1 GP [50][3]	[50]

Underlined in green: overlap with GP but different values for the option1 at the moment

New: Proposed distinction between new and old installations f or option 2

Limit values for heavy metals for sinter plants

HM Protocol 1998	Draft revised HM protocol
No values	**14.** Limit value for cadmium emissions: [0.05] mg/m^3. **15.** Limit value for lead emissions: [1] mg/m^3. **16.** Limit value for mercury emissions: [0.05] mg/m^3.

[3] This ELV should be considered as averaged over a substantial period of time

17. Limit values for particulate emissions for pellet plants

	HM Protocol 1998	Option 1	Option 2	Option 3
Limit value for particulate emissions	9.(a) Grinding, 25 mg/m^3 9. (b) Drying, 25 mg/m^3	[5]	[10]	[25]

Limit values for heavy metals for pellet plants

HM Protocol 1998	Draft revised HM protocol
No values	**18.** Limit value for cadmium emissions: [0.05] mg/m^3. **19.** Limit value for lead emissions: [0.5] mg/m^3. **20.** Limit value for mercury emissions: [0.05] mg/m^3.

21. Limit values for particulate emissions for blast oxygen furnaces including continuous casting (annex II, category 2)

	HM Protocol 1998	Option 1	Option 2	Option 3
Blast furnace: hot stove	11.) 50 mg/m^3	[5][4]	[10][4]	[50]
Basic oxygen steelmaking and casting		[10][4]	[30][4]	[50]

[4] This ELV should be considered as averaged over a substantial period of time

Limit values for heavy metals for blast oxygen furnaces including continuous casting

HM Protocol 1998	Draft revised HM protocol
No values	**22.** Limit value for cadmium emissions: [0.05] mg/m³. **23.** Limit value for lead emissions: [0.5] mg/m³. **24.** Limit value for mercury emissions: [0.05] mg/m³.

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 27 to 30 and table 4 (Please note : numbers for paras 27 and 28 are used twice by mistake in this document) http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust of GP Protocol http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf
- Best Available Techniques Reference Document on the Production of Iron and Steel http://www.bvt.umweltbundesamt.de/archiv-e/bvt_eisen-stahl_vv.pdf
- second draft of BREF document 2009 http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_IS_D2.cfm
- Please note: electric arc furnaces were shifted to the next category

III. Secondary Iron and Steel Industry (annex II, category 3) electric arc furnaces

25. Limit values for particulate emissions for blast oxygen furnaces including continuous casting (annex II, category 2)

	HM Protocol 1998	Option 1	Option 2	Option 3
Existing installations	12.) 20 mg/m^3	[10][5]	[15][5]	[20] daily average
New installations	12.) 20 mg/m^3	[5][5]	[5][5]	[20] daily average

Limit values for heavy metals for electric arc furnaces (EAF)

HM Protocol 1998	Draft revised HM protocol
No values	**26.** Limit value for cadmium emissions: [0.05] mg/m^3. **27.** Limit value for lead emissions: [0.5] mg/m^3. **28.** Limit value for mercury emissions: [0.05] mg/m^3.

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 31 to 34 and table 5 http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust of GP Protocol http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf

[5] This ELV should be considered as averaged over a substantial period of time

IV. Iron foundries (annex II, category4)

29. Limit values for particulate emissions for iron foundries

	HM Protocol 1998	Option 1	Option 2	Option 3
All furnaces (cupola, induction, rotary) All mouldings (lost, permanent)	No values	[10]	[20]	[50]
Hot and cold rolling	No values	[10]	[20]	[30]

Limit values for heavy metals for iron foundries

HM Protocol 1998	Draft revised HM protocol
No values	**30.** Limit value for cadmium emissions: [0.05] mg/m³. **31.** Limit value for lead emissions: [0.5] mg/m³. **32.** Limit value for mercury emissions: [0.05] mg/m³.

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 35 and 36 and table 6 http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust of GP Protocol http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf
- Technical information on iron foundries can be found already in ANNEX III of the HM protocol of 1998 (paragraphs 34 and 35 and table 6). Also it is mentioned that technical measures can reduce dust concentration to 20 mg/m3 a limit value for annex V was not agreed at this time.
- BREF Document (2005) http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_SF.cfm

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

33. Limit values for particulate emissions

Limit value for particulate emissions	HM Protocol 1998	Option 1	Option 2	Option 3
- Fabric filters, ceramic filters - Electrostatic precipitators - Scrubbers	20 mg/m^3 (for annex II, category 5) no distinction for type of filters	[3] [7] [10]	[5] [12] [20]	[20] [20] [20]

34. The preferred technique for dust abatement is the use of fabric filters or ceramic filters. Electrostatic precipitators should be used for gases containing to much moist, for hot gases, or when the dust is too sticky. Scrubbers should be used as the temperature or the nature of the gases precludes the use of other techniques, or when gaseous elements or acids have to be removed simultaneously with dust.

(Note: This paragraph 34 is comparable but not identical to footnote a) of table 8 , draft technical annex on dust http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf)

Limit values for heavy metals for primary and secondary non-ferrous metal industry

HM Protocol 1998	Draft revised HM protocol
No values	**35.** Limit value for cadmium emissions: [0.05] mg/m^3. **36.** Limit value for lead emissions: [1] mg/m^3. **37.** Limit value for mercury emissions: [0.05] mg/m^3.

Under this category would fall the proposed inclusion of the **production of manganese and secondary aluminium**. The same requirements would apply.

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 37 to 53 and tables 7 a/b/c. http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust of GP Protocol http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf
- http://www.bmu.de/foerderprogramme/pilotprojekte_inland/doc/47011.php (values below 1 mg/m3 with secondary filters which can be regenerated, article in German)
- BREF Document (2005) http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_NFM.cfm
- BREF Document Draft 2 (2009) http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_NFM_D2.cfm
- For information on manganese and aluminium see:
    - "The need for mercury abatement in manganese production", contribution by Norway for UNEP INC2, the original document is copied at the end of this document
    - Informal document 11, 47th session of WGSR (contains information on secondary aluminium and manganese production) http://www.unece.org/env/documents/2010/eb/wg5/wg47/Informal%20documents/Info.%20dic%2011_Information%20on%20Emissions%20from%20the%20Secondary%20aluminiu%20and%20Manganese%20Industries%20by%20the%20Chair%20of%20the.pdf
    - Data on manganese (Mn) production presented by Tor Faerden, Norwegian Pollution Control Authority (SFT) at the Vienna meeting of the TF HM in June 2007. Data documentation Manganese Industry: http://www.unece.org/env/lrtap/TaskForce/tfhm/fourth%20meetingdocs/AddInfofromNorwayonHgreductionmeasuresWien.ppt
    - Erhebung von Quecksilberkonzentrationen in Fraktionen der Leuchtmittelverarbeitung, Hug, E. und Renner, N. , im Auftrag von SENS und SLRS, Schweiz– this is a brochure on adherence of mercury on aluminium parts of recycled fluorescent lamps (in German), not available on internet

VI. Production of lead (annex II, categories 5 and 6)

38. Limit values for particulate emissions from production of lead

Limit value for particulate emissions	HM Protocol 1998	Option 1	Option 2	Option 3
- production of lead	14.) 10 mg/m^3	[3]	[5]	[10]

Note: In this case for PM no overlap with the GP.

HM Protocol 1998	Draft revised HM protocol
No values	**39.** Limit value for cadmium emissions: [0.05] mg/m^3. **40.** Limit value for lead emissions: [2] mg/m^3. **41.** Limit value for mercury emissions: [0.05] mg/m^3.

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 42 to 44 and tables 7 a/b/c. http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- BREF Document Draft 2 (2009) chapter 5 http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_NFM_D2.cfm

VII. Cement Industry (annex II, category 7)

42. Installations for the production of cement clinker in rotary kilns with a capacity > 500 Mg/day or in other furnaces with a production capacity exceeding 50 Mg/day.

43. Limit values for particulate emissions refer to 10% O2 concentration in flue gas.

Limit value for particulate emissions	HM Protocol 1998	Option 1	Option 2	Option 3
cement industry	15.) 50 mg/m^3	[15]	[20]	[50]

HM Protocol 1998	Draft revised HM protocol
No values	**44.** Limit value for cadmium emissions: [0.05] mg/m^3. **45.** Limit value for lead emissions: [0.5] mg/m^3. **46.** Limit value for mercury emissions: [0.05] mg/m^3.

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 54 to 61 and table 8. http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust of GP Protocol http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf
- BREF document (2010) http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_CLM.cfm

VIII. Glass Industry (annex II, category 8)

HM Protocol 1998	Draft revised HM protocol
16. Limit values refer to different O2 concentrations in flue gas depending on furnace type: tank furnaces:8%; pot furnaces and day tanks: 13%.	**47.** Limit values refer to different O2 concentrations in flue gas depending on furnace type: tank furnaces (continuous melters): 8%; pot furnaces and day tanks (discontinuous melters): 13%

48. Limit value for particulate emissions:

Limit value for particulate emissions	HM Protocol 1998	Option 1	Option 2	Option 3
glass industry	no value	[10] GP,new installations: [10] existing instal.: [15]	[20] GP [30]	[50]

HM Protocol 1998	Draft revised HM protocol
17. Limit value for lead emissions: 5 mg/Nm³	**49.** Limit value for lead emissions: [0.5] mg/Nm³ **50.** Limit value for lead emissions in container glass production using foreign cullet: [0.8] mg/Nm³ **51.** Limit value for lead emissions in glass production if lead is required for product quality: [3] mg/Nm³ **52.** Limit value for cadmium emissions:[0.05] mg/Nm³ **53.** Limit value for cadmium emissions in container glass production: [0.5] mg/Nm³ **54.** Limit value for cadmium emissions if cadmium compounds are used as colouring agents for quality reasons: [0.2] mg/Nm³ **55.** Limit value for mercury emissions: [0.05] mg/Nm³

56. For oxy-fuel burners and electrical heating it is necessary to evaluate the performances only in terms of specific mass emissions (kg/tonne of glass melted).

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 62 to 67 and table 9. http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust of GP Protocol http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf
- BREF document (2001) http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_GLS.cfm
- BREF document Draft 2 (2009) http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_GLS_D2.cfm

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

57. Limit values refer to the total quantity of mercury released by a plant into the air, regardless of the emission source and expressed as an annual mean value.

58. Limit values for existing chlor-alkali plants using the mercury cell process: [1.0 g per Mg] chlorine produced.

59. New chlor-alkali plants are to be operated mercury free.

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 68 to 72 and table A and B. http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- Report of the TF HM ECE/EB.AIR/WG.5/2006/2, page 15, chapter III, paragraphs 61 to 63 a) and 64 http://www.unece.org/env/documents/2006/eb/wg5/ece.eb.air.wg.5.2006.2.e.pdf
- Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing industry http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_CAK.cfm

X. Municipal waste incineration (> 3 t/hour), medical and hazardous waste incineration (> 1 t/hour) (annex II, categories 10 and 11)

60. Limit values refer to 11% O2 concentration in flue gas for waste incineration; co-incineration in combustion installations: 6% O2 for solid fuels and 6% O2 for liquid fuels; co-incineration in cement kilns: 10% O2.

61. Limit value for particulate emissions:

Limit value for particulate emissions	HM Protocol 1998	Option 1	Option 2	Option 3
For waste incineration, co-incineration of waste with a thermal input from waste > 25%, and co-incineration in cement kilns with a thermal input from waste > 60%	22.(a) 10 mg/m3 for hazardous and medical waste incineration; 22 (b) 25 mg/m3 for municipal waste incineration.	[3]	[5]	[10]
For co-incineration of waste with a thermal input from waste < 25%, and co-incineration in cement kilns with a thermal input from waste < 60%		[5] no proposal	[10]	no proposal in GP

62. Limit value for mercury emissions:

HM Protocol 1998	Draft revised HM Protocol
22.(a) 10 mg/m³ for hazardous and medical waste incineration	**62. (a)** [0.03] mg/m³ for waste incineration and co-incineration

22.(b) 25 mg/m³ for municipal waste incineration	**62. (b)** [0.05] mg/m³ for co-incineration of waste in cement kilns if mercury emissions are due to raw material input

63. Limit value for cadmium emissions: [0.05] mg/m³.

64. Limit value for lead emissions: [0.5] mg/m³."

Relating technical information on BAT:

- proposal forAnnex III (Informal document No. 7, 46th session of WGSR), paragraphs 73 to 82 and table 10. http://www.unece.org/env/documents/2010/eb/wg5/Informal%20documents/Info%207.%20Options%20proposed%20by%20Switzerland%20for%20amending%20annex%20III%20to%20the%20Heavy%20Metals%20Protocol.pdf
- background document on dust of GP Protocol http://www.unece.org/env/documents/2009/EB/wg5/wgsr45/ece.eb.air.wg.5.2009.21.e.pdf
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Annex

The need for mercury abatement in manganese production

According to the para 29 study the global share of the emissions from the non ferrous metals industry is 7 % when zink, cobber and lead are included. According to the International Manganese institute (http://www.manganese.org/about_mn/production) the global manganese production was 11.7 million tons in 2009, which was a reduction by 18 % from the year before.

All of the Norwegian manganese plants have installed mercury abatements systems to minimize the mercury emissions. The last five years the plant at Porsgrunn has reported an average of 13 kg of mercury as atmospheric emissions. The production level of the plant is about 100 000 tons of ferromangense a year. Hence, the mercury emission per ton of ferromanganese produced is about 0.13 grams. This level represents the emission level when mercury is actively removed from the off-gas by applying abatement systems.

By applying the numbers from the plant at Porsgrunn to the global production of manganese, the emissions globally from the manganese production will sum up to about 1.5 tons of mercury *if all manganese plants had abatement systems for removal of mercury*. However, without abatement the level of mercury per ton of manganese produced can be at about 3 grams per ton manganese produced. Hence, the global emissions level accounts to about 35 tons a year, which represents about 1.5 % of the global emissions when compared to the total in the para 29 study. The total could be somewhat too high due to the fact that some manganese producers use low mercury ore. Anyway, the difference illustrate the possibility to reduce the global emissions of mercury significantly by to a larger extent introduce abatement of mercury at manganese plants.

The costs of installing mercury abatement systems should not be too high compared to the positive effect the emission reduction will represent. The costs at Eramet Porsgrun to install the mercury abatement unit were about 5 million Euro or 6.7 million US Dollars for one smelter.

Annex X: Limit values for emissions from production of manganese

I. Introduction

1. Two types of limit values are important for mercury emission control:

(a) Limit values for total mercury, both as particulate matter and gas; and

(b) Limit values for emissions of particulate matter in general.

2. In principle, limit values for particulate matter cannot replace specific limit values for mercury, because the quantity of metals associated with particulate emissions differs from one process to another. Secondly, a large share of mercury emissions is emitted in gas phase, and will not be included in the particulate matter. However, compliance with these limits contributes significantly to reducing mercury metal emissions. Moreover, monitoring particulate emissions is generally less expensive than monitoring individual species. Therefore, particulate limit values are of great practical importance.

3. Limit value means the quantity of a substance contained in the waste gases from an installation that is not to be exceeded. Limit values for particulate matter refer to the solid substance in the waste gases. Limit values for mercury include the solid, gaseous and vapour form of the metal and its compounds, expressed as the metal. Unless otherwise specified, it shall be calculated in terms of mass of pollutant per volume of the waste gases (expressed as $\mu g/Nm^3$), assuming standard conditions for temperature and pressure for dry gas (volume at 273.15 K, 101.3 kPa).

4. Emissions shall be monitored in all cases. Compliance with limit values shall be verified. The methods of verification can include continuous or discontinuous measurements, type approval, or any other technically sound method. In case of discontinuous measurement or other appropriate determination procedures, compliance with the emissions standards is achieved if the mean value based on an appropriate number of measurements under representative conditions does not exceed the value of the emission standard. The inaccuracy of the continuous and discontinuous measurement methods may be taken into account for verification purposes.

5. Sampling and analysis of relevant polluting substances and measurements of process parameters, as well as the quality assurance of automated measuring systems and the reference measurement methods to calibrate those systems shall be carried out in accordance with CEN standards. If CEN standards are not available, ISO standards, national or international standards which will ensure the provision of data of an equivalent scientific quality shall apply.

6. Limit values for mercury emissions from production of ferromanganese and silicomanganese. The limit is given as specific emission, mercury emissions per unit manganese produced.

Installation category	Emission limit	Unit of measurement
Existing manganese plants	200	mg/ton produced
New manganese plants	150	mg/ton produced

Alternatively;

Emission limits given as concentration values of mercury in the off-gas. The

Installation category	Emission limit	Unit of measurement
Existing manganese	5	µg/Nm³
New manganese plants	5	µg/Nm³

Table: Limit values for atmospheric emissions from secondary steel production expressed as concentration limits.

Non-Ferrous metal production: Ferromanganese/silicomanganese

MERCURY ABATEMENT

Market and use

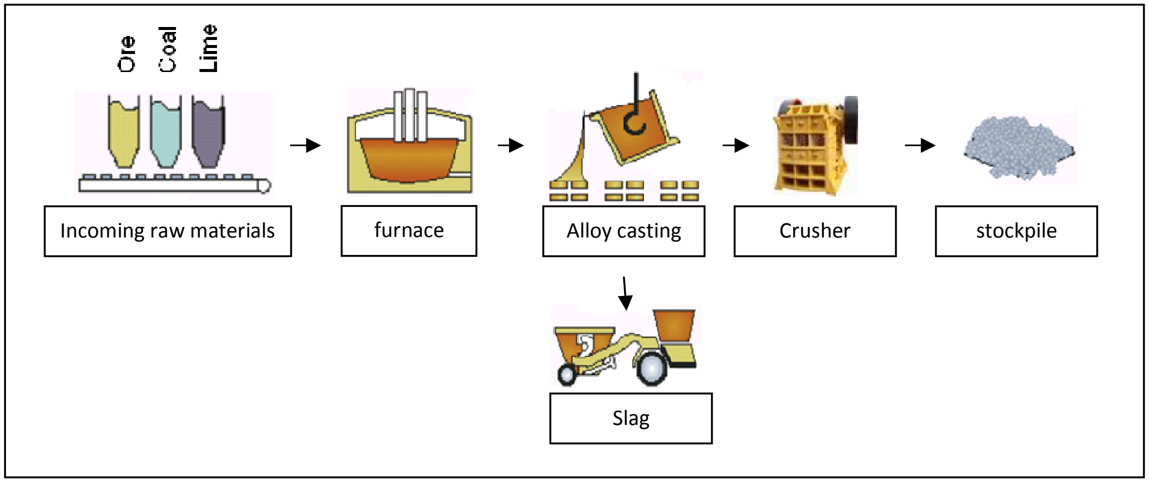
Manganese is a metal used mainly as an alloy in the steel industry. The world demand for manganese is therefore strongly influenced by the demand for steel. The world production of different manganese alloys was approximately 13 million tons in 2007, where China was the indisputable largest producing country with close to half the worldwide production.

Three of the world's largest manganese ferroalloy producers have plants in European countries. Private Group, with 20% share of the world market, has plants in Romania, Poland, Ukraine and Russia. Eramet and Vale have both plants in France, Italy and Norway. The EEA countries, Poland and Romania produce approximately. 1, 3 million tons annually. Russia and Ukraine, together with other producing CIS countries are estimated to have an annual production of nearly 2 million tons[6].

Production process

[6] ENRC : *www.enrc.com/files/Manganese_Presentation_ENG4.ppt*

Manganese ferroalloys are commercially produced by carbothermic reduction of manganese oxide ores. Coke, coal, and petrol coke are all used in various degrees as reduction agents. There are two main processes used commercially in the production of manganese ferroalloys, namely the blast furnace process and the electrical smelting process. Today, the electrical smelting process (submerged arc furnace) is by far the most widely used process due to the lower consumption of high quality carbon products, higher manganese yield, and more flexibility to produce different grades of manganese ferroalloys.



Figur 1: Overview of the production process of manganese ferroalloys

Mercury emission aspects and abatement Technology

Heavy metals emitted from manganese ferroalloy production originate from the ones present in the raw materials. A large share of the heavy metals introduced in the process, however, ends up in the finished product and slag, or in particulate form in the dust that potentially are collected at end of pipe. Mercury, on the other hand, evaporates at low temperatures and is therefore emitted as vapor in the off-gas from the manganese ferroalloy production. The amount emitted is however largely dependent on the mercury content in the manganese ore used, and to some degree also by the content in the selected reduction materials. Especially one ore, which is used to a large extent, contains significant quantities of mercury. Facilities using this mercury-rich manganese ore are therefore especially exposed to emit high concentrations of mercury.

Increased environmental awareness and stricter environmental legislation in the 1990s contributed so that three Norwegian manganese producers were forced to install off-gas cleaning units for mercury in the early 2000. This made it possible for the manganese plant to still use mercury–rich manganese ore, and similarly stay within the strict emission limits set by the governmental pollution control authority.

Norway has today four manganese plants; Eramet Sauda, Eramet Porsgrunn, Eramet Kvinesdal, and Vale Manganese. All plants have an upper emission limit of 15-36 kg of mercury to air per year. The cleaning processes on Eramet Kvinesdal, Sauda and Porsgrunn are installed on the off-gas stream from the reduction process itself, while Vale Manganese has installed the cleaning step on their sintering process only. The explanation of the different approaches is due to that only Vale Manganese sinter the manganese ore themselves. The Eramet plants buy already sintered ore and mercury emissions from the sintering process happen elsewhere. Simultaneously, Vale Manganese does not use such mercury-rich ore as the Eramet plants, which makes abatement of mercury from the reduction process redundant in order to reach their emission limits for mercury.

MILTEC cleaning process – Eramet Kvinesdal

In the late 1990s, Tinfos Manganese (now Eramet Kvinesdal), developed the MILTEC process together with MILTEC AS. The MILTEC process removes mercury from the off-gas by washing it co-currently with seawater containing sodium hypochlorite, which oxides the mercury. In addition, the wash water collects the dust, and reduces SO_2 emissions to air.

The wash water after gas cleaning contains the mercury as mercury salts, which is added disodium sulfite (Na_2S). This leads to the formation of mercury sulfate (HgS) and other metal sulfite precipitate, which can be removed from the process using a press filter.

The MILTEC process is adapted to clean the off-gas from Eramet Kvinesdal after it has been through several additional cleaning steps such as venturi scrubbers and cyclones. The cleaning process reduces the mercury emissions to air to over 95%. The sludge from the process is categorized as hazardous, and treated at a certified waste disposal site.

The cleaning step was introduced at Tinfos in 2001, and has since reduced the emission of mercury to air from over 100 kg a year to less than 10 kg a year. This accounts for approximately 40g/Nm3, and makes Eramet Kvinesdal able to meet the restrictions of 15kg mercury emitted per year set by the Norwegian pollution control authority.

The Miltec process for the removal of mercury has not yet been installed elsewhere, but the company has at present time interested costumers’ in Australia and Canada.

MRU units (LURGI) – Eramet Sauda/Porsgrunn
Both Eramet Sauda and Porsgrunn use LURGI mercury removal units (MRU) which uses wet-electrostatic precipitator (WESP) and a packed bed absorber using sulfur-impregnated coal in their removal of mercury from the off-gas. The WESP removes dust and tars before the mercury contaminated off-gas is heated to 60-85 degree Celsius and is absorbed in 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.

Eramet Sauda and Porsgrunn also considered the MILTEC process for the removal of mercury. The Miltec proces, despite being cheaper, was however not selected. This was because the process showed to be problematic for cleaning non combusted off-gas from the process which was needed in Porsgrunn and Sauda. Eramet Kvinesdal, on the other hand, combust their off-gas before it entered to the Miltec`s mercury cleaning step.

The MRU is able to absorb over 95% of the mercury in the off-gas. The units were installed in 2001/2002 after new strict legislations from the Norwegian Pollution Control Authority implemented in 1999. Without cleaning, the two plants would have a total emission of 600-900 kg Hg per year with the use of the mercury-rich ore, while the companies now meet the emission requirements set to 15 and 36 kg per year for Eramet Porsgrunn and Sauda, respectively. The process also abates emissions of other heavy metals, organic matter and dust. Waste from the removal process is categorized as hazardous and is treated by a certified waste disposal company. The investment of the MRU was 5 million EUR per smelter.

Vale manganese – injection of active carbon in the off-gas
Vale manganese do not use as mercury-rich manganese ore as Eramet. They do, however, sinter their manganese ore. Mercury is released in the sintering process, and Vale was therefore needed to install a cleaning step in 2008 in order to reach their emission limits. The cleaning step works by injecting active carbon particles into the off-gas stream from the sintering process. These particles are fine-grained and absorb the mercury which consists as gas coming from the process. The particles are collected in a fabric filter at end of pipe and are treated by a certified waste disposal company. The cleaning step absorbs over 95% of the mercury in the off-gas. Note that Vale`s cleaning step is installed on the off-gas from the company`s sintering process only.

Year	Eramet Kvinesdal [kg]	Eramet Sauda [kg]	Eramet Porsgrunn [kg]	Vale manganese Norway [kg]
1995	92,00	-	-	
1996	71,40	-	-	
1997	71,00	-	-	

1998	92,00	17,60	-	
1999	99,10	72,00	29,00	
2000	70,00	10,40	51,00	
2001	20,15	11,00	33,00	
2002	6,67	13,80	13,40	[7]
2003	4,30	13,60	13,00	1,60
2004	11,19	9,00	24,00	22,00
2005	5,95	7,00	15,00	11,00
2006	3,67	15,00	19,00	9,80
2007	5,21	10,00	17,00	57,20[8]
2008	5,61	7,00	8,00	5,00
2009	4,82	4,00	5,00	1,40

Figur 2: The table shows mercury emissions from the four norwegian ferromanganese/silicomanganese plants. The emissions are listed in kilograms. Change of ore for the Eramet Sauda and Porsgrunn would have increased the emissions to hundreds of kg og Mercury if not the MRU abatement units were installed in 2001.

Typical concentration of mercury in the off-gases from the Porgrunn and Sauda plants after removal of mercury are 1-2 µg/Nm^3 as gaseous mercury in the off gas. In addition about 0,5 µg/Nm^3 is contained in particulate matter.

[7] The production of manganese at Vale in Mo i Rana was establisted in 2003.

[8] Due to higher mercury content in the ore, the mercury emissions increased significantly in 2007. The facility had to install a mercury abatement unit to ensure emissions lower than the permit. The low emissions of 2008 and 2009 is a result of the abatement.