REVISED DRAFT
GUIDELINES ON BEST AVAILABLE TECHNIQUES AND PROVISIONAL GUIDANCE ON BEST ENVIRONMENTAL PRACTICES RELEVANT TO ARTICLE 5 AND ANNEX C OF THE STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS

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Section I

Introduction

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I.A Purpose

Under the Stockholm Convention on Persistent Organic Pollutants, Parties shall promote in some cases and require in others the use of best available techniques, and promote the application of best environmental practices. In short, each Party shall:

- Develop, within two years of the date of entry into force of the Convention for it, an action plan (national or regional) where releases of chemicals listed in Annex C of the Convention are identified, characterized and addressed; the plan shall include source inventories and take into consideration the source categories listed in Parts II and III of Annex C (subparagraph (a) of Article 5);
- For **new sources**:
  - Promote and, in accordance with the implementation schedule of its action plan, require the use of best available techniques within source categories identified as warranting such action, with particular initial focus on source categories identified in Part II of Annex C; the requirement to use best available techniques for Part II source categories shall be phased in as soon as practicable, but no later than four years after entry into force of the Convention for the Party (subparagraph (d) of Article 5);
  - Promote, for those categories identified above, the use of best environmental practices (subparagraph (d) of Article 5);
  - Promote, in accordance with its action plan, best available techniques and best environmental practices within source categories such as those listed in Part III of Annex C which a Party has not addressed above (subparagraph (e) (ii) of Article 5);
- For **existing sources**:
  - Promote, in accordance with its action plan, the use of best available techniques and best environmental practices for source categories listed in Part II of Annex C and such sources as those in Part III of the Annex (subparagraph (e) (i) of Article 5).

When applying best available techniques and best environmental practices for the above, Parties should take into consideration the general guidance on prevention and release reduction measures in Annex C and guidelines on best available techniques and best environmental practices to be adopted by decision of the Conference of the Parties (see subparagraphs (d) and (e) of Article 5).

The Conference of the Parties to the Stockholm Convention, at its first meeting held in Punta del Este, Uruguay, 2–6 May 2005, in its decision SC-1/19, established an Expert Group on Best Available Techniques and Best Environmental Practices with a mandate to complete further work on the enhancement and strengthening where need be of the "draft guidelines on best available techniques and guidance on best environmental practices relevant to Article 5 and Annex C of the Convention"[1] as contained in document UNEP/POPS/COP.1/INF/7.

The Expert Group has submitted the guidelines and guidance for consideration and possible adoption by the third meeting of the Conference of the Parties to the Stockholm Convention to be held from 30 April to 4 May 2007.

In accordance with Article 5 of the Convention, the guidelines and guidance, upon adoption by decision of the Conference of the Parties, should be taken into consideration when applying best available techniques and best environmental practices pursuant to subparagraphs (d) and (e) of Article

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[1] The draft guidelines on best available techniques and guidance on best environmental practices relevant to Article 5 and Annex C of the Convention were developed by the Expert Group on Best Available Techniques and Best Environmental Practices established for this purpose by the sixth session of the Intergovernmental Negotiating Committee for an International Legally Binding Instrument for Implementing International Action on Certain Persistent Organic Pollutants (see UNEP/POPS/INC.6/22, paragraph 75).

5. They may also be used to assist decision-making at the country level in the implementation of action plans and other actions related to the obligations under Article 5 and Annex C.

I.B Structure of document and using guidelines and guidance

Section I of this document is an introduction and includes the purpose and structure of the document; a brief description of the characteristics and risks of chemicals listed in Annex C of the Stockholm Convention; directly relevant provisions of the Stockholm Convention, Article 5 and Annex C; a summary of required measures under these provisions; and an explanation of the relationship of these provisions to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal.

Section II provides guidance on consideration of alternatives, including a checklist that may be used in applying best available techniques to new sources, and information on other considerations of the Stockholm Convention.

Section III includes general guidance, applicable principles and descriptions of considerations that cut across multiple source categories.

Section IV is a compilation of the summaries provided for each category source in sections V and VI.

Sections V and VI contain specific guidelines for each source category listed in Part II and Part III of Annex C of the Stockholm Convention. For each of the source-specific guidelines, the following information is provided:

- Process description;
- Sources of chemicals listed in Annex C;
- Primary and secondary measures;
- Performance standards;
- Performance reporting;
- Case studies.

References and bibliographic information are provided for each of the guidelines.

The complete list of references and bibliographic information for the guidelines and guidance is available at www.pops.int. This site can be updated as relevant new information becomes available.

I.C Chemicals listed in Annex C: Definition, risks, toxicity

1. What are the chemicals listed in Annex C?

1.1 Definition

The chemicals listed in Annex C of the Stockholm Convention include polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB).

1.2 Characteristics

The chemicals listed in Annex C, in addition to their documented toxicity, are persistent and bioaccumulative and undergo long-range transport. Persistent chemicals do not easily degrade in the environment. Bioaccumulative chemicals are usually fat soluble and build up in higher trophic levels, including in humans. The chemicals listed in Annex C, as semi-volatile compounds, undergo a series of evaporations and condensations in the environment, making them mobile.

1.3 Uses

PCDD and PCDF have never been used as commercial products nor were they intentionally manufactured for any reason other than laboratory purposes.

PCB have been used as coolants and lubricants in transformers, capacitors and other electrical equipment because they do not burn easily and are good insulators. Among other things, products that may contain PCB include old fluorescent lighting fixtures and electrical devices containing PCB capacitors.

HCB has been widely used as a pesticide to protect the seeds of onions and sorghum, wheat and other grains against fungus. It has also been used to make fireworks, ammunition and synthetic rubber. It is also used as a solvent in the production of pesticide.

The following guidelines and guidance, however, do not apply to the commercial production of PCB and HCB, but rather to those processes that inadvertently lead to their formation and release.

2. What are the risks to humans of chemicals listed in Annex C?

2.1 Exposure

Because these chemicals exist throughout the environment, almost all living creatures, including humans, have been exposed to the chemicals listed in Annex C. Exposure arises mainly through fatty foods, including breast milk, but can also arise from accidental or occupational situations. The health effects that have been associated with these exposures depend on a variety of factors, including the level of exposure and the duration and frequency of exposure.

2.2 PCDD and PCDF

Much of the information on the toxicity of these chemicals is based on extensive studies of the most toxic member of the family, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in experimental animals. TCDD and related compounds can produce a wide variety of effects in animals and might produce many of the same effects in humans.

The International Agency for Research on Cancer (IARC) under the World Health Organization (WHO) identified 2,3,7,8-TCDD as the most toxic of all dioxin compounds, and as carcinogenic to humans, based mainly on studies of cases involving accidental or occupational heavy exposure. Animal studies have also shown an increased risk of cancer from long-term exposure to PCDD/PCDF.

TCDD exposure results in a wide variety of reproductive and developmental effects in a number of species of experimental animals, including reduced viability, structural alterations, growth retardation and functional alterations. There is also evidence of neurobehavioural effects and effects on immune and various endocrine functions, including those of the thyroid. Because of this evidence in animals, particularly at high doses but in some cases at doses close to those with relevance for human beings, scientists are concerned about the potential for these same effects to occur in humans, especially the effects of prenatal exposure on developing children.

2.3 PCB

The most commonly observed health effects in people exposed to large amounts of PCB are skin conditions. Studies in exposed workers have shown changes in blood and urine that may indicate liver damage. In the Yusho and Yucheng incidents, each involving about 2,000 cases, Japanese and Taiwanese people were exposed to high concentrations of PCB and PCDF through consumption of contaminated rice oil. Fatal liver disease (among other indicators) was found to be 2–3 times more frequent than national rates in both cohorts (IARC)**.** PCB exposures in the general population are not likely to result in skin and liver effects. Most of the studies of health effects of PCB in the general population examined children of mothers who were exposed to PCB.

IARC has determined that PCB are probably carcinogenic to humans. A few studies of workers indicated that PCB were associated with certain kinds of cancer in humans, such as cancer of the liver and biliary tract. Rats that ate food containing high levels of PCB for two years developed liver cancer.

PCB may be associated with developmental or endocrine effects. Women who were exposed to relatively high levels of PCB in the workplace or ate large amounts of fish contaminated with PCB had babies that weighed slightly less than babies of women who did not have these exposures. Babies born to women who ate PCB-contaminated fish also showed abnormal responses in tests of infant behaviour. Some of these behaviours, such as problems with motor skills and a decrease in short-term memory, lasted for several years.

2.4 HCB

The United States Department of Health and Human Services has determined that HCB may reasonably be expected to be a carcinogen. Studies in animals show that long-term ingestion of large amounts of HCB can damage the liver, thyroid, nervous system, bones, kidneys, blood, and immune and endocrine systems.

3. How is the toxicity of chemicals listed in Annex C measured?

3.1 Toxic equivalency

For PCDD/PCDF the most toxic compounds have chlorines in the 2, 3, 7 and 8 positions. For PCB, the highest toxicity is with compounds where the molecule can assume a planar conformation, analogous to that of the PCDD/PCDF. Toxicity of mixtures of these materials is evaluated as a single number called the toxic equivalent (TEQ).

To determine the TEQ of a mixture, the amount of each of the toxic members of the family is multiplied by a weighting factor relative to the most toxic chemical, 2,3,7,8-TCDD. This weighting factor is called a toxic equivalency factor (TEF). The first scheme, derived by the Committee on the Challenges of Modern Society of the North Atlantic Treaty Organisation in 1988 and called I-TEFs, covered 17 PCDD/PCDF. Twenty-nine of the 419 individual PCDD, PCDF and PCB have TEFs assigned by WHO in 1997 and revised in 2005 (Table 1). HCB does not have a TEF.

3.2 Tolerable intakes

The tolerable daily intake (TDI) is the amount of intake per kg of body weight per day of a chemical substance judged not to give rise to manifestations of health effects if such an amount is taken every day for an entire lifetime. The TDI established by WHO in 1998 for chemicals contributing to TEQ was set at 1–4 pg/kg body weight/day.[2] In 2001, the Joint FAO/WHO Expert Committee on Food Additives set a provisional tolerable monthly intake (PTMI) of 70 pg/kg body weight/month, which approximates to 2.3 pg/kg body weight/day.

Table 1. Toxic equivalency factors

Congener	**WHO/97 Mammalian TEFs**	**I-TEFs**	**WHO/2005 Mammalian TEFs**
PCDD			
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01
1,2,3,4,6,7,8,9-OCDD	0.0001	0.001	0.0003
PCDF			
2,3,7,8-TCDF	0.1	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
1,2,3,4,6,7,8,9-OCDF	0.0001	0.001	0.0003

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[2] 1 pg (picogram) = 1 × 10^{-15} kilogram (1 × 10^{-12} gram).

Congener		**WHO/97 Mammalian TEFs**	**I-TEFs**	**WHO/2005 Mammalian TEFs**
PCB				
IUPAC No.	**Structure**			
77	3,3',4,4'-TCB	0.0001	n.a.	0.0001
81	3,4,4',5-TCB	0.0001		0.0003
105	2,3,3',4,4'-PeCB	0.0001		0.00003
114	2,3,4,4',5-PeCB	0.0005		0.00003
118	2,3',4,4',5-PeCB	0.0001		0.00003
123	2',3,4,4',5-PeCB	0.0001		0.00003
126	3,3',4,4',5-PeCB	0.1		0.1
156	2,3,3',4,4',5-HxCB	0.0005		0.00003
157	2,3,3',4,4',5'-HxCB	0.0005		0.00003
167	2,3',4,4',5,5'-HxCB	0.00001		0.00003
169	3,3',4,4',5,5'-HxCB	0.01		0.03
189	2,3,3',4,4',5,5'-HpCB	0.0001		0.00003

IUPAC No.	**Structure**			
non-*ortho* substituted				
77	3,3',4,4'-TCB	0.0001	n.a.	0.0001
81	3,4,4',5-TCB	0.0001		0.0003
126	3,3',4,4',5-PeCB	0.1		0.1
169	3,3',4,4',5,5'-HxCB	0.01		0.03
mono-ortho substituted				
105	2,3,3',4,4'-PeCB	0.0001		0.00003
114	2,3,4,4',5-PeCB	0.0005		0.00003
118	2,3',4,4',5-PeCB	0.0001		0.00003
123	2',3,4,4',5-PeCB	0.0001		0.00003
156	2,3,3',4,4',5-HxCB	0.0005		0.00003
157	2,3,3',4,4',5'-HxCB	0.0005		0.00003
167	2,3',4,4',5,5'-HxCB	0.00001		0.00003
189	2,3,3',4,4',5,5'-HpCB	0.0001		0.00003

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I.D Article 5 and Annex C of the Stockholm Convention

Box 1. Article 5 of the Stockholm Convention

ARTICLE 5

Measures to reduce or eliminate releases from unintentional production

Each Party shall at a minimum take the following measures to reduce the total releases derived from anthropogenic sources of each of the chemicals listed in Annex C, with the goal of their continuing minimization and, where feasible, ultimate elimination:

(a) Develop an action plan or, where appropriate, a regional or subregional action plan within two years of the date of entry into force of this Convention for it, and subsequently implement it as part of its implementation plan specified in Article 7, designed to identify, characterize and address the release of the chemicals listed in Annex C and to facilitate implementation of subparagraphs (b) to (e). The action plan shall include the following elements:

  (i) An evaluation of current and projected releases, including the development and maintenance of source inventories and release estimates, taking into consideration the source categories identified in Annex C;

  (ii) An evaluation of the efficacy of the laws and policies of the Party relating to the management of such releases;

  (iii) Strategies to meet the obligations of this paragraph, taking into account the evaluations in (i) and (ii);

  (iv) Steps to promote education and training with regard to, and awareness of, those strategies;

  (v) A review every five years of those strategies and of their success in meeting the obligations of this paragraph; such reviews shall be included in reports submitted pursuant to Article 15;

  (vi) A schedule for implementation of the action plan, including for the strategies and measures identified therein;

(b) Promote the application of available, feasible and practical measures that can expeditiously achieve a realistic and meaningful level of release reduction or source elimination;

(c) Promote the development and, where it deems appropriate, require the use of substitute or modified materials, products and processes to prevent the formation and release of the chemicals listed in Annex C, taking into consideration the general guidance on prevention and release reduction measures in Annex C and guidelines to be adopted by decision of the Conference of the Parties;

(d) Promote and, in accordance with the implementation schedule of its action plan, require the use of best available techniques for new sources within source categories which a Party has identified as warranting such action in its action plan, with a particular initial focus on source categories identified in Part II of Annex C. In any case, the requirement to use best available techniques for new sources in the categories listed in Part II of that Annex shall be phased in as soon as practicable but no later than four years after the entry into force of the Convention for that Party. For the identified categories, Parties shall promote the use of best environmental practices. When applying best available techniques and best environmental practices, Parties should take into consideration the general guidance on prevention and release reduction measures in that Annex and guidelines on best available techniques and best environmental practices to be adopted by decision of the Conference of the Parties;

(e) Promote, in accordance with its action plan, the use of best available techniques and best environmental practices:

(i) For existing sources, within the source categories listed in Part II of Annex C and within source categories such as those in Part III of that Annex; and

(ii) For new sources, within source categories such as those listed in Part III of Annex C which a Party has not addressed under subparagraph (d).

When applying best available techniques and best environmental practices, Parties should take into consideration the general guidance on prevention and release reduction measures in Annex C and guidelines on best available techniques and best environmental practices to be adopted by decision of the Conference of the Parties;

(f) For the purposes of this paragraph and Annex C:

(i) "Best available techniques" 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 in principle the basis for release limitations designed to prevent and, where that is not practicable, generally to reduce releases of chemicals listed in Part I of Annex C and their impact on the environment as a whole. In this regard:

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

(iii) “Available” techniques means those techniques that are accessible to the operator and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages; and

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

(v) "Best environmental practices" means the application of the most appropriate combination of environmental control measures and strategies;

(vi) “New source” means any source of which the construction or substantial modification is commenced at least one year after the date of:

a. Entry into force of this Convention for the Party concerned; or

b. Entry into force for the Party concerned of an amendment to Annex C where the source becomes subject to the provisions of this Convention only by virtue of that amendment.

(g) Release limit values or performance standards may be used by a party to fulfil its commitments for best available techniques under this paragraph.

Box 2. Annex C of the Stockholm Convention

Annex C

UNINTENTIONAL PRODUCTION

Part I: Persistent organic pollutants subject to the requirements of Article 5

This Annex applies to the following persistent organic pollutants when formed and released unintentionally from anthropogenic sources:

Chemical
Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) Hexachlorobenzene (HCB) (CAS No: 118-74-1) Polychlorinated biphenyls (PCB)

Part II: Source categories

Polychlorinated dibenzo-p-dioxins and dibenzofurans, hexachlorobenzene and polychlorinated biphenyls are unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions. The following industrial source categories have the potential for comparatively high formation and release of these chemicals to the environment:

(a) Waste incinerators, including co-incinerators of municipal, hazardous or medical waste or of sewage sludge;

(b) Cement kilns firing hazardous waste;

(c) Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching;

(d) The following thermal processes in the metallurgical industry:

  (i) Secondary copper production;

  (ii) Sinter plants in the iron and steel industry;

  (iii) Secondary aluminium production;

  (iv) Secondary zinc production.

Part III: Source categories

Polychlorinated dibenzo-p-dioxins and dibenzofurans, hexachlorobenzene and polychlorinated biphenyls may also be unintentionally formed and released from the following source categories, including:

(a) Open burning of waste, including burning of landfill sites;

(b) Thermal processes in the metallurgical industry not mentioned in Part II;

(c) Residential combustion sources;

(d) Fossil fuel-fired utility and industrial boilers;

(e) Firing installations for wood and other biomass fuels;

(f) Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil;

(g) Crematoria;

(h) Motor vehicles, particularly those burning leaded gasoline;

(i) Destruction of animal carcasses;

(j) Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction);

(k) Shredder plants for the treatment of end of life vehicles;

(l) Smouldering of copper cables;

(m) Waste oil refineries.

Part IV: Definitions

1. For the purposes of this Annex:

(a) "Polychlorinated biphenyls" means aromatic compounds formed in such a manner that the hydrogen atoms on the biphenyl molecule (two benzene rings bonded together by a single carbon-carbon bond) may be replaced by up to ten chlorine atoms; and

(b) "Polychlorinated dibenzo-p-dioxins" and "polychlorinated dibenzofurans" are tricyclic, aromatic compounds formed by two benzene rings connected by two oxygen atoms in polychlorinated dibenzo-p-dioxins and by one oxygen atom and one carbon-carbon bond in polychlorinated dibenzofurans and the hydrogen atoms of which may be replaced by up to eight chlorine atoms.

2. In this Annex, the toxicity of polychlorinated dibenzo-p-dioxins and dibenzofurans is expressed using the concept of toxic equivalency which measures the relative dioxin-like toxic activity of different congeners of polychlorinated dibenzo-p-dioxins and dibenzofurans and coplanar polychlorinated biphenyls in comparison to 2,3,7,8-tetrachlorodibenzo-p-dioxin. The toxic equivalent factor values to be used for the purposes of this Convention shall be consistent with accepted international standards, commencing with the World Health Organization 1998 mammalian toxic equivalent factor values for polychlorinated dibenzo-p-dioxins and dibenzofurans and coplanar polychlorinated biphenyls. Concentrations are expressed in toxic equivalents.

Part V: General guidance on best available techniques and best environmental practices

This Part provides general guidance to Parties on preventing or reducing releases of the chemicals listed in Part I.

A. General prevention measures relating to both best available techniques and best environmental practices

Priority should be given to the consideration of approaches to prevent the formation and release of the chemicals listed in Part I. Useful measures could include:

(a) The use of low-waste technology;

(b) The use of less hazardous substances;

(c) The promotion of the recovery and recycling of waste and of substances generated and used in a process;

(d) Replacement of feed materials which are persistent organic pollutants or where there is a direct link between the materials and releases of persistent organic pollutants from the source;

(e) Good housekeeping and preventive maintenance programmes;

(f) Improvements in waste management with the aim of the cessation of open and other uncontrolled burning of wastes, including the burning of landfill sites. When considering proposals to construct new waste disposal facilities, consideration should be given to alternatives such as activities to minimize the generation of municipal and medical waste, including resource recovery, reuse, recycling, waste separation and promoting products that generate less waste. Under this approach, public health concerns should be carefully considered;

(g) Minimization of these chemicals as contaminants in products;

(h) Avoiding elemental chlorine or chemicals generating elemental chlorine for bleaching.

B. Best available techniques

The concept of best available techniques 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. Appropriate control techniques to reduce releases of the chemicals listed in Part I are in general the same. In determining best available techniques, special consideration should be given, generally or in specific cases, to the following factors, bearing in mind the likely costs and benefits of a measure and consideration of precaution and prevention:

(a) General considerations:

- (i) The nature, effects and mass of the releases concerned: techniques may vary depending on source size;
- (ii) The commissioning dates for new or existing installations;
- (iii) The time needed to introduce the best available technique;
- (iv) The consumption and nature of raw materials used in the process and its energy efficiency;
- (v) The need to prevent or reduce to a minimum the overall impact of the releases to the environment and the risks to it;
- (vi) The need to prevent accidents and to minimize their consequences for the environment;
- (vii) The need to ensure occupational health and safety at workplaces;
- (viii) Comparable processes, facilities or methods of operation which have been tried with success on an industrial scale;
- (ix) Technological advances and changes in scientific knowledge and understanding.

(b) General release reduction measures: When considering proposals to construct new facilities or significantly modify existing facilities using processes that release chemicals listed in this Annex, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of such chemicals. In cases where such facilities will be constructed or significantly modified, in addition to the prevention measures outlined in section A of Part V the following reduction measures could also be considered in determining best available techniques:

- (i) Use of improved methods for flue-gas cleaning such as thermal or catalytic oxidation, dust precipitation, or adsorption;
- (ii) Treatment of residuals, wastewater, wastes and sewage sludge by, for example, thermal treatment or rendering them inert or chemical processes that detoxify them;
- (iii) Process changes that lead to the reduction or elimination of releases, such as moving to closed systems;
- (iv) Modification of process designs to improve combustion and prevent formation of the chemicals listed in this Annex, through the control of parameters such as incineration temperature or residence time.

C. Best environmental practices

The Conference of the Parties may develop guidance with regard to best environmental practices.

1.E Relationship to the Basel Convention

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal was adopted in 1989 and entered into force in 1992. The Basel Convention is the one other global agreement, besides the Stockholm Convention, directly relevant to the application of best available techniques and best environmental practices to the control of chemicals listed in Annex C of the Stockholm Convention. The Convention places obligations on countries that are Parties to, inter alia: minimize generation of hazardous waste; ensure that adequate disposal facilities are available; and ensure environmentally sound management of wastes.

Paragraph 2 of Article 6 of the Stockholm Convention, which addresses measures to reduce or eliminate releases from stockpiles and wastes, contains the following provisions:

> "The Conference of the Parties shall cooperate closely with the appropriate bodies of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal to, inter alia:
>
> (a) Establish levels of destruction and irreversible transformation necessary to ensure that the characteristics of persistent organic pollutants are not exhibited;
>
> (b) Determine what they consider to be the methods that constitute environmentally sound disposal referred to above; and
>
> (c) Work to establish, as appropriate, the concentration levels of the chemicals listed in Annexes A, B and C in order to define the low persistent organic pollutant content referred to in paragraph 1 (d) (ii)."[3]

The Conference of the Parties to the Basel Convention, at its eighth meeting in December 2006 adopted updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants and updated guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls, polychlorinated terphenyls or polybrominated biphenyls. The general technical guidelines developed under the Basel Convention address matters related to all three of the outstanding definitional issues raised in paragraph 2 of Article 6 of the Stockholm Convention.

In addition the eighth meeting of the Conference of the Parties to the Basel Convention also adopted the following three new specific technical guidelines: Technical guidelines for the environmentally sound management of wastes consisting of, containing off contaminated with the pesticides aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex or toxaphene or with hexachlorobenezene as an industrial chemical; Technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with 1, 1,1 trichloro-2,2 bis (chlorophenyl) ethane (DDT); and Technical guidelines for the environmentally sound management of wastes containing or contaminated with unintentionally produced polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), hexachlorobenzene or polichorinated biphenyls.

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[3] Article 6, paragraph 1 (d) (ii) of the Stockholm Convention states that each party shall: "(d) Take appropriate measures so that such wastes, including products and articles upon becoming wastes, are … (ii) Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option or the persistent organic pollutant content is low, taking into account international rules, standards, and guidelines, including those that may be developed pursuant to paragraph 2, and relevant global and regional regimes governing the management of hazardous wastes."

I.F Relationship to other environmental concerns

There has been global recognition of the adverse impacts of mercury and its compounds. This has resulted in decisions on the need for further international action and measures which will reduce or eliminate releases of mercury and its compounds into the environment. A number of the sources of release of the persistent organic pollutants listed in Annex C to the Stockholm Convention may also release high levels of mercury into the environment. Releases of other environmental pollutants or greenhouse gases are also possible. In recognition of these effects, when applying the best available techniques and best environmental practices set out in the present guidelines in relation to the release of persistent organic pollutants, Parties should consider also applying appropriate measures to ensure that releases of mercury and other pollutants are minimized at the same time.

Under the definitions in the Stockholm Convention, specifically in relation to Article 5 and Annex C, the term “best environmental practices” means the application of the most appropriate combination of environmental control measures and strategies, while the term “best” is defined as being the most effective in achieving a high general level of protection of the environment as a whole.

Efforts should be made to avoid increasing the release of other pollutants while decreasing the release of persistent organic pollutants.

Section II

Consideration of Alternatives in the Application of Best Available Techniques

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II.A Consideration of alternatives in the Stockholm Convention

The Stockholm Convention provides general guidance on best available techniques and best environmental practices in which Parties are encouraged to give priority to the consideration of approaches that prevent the formation and release of the chemicals listed in Part I of Annex C of the Convention.[1] The Convention addresses the "consideration of alternatives" with specific reference to best available techniques as follows:

> "When considering proposals to construct new facilities or significantly modify existing facilities using processes that release chemicals listed in this Annex, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of such chemicals."[2]

II.B The Stockholm Convention and new sources

Parties are obliged to require the use of best available techniques for new sources within source categories that a Party has identified as warranting such action in its action plan. Initial focus should be given to the source categories identified in Part II of Annex C of the Convention.[3]

When a Party implements this obligation, it should assure that priority consideration is given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of chemicals listed in Part I of Annex C.

In this regard, the Stockholm Convention is ambitious. It encourages a search for processes, techniques and practices that avoid generation and release of persistent organic pollutants and it encourages Parties to give them priority consideration. This encouragement should not be interpreted to mean that facilities that have the potential to form and release to the environment chemicals listed in Part I of Annex C should always be avoided. Complete elimination may not be practical or feasible. Sources that are listed in Parts II and III of Annex C have useful purposes despite the potential to form and release persistent organic pollutants.

A key factor in deciding when it is best to avoid a Part II source, a Part III source or some other prioritized source is a consideration of both the originally proposed new facility as well as the possible alternatives, taking into account the feasibility of the various options under consideration.

II.C An approach to consideration of alternatives

When a Party requires the application of best available techniques for a proposed new source of chemicals listed in Annex C, decision makers are encouraged to assure that consideration is also given to alternatives that avoid the formation and release of such chemicals. In doing this, they should undertake a comparison of the proposed process, the available alternatives and the applicable legislation using what might be termed a "checklist approach", keeping in mind the overall sustainable development context and taking fully into account environmental, health, safety and socio-economic factors.

The following are elements of such an approach:

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[1] See Stockholm Convention, Annex C, Part V, section A, chapeau.

[2] See Stockholm Convention, Annex C, Part V, section B, subparagraph (b).

[3] See Stockholm Convention, Article 5 (d).

1. Review the proposed new facility in the context of sustainable development

Decision makers should carry out a review of both the originally proposed new facility and of possible alternatives in the context of the country's plans for sustainable development. The purpose of such a review is to enable decision makers to understand better the proposed facility and its intended usefulness in relation to social, economic and environmental considerations, and its potential contribution to sustainable development. They should also review the availability of and the practicality of implementing general measures to reduce releases of chemicals listed in Annex C, such as those measures listed in Annex C, Part V, section B, subparagraph (b), points (i) through (iv).

2. Identify possible and available alternatives

An effort should be made to identify available alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of chemicals listed in Annex C. Available guidance comprising options for those processes, techniques and practices should be taken into account (for example, guidance from the Basel Convention, the World Health Organization (WHO), the Food and Agriculture Organization of the United Nations (FAO), other intergovernmental bodies and governments).

In order to assist Parties to identify possible available and appropriate alternatives, the Convention Secretariat will, in its role as clearing-house mechanism for information mandated under Article 9, produce, manage and facilitate a compendium of available processes, techniques or practices that avoid the generation and release to the environment of chemicals listed in Annex C, and that may be utilized as appropriate alternatives to facilities and processes that do generate and release such chemicals. The development and maintenance of this element of the clearing-house mechanism must:

- Be done in a transparent manner;
- Be kept up to date;
- Provide information that Parties can use in ways that take fully into account the particular circumstances of developing countries and some countries with economies in transition;
- Provide information that Parties can use to give consideration to regional differences and to help them to focus on sustainable development, taking into account environmental, health, safety and socio-economic factors.

3. Undertake a comparative evaluation of both the proposed and identified possible and available alternatives

After possible and available alternatives have been identified, decision makers should undertake comparative evaluations of the various options, namely the originally proposed new facility and all possible alternatives that may be under consideration. In some cases, and for some kinds of facilities, it may be most appropriate for this comparative evaluation to be done by local or district authorities. However, in many cases, it may be more appropriate, from a sustainable development perspective, for the comparative evaluation to be made at some other strategic or policy level. In carrying out the comparative evaluation, consideration should be given to appropriate items of the indicative list contained in Annex F[4], Information on Socio-Economic Considerations; and also relevant criteria from Annex C, Part V, sections A and B.

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[4] The list of items provided in Annex F to the Convention for chemicals being assessed under Article 8 (listing of chemicals in Annexes A, B and C) is also relevant to the comparative evaluation.

4. Priority consideration

A proposed alternative should be given priority consideration over other options, including the originally proposed facility, if, based on the comparative evaluation described in paragraph 3 above, and using relevant considerations and criteria from Convention Annex F and Annex C, an identified, available alternative is determined to:

- Avoid the formation and release of chemicals listed in Annex C;
- Have similar usefulness;
- Fit comparatively well within a country's sustainable development plans, taking into account effective integration of social, economic, environmental, health and safety factors.

II.D Other considerations of the Stockholm Convention

1. Health, safety and environmental considerations

Article 1 of the Convention states that "the objective of this Convention is to protect human health and the environment from persistent organic pollutants". In carrying out comparative evaluations of originally proposed facilities and possible and available alternatives (as in section II.C, paragraph 3 of the present guidelines), health, safety and environmental considerations should be taken into account.

Health, safety and environmental impacts of proposed alternatives should be compared with the corresponding impacts of the originally proposed facility. The outcome of this comparison should constitute an important component in the consideration of "similar usefulness" and in a determination of practicality and feasibility.

2. Social and economic considerations

Annex F of the Stockholm Convention addresses relevant information relating to socio-economic considerations associated with possible control measures to enable decisions by the Conference of the Parties. However, it is also a starting point for a useful list of social and economic considerations and criteria that can be used by authorities in carrying out comparative evaluations of originally proposed facilities and identifying possible and available alternatives. The creation of a country-specific checklist is strongly recommended; it should include the following items, many of which are included in Annex F of the Convention:

- Technical feasibility;
- Costs, including environmental and health cost;
- Cost efficiency;
- Efficacy (infrastructural capacity, including availability of well-trained staff);
- Risk;
- Availability;
- Accessibility;
- Operator friendliness (ease of use);
- Positive or negative impacts on society, including health (public, environmental and occupational health); agriculture (including aquaculture and forestry); biodiversity; economic aspects; movement towards sustainable development; and social costs.

In many cases, a proposed new facility may have the potential to contribute to a country's economic development and poverty reduction plans. Proper implementation of the Stockholm Convention should not significantly interfere with this potential. Rather, if properly implemented, the Stockholm Convention should contribute positively to sustainable development and poverty reduction.

The Convention[5] provides that developing country Parties and Parties with economies in transition will have access to new and additional financial resources to enable them to meet the agreed full incremental costs of implementing measures that fulfil their Convention obligations. Therefore, insofar as a Party is obliged to require best available techniques under the well-defined circumstances specified in the Convention, the Party should receive access to the agreed full incremental costs of implementing this obligation.

In some cases, appropriate alternatives to proposed sources of chemicals listed in Annex C require less expenditure on imported capital goods, relying rather on locally available labour sources and building on local knowledge. Such alternatives may avoid formation and release of chemicals listed in Annex C; fit well into a country's sustainable development plans; and provide usefulness that is as good as or better than the originally proposed facility.

Finally, all obligations under the Convention contribute to the Convention's objective to protect human health and the environment from chemicals listed in Annex C.[6]The Convention recognizes in its preamble[7] "health concerns, especially in developing countries, resulting from local exposure to persistent organic pollutants, in particular impacts upon women and, through them, upon future generations". By minimizing releases of chemicals listed in Annex C, as part of a robust and balanced sustainable development process, proper implementation of the Stockholm Convention can reduce the burdens of disease and health deficits that undermine efforts aimed at sustainable development and poverty reduction.

3. Annex C considerations

All relevant sections of Annex C, Part V, sections A and B should be taken into consideration in applying the present guidelines.

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[5] See Stockholm Convention, Article 13.2.

[6] See Stockholm Convention, Article 1.

[7] See Stockholm Convention, page 2 (English text).

Section III

Best available techniques and best environmental practices: Guidance, principles and cross-cutting considerations

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III.A Guidance

1. General considerations

Article 5 of the Stockholm Convention requires Parties to develop, within two years of entry into force for them, an action plan to identify, characterize and address the release of chemicals listed in Annex C. Currently listed are polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), as well as hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) when produced unintentionally.

The action plan, which is also to be a component of a Party's national implementation plan to be developed pursuant to Article 7 of the Convention, will include strategies for meeting obligations to reduce or eliminate releases of chemicals listed in Annex C of the Stockholm Convention, and a schedule for the action plan. The plan will identify priorities for action, including for those source categories that provide the most cost-effective opportunities for release reduction or elimination. It will also include an inventory of releases of chemicals listed in Annex C.

In accordance with the implementation schedule of its action plan and taking into account the guidelines to be adopted by the Conference of the Parties, Parties are to promote and in some cases require the use of best available techniques and to promote the use of best environmental practices by identified sources of release. Parties are also to promote the development of and, where appropriate, require the use of substitute materials or processes to prevent the formation and release of chemicals listed in Annex C.

2. Policy, legal and governance issues

Just how a government promotes or requires the use of best available techniques and best environmental practices will vary from country to country, depending on its legal structure and socio-economic conditions. Possible implementation strategies would include release estimate reporting, public information and education programmes, voluntary industry programmes, economic instruments and regulation. These issues should be addressed in the Party's national action plan.

The types of measures that may be promoted or required as best available techniques to reduce or eliminate the release of Annex C chemicals can be categorized as follows: shifting to alternative processes; primary measures that prevent the formulation of chemicals listed in Annex C; and secondary measures that control and reduce the release of those chemicals.

3. Scientific and technical issues

The state of the science with regard to both the measurement of releases and levels present in the environment of chemicals listed in Annex C and what is considered "best" available techniques and "best" environmental practices will advance with time. This guidance will be periodically updated to keep up with these changes.

The Convention identifies the term "best" as "most effective in achieving a high general level of protection of the environment as a whole" (see subparagraph (f) (iv) of Article 5).

Consistent with decision SC-1/15 of the Conference of the Parties of the Stockholm Convention efforts should be made to ensure that mechanisms are set in place for providing technical assistance and promoting transfer of technology. A particular case is that of Parties that currently do not have access to those techniques that are subject to intellectual property rights.

These guidelines should be taken into consideration, and the performance levels associated with best available techniques and best environmental practices for PCDD/PCDF releases, may be used by a Party in fulfilling its commitments to apply best available techniques. It is within the jurisdiction of each Party to establish its regulatory release limits based on such guidance.

4. Economic and social implications

Depending on the process that is a source of chemicals listed in Annex C, economic and social conditions in a country are a factor in determining what are “best” available techniques and “best” environmental practices. Where processes are relatively large scale, capital intensive and involve large and continuous throughputs (e.g. cement kilns firing hazardous wastes, sinter plans in the iron and steel industry, fossil fuel-fired utilities, large waste incinerators) the technologies and practices used and enterprises that manage them are rather similar worldwide. In such cases, best available techniques and best environmental practices can be applied in much the same way in all countries. Where processes are relatively smaller in scale (crematoria, home heating and cooking, industrial boilers, motor vehicles) or involve smaller scale management of wastes (waste incineration, open burning), the technologies and practices available may vary greatly from country to country. In these cases, determining what are best available techniques and best environmental practices will need to include an analysis of economic feasibility of the various options available. As such, “best” may mean best option that is economically feasible under the socio-economic conditions present.

5. New versus existing sources

For new sources of chemicals within source categories that warrant the use of best available techniques, as identified in their national action plans, Parties are to focus initially on source categories identified in Part II of Annex C. Parties shall phase in requirements for best available techniques for new sources in the categories in Part II of Annex C as soon as practicable, but no later than four years after entry into force of the Convention for the Party. For existing source categories, identified in the action plans as warranting the use of best available techniques, best available techniques are to be promoted. The use of best available techniques and best environmental practices are to be promoted for those new sources that do not warrant action in a Party’s action plan.

The use of best available techniques and best environmental practices for new sources ensures that releases of chemicals listed in Annex C are minimized to the greatest extent possible. It also allows such techniques and practices to be considered in the design and operation of the facility at a stage when they can be incorporated cost-effectively. Given the range of industrial and other activities involved, national sustainable development strategy should take into account the need to ensure that the investments into the national economy comply with this guidance and guidelines.

The use of best available techniques and best environmental practices for existing sources identified in a Party’s national action plan are to be promoted in accordance with the Party’s action plan.

Addressing existing sources is a good opportunity for a Party to reduce overall releases. In considering priority existing sources identified in its national action plan, a Party will need to consider measures to encourage necessary changes to the process or management practices that could lead to eventual attainment of best available techniques and best environmental practices. Such modifications could be phased in over time and could be part of plans to modernize a facility.

III.B General principles and approaches

When applying these guidelines and guidance to sources of chemicals listed in Annex C of the Stockholm Convention, Parties may find it useful to consider some general environmental management principles and approaches that may be supportive of the Convention. The following is indicative of some of these general environmental management principles and approaches.

1. **Sustainable development.** “Development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”[1]
2. **Sustainable consumption.** “The use of services and related products which respond to basic needs and bring a better quality of life while minimizing the use of natural resources and toxic

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[1] World Commission on Environment and Development. 1987. www.un.org/documents/ga/res/42/ares42-187.htm.

materials as well as the emissions of waste and pollutants over the life cycle of the service or product so as not to jeopardize the needs of future generations."[2]

3. **Development and implementation of environmental management systems.** "A structured approach for determining, implementing and reviewing environmental policy through the use of a system which includes organizational structure, responsibilities, practices, procedures, processes and resources."[3]

4. **Use of science, technology and indigenous knowledge to inform environmental decisions.** "Increase the use of scientific knowledge and technology and increase the beneficial use of local and indigenous knowledge in a manner respectful of the holders of that knowledge and consistent with national law;" and "Establish partnerships between scientific, public and private institutions, including by integrating the advice of scientists into decision-making bodies to ensure a greater role for science, technology, development and engineering sectors."[4]

5. **Precautionary approach.** "In order to protect the environment, the precautionary approach shall be widely applied by States according to their capabilities. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation."[5]

6. **Internalizing environmental costs and polluter pays.** "National authorities should endeavour to promote the internalization of environmental costs and the use of economic instruments, taking into account the approach that the polluter should, in principle, bear the cost of pollution, with due regard to the public interest and without distorting international trade and investment."[6]

7. **Pollution prevention.** "The use of processes, practices, materials, products or energy that avoid or minimize the creation of pollutants and waste, and reduce overall risk to human health or the environment."[7]

8. **Integrated pollution prevention and control.** "This principle aims to achieve integrated prevention and control of pollution arising from large-scale industrial activities. It lays down measures designed to prevent or, where that is not practicable, to reduce emissions in the air, water and land from these activities, including measures concerning waste, in order to achieve a high level of protection of the environment taken as a whole."[8]

9. **Co-benefits of controlling other pollutants.** For instance, pollution prevention and control of other contaminants may also contribute to the reduction and elimination of chemicals listed in Annex C.

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[2] UNEP (United Nations Environment Programme). 1994. Oslo Symposium: Sustainable Consumption. Oslo, Norway, January 1994. www.iisd.org/susprod/principles.htm.

[3] UNEP (United Nations Environment Programme). 2002. Environmental Impact Assessment Training Resource Manual. Page 558. www.iaia.org/Non_Members/EIA/ManualContents/Vol1_EIA_Manual.pdf.

[4] UN DESA (United Nations Department of Economic and Social Affairs) 2002 Plan of Implementation of the World Summit on Sustainable Development, page 50. http://www.un.org/esa/sustdev/documents/WSSD_POI_PD/English/WSSD_PlanImpl.pdf

[5] UNEP (United Nations Environment Programme). 1992. Rio Declaration on Environment and Development. Principle 15. Rio de Janeiro, Brazil, 1992. www.unep.org/Documents/Default.asp?DocumentID=78&ArticleID=1163.

[6] Preamble to Stockholm Convention and Principle 16 of the Rio Declaration on Environment and Development.

[7] Environment Canada. 1995. Pollution Prevention – A Federal Strategy for Action. www.ec.gc.ca/cppic/aboutp2/en/glossary.cfm.

[8] European Commission. 1996. Integrated Pollution Prevention and Control Directive. 96/61/EC. europa.eu.int/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc&lg=EN&numdoc=31996L0061&model=guichet.

10. **Cleaner production.** "The continuous application of an integrated preventive environmental strategy to processes, products and services to increase overall efficiency and reduce risks to humans and the environment. Cleaner production can be applied to the processes used in any industry, to products themselves and to various services provided in society."[9]

11. **Life cycle analysis.** "A system-oriented approach estimating the environmental inventories (i.e. waste generation, emissions and discharges) and energy and resource usage associated with a product, process or operation throughout all stages of the life cycle."[10]

12. **Life cycle management.** "An integrated concept for managing the total life cycle of goods and services towards more sustainable production and consumption, building on the existing procedural and analytical environmental assessment tools and integrating economic, social and environmental aspects."[11]

13. **Virtual elimination.** "The ultimate reduction of the quantity or concentration of the toxic substance in an emission, effluent, or waste released to the environment below a specified level of quantification. The 'level of quantification' means, in respect of a substance, the lowest concentration that can be accurately measured using sensitive but routine sampling and analytical methods."[12]

14. **Community Right to Know.** "In the field of environment, improved access to information and public participation in decision-making enhance the quality and the implementation of decisions, contribute to public awareness of environmental issues, give the public the opportunity to express its concerns and enable public authorities to take due account of such concerns."[13]

III.C Cross-cutting considerations

(i) Chemicals listed in Annex C: Formation mechanisms

1. Formation of chemicals listed in Annex C: An overview

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) are unintentionally formed in industrial-chemical processes, such as chemical manufacture, and thermal processes, such as waste incineration. PCDD/PCDF are the only by-product persistent organic pollutants whose mechanism of formation has been studied extensively in combustion-related processes and to a lesser extent in non-combustion-related chemical processes; even so, the mechanisms and exact formation conditions are not fully resolved. It is clear that the predominant mechanism or pathway can vary from process to process so that different factors become controlling and there is no universal controlling factor.

There is far less information as to the formation of PCB and HCB, especially in combustion processes. Since there are similarities in the structure and occurrence of PCDD/PCDF, PCB and HCB, it is usually assumed that, with the exception of oxygen-containing species, those parameters and factors that favour formation of PCDD/PCDF also generate PCB and HCB.

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[9] UNEPTIE. www.uneptie.org/pc/cp/understanding_cp/home.htm.

[10] European Environment Agency. glossary.eea.eu.int/EEAGlossary.

[11] UNEPTIE. www.uneptie.org/pc/sustain/reports/lcini/lc-initiative-barcelona-workshop.pdf.

[12] Environment Canada. 1999. Canadian Environmental Protection Act, 1999. Section 65. www.ec.gc.ca/CEPARegistry/the_act/.

[13] Aarhus Convention on Access to Information, Public Participation in Decision Making and Access to Justice in Environmental Matters, United Nations Economic Commission for Europe, www.unece.org/env/pp

On the other hand, in some industrial processes HCB is formed to a greater extent than PCDD/PCDF or PCB. The guidance chapters (sections V and VI) on various types of incineration and chemical processes contain more specific process and by-product information.

2. Formation of PCDD/PCDF

2.1 Thermal processes[14]

Carbon, oxygen, hydrogen and chlorine, whether in elemental, organic or inorganic form, are needed. At some point in the synthesis process, whether present in a precursor or generated by a chemical reaction, the carbon must assume an aromatic structure.

There are two main pathways by which these compounds can be synthesized: from precursors such as chlorinated phenols or de novo from carbonaceous structures in fly ash, activated carbon, soot or smaller molecule products of incomplete combustion. Under conditions of poor combustion, PCDD/PCDF can be formed in the burning process itself.

The mechanism associated with this synthesis can be homogeneous (molecules react all in the gas phase or all in the solid phase) or heterogeneous (involving reactions between gas phase molecules and surfaces).

PCDD/PCDF can also be destroyed when incinerated at sufficient temperature with adequate residence time and mixing of combustion gases and waste or fuel feed. Good combustionpractices include management of the “3 Ts” – time of residence, temperature and turbulence, and sufficient excess oxygen to allow complete oxidation. Use of a fast temperature quench and other known processes are necessary to prevent reformation.

Variables known to impact the thermal formation of PCDD/PCDF include:

- Technology: PCDD/PCDF formation can occur either in poor combustion or in poorly managed post-combustion chambers and air pollution control devices. Combustion techniques vary from the very simple and very poor, such as open burning, to the very complex and greatly improved, such as incineration using best available techniques;
- Temperature: PCDD/PCDF formation in the post-combustion zone or air pollution control devices has been reported to range between 200° C and 650° C; the range of greatest formation is generally agreed to be 200–450° C, with a maximum of about 300° C;
- Metals: Copper, iron, zinc, aluminium, chromium and manganese are known to catalyse PCDD/PCDF formation, chlorination and dechlorination;
- Sulphur and nitrogen: Sulphur and some nitrogen-containing chemicals inhibit the formation of PCDD/PCDF, but may give rise to other unintended products;
- Chlorine must be present in organic, inorganic or elemental form. Its presence in fly ash or in the elemental form in the gas phase may be especially important;
- PCB are also precursors for the formation of PCDF.

Research has shown that other variables and combinations of conditions are also important.

2.2 Industrial-chemical processes

As with thermal processes, carbon, hydrogen, oxygen and chlorine are needed. PCDD/PCDF formation in chemical processes is thought to be favoured by one or more of the following conditions:

- Elevated temperatures (> 150° C);

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[14] PCDD/PCDF may also be introduced as contaminants in raw materials or wastes and may therefore appear in processes in which PCDD/PCDF formation does not occur.

- Alkaline conditions;
- Metal catalysts;
- Ultraviolet (UV) radiation or other radical starters.

In the manufacture of chlorine-containing chemicals, the propensity for PCDD/PCDF formation has been reported as follows:

Chlorophenols > chlorobenzenes > chlorinated aliphatics > chlorinated inorganics

(ii) Waste management considerations

1. Summary

Burning of waste has the potential for comparatively high unintentional formation and release of persistent organic pollutants to the environment. Waste incinerators are therefore listed as Part II source categories in Annex C of the Stockholm Convention. Open burning of waste, including burning of landfill sites, can also lead to the unintentional formation and release of persistent organic pollutants, and is listed as a Part III source category in Annex C. The application of best available techniques and best environmental practices to these sources should take into consideration environmentally sound waste management practices. Environmentally sound waste management reduces the release of persistent organic pollutants and is also an important factor in avoiding health problems and in promoting sustainable use of resources.

Important principles applicable to the prevention and reduction of waste include the source reduction principle; the integrated life cycle principle; and the principle of recovery of reusable and recyclable components, to the greatest possible extent. In many cases, this will be facilitated by separating at the source those wastes that can be composted, reused or recycled. The remaining waste should be treated and disposed of in an environmentally sound way. Reliable solutions for all steps – the collection system, the recycling actions, and the final disposal – should be adapted to the local circumstances, taking into account such factors as opportunities for waste prevention, the composition of waste, the available recycling processes, the existing structures, and financial, economic and social aspects.

In general priority should be given to approaches that prevent the formation and release of chemicals listed in Annex C of the Convention. Improved waste management approaches should be employed with the aim of avoiding open and other uncontrolled burning of wastes, including burning of landfill sites. When considering proposals to construct new waste disposal facilities, consideration should be given to alternatives such as activities to minimize the generation of municipal and medical waste, including resource recovery, reuse, recycling, waste separation and promoting products that generate less waste. Under this approach, public health concerns should be carefully considered.

The present chapter deals with these issues but it cannot replace a comprehensive examination of all the specific questions related to waste management.

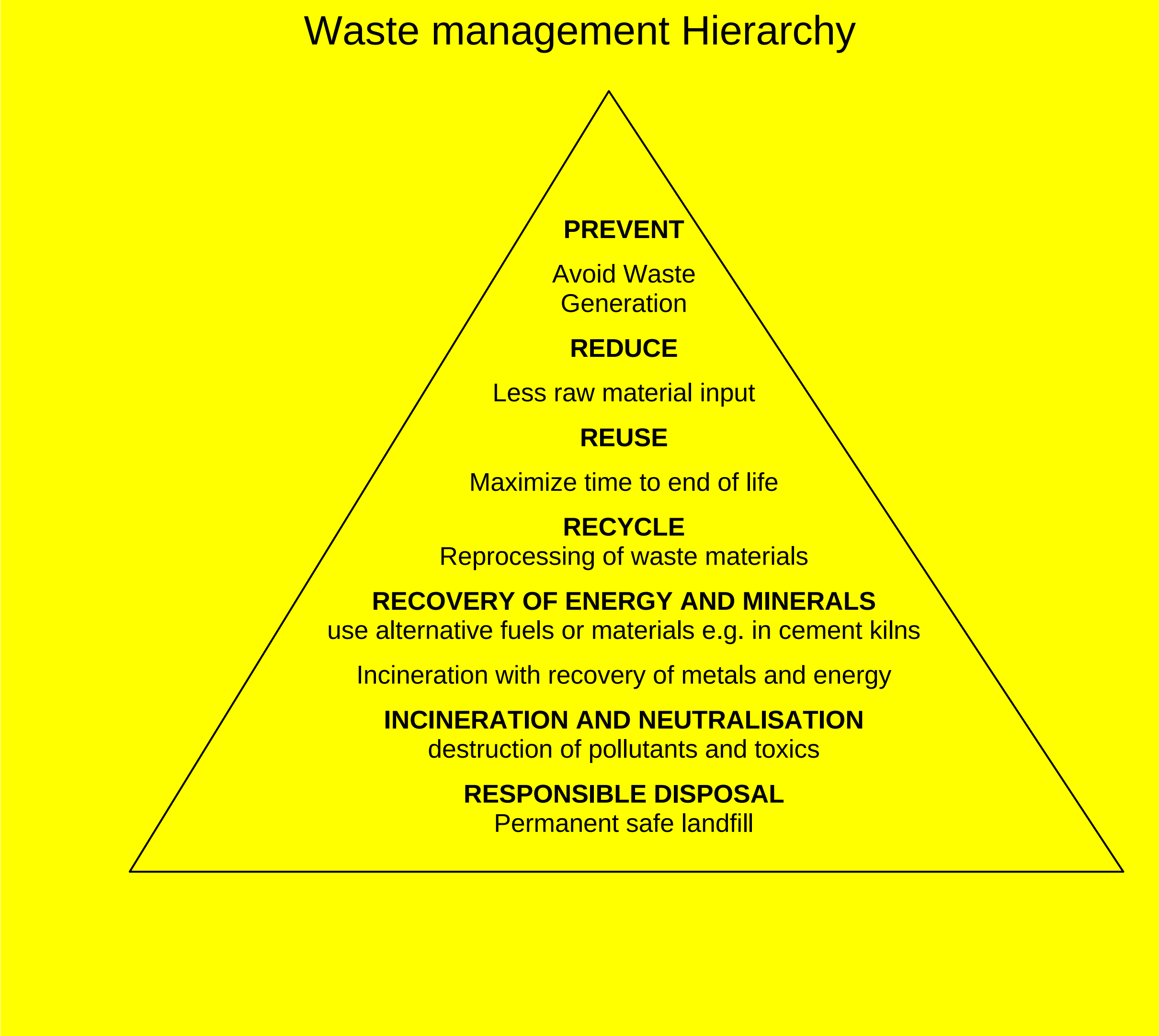
2. Introduction

2.1 The importance of waste management to the environment and health

Sound waste management is an important element in the protection of human health and the protection of the environment. It also helps to avoid the loss of resources. Careless landfilling may pollute water bodies; burning of waste on landfills or in inappropriate incinerators or open burning can release high levels of chemicals listed in Annex C and other toxic substances such as polycyclic aromatic hydrocarbons, heavy metals and particulate matter. For this reason a holistic approach to improving the waste management system will have positive effects in a number of areas.

Waste management consists of many different areas of intervention. As a first step waste prevention and reduction can help reduce the generation of waste, and its hazard potential, to a minimum. In industrial processes the development and use of low-waste and non-waste technologies have had a positive effect in decreasing the amount of waste requiring treatment. Greater emphasis on producer responsibility may also help to solve or at least reduce waste management problems. (See figure 1)

Figure 1: Waste management hierarchy



2.2 Definitions

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal gives the following definition for wastes in general:

> “Wastes are substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law.”

The Basel Convention defines “disposal” as operations which may or may not lead to the possibility of “resource recovery, recycling, reclamation, direct re-use or alternative uses.”

Annex I of the Basel Convention lists 45 categories of hazardous wastes subject to transboundary movement requiring control, unless they do not fall into any of the following categories, the characteristics of which are listed in Annex III of the Basel Convention:

- Explosives;
- Flammable liquids;

- Flammable solids;
- Substances or wastes liable to spontaneous combustion;
- Substances or wastes which, in contact with water, emit flammable gases;
- Oxidizing substances;
- Organic peroxides;
- Poisonous (acute) substances;
- Infectious substances;
- Corrosives;
- Substances that liberate toxic gases in contact with air or water;
- Toxic (delayed or chronic) substances;
- Ecotoxic substances;
- Substances capable, by any means, after disposal, of yielding another material, e.g. leachate, which possesses any of the characteristics listed above.

2.3 The importance of developing national waste management strategies

Waste management influences all parts of society and of its economy. It concerns local, regional and national authorities; it requires a legal base, a financial mechanism, and a great deal of coordination between citizens and authorities at all levels. Furthermore, good waste management is not feasible without a minimal level of investment. To ensure a coherent waste management system, all the actions at different levels should follow a commonly agreed strategy; it is therefore necessary or at least useful to discuss and decide upon a national waste management strategy. The successful implementation of any waste management system, particularly in developing countries, may require the transfer of appropriate technologies and capacity building in accordance with article 12 of the Convention (see also Scientific and technical issues in III.A).

2.4 Some principles to be applied

Basel Convention guidance to be considered in the development of waste and hazardous waste strategies (Basel Convention Secretariat 1993) includes:

- The source reduction principle, “by which the generation of waste should be minimized in terms of its quantity and its potential to cause pollution. This may be achieved by using appropriate plant and process designs”;
- The integrated life cycle principle, “by which substances and products should be designed and managed such that minimum environmental impact is caused during their generation, use, recovery and disposal”.

Discards with the potential for reuse or recycling should be recovered for those purposes to the greatest extent possible.

2.5 Approach proposed in the WSSD Plan of Implementation

The 2002 Johannesburg World Summit on Sustainable Development (WSSD) Plan of Implementation, paragraph 22, states:

> “Prevent and minimize waste and maximize reuse, recycling and use of environmentally friendly alternative materials, with the participation of government authorities, and all stakeholders, in order to minimize adverse effects on the environment and improve resource efficiency, with financial, technical and other assistance for developing countries.
>
> This would include actions at all levels to:

(a) Develop waste management systems with the highest priority placed on waste prevention and reduction, reuse and recycling, and environmentally sound disposal facilities, including technology to recapture the energy contained in waste, and encourage small-scale waste-recycling initiatives that support urban and rural waste management and provide income-generating opportunities with international support for developing countries;

(b) Promote waste prevention and reduction by encouraging production of reusable consumer goods and biodegradable products and developing the infrastructure required."

2.6 The importance of public education

Successful implementation of a general waste management plan needs the assistance of different actors: consumers, authorities, waste management operators. All these stakeholders have to be informed about coherent waste management and have to be convinced to contribute to its successful implementation. There is a clear need for awareness building at all levels: for example, consumers should be informed about strategies for avoiding waste and the advantages of using recycling opportunities; and information about the health hazards of open burning of waste and promotion of better alternatives are necessary if this way of disposal is to be reduced and eventually stopped.

2.7 The importance of training of personnel

In order to manage wastes effectively, it is important that adequate training is provided to decision makers and technical personnel (refer to Section III 2.4 (v) of the Cross-cutting Considerations).

3. Influencing production and products

All industrial or artisanal products will at some point become waste. Hence, the quality and especially the technical lifetime of products have a crucial impact on the quantities of waste that have to be eliminated.

National authorities are limited in their ability to directly prescribe the general life cycle quality of products and encourage the production of long-life products. There are however several quite efficient indirect ways to influence these aspects of production.

In many countries public procurement is an important part of the overall market. By defining quality standards and minimum requirements, public procurement allows the quality of the products offered to be influenced. As a follow-up to the World Summit on Sustainable Development, several nations are developing toolkits for sustainable procurement following the definition developed by the Sustainable Procurement Task Force set up by the Government of the United Kingdom: "Sustainable procurement is a process whereby organizations meet their needs for goods, services, works and utilities in a way that achieves value for money on a whole life basis in terms of generating benefits to society and the economy, whilst minimizing damage to the environment" (Sustainable Procurement Task Force 2006).

In general it is useful to avoid unnecessary packaging, to promote durable and reusable products, and to utilize materials and product designs that avoid toxicity and other hazard characteristics and that enable end-of-life remanufacture, material recovery and recycling.

Labelling is another powerful instrument: it enables the consumers to select products based on environmental performance, price and quality, thus directing their demand towards goods produced with respect for the principles of sustainable development.

3.1 Product warranties

Products become wastes at the end of their life. If the use of a product is limited by careless design or production, this may lead to an unnecessarily short technical lifetime. Electronic appliances or tyres of low quality may become waste after a comparatively short period of use, thereby increasing the amount of waste. One possible way of influencing quality is by legally defining a minimum period of warranty for products.

3.2 Encourage companies to use environmental management systems

The use of environmental management systems (for example those developed by the International Standards Organization and the European Union Eco-Management and Audit Scheme, or EMAS) leads to better knowledge about industrial processes and their influence on the environment. This may also help to reduce the amount of waste and its hazardous characteristics. The responsible management of products and processes from an environmental point of view can stimulate greater awareness throughout a company, improve corporate credibility and reputation, enhance business development opportunities and facilitate dialogue and partnership with key stakeholders.

3.3 Producer responsibility

Producers and other stakeholders have responsibilities that can be established through approaches such as the European Union's draft Integrated Product Policy and forthcoming thematic strategy on the prevention and recycling of waste, the Extended Producer Responsibility programme of the Organisation for Economic Co-operation and Development (OECD 2000), the concept of product stewardship, or through other means. In some cases it may be useful to oblige producers to take back certain end-of-life products and to assure their environmentally sound treatment.

4. Source reduction as a priority

In general, a society should give careful consideration to the full range of waste management options and considerations before reaching a decision to make a large-scale investment in the construction of any new incinerator, a new sanitary landfill, mechanical or biological treatment, or other similar investments, or to retrofit an existing facility for these purposes.

The first priority among waste management options is source reduction – minimization of the quantity of waste, alongside the reduction of its toxicity and other hazard characteristics. This is a responsibility shared by all sectors of society. One measure of success is the percentage of discards that can be diverted from landfills and incinerators, but this should always be considered in the context of total waste generated.

In some situations, the decision to construct a new large-scale waste treatment facility can undermine efforts at waste reduction and waste-derived resource recovery. Those who invest in these new facilities will often face pressures to assure sufficient incoming waste in order to recover their investments. When this happens, the new facility can sometimes serve as a counterforce and as a disincentive to effective waste reduction efforts. Therefore, any such consideration should take place in the framework of holistic waste management policies.

5. Collection

Households usually keep waste to be discarded in designated containers. These may be metal or plastic dustbins or plastic and paper bags. In large buildings and apartment blocks, centralized containers are sometimes provided into which occupants place their waste. In most developed countries, it is usual for household waste to be collected from premises on a regular basis since food waste, in particular, decays rapidly. In cities and urban areas, waste is collected for disposal in specially designated vehicles fitted with compaction equipment to increase the payload that can be transported, often over significant distances, to sanitary landfill sites. In large conurbations, studies show that transferring the collected waste to railway containers for transport to a landfill site is economically viable; large barges are also used for transport. In some instances, waste is baled to facilitate mechanical handling.

Even though there exist quite efficient mechanical sorting systems for mixed waste, source separation and collection of recyclable goods is in many cases cheaper and will provide cleaner products for recycling. This is particularly true when, without source separation, paper and cardboard would be mixed up with wet waste from the kitchen, or when vegetable waste, designed to be composted or fermented, is at risk of being mixed with hazardous waste from small industries.

5. Recycling

Generally a large proportion of municipal solid waste can be composted, reused or recycled. In several industrial countries more than 50% of municipal solid waste is recycled. Some regions achieve even higher recycling rates. NGOs such as Zero Waste International Alliance are following such ambitious goals for the diversion of wastes from landfills or incinerators in a number of countries. Zero waste means designing and managing products and processes to reduce the volume and the toxicity of waste and materials, conserve and recover all resources and not to burn or bury them. Zero waste programmes have been implemented in many countries, for example in Palarikovo, Slovakia and in Canberra, Australia – refer to the web-sites reference for further information.

The sound disposal of mixed waste is in most cases more expensive than source reduction through the use of long-life products, repairing goods and efficient recycling. The possibilities of composting, reuse and recycling have to be examined and developed taking into account the composition of the waste, the existing collection and recycling systems and the economic possibilities

As an example, the recycling of paper and cardboard, metals and glass in many cases creates a positive revenue or is at least cheaper than the transportation and elimination of these materials together with other wastes. Similarly, collection and recycling of polyethylene terephthalate (PET) bottles or other plastic containers can produce a feedstock for the plastic recycling industry.

In many developing countries, waste-derived resources can provide important raw materials for small-scale resource recovery and remanufacturing activities. These small-scale activities can be encouraged. When this is done, efforts should also be made to promote improvements in the health and safety of this sector, which in many countries is presently an informal sector.

The collection of recyclable goods may be done by source separation followed by collection of the recyclable goods by either public authorities or private companies. In many cases the informal sector has also built up quite efficient structures for the collection of those wastes. The use and even the reinforcement of existing structures may have economic and social advantages, and should therefore be taken into account when developing or adapting waste management systems. Interesting examples of neighbourhood associations that successfully recycle and compost come from Mumbai in India and from Cairo in Egypt (Kumar 2000; Faccini 1999).

6. Final disposal

Even with good results in prevention of waste and with ambitious goals for recycling, some waste remains for disposal. The quantity of waste, its composition and hazardous characteristics, and the technical and economic possibilities for its disposal, are factors that have to be taken into account in choosing the final disposal method.

If the mixed waste contains a large percentage of vegetable waste, the possibilities for composting or anaerobic digestion should be examined. In some cases the waste consists predominantly of vegetable material, dust and sand, and composting of the waste after sorting out some other fractions (e.g. plastics) may be a viable option. The quality and use of the produced compost has to be evaluated.

Biological treatment or mechanical biological treatment of waste are options when the mixed waste contains, besides biodegradable material, a larger proportion of plastics, metals and other waste fractions. Mechanical biological treatment processes incorporate mechanical sorting and separation of the waste stream to separate the biodegradable materials, which are sent to a biological process, from the non-biodegradable materials. The mechanical process can be configured to further separate the non-biodegradable materials into fractions that can be recycled. The recovery of combustible parts of waste is also possible. This combustible fraction, also called waste-derived fuel, will in most cases be polluted by heavy metals and will contain more chlorine than normal fuels. For this reason, such products of waste management can only be used as fuel in installations with air pollution control equipment and careful disposal of ashes. The products of the biological treatment may be used as composts if the quality is sufficient, or can be landfilled.

6.1 Landfill

In many countries household waste has always been disposed of by landfilling. Significant changes in the composition of waste (e.g. more plastics), and the increasing quantities requiring disposal, led to designated areas of land being set aside as local waste disposal sites.

In a landfill, the waste is deposited in layers in prepared cells and compacted to decrease its volume. It is then covered, at least daily, with a suitable soil-like material to deter vermin, flies, birds and other scavengers and to prevent injuries from sharps. Many wastes, especially hazardous wastes, should only be disposed of in specially engineered landfills. (For further information see Basel Convention technical guidelines: on specially engineered landfill (D5)).

The putrescible fraction of waste undergoes aerobic and anaerobic processes. Landfill gas, a mixture of methane and carbon dioxide, is produced, and other organic compounds are formed. Many of these are soluble in water and become dissolved in any surplus moisture in the landfill site to produce a liquid mixture termed leachate. Leachate can be highly polluting, and it is necessary to prevent it from mixing with groundwater and surface water. The treatment of leachate and the safe disposal or even use of landfill gas are components of an environmentally sound waste management policy. In any case it is necessary to prevent leachate migration since it can continue to produce landfill gas away from a landfill site.

Landfill is by far the most commonly practised waste disposal method in the majority of countries. As a result of serious environmental and health problems experienced with historic and abandoned dump sites and the very high costs associated with clean-up measures at contaminated sites, many countries have introduced the specially engineered landfill concept, whereby the wastes are only consigned to sites selected for their containment properties. They may be natural, or augmented by or provided directly by liners, the overall engineering being such as to ensure as far as possible the isolation of wastes from the environment. Such landfills are considered a final resort option only to be used after every effort has been made to reduce, mitigate or eliminate the hazards posed by such wastes.

7. Incineration

In some countries with high population density and a lack of suitable areas for landfills, incineration of waste has become the main way for the treatment and disposal of the not recyclable waste over the last 50 years. As there are many combustible components in municipal solid waste, surplus heat can be produced. Pathogenic germs and organochemical constituents in waste can be destroyed almost completely. Because household waste contains a large variety of materials, including those that are not combustible, incinerators need to be rugged and versatile to cope with a highly variable feedstock both in terms of waste composition and calorific value. Traditionally, furnaces are based on either the chain or rocking grate principle or to a lesser extent a rotary kiln. For sewage sludge and for industrial wastes fluidized bed combustion is used. To ensure high combustion efficiency the temperature range at which the furnace is operated and burns waste, the time during which the waste reaches and is maintained at furnace temperature and turbulence within the furnace chamber all need to be strictly controlled. The so-called “3 Ts principle” – temperature, time and turbulence in the presence of sufficient oxygen - are the basic requirements for good combustion (see also section V.A of the present guidelines, on waste incinerators).

In order to avoid gaseous or particulate emissions, incinerators have to be equipped with efficient flue gas cleaning systems, which may in many cases include catalytic converters or addition of activated carbon to the flue gas and scrubbers. If water from scrubbers is discharged, it has to be treated. Fly ash from electrostatic precipitators and residues from air pollution equipment almost certainly contain significant amounts of chemicals listed in Annex C of the Convention, so these wastes have to be disposed of in a controlled way.

The need for reliable control of the parameters of combustion, the requirements of high-tech flue gas cleaning systems and the investment necessary for energy recovery (boilers, turbines, electrical generators) may explain why incinerators are highly developed, efficient but also rather expensive technology. Smaller installations exist, but in order to achieve economies of scale, in most cases at least 100,000 tons of waste per year are needed.

Over the last years some new methods for combustion of the non-recyclable components of municipal solid waste have been developed. In some cases the waste is first crushed or milled and then burnt in a specially designed plant. This offers the possibilities to use degasification at lower temperatures or to treat with very low or non oxygen as a first step (known as pyrolysis).and to omit oxygen excess as a first step. The resulting gas is then burnt – eventually after cleaning - at high temperatures in a second step. This high-temperature step allows vitrification of the combustion residues and offers some possibilities for controlled destruction of waste contaminated with chemicals listed in Annex C. Particular care must be taken with this processes that products of incomplete combustion are not released into the environment.

Annex 1 Treatment of quarantine waste

Quarantine controls at a country’s border provide significant protection from the introduction of disease, pests and pathological organisms. Products and substances intercepted at a quarantine barrier can vary widely and include aeroplane or ship wastes (including food and paper waste) raw or processed materials, such as baskets or souvenirs, materials infested with organisms (e.g. borer in wood) or grain with weed seeds, building materials or machinery contaminated with soil.

In all cases, priority must be given to the appropriate treatment to destroy the organism and/or material of concern. Historically, incineration has been the preferred method of treatment, however use of non-combustion technologies, such as steam sterilization, should also be considered. An example of a commercial decision, with local community input, to convert from high temperature incineration to steam sterilization occurred at Auckland International Airport in New Zealand in 2005. The 22 tonnes per day unit was commissioned in early 2006 and reports trouble-free, continuous operation at time of publication, December 2006.

Annex 2 Case study on health-care waste management [15]

The New Delhi-based non-governmental organizations Srishti and ToxicsLink have been supporting health-care facilities to solve health-care waste management problems since 1996. In their experience, administrative willingness was the most essential quality needed in a health-care institution. Several private hospitals in New Delhi started to work on this issue in 1998, soon after national rules on health-care waste were passed. In these cases, the senior administrator led the systems and policy change. Today these hospitals have established systems because of their commitment in 1998 and subsequent years. Hospitals typically failed if their senior staff viewed waste management as an unnecessary burden for themselves and their health-care workers.

In a successful waste management programme, the leading authority made regular rounds to identify and address problems directly with appropriate personnel. The head of the medical staff and the nursing superintendent also played an active role in waste management programmes. In other cases, a successful hospital programme was built around a team effort. While the top administrator was fully supportive, a full waste management committee was appointed and headed by the Deputy Director.

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[15] Information obtained from: Srishti (New Delhi, India): http://www.toxicslink.org/ovrvw-prog.php?prognum=1 and *Safe Management of Bio-Medical Sharps Waste in India*, SEA-EH-548, World Health Organization South-East Asia Regional Office, 2005.

The programme's success required regular and tailored training for all personnel. Necessary staff time was allocated for training and the importance of training was emphasized.

Since about 80% of wastes generated in health-care facilities were general, non-infectious or non-hazardous wastes, segregation and waste recycling were important activities. Many hospitals installed autoclaves, an advanced steam treatment system known as a hydroclave, or a microwave unit to treat much of their infectious waste. Pathological waste was sent to crematoria. Non-infectious waste was disposed of as regular domestic waste. The treatment and disposal of sharps were a particular concern in view of the particular hazards posed by contaminated needles. Some sharps waste was buried in specially designed sharps pits. Others treated sharps in autoclaves, shredded the treated sharps, and re-processed the separated plastic and metal pieces. Thirteen specific case studies were published by the World Health Organization in S*afe Management of Bio-Medical Sharps Waste in India*. The non-governmental organizations also promoted small-scale, low-cost treatment systems for small rural facilities, such as small solar-powered autoclaves and other designs from the Health-Care Without Harm international competition on alternative treatment technologies for rural areas (www.medwastecontest.org).

(iii) Co-benefits of best available techniques for chemicals listed in Annex C

1. General considerations

The application of best available techniques for chemicals listed in Annex C of the Stockholm Convention will often have various co-benefits. Conversely, measures to protect human health and the environment from other pollutants will also help to reduce and eliminate chemicals listed in Annex C.

These other pollutants include particulate matter, certain metals (such as mercury), nitrogen oxides (NO_x), sulphur dioxide (SO_2), and volatile organic compounds. Measures include flue gas cleaning processes, wastewater and solid residue treatment and monitoring and reporting.

Examples of some of these linkages and co-benefits are outlined below, with further details on best available techniques and best environmental practices provided in sections of the document dealing with specific source categories.

2. Information, awareness and training

Information, awareness and training activities associated with environmental and health concerns and protection may have co-benefits for the reduction of chemicals listed in Annex C and other pollutants.

3. Flue gas cleaning processes

Various flue gas treatment processes will have co-benefits for chemicals listed in Annex C and other pollutants. Examples include:

3.1 Containment, collection and ventilation

These measures will reduce residential and occupational human exposure to total particulate matter, particulate matter less than 10 microns (PM10) and particulate matter less than 2.5 microns (PM2.5). Pollutants associated with particulate matter, such as metals and metal compounds (e.g. lead), and gaseous pollutants such as volatile organic compounds, may also be reduced.

3.2 Dust separation processes

Measures such as cyclones, electrostatic precipitators and fabric filters will reduce emissions of particulate matter and pollutants associated with particulate matter to the environment.

3.3 Scrubbing processes

These measures will reduce emissions of particulate matter using effective mist eliminators and may reduce gaseous pollutants such as acid gases and mercury. Flue gas desulphurization will reduce emissions of SO_2.

3.4 Sorption processes

Measures such as activated carbon adsorption will reduce emissions of mercury, volatile organic compounds, SO_2, hydrogen chloride (HCl), hydrogen fluoride (HF) and polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) as applicable.

3.5 Catalytic processes

Measures such as selective catalytic reaction for reduction of NO_x may also reduce gas phase emission of chemicals listed in Annex C if catalytic oxidation also occurs in the system. Selective catalytic reaction may also oxidize elemental mercury, which is water soluble and can be removed in flue gas desulphurization systems. Catalytic fabric filters may also reduce volatile organic compounds.

4. Wastewater treatment processes

Primary wastewater treatment will remove suspended solids. Tertiary treatment such as activated carbon may remove various organics.

Filter cake from wastewater treatment is regarded as hazardous waste and has to be disposed of in an environmentally sound manner (e.g. specially engineered landfill).

5. Solid residue treatment processes

Measures such as waste residue solidification and thermal treatment will reduce the total content of pollutants and leaching of various pollutants to the environment.

6. Monitoring and reporting

Facilities may be required to monitor, measure, estimate and report releases to the environment. These could provide public information on various pollutants and incentives for continual improvements in the environmental performance of the facilities.

Periodic comprehensive measurement scans of a wide range of pollutants, including PCDD/PCDF, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB), in addition to routine monitoring of common pollutants, could provide useful information on many potential sources of chemicals listed in Annex C and other pollutants.

(iv) Management of flue gas and other residues

1. Flue gas treatment techniques (air pollution control devices)

In principle, reduction of emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) can be achieved with the following exhaust gas cleaning processes:

- Afterburners;
- Rapid quench systems;
- Dust separation;
- Scrubbing processes;

- Sorption process;
- Catalytic oxidation.

Air pollution control devices may be wet, dry, or semi-dry, depending on the role of water in the process. Wet and, sometimes, semi-dry air pollution control devices require additional processes to clean any wastewater generated before it leaves the facility.[16] Solid waste arising from semi-dry and dry processes (and also from wet processes after wastewater treatment) has to be disposed of in an environmentally sound manner or undergo additional treatment before disposal or potential reuse.

Further information with regard to applications for waste incineration can be found in Section V.A, 6.4.

1.1 Comparison of PCDD/PCDF control techniques

The techniques that have been found to be most effective at reducing persistent organic pollutants in flue gases are those that utilize adsorbents and particulate control and those that utilize catalysts. Table 1 summarizes the collection efficiencies of selected PCDD/PCDF control techniques.

Costs for PCDD/PCDF control at existing facilities can be reduced by using synergies with existing air pollution control devices:

- Through activated coke injection an existing fabric filter or electrostatic precipitator can be extended to a flow injection reactor to reduce PCDD/PCDF. The additional costs for PCDD/PCDF reduction arise from the storage, transport, injection and disposal of the activated coke, which is used as an additional adsorbent, and safe handling of the carbon and disposal of the residues, which may change in character.
- PCDD/PCDF can be destroyed with an oxidation catalyst. An existing catalyst for the selective removal of nitrogen oxides (NO_x) can be used for this purpose. Additional costs arise from enlarging the surface of the catalyst by adding one or two layers of catalyst to achieve PCDD/PCDF concentrations below 0.1 ng I-TEQ/Nm^3.[17]

In addition to the removal or destruction of PCDD/PCDF, other pollutants such as heavy metals, aerosols or other organic pollutants will be reduced.

Table 1. Comparison of PCDD/PCDF control systems

Control option	**PCDD/PCDF removal efficiency**	**Co-benefits**
Cyclone	Low efficiency	Coarse dust removal
Electrostatic precipitator	Low efficiency	Designed for dust removal
Bag filter	Medium efficiency	Designed for dust removal
Wet scrubber	Medium efficiency	Designed for dust or acid gas removal
Quenching and subsequent high-efficiency wet scrubber	Medium to high efficiency	Simultaneous reduction of dust, aerosols, HCl, HF, heavy metals and SO_2
Afterburner	High efficiency	No residues, but quenching

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[16] Combustion controls and other factors that affect formation and release of chemicals listed in Annex C of the Stockholm Convention upstream of the flue gases are described in the sector-specific guidance notes (sections V and VI).

[17] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on reporting PCDD/PCDF results see section I.C, subsection 3 of the present guidelines.

		of flue gases required
Catalytic oxidation (selective catalytic reaction)	High efficiency; destruction of PCDD/PCDF and other organics	No residues, simultaneous reduction of NO_x
Catalytic bag filter	High efficiency	Simultaneous dust removal
Dry absorption in resins (carbon particles dispersed in a polymer matrix)	Depends on the amount of installed material	Selective for PCDD/PCDF; material can be incinerated after use
Entrained flow reactor with added activated carbon or coke/lime or limestone solutions and subsequent fabric filter	Medium to high efficiency	Simultaneous reduction of various pollutants such as PCDD/PCDF and mercury; material can be incinerated after use[a]
Fixed bed or circulating fluidized bed reactor, adsorption with activated carbon or open hearth coke	High efficiency	Simultaneous reduction of various pollutants such as PCDD/PCDF and mercury; material can be incinerated after use[a]

a. As a carbon adsorber will also adsorb mercury, care has to be taken about mercury circulation if the spent carbon is reburnt. Additional mercury removal is therefore needed.

1.2 Rapid quenching systems

Water quench systems are also used to bring flue gas temperatures down quickly to below the formation threshold for chemicals listed in Annex C of the Stockholm Convention. These systems and associated wastewater treatment systems must be designed to deal with the higher particulate matter loadings that will end up in the scrubber water as a consequence.

1.3 Afterburners

Afterburners are either separate from or integrated into the main combustion chamber for destroying unburnt or partially burnt carbon compounds in the exhaust gas. Depending on the actual conditions a catalyst, additional combustion air or a (natural gas-fired) burner may be required. Where appropriate, legislation would indicate minimum temperatures to achieve this destruction for a given process. Measures are required to ensure that the afterburners are actually used as required.

1.4 Dust separation

PCDD/PCDF are released with flue gases via the gas phase as well as particle bound. The fine dust fraction may be enriched in particular due to its high specific surface. Since the separation of the fine dust fraction is not always achieved with electrostatic precipitators, well-designed fabric filters are often more efficient for PCDD/PCDF emission reduction. Addition of sorbents may enhance the removal efficiency (Hübner et al. 2000).

1.4.1 Cyclones and multicyclones

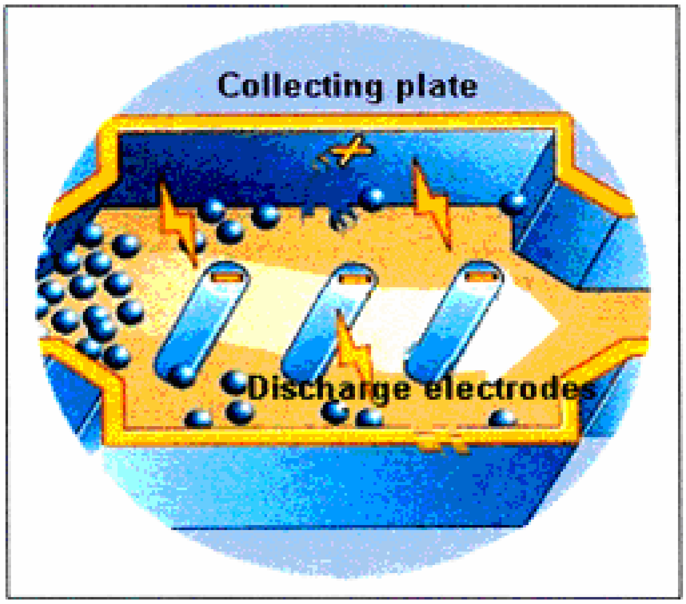
Cyclones and multicyclones (consisting of several small cyclones) extract particulate matter from the gas stream through the use of centrifugal force. Cyclones are much less effective than devices such as electrostatic precipitators or fabric filters in controlling particulate matter releases and are not used alone in advanced flue gas cleaning applications.

1.4.2 Electrostatic precipitators

Electrostatic precipitators (in Europe these systems are usually referred to as electrostatic filters) are generally used to collect and control particulate matter in combustion gas by introducing a strong electrical field into the flue gas stream (Figure 1). This acts to charge the particles entrained in the combustion gases.

Large collection plates receive an opposite charge to attract and collect the particles. The efficiency of collection is a function of the electrical resistivity of the entrained particles. Electrostatic precipitators efficiently remove most particulate matter, including chemicals listed in Annex C adsorbed to particles.

Figure 2. Electrostatic precipitator principle



Source: European Commission 2005.

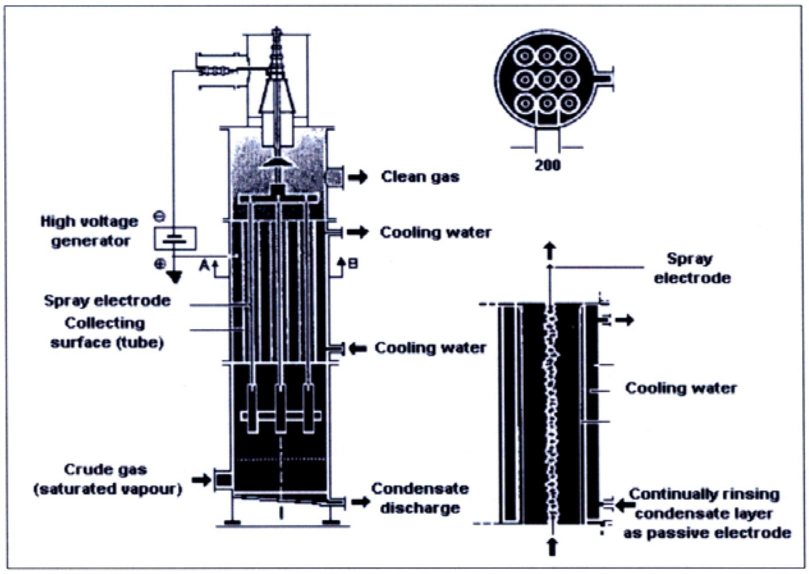
Formation of chemicals listed in Annex C can occur within the electrostatic precipitator at temperatures in the range of 200º C to about 450º C. As temperatures at the inlet to the electrostatic precipitator increase from 200° to 300º C, PCDD/PCDF concentrations have been observed to increase with increase in temperature. As the temperature increases beyond 300º C, formation rates decline.

Typical operational temperatures for electrostatic precipitators are 160°–260° C. Operation at higher temperatures (e.g. above 250° C) is generally avoided as this may increase the risk of PCDD/PCDF formation.

Wet electrostatic precipitators use liquids, usually water, to wash pollutants off the collection plates. These systems operate best when the incoming gases are cooler or moist.

Condensation electrostatic precipitators use externally water-cooled bundles of plastic tubes that collect fine liquids or solids by facilitating condensation with a water quench (Figure 3).

Figure 3. Condensation electrostatic precipitator

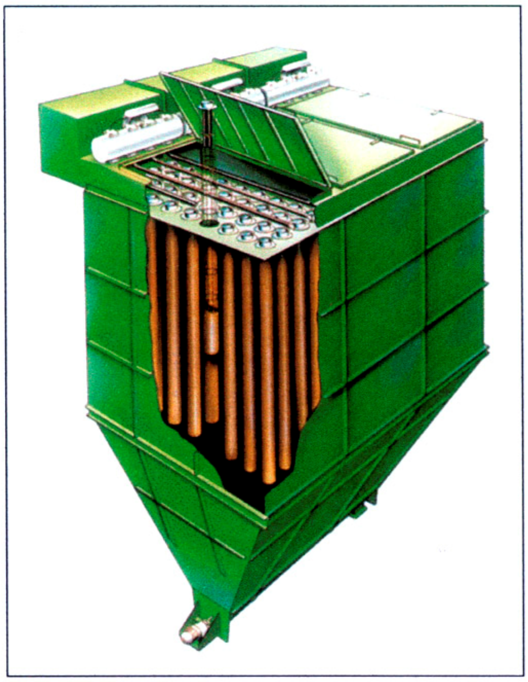


Source: European Commission 2005.

1.4.3 Fabric filters

Fabric filters are also referred to as baghouses or bag or sleeve filters (Figure 3). These particulate matter control devices are highly effective in removing chemicals listed in Annex C that may be associated with particles and any vapours that adsorb to the particles in the exhaust gas stream.

Figure 4. Schematic of a fabric filter



Source: European Commission 2005.

Filters are usually bags of 16 to 20 cm diameter, 10 m long, made from woven fibreglass material or polytetrafluoroethylene (PTFE), and arranged in series (see Table 2). An induction fan forces the combustion gases through the tightly woven fabric, which provides a bed for filter cake formation. The porosity of the fabric and the resulting filter cake allows the bags to act as filter media and retain a broad range of particle sizes down to less than 1 µm in diameter (although at 1 µm capture efficiency begins to decrease).[18] Fabric filters are subject to water damage and corrosion and gas streams must be maintained above the dew point (130°-140°C) to prevent these effects. Some filter materials are more resistant to damage. Fabric filters are sensitive to acids; therefore, they are commonly operated in combination with spray dryer adsorption systems for upstream removal of acid gases. Spray drying also serves to cool the inlet gases. Without such cooling, chemicals listed in Annex C may be formed in the fabric filters, similar to the situation with electrostatic precipitators. Dust removal systems are compared in Table 3.

Table 2. Characteristics of fabric filter materials

Fabric	Maximum temperature (° C)	Resistance		
		Acid	**Alkali**	**Physical flexibility**
Cotton	80	Poor	Good	Very good
Polypropylene	95	Excellent	Excellent	Very good
Wool	100	Fair	Poor	Very good
Polyester	135	Good	Good	Very good
Nylon	205	Poor to fair	Excellent	Excellent
PTFE	235	Excellent	Excellent	Fair
Polyamide	260	Good	Good	Very good
Fibreglass	260	Fair to good	Fair to good	Fair

Source: European Commission 2005.

Table 3. Comparison of dust removal systems

Dust removal system	Typical dust emission concentrations	Advantages	Disadvantages
Cyclone and multicyclone	Cyclones: 200–300 mg/m³ Multicyclones: 100–150 mg/m³	Robust, relatively simple and reliable Applied in waste incineration	Only for pre-dedusting Relatively high energy consumption (compared to electrostatic precipitator)
Electrostatic precipitator, dry	< 5–25 mg/m³	Relatively low power requirements Can use gas temperatures in the range 150°–350° C but effectively limited to 200° C by PCDD/PCDF issue (see right)	Formation of PCDD/ PCDF if used in range 200°–450° C
Electrostatic precipitator,	< 5–20 mg/m³	Able to reach low pollutant concentrations	Mainly applied for post-dedusting

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[18] 1 µm (micrometre) = 1×10^{-6} metre.

Dust removal system	Typical dust emission concentrations	Advantages	Disadvantages
wet			Generation of process wastewater Increase of plume visibility
Bag filter	< 5 mg/m³	Layer of residue acts as an additional filter and as an adsorption reactor	Relatively high energy consumption (compared to electrostatic precipitator) Sensitive to condensation of water and to corrosion

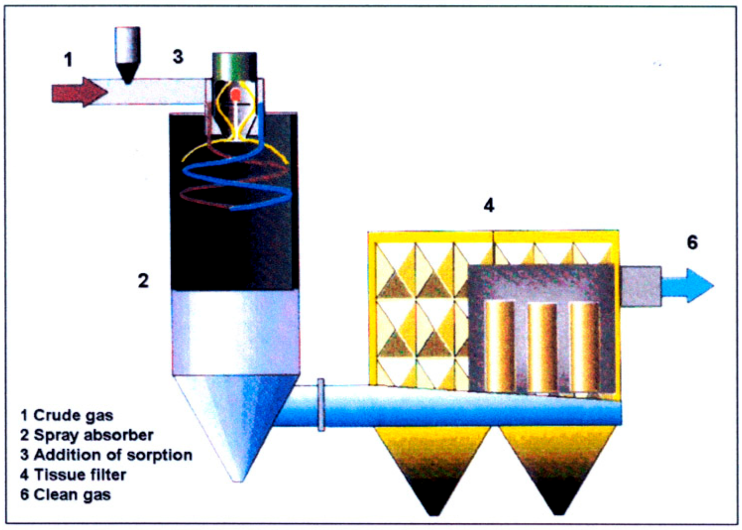
Source: European Commission 2005.

1.5 Scrubbing processes

1.5.1 Spray dry scrubbing

Spray dry scrubbing, also called spray dryer adsorption or semi-wet scrubbing, removes both acid gas and particulate matter from the post-combustion gases. In a typical spray dryer, hot combustion gases enter a scrubber reactor vessel (Figure 4).

Figure 5. Spray dry scrubbing/adsorption



Source: European Commission 2005.

An atomized hydrated lime slurry (water plus lime) is injected into the reactor at a controlled velocity. The slurry rapidly mixes with the combustion gases within the reactor. The water in the slurry quickly evaporates, and the heat of evaporation causes the combustion gas temperature to rapidly decrease. The neutralizing capacity of hydrated lime can reduce the acid gas constituents of the combustion gas (e.g. HCl and SO_2) by as much as 90%. However at waste incinerator plants spray dry scrubbing systems also typically achieve 93% SO_2 and 98% HCl control.A dry product consisting of particulate matter and hydrated lime either settles to the bottom of the reactor vessel or is captured by the downstream particulate capture device (electrostatic precipitator or fabric filter).

Spray drying technology is used in combination with fabric filters or electrostatic precipitators. In addition to reducing acid gas and particulate matter and control of volatile metals, spray drying reduces inlet temperatures to help reduce formation of chemicals listed in Annex C. PCDD/PCDF formation and release is substantially prevented by quenching combustion gases quickly to a temperature range that is unfavourable to their formation, and by the higher collection efficiency of the resulting particulate matter.

Solid residue from spray dry usually contains a mixture of sulphates, sulphites, fly ash, pollutants and unreacted adsorbents and has to be landfilled.

1.5.2 Wet scrubbers

Wet scrubbers encompass a number of processes designed for acid gas and dust removal. Alternative technologies include jet, rotation, venturi, spray, dry tower and packed tower scrubbers (European Commission 2005). Wet scrubbers help reduce formation and release of chemicals listed in Annex C in both vapour and particle forms. In a two-stage scrubber, the first stage removes hydrogen chloride (HCl) through the introduction of water, and the second stage removes sulphur dioxide (SO_2) by addition of caustic or hydrated lime. In the wet scrubbing process gypsum can be produced, which reduces the amount of waste going to landfills.

In the case of packed tower scrubbers, packing that contains polypropylene embedded with carbon can be used for specific removal of PCDD/PCDF.

Wet scrubbers have the highest removal efficiencies for soluble acid gases among the demonstrated techniques where removal efficiency is a function of pH of scrubber water. Solid particles in scrubber water may also cause interaction with PCDD/PCDF in the mobile gas stream, thus influencing the reliability of the relationship between results obtained from periodic stack gas monitoring and the destruction efficiency of the plant.

Memory effects are mainly due to the accumulation of various PCDD/PCDF congeners in plastic materials used in wet scrubbers. The effect may last several hours or may be long-term. As such, there is a preference for the removal of PCDD/PCDFF before wet scrubbing to reduce memory effects. An assessment should be carried out regarding PCDD/PCDF build-up in the scrubber and suitable measures adopted to deal with this build-up and prevent scrubber breakthrough releases. Particular consideration should be given to the possibility of memory effects during shut-down and start-up periods.

1.5.3 Fine dust absorber

Fine dust absorbers are equipped with a large number of pneumatic two-component jets (water and compressed air). Such high-efficiency absorbers can separate the PCDD/PCDF-covered fine dust through the very fine spray-like dispersal of the absorption solution and the high speed of the water droplets. In addition, the cooling of the exhaust gases and the undercooling in the dust absorber initiate condensation and improve the adsorption of volatile compounds on the dust particles. The absorption solution is treated by wastewater processing. The addition of adsorbents may further improve PCDD/PCDF reduction. With simple scrubbers for the separation of acid exhaust gases appreciable PCDD/PCDF removal is not possible. The achievable emission values of high-efficiency absorbers are in a range of 0.2–0.4 ng I-TEQ/Nm^3. This is equal to a separation efficiency of approximately 95% (Hübner et al. 2000). Waste arising from this process is normally disposed in a specially engineered landfill.

1.6 Sorption processes

1.6.1 Fixed bed filters

In the fixed bed process, precleaned exhaust gases are conducted at temperatures of 110°–150° C through an activated carbon based adsorbent material. Necessary devices include fresh adsorbent supply, fixed bed reactor and spent adsorbent system. The activated coke bed separates residual dust, aerosols and gaseous pollutants. It is moved cross-current and countercurrent in order to prevent blockage of the bed through, for example, residual dust.

Usually, the PCDD/PCDF-covered coke is disposed off through (internal) combustion, by which organic pollutants are to a large extent destroyed. Inorganic pollutants are released via slags or separated in the exhaust gas fine cleaning again. The fixed bed process achieves PCDD/PCDF reductions of 99.9%. Compliance with a performance standard of 0.1 ng I-TEQ/Nm^3 is state-of-the-art (Hübner et al. 2000; Hartenstein 2003).

1.6.2 Flow injection process

In order to enhance the separation efficiency of fabric filters, adsorbents with high PCDD/PCDF take-up capacities are injected into the exhaust gas stream. In general, activated coal or hearth-type coke are used as adsorbents together with lime hydrate. The separation is carried out in a fabric filter located at the end of the process, where adsorbents and dust are separated and a filter layer is formed. The appropriate disposal of the PCDD/PCDF-containing filter dust has to be assured. Conventional operation temperatures range from 135° to 200° C.

Usually, the PCDD/PCDF-covered coke is disposed off through (internal) combustion. By (internal) combustion organic pollutants are destroyed to a large extent. Inorganic pollutants are released via slags or separated in the exhaust gas fine cleaning again.

With the flow injection process, filtration efficiencies of 99% are achieved. The PCDD/PCDF removal efficiency depends on the quality of the adsorbent injection, the effectiveness of the adsorbent-flue gas mixing system, the type of particulate filter and the operation of the system. Another critical parameter is the mass flow rate of the injected adsorbent. For applying this technology most effectively a baghouse should be used. Compliance with a performance standard of 0.1 ng I-TEQ/Nm^3 is state-of-the-art (Hübner et al. 2000; Hartenstein 2003).

1.6.3 Entrained flow reactor

For this technology the same adsorbents are applied as used for the adsorbent injection process. However, the adsorbent is usually applied in a mixture with hydrated lime or other inert materials such as limestone, quicklime or sodium bicarbonate. Upstream of the entrained flow reactor for flue gas polishing, a conventional flue gas cleaning system is required for removing the bulk of the fly ash and the acid gases. Necessary devices include fresh adsorbent supply, fabric filter, recirculation system and spent adsorbent system. Conventional operation temperatures range from 110° to 150° C. Compliance with a performance standard of 0.1 ng I-TEQ/Nm^3 is state-of-the-art (Hartenstein 2003).

1.6.4 Dry absorption (in resins)

A new flue gas cleaning technology has been developed that combines adsorption and absorption of PCDD/PCDF into plastic structures containing dispersed carbon particles. In this new material, the PCDD/PCDF are first adsorbed in the polymer matrix and then diffuse to the surface of the carbon particles where they are irreversibly absorbed. The most common application of Adiox^{TM} is tower packings employed in gas cleaning systems. Until now, more than 30 full-scale incineration lines with flow gases ranging from 5,000 to 100,000 Nm^3/h are installed in wet flue gas cleaning systems. The removal efficiency depends on the amount of installed material. The technology can be applied as the main PCDD/PCDF cleaning system or to increase the safety margins or to reduce the memory effect in wet scrubbers. If Adiox is employed in dry adsorbers, the removal efficiency per installed amount is higher (Andersson 2005).

1.7 Catalytic oxidation of PCDD/PCDF

1.7.1 Selective catalytic reactions

Catalytic oxidation processes, which are normally used for reducing nitrogen oxide emissions, are applied for PCDD/PCDF destruction as well. Therefore, effective dedusting (e.g. emission values of particulate matter of below 5 mg/m^3) is a requirement for achieving low overall emissions of chemicals listed in Annex C. For the removal of PCDD/PCDF only (e.g. with the DeDiox process), ammonia injection is not necessary. In this case, operation temperatures range from 130° to 350° C.

The main advantages of this process are an easy operation and no residues apart from very little spent catalyst. Therefore, catalytic oxidation does not cause disposal problems.

Decomposition reaction for Cl_4DD: $C_{12}H_4Cl_4O_2 + 11\ O_2 \rightarrow 12\ CO_2 + 4\ HCl$

In general, the installations are operated in clean gas circuits, i.e., dust and heavy metals are separated before the catalyst in order to prevent rapid wear and deactivation of the catalysts through catalyst poisons.

With catalytic oxidation, only the PCDD/PCDF fraction in the gas phase can be captured. Nevertheless, emission reductions of 95 to 99% can be achieved. PCDD/PCDF reduction rate depends on the installed catalyst volume, the reaction temperature and the space velocity of the flue gas through the catalyst. PCDD/PCDF testing showed emission values lower than 0.01 ng I-TEQ/Nm^3 (dry basis, 11% O_2).

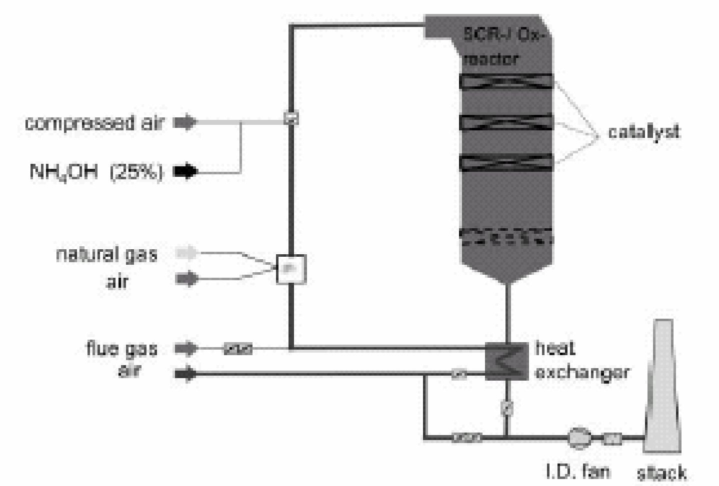
In the selective catalytic reaction process for combined removal of PCDD/PCDF and NO_x an air-ammonia mix is injected into the flue gas stream and passed over a mesh catalyst (Figure 5). The ammonia and NO_x react to form water and N_2 (European Commission 2005; Hübner et al. 2000; Hartenstein 2003).

1.7.2 Catalytic bag filters

Catalytic bag filters with PTFE membrane enable dust concentrations in cleaned flue gases of about 1–2 mg/Nm^3. Currently applications are known in waste incineration, crematoria, metal industries and cement plants. Filter bags that are impregnated with a catalyst, or contain a powdered catalyst directly mixed in fibre production, have been used to reduce PCDD/PCDF emissions. This type of filter bag is generally used without the addition of activated carbon so that the PCDD/PCDF can be destroyed on the catalyst rather than absorbed in the carbon and discharged as solid residues. They operate at temperatures between 180° and 250° C.

A catalytic filter system incorporates microporous PTFE fibre with the catalyst particles built into the fibre structure. In this process, PTFE particles are mixed with the catalyst and processed to produce fibres. A microporous ePTFE membrane is laminated to the ePTFE/catalyst microporous fibres to produce the filtration medium. This material is then sewn into filter bags, which can be installed in a baghouse. Applications at German and Japanese crematoria gave emissions below 0.1 ng I-TEQ/Nm^3 (Xu et al. 2003).

Figure 6. High-temperature selective catalytic reduction reactor for simultaneous NO_x and PCDD/PCDF removal



Source: Hartenstein 2003.

2. Treatment of flue gas treatment residues

The treatment of flue gases to remove contaminants (as described above) will generate a number of residues, which must either be disposed of or undergo additional treatment before disposal and potential reuse. Appropriate options for disposal or reuse of these residues will depend on the type and degree of contamination, as well as the waste matrix (inert fraction). Flue gas treatment residues may be solids (e.g. baghouse or electrostatic precipitator dust), wastewaters or slurries containing varying amounts of dissolved and suspended solids (e.g. from wet electrostatic precipitators and other wet scrubbers) or spent adsorbent materials (e.g. saturated resins). These residues may contain, in addition to the inert materials, toxic metals, such as arsenic, lead, cadmium, mercury or others, as well as PCDD/PCDF.[19] These residues could be handled in one of several different ways, as discussed below. Current practices for the treatment and disposal of flue gas treatment residues include reuse in the process from which they were derived, disposal to landfill, stabilization and subsequent disposal, vitrification, incorporation into road-making materials, disposal or valorization in salt or coal mines, and catalytic or thermal treatment.

According to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal, Annex I wastes, including fly ashes, containing PCDD or PCDF are classified as hazardous waste.

2.1 Management of solid flue gas treatment residues[20]

One major flue gas treatment residue (or air pollution control residue) is fly ash. Fly ash removal from flue gas by use of dry scrubbers, cyclones or fabric filters will result in dry fine solid particulate material having a range of properties and contaminants depending on the combustion source that produced it. Air pollution control of many types of combustion sources, including municipal and hazardous waste incinerators, steel-making electric arc furnaces and cement kilns, can generate such a fine dry particulate material when dry controls are used. These dry particulate residues will contain different levels of metals (depending on feedstocks) and may also have some PCDD/PCDF and other polycyclic aromatic hydrocarbons adsorbed onto them, depending on the combustion conditions.

Contaminant releases to the environment from these dry materials may be by a number of routes, including leaching to groundwater, wind-blown dust, crop plant uptake or direct ingestion by humans or wildlife (potentially including farm animals). All management of these materials must be done with consideration of these potential releases, as required by the particular residue. A number of management options, including both beneficial reuse and treatment or disposal, are available for these dry residues, depending on the properties of the inert fraction and the type and level of contamination with metals and organics.

2.1.1 Residue reuse

Limited reuse is appropriate for dry, solid residues.

A major reuse of coal fly ash is in the construction of roads or buildings because of its pozzolanic properties. It can be used in cement and concrete production.

Fly ashes should never be used as soil amendment in agricultural or similar applications. Addition to soil may result in subsequent dispersion of the ash and any contaminants. In agricultural uses plants may take up contaminants, resulting in exposure to human or animals that consume the plants. Pecking or grazing animals may directly ingest contaminants, with subsequent exposure to humans when they consume the animals or animal products (e.g. milk and eggs).

2.1.2 Stabilization and solidification

Treatment and disposal options for solid residues from flue gas control systems include solidification or stabilization with Portland cement (or other pozzolanic materials), alone or with additives or a number of thermally based treatments, followed by appropriate disposal (based on anticipated releases

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[19] For additional guidance on management of residues based on their concentration of persistent organic pollutants (including when the persistent organic pollutant content is low, as per Stockholm Convention Article 6.1 (d) (ii)), see Basel Convention Secretariat 2005.

[20] The subparagraphs in paragraph 2 are cited from European Commission 2005, chapter 2.7.3.

from the treated residuals). Some residues with low levels of contamination may require no treatment before disposal in a landfill, based on an assessment of their contaminant release potential.

The main purpose of solidification is to produce a material with physical and mechanical properties that promote a reduction in contaminant release from the residue matrix. An addition of cement, for example, generally decreases hydraulic conductivity and porosity of the residue, while increasing durability, strength and volume.

Solidification methods commonly make use of several, mostly inorganic, binder reagents: cement, lime and other pozzolanic materials such as coal fly ash, blast furnace bottom ash or cement kiln dust, although some organic binders such as bitumen/asphalt or paraffin and polyethylene can also be used. Combinations of binders and various types of proprietary or non-proprietary additives are used as well. By far the most prevalent solidification technique is cement stabilization.

The main concept of chemical stabilization is to bind the heavy metals in more insoluble forms than those in which they occur in the original untreated residues. These stabilization methods make use of both the precipitation of metals in new minerals and the binding of metals to minerals by sorption. This process includes the solubilization of the heavy metals in the residues and a subsequent precipitation in, or sorption to, new minerals.

Several of the stabilization methods incorporate an initial washing step whereby a major part of soluble salts and to some extent metals are extracted before chemical binding of the remaining metals. These methods are completed by dewatering the stabilized product.

Treatment options using extraction and separation processes can, in principle, cover all types of processes for extracting specific components from the residues. However, most emphasis has been put on processes involving the extraction of heavy metals and salts with acid.

While stabilization and solidification approaches to waste treatment are typically directed at controlling the release of contaminant metals, PCDD/PCDF and other polycyclic aromatic hydrocarbons may be only partially controlled by these treatments (although these compounds are very hydrophobic and so generally do not leach very fast or at very high concentrations). Addition of adsorbents (such as clays or activated carbon), which are then incorporated into the treated waste matrix, can improve control of these organics. Laboratory leaching tests or other evaluations should be applied for assessing the effectiveness of any of these treatment approaches.

2.2 Thermal treatment of flue gas treatment residues

Thermal treatment can be grouped into three categories: vitrification, melting and sintering. The differences between these processes are chiefly related to the characteristics and properties of the final product.

- Vitrification is a process whereby residues are treated at high temperature (currently 1,300° to 1,500° C) and then quickly quenched (with air or water) to obtain an amorphous glassy matrix. After cooling down, the melt forms a single-phase product called a vitrificate. The vitrificate can be a glass-like or stone-like product, depending on the melt composition. Additives are sometimes (but not usually) added to the residues to favour the formation of the glassy matrix.
- Melting is similar to vitrifying, but the quenching step is controlled to allow crystallization of the melt as much as possible. It results in a multiphase product. Temperatures and the possible separations of specific metal phases are similar to those used in vitrifying. It is also possible to add specific additives to favour the crystallization of the matrix.
- Sintering involves the heating of residues to a level where bonding of particles occurs and the chemical phases in the residues reconfigure. This leads to a denser product with less porosity and a higher strength than the original product. Typical temperatures are around 900° C. When municipal solid waste is incinerated some level of sintering will typically take place in the incineration furnace. This is especially the case if a rotary kiln is used as part of the incineration process.

Regardless of the actual process, the thermal treatment of residues in most cases results in a more homogeneous, denser product with improved leaching properties. The energy requirements of stand-alone treatments of this type are generally very high.

These processes are generally employed to immobilize metals or radiological contaminants, and will significantly reduce the potential for leaching of many contaminants likely to be found in flue gas treatment solid residues. Again, leaching tests may be useful in evaluating the effectiveness of these treatments. Because these are high-temperature processes, any PCDD/PCDF or other polycyclic aromatic hydrocarbons adsorbed onto the original dry solids may well be destroyed as part of the treatment process. However, as high-temperature processes, air emissions must be monitored from the treatment itself, as it may result in air pollution control residues of its own, which will then need to be managed in an environmentally sound manner.

2.3 Treatment of spent dry adsorption resins

Use of specialized dry resins to remove flue gas contaminants such as PCDD/PCDF before release to the air will also generate a treatment residue in the form of the spent resin cartridge or bulk resin material. If such resins are designed to be regenerated, either through thermal desorption or by other means, then the regeneration process will itself generate residues or releases to the air that must be controlled and managed. If spent resins are to be disposed of after a single use (or for regenerated resins that are no longer useful), evaluation of the level and type of contaminants on the resin will help determine whether it can be landfilled without treatment, or requires some treatment before disposal. For some resins, incineration or some other treatment that destroys both the resin and adsorbed contaminants may also be a possibility.

2.4 Treatment of wastewaters

Many processes have wastewater streams that cannot reasonably be released to the open environment without treatment. Flue gas treatment systems are similar to chemical processes in that they each may have wastewater treatment needs.

Various wet processes may also be used to remove pollutants from flue gas streams and so prevent their release to the air. Resultant wastewaters will contain some amount of dissolved as well as suspended materials.

As with many chemical processes, the first step in handling these flue gas treatment residues, particularly where metals are the main concern, is often separation of the liquid and solid portions. This can often be accomplished using settling ponds or tanks, although land-based ponds may require liner systems to prevent leaching of contaminants into groundwater. The solid fraction may be further dewatered and dried and then handled as a solid material as discussed above. The water portion may require further removal of contaminants before meeting requirements for discharge to surface water or groundwater recharge areas. Treatments could include addition of chemicals to precipitate out metal salts, or use of adsorbent materials to remove organics. These wastewater treatment residuals would then also require appropriate treatment and disposal.

Flue gas treatment residues from wet processes may also contain organic constituents, including PCDD/PCDF or other polycyclic aromatic hydrocarbons. Biological treatment in ponds or impoundments can usually reduce the concentration of these and other organic constituents that may occur in flue gas treatment residues.

Most wastewaters do not present opportunities for reuse. However, treatment of flue gas to remove sulphur, using ground and slaked lime, presents one such opportunity. In the fully oxidized form of this treatment, the solid residue in the wastewater is a high-quality calcium sulphate, or gypsum. This gypsum can be dewatered and used to manufacture wallboard for residential or other buildings, sometimes at costs that are much lower than those for wallboard from mined gypsum.

(v) Training of decision makers and technical personnel

The importance of technical assistance, in particular training, as a need to strengthen the national capabilities of developing countries (in particular the least developed) and countries with economies in transition, is recognized in the preambular paragraphs of the Stockholm Convention, and Article 12 states: "Parties recognize that rendering of timely and appropriate technical assistance in response to requests from developing country Parties and Parties with economies in transition is essential to the successful implementation of this Convention."

In this regard capacity-building technical assistance, in particular training in available environmental methodologies, practices and tools, with specific reference to the particular needs of a Party, may give a better understanding of procedures for conducting, on a sustained basis, daily operational practices and preventive maintenance of the best available techniques and best environmental practices being introduced as components of the Party's national implementation plan. It is of utmost importance that capacity-building technical assistance, in particular training, should be provided at both managerial and technical or operating levels in public and private sector organizations involved in the implementation of the guidelines for best available techniques and best environmental practices. Taking into consideration the complexity of many best available techniques and the required holistic and preventive approach for introducing best environmental practices, life cycle management, in addition to relevant health and safety issues, should be given priority consideration in capacity-building, with a risk prevention and reduction approach.

(vi) Testing, monitoring and reporting

1. Testing and monitoring

Monitoring of releases of chemicals listed in Annex C of the Stockholm Convention is critical to achieving the goals of the Convention. However, many developing countries and countries with economies in transition do not have the necessary capacity in terms of costs, technical expertise and laboratories and, in some cases, the economic returns for facilities may not be sufficient to cover all costs associated with monitoring. Consequently, it is necessary to establish and strengthen regional, subregional and national technical capacity and expertise, including laboratories. This enhanced capacity may also promote monitoring at specified intervals for existing sources.

Proposals for new facilities or proposals to significantly modify existing facilities should, as part of best available techniques and best environmental practices, include plans for the evaluation of compliance with the target values for releases of chemicals listed in Annex C in stack gases and other outputs that are given in this guidance document. Accordingly, as part of ongoing operation, these facilities should demonstrate, through monitoring at specified intervals, as appropriate, that the performance levels continue to be achieved.[1, 2]

1.1 Sampling and analysis of PCDD/PCDF and dioxin-like PCB

Validated, standardized methods of sampling and analysis are available for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) but not yet for all chemicals listed in Annex C (Table 4). The methods for sampling and monitoring for polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) must be developed and validated. Methods for sampling stack gases include those with sampling periods of 4 to 8 hours as well as those that are quasi-continuous. Most if not all regulatory regimes for PCDD/PCDF are currently based on toxic equivalents (TEQ).[3]

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[1] Determination of the mass concentration of chemicals listed in Annex C in releases from a given source should follow nationally or internationally recognized standard methods of sampling, analysis and evaluation of compliance.

[2] In most cases, target values currently exist only for PCDD/PCDF.

[3] To determine TEQ concentrations, each of the 17 PCDD/PCDF congeners that are of greatest toxicological concern are quantified using a high-resolution gas chromatograph/mass spectrometer.

Sampling of PCDD/PCDF emissions to date is mainly undertaken by using one of the methods listed in Table 4.

Table 4: Methods for stack sampling and analysis of PCDD/PCDF and PCB

Method	**Substances analyzed**	**Analytical principle**	**Reference**
EN 1948	PCDD/PCDF	HRGC/HRMS	European Committee for Standardization
US EPA Method 23	PCDD/PCDF	HRGC/HRMS	U.S. Environmental Protection Agency
VDI Method 3499	PCDD/PCDF	HRGC/HRMS	Association of German Engineers (VDI)
Canada Methods EPS 1/RM/2 and EPS 1/RM/3	PCDD/PCDF, PCB	HRGC/HRMS	Environment Canada
Japanese Industrial Standard K 0311	PCDD/PCDF, dioxin-like PCB	HRGC/HRMS	Japanese Industrial Standards Committee

PCDD/PCDF analysis is carried out using high-resolution mass spectrometry. Quality control procedures are required at each stage of the analysis and recovery spike concentrations associated with both sampling and extraction. United States EPA Method 23 specifies that all recoveries should be between 70% and 130%. Canada provides detailed quality assurance guidance on the analysis of samples containing dioxins and furans in a range of matrices in its Reference Method EPS 1/RM/2.

The European Standard EN 1948 has been developed for separation detection, and quantification of PCDD/PCDF and dioxin-like PCB in emission samples from stationary sources at concentrations at about 0.1 ng TEQ/Nm³. Parts 1-3 detail sampling; extraction and clean-up; and identification and quantification of PCDD/PCDF (adopted in 1996, revision to be adopted in 2006). Part 4 will detail the standard for dioxin-like PCB (to be adopted in 2006).

The lower detection limits measured during the validation test of EN 1948 at a municipal solid waste incinerator varied between 0.0001 and 0.0088 ng/Nm^3 for the 17 individual PCDD/PCDF toxic congeners (CEN 1996c; . See also CEN 1996a, 1996b)

In the new draft of EN 1948-3 of February 2004 (updating CEN 1996c), Annex B, the uncertainty for the complete procedure is given to be 30–35% and the external variability is estimated to be ± 0.05 ng I-TEQ/m^3 at a mean concentration 0.035 ng I-TEQ/Nm^3.

Taking into account the toxic equivalence factors for the individual congeners the resulting overall detection limits vary between 0.001 and 0.004 ng I-TEQ/Nm^3. It is reasonable to assume that concentrations lower than 0.001 ng I-TEQ/m^3 should be considered as being below the detection limit.

A study performed by Environment Canada assessed the variability of sampling and analysis of 53 sets of PCDD/PCDF emission data from 36 combustion facilities. The limit of quantification for PCDD/PCDF emissions was estimated to be 0.032 I-TEQ ng/m^3, although this limit may vary depending on sampling volume, interfering substances and other factors.

Interferences should be expected to occur from compounds that have similar chemical and physical properties to PCDD/PCDF (CEN 1996c).

1.2 Limit of detection and limit of quantification

The “limit of detection” (LOD) is the smallest amount or concentration of analyte in the test sample that can be reliably distinguished, with stated significance, from the background or blank level.

The “limit of quantification” (LOQ) of an analytical procedure is the lowest amount or concentration of analyte in a sample which can be quantitatively determined with an acceptable level of precision and accuracy. The limit of quantification should be stated if it is necessary to specify a lower limit of measurement below which acceptable accuracy and precision is not attained. Using the method, carry out a number of independent determinations, preferably >20, using a sample which is known to contain the analyte at between 2 and 5 times the estimated detection limit. The limit of quantification is the concentration at which an acceptable degree of performance, in terms of RSD% (relative standard deviation), is obtained. It is usually the case that the limit of quantification corresponds to the lowest standard concentration level in the calibration range.

In the context of regulatory limit values, or for reporting measured concentrations, there is no general rule how to treat results below LOQ. Very often, the regulations or laws define the way of reporting results. For reporting, the following definitions should be taken into account:

– Lower-bound:	Non-quantifiable peaks are set to zero
– Upper-bound:	Full LOQ included in presentation of result

Criteria should be set to define lower-bound and upper-bound concentrations and the reporting value and therefore the LOQ should be at least 1/5 of the regulatory limit or level of interest or baseline concentration.

1.3 Gas reference conditions

Table 5 presents reference condition conversions used in Canada, the European Union and the United States of America.

Table 5: Reference Condition Conversions

Unit	Country/Region	Temperature (°C)	Pressure (atm)	Gas conditions
Nm^3 (Normal cubic meter)	European Union (EU)	0	1	Dry; 11% oxygen for municipal waste incinerators and co-combustion of waste; 10% oxygen for cement plants; no oxygen level requirements for all other plants (i.e., concentrations are reported at the actual oxygen content and are not normalized to any fixed O2 content)
Rm^3 (Reference cubic meter)	Canada	25	1	Dry; 11% oxygen for incinerators and coastal pulp and paper mill boilers, operating oxygen levels for sinter plants and steel manufacturing electric arc furnaces.
Sm^3 (or dscm) (Dry standard cubic meter)	United States (U.S.)	20	1	Dry; 7% oxygen or 12% carbon dioxide for incinerators and most combustion sources.

0.1 ng TEQ/Nm^3 (EU) = **0.131** ng TEQ/Sm^3 (U.S.) = **0.092** ng TEQ/Rm^3 (Canada

1.4 Bioassay methods

Four bioassay methods, three reporter gene bioassay methods and an enzyme imunoassay method, have been approved in Japan for measuring dioxins in emission gas, dust and cinders from waste incinerators. The methods provide a less costly alternative to high-resolution gas chromatography/mass spectrometry and are approved for measuring emissions from incinerators with a capacity less than 2 tons/hour (emission standards for new facilities: 5 ng WHO-TEQ/Nm^3) and dust and cinders from all waste incinerators (treatment standard 3 ng WHO-TEQ/g).

Table 6: Bioassay methods for stack and residue measurements at small waste incinerators

Method	Analytical Principle	Reference
CALUX Assay	Reporter gene assay	Xenobiotic Detection Systems International
P450 Human Reporter Gene System	Reporter gene assay	Columbia Analytical Services
AhR Luciferase Assay	Reporter gene assay	Sumitomo Chemical Co., Ltd

Guidelines for appropriate monitoring programmes are also necessary. In that regard, the United Nations Environment Programme (UNEP, 2004) has developed guidance for prioritizing measurements and minimizing the number of measurements for impact assessment. The European Commission has prepared a reference document on the general principles of monitoring; and some companies and industry associations have agreed monitoring requirements. Model legislation and regulations will also facilitate the establishment and implementation of programmes to monitor releases of chemicals listed in Annex C, including such approaches as bioassay monitoring.

2. Reporting

Reporting of releases and other relevant information is a key part of meeting Party obligations under Article 9 (Information exchange), Article 10 (Public information, awareness and education) and Article 11 (Research, development, and monitoring) of the Stockholm Convention. Parties seeking to employ best environmental practices for Annex C sources should include measures described in these articles, including:

- Mechanisms such as pollutant release and transfer registers to collect and disseminate comprehensive and chemically specific information on production and releases of chemicals listed in Annexes A, B or C together with their sources;
- Public participation in the regulation of sources of chemicals listed in Annex C;
- Public availability of monitoring data collected from sources in Annex C (taking into account paragraph 5 of Article 9);
- Making the results of their research, development and monitoring activities accessible to the public on a timely and regular basis (Article 11, paragraph 2 (e)).

Full provision of relevant information can encourage and facilitate public participation.

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Section IV

Compilation of summaries from the source categories included in sections V and VI

Table of contents

Preamble

This section includes a compilation of all the summaries from the source categories in sections V and VI of the draft guidelines on Best Available techniques and Provisional Guidance on Best Environmental Practices Relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants.

Each summary may include the following information, as appropriate:

- A brief description of the source, its purpose and the processes involved;
- Potential of the source for generation of chemicals listed in Annex C of the Stockholm Convention, namely: polychlorinated dibenzo-p-dioxins (PCDD); polychlorinated dibenzofurans (PCDF); polychlorinated biphenyls (PCB); and hexachlorobenzene (HCB);
- Best available techniques and best environmental practices to minimize emissions of chemicals listed in Annex C;
- Primary and secondary measures that may assist in reducing emissions;
- Alternatives, where applicable, that may be preferable to current processes and practices;
- Performance levels associated with best available techniques.

Summaries of section V: source categories included in Part II of Annex C

A. Waste incinerators

(i) Municipal solid waste, hazardous waste and sewage sludge

Summary

Waste incinerators are identified in the Stockholm Convention as having the potential for comparatively high formation and release of chemicals listed in Annex C to the environment.

The potential purposes of waste incineration include volume reduction, energy recovery, destruction or at least minimization of hazardous constituents, disinfection and the recovery of some residues.

When considering proposals to construct new waste incinerators, priority consideration should be given to alternatives such as activities to minimize the generation of waste, including resource recovery, reuse, recycling, waste separation and promoting products that generate less waste. Priority consideration should also be given to approaches that prevent the formation and release of persistent organic pollutants.

The environmentally sound design and operation of waste incinerators requires the use of both best available techniques and best environmental practices (which are to some extent overlapping) to prevent or minimize the formation and release of chemicals listed in Annex C.

Best environmental practices for waste incineration include appropriate off site procedures (such as overall waste management and consideration of environmental impacts of siting) and on site procedures (such as waste inspection, proper waste handling, incinerator operation and management practices and handling of residues).

Best available techniques for waste incineration include appropriate selection of site; waste input and control; techniques for combustion, flue gas, solid residue and effluent treatment.

To achieve best results for environmental protection as a whole it is essential to coordinate the waste incineration process with upstream activities (e.g. waste management techniques) and downstream activities (e.g. disposal of solid residues from waste incineration).

Releases of chemicals listed in Annex C from municipal solid waste incinerators designed and operated according to best available techniques and best environmental practices occur mainly via fly ash, bottom ash and filter cake from wastewater treatment. Therefore it is of major importance to provide for a safe sink of these waste types, for example by pretreatment and final disposal in dedicated landfills, which are designed and operated according to best available techniques.

With a suitable combination of primary and secondary measures, PCDD/PCDF performance levels in air emissions no higher than 0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluents, are associated with PCDD/PCDF concentration levels well below 0.1 ng I-TEQ/l.

(ii) Medical waste

Summary

Incineration of medical waste (infectious health-care waste, biological health-care waste and sharps in dedicated waste incineration plants is performed in order to minimize chemical, biological and physical risks, and to reduce the volume of waste as a pretreatment step to environmentally sound landfilling.

If medical waste is incinerated in conditions that do not constitute best available techniques or best environmental practices, there is potential for the release of PCDD and PCDF in relatively high concentrations. For small medical waste incinerators, application of best available techniques is often difficult, given the high costs associated with building, operating, maintaining and monitoring such facilities.

Possible alternatives to incineration are sterilization (steam, advanced steam, dry heat), microwave treatment, alkaline hydrolysis, biological treatment or in certain cases landfilling. The most important step in managing medical waste is segregating different types of waste at the source. As between 75% and 90% of waste in hospitals is comparable to municipal solid waste, segregation greatly reduces the volume of medical waste. Effective waste management, including waste minimization and segregation at the source, is essential.

Appropriate treatment of bottom ashes and residues from flue gas cleaning is essential for the reduction of PCDD/PCDF releases into the environment. The use of best available techniques in incinerators will also reduce emissions of hydrochloric acid and metals (in particular mercury) and will also, in effect, reduce subsequent releases from residues disposed of into landfills.

With regard to incineration, primary measures alone will significantly reduce emission of the chemicals listed in Annex C of the Stockholm Convention. However, implementation of best available techniques requires both primary and secondary measures. .

With a suitable combination of primary and secondary measures, PCDD/PCDF emission levels in air emissions no higher than 0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluents, are associated with PCDD/PCDF concentration levels well below 0.1 ng I-TEQ/l.

B. Cement kilns firing hazardous waste

Summary

The main purpose of cement kilns is clinker production. Firing wastes in cement kilns aims at energy recovery and substitution of fossil fuels or substitution of minerals. In some cases hazardous wastes are disposed of in these installations.

The manufacturing process includes the decomposition of calcium carbonate ($CaCO_3$) at about 900° C to calcium oxide (CaO, lime) (calcination) followed by the clinkering process at about 1450C° in a rotary kiln. The clinker is then ground together with gypsum and other additives to produce cement. According to the physical and chemical conditions the main process routes for the manufacture of cementare termed dry, wet, semi-dry and semi-wet.

The combustion process in the kiln, has the potential to result in the formation and subsequent release of chemicals listed in Annex C of the Stockholm Convention. In addition, releases from storage sites may occur.

Well-designed process conditions, and the installation of appropriate primary measures, should enable cement kilns firing hazardous waste to be operated in such a manner that the formation and release of chemicals listed in Annex C can be minimized sufficiently to achieve concentrations of PCDD and PCDF in flue gases of < 0.1 ng I-TEQ/Nm^3 (oxygen content 10%), depending on such factors as the use of clean fuels, waste feeding, temperature and dust removal. Where necessary, additional secondary measures to reduce such emissions should be applied.

Many data on PCDD/PCDF emissions to air are available

PCDD/PCDF releases via cement kiln dust and possibly clinker have been reported and are currently under further investigation. Data on PCB and HCB releases are still scarce

The performance level associated with best available techniques and best environmental practice for control of PCDD/PCDF in flue gases is < 0.1 ng I-TEQ/Nm^3 with reference conditions of 273 K, 101.3 kPa, 10% O_2 and a dry gas basis.

C. Production of pulp using elemental chlorine or chemicals generating elemental chlorine

Summary

The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, deknotting, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing.

Of the chemicals listed in Annex C of the Stockholm Convention, only PCDD and PCDF have been identified as being produced during the production of pulp using elemental chlorine. Of the 17 PCDD/PCDF congeners with chlorine in the 2,3,7 and 8 positions, only two congeners – namely 2,3,7,8-TCDD and 2,3,7,8-TCDF – have been identified as potentially being produced during chemical pulp bleaching using chlorine. Most of the formation of the 2,3,7,8-TCDD and 2,3,7,8-TCDF is generated in the C-stage of bleaching via the reaction of chlorine with precursors of TCDD and TCDF. HCB and PCB are not formed during pulp bleaching.

As a summary, the following primary measures can be taken for decreasing or eliminating the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in wood and non-wood bleaching processes: eliminate elemental chlorine by replacing it with chlorine dioxide (elemental chlorine-free bleaching) or in some cases with totally chlorine-free processes; reduce application of elemental chlorine by decreasing chlorine multiple or increasing the substitution of chlorine dioxide for molecular chlorine; minimize precursors such as dibenzo-p-dioxin and dibenzofuran entering the bleach plant by using precursor-free additives and thorough washing; maximize knot removal; and eliminate pulping of furnish contaminated with polychlorinated phenols.

D. Thermal processes in the metallurgical industry

(i) Secondary copper production

Summary

Secondary copper smelting involves copper production from sources that may include copper scrap, sludge, computer and electronic scrap, and drosses from refineries. Processes involved in copper production are feed pretreatment, smelting, alloying and casting. Factors that may give rise to chemicals listed in Annex C of the Stockholm Convention include the presence of catalytic metals (of which copper is a highly effective example); organic materials in feed such as oils, plastics and coatings; incomplete combustion of fuel; and temperatures between 250° and 500° C.

Best available techniques include presorting, cleaning feed materials, maintaining temperatures above 850° C, utilizing afterburners with rapid quenching, activated carbon adsorption and fabric filter dedusting.

Performance levels associated with best available techniques and best environmental practices for secondary copper smelters: < 0.5 ng I-TEQ/Nm3 (at operating oxygen concentrations).

(ii) Sinter plants in the iron and steel industry

Summary

Sinter plants in the iron and steel industry are a pretreatment step in the production of iron whereby fine particles of iron ores and, in some plants, secondary iron oxide wastes (collected dusts, mill scale) are agglomerated by combustion. Sintering involves the heating of fine iron ore with flux and coke fines or coal to produce a semi-molten mass that solidifies into porous pieces of sinter with the size and strength characteristics necessary for feeding into the blast furnace.

Chemicals listed in Annex C appear to be formed in the iron sintering process mainly via de novo synthesis. PCDF generally dominate in the waste gas from sinter plants. The PCDD/PCDF formation mechanism appears to start in the upper regions of the sinter bed shortly after ignition, and then the dioxins, furans and other compounds condense on cooler burden beneath as the sinter layer advances along the sinter strand towards the burn-through point.

Primary measures identified to prevent or minimize the formation of PCDD/PCDF during iron sintering include the stable and consistent operation of the sinter plant, continuous parameter monitoring, recirculation of waste gases, minimization of feed materials contaminated with persistent organic pollutants or contaminants leading to formation of such pollutants, and feed material preparation.

Secondary measures identified to control or reduce releases of PCDD/PCDF from iron sintering include adsorption/absorption (for example, activated carbon injection), suppression of formation using urea addition, and high-efficiency dedusting, as well as fine wet scrubbing of waste gases combined with effective treatment of the scrubber wastewaters and disposal of wastewater sludge in a secure landfill.

Performance levels associated with best available techniques and best envioronmental practices for an iron sintering plant operating according to best available techniques: < 0.2 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

(iii) Secondary aluminium production

Summary

Secondary aluminium smelting involves the production of aluminium from used aluminium products or process waste to recover metals by pretreatment, smelting and refining.

Fuels, fluxes and alloys are used, while magnesium removal is practised by the addition of chlorine, aluminium chloride or chlorinated organics. Chemicals listed in Annex C of the Stockholm Convention probably result from demagging additions, incomplete combustion, organics in the feed, chlorine compounds and formation in the system at temperatures between 250° and 500° C.

Best available techniques include high-temperature advanced furnaces, oil- and chlorine-free feeds (if alternatives are available), afterburners with rapid quench, activated carbon adsorption and dedusting fabric filters, as well as avoiding the use of hexachloroethane for the removal of magnesium from the melt (demagging) and maintaining careful control over demagging in general.

Performance levels associated with best available techniques and best environmental practices for secondary aluminium smelters: < 0.5 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

(iv) Secondary zinc production

Summary

Secondary zinc smelting involves the production of zinc from materials such as dusts from copper alloy production and electric arc steel making, and residues from steel scrap shredding and galvanizing processes.

Production processes include feed sorting, pretreatment cleaning, crushing, sweating furnaces to 364°C, melting furnaces, refining, distillation and alloying. Contaminants in the feed (including oils and plastics), poor combustion and temperatures between 250° and 500° C may give rise to chemicals listed in Annex C of the Stockholm Convention.

Best available techniques include feed cleaning, maintaining temperatures above 850° C, fume and gas collection, afterburners with quenching, activated carbon adsorption and fabric filter dedusting.

Performance levels associated with best available techniques and best environmental practices for secondary zinc smelters: < 0.5 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

Summaries of section VI: source categories included in Part III of Annex C

A. Open burning of waste, including burning of landfill sites

Summary

Open burning is an environmentally unacceptable process that generates chemicals listed in Annex C of the Stockholm Convention and numerous other pollutant products of incomplete combustion. Consistent with Annex C, Part V, section A, subparagraph (f) of the Stockholm Convention, the best guidance is to reduce the amount of material disposed of via this method with the goal of elimination altogether.

Other techniques which may effect improvement include, with respect to the materials burned: avoid including non-combustible materials, such as glass and bulk metals, wet waste and materials of low combustibility; avoid waste loads containing high chlorine content, whether inorganic chloride such as salt, or chlorinated organics such as PVC; and avoid materials containing catalytic metals such as copper, iron, chromium and aluminum, even in small amounts. Materials to be burned should be dry, homogeneous or well blended, and of low density, such as non-compacted waste.

With respect to the burning process, aims should include: supply sufficient air; maintain steady burning or rate of mass loss; minimize smouldering, possibly with direct extinguishment; and limit burning to small, actively turned, well-ventilated fires, rather than large poorly ventilated dumps or containers.

B. Thermal processes in the metallurgical industry not mentioned in Annex C, Part II

(i) Secondary lead production

Summary

Secondary lead smelting involves the production of lead and lead alloys, primarily from scrap automobile batteries, and also from other used lead sources (pipe, solder, drosses, lead sheathing). Production processes include scrap pretreatment, smelting and refining. Incomplete combustion; high levels of oils, plastics and other organic materials in feed; and temperatures between 250° and 500° C may all give rise to chemicals listed in Annex C of the Stockholm Convention.

Best available techniques include the use of plastic-free and oil-free feed material, high furnace temperatures above 850° C, effective gas collection, afterburners and rapid quench, activated carbon adsorption, and dedusting fabric filters.

Performance levels associated with best available techniques for secondary lead smelters: < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

(ii) Primary aluminium production

Summary

Primary aluminium is produced directly from the mined ore, bauxite. The bauxite is refined into alumina through the Bayer process. The alumina is reduced into metallic aluminium by electrolysis through the Hall-Héroult process (either using self-baking anodes – Söderberg anodes – or using prebaked anodes).

Primary aluminium production is generally thought not to be a significant source of chemicals listed in Annex C of the Stockholm Convention. However, contamination with PCDD and PCDF is possible through the graphite-based electrodes used in the electrolytic smelting process.

Possible techniques to reduce the production and release of chemicals listed in Annex C from the primary aluminium sector include improved anode production and control, and using advanced smelting processes. The performance level associated with best available techniques for emissions of PCDD/PCDF in the primary aluminium sector is < < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations)..

(iii) Magnesium production

Summary

Magnesium is produced either from raw magnesium chloride with molten salt electrolysis, or magnesium oxide reduction with ferrosilicon or aluminium at high temperatures, as well as through secondary magnesium recovery (for example, from asbestos tailings).

The addition of chlorine or chlorides, the presence of carbon anodes and high process temperatures in magnesium production can lead to the formation of chemicals listed in Annex C of the Stockholm Convention and their emission to air and discharge to water.

Alternative techniques may include the elimination of the carbon source by using non-graphite anodes, and the application of activated carbon. However, performance levels associated with best available techniques depend on the type of process and controls utilized for air and water releases.

(iv) Secondary steel production

Summary

Secondary steel is produced through direct smelting of ferrous scrap using electric arc furnaces. The furnace melts and refines a metallic charge of scrap steel to produce carbon, alloy and stainless steels at non-integrated steel mills. Ferrous feed materials may include scrap, such as shredded vehicles and metal turnings, or direct reduced iron. In addition scrap may be added to other melting furnaces in the foundry and primary iron and steel sectors.

Chemicals listed in Annex C of the Stockholm Convention, such as PCDD and PCDF, appear to be most probably formed in the electric arc furnace steel-making process via de novo synthesis by the combustion of non-chlorinated organic matter such as plastics, coal and particulate carbon in the presence of chlorine donors. Many of these substances are contained in trace concentrations in the steel scrap or are process raw materials such as injected carbon.

Primary measures include adequate off-gas handling and appropriate off-gas conditioning to prevent conditions leading to de novo synthesis formation of PCDD/PCDF. This may include post-combustion afterburners, followed by rapid quench of off-gases. Secondary measures include adsorbent injection (for example, activated carbon) and high-level dedusting with fabric filters.

Performance levels associated with best available techniques for secondary steel production is < 0.1 ng/Nm^3 (at operating oxygen concentrations).

(v) Primary base metals smelting

Summary

Primary base metals smelting involves the extraction and refining of nickel, lead, copper, zinc and cobalt. Generally, primary base metals smelting facilities process ore concentrates. Most primary smelters have the technical capability to supplement primary concentrate feed with secondary materials (e.g. recyclables).

Production techniques may include pyrometallurgical or hydrometallurgical processes. Chemicals listed in Annex C of the Stockholm Convention are thought to originate through high-temperature thermal metallurgical processes; hydrometallurgical processes are therefore not considered in this section on best available techniques for primary base metals smelting.

Available information on emissions of PCDD and PCDF from a variety of source sectors (e.g. incinerators, steel electric arc furnaces, iron sintering plants) suggests that process technologies and techniques, and associated off-gas conditioning, can influence the formation and subsequent release of PCDD/PCDF. Consideration should be given to hydrometallurgical processes, where technically and economically feasible, as alternatives to pyrometallurgical processes when considering proposals for the construction and commissioning of new base metals smelting facilities or processes.

Primary measures include the use of hydrometallurgical processes, quality control of feed materials and scrap to minimize contaminants leading to PCDD/PCDF formation, effective process control to avoid conditions leading to PCDD/PCDF formation, and use of flash smelting technology. Identified secondary measures include high-efficiency gas cleaning and conversion of sulphur dioxide to sulphuric acid, effective fume and gas collection and high-efficiency dust removal.

A performance level associated with best available techniques for base metals smelters is < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations)

C. Residential combustion sources

Summary

This section considers the combustion of wood, coal, gas, as well as other organic matter mainly for residential heating and cooking. Combustion takes place in hand-fired stoves or fireplaces or, in the case of larger central heating systems, in automatically fired installations. Studies have shown that significant levels of chemicals listed in Annex C of the Stockholm Convention are released from residential combustion sources. The amount of chemicals released depends primarily on the fuel used (household waste, sea-salt laden driftwood and treated wood are significant sources of PCDD/F) as well as combustion efficiency. The efficiency of combustion depends upon the combustion temperature, how well the gases are mixed, residence time, sufficient oxygen and the fuel properties. Given their large numbers, residential combustion appliances contribute noticeably to overall releases of chemicals listed in Annex C.

The use of efficient combustion of clean, untreated fuels for cooking and heating is of primary importance for reducing the formation and release of chemicals listed in Annex C. Strategies to minimize releases of chemicals listed in Annex C from residential combustion sources include public education, awareness and training programmes on the proper use of the appliances, use of appropriate fuels and the health impacts from uncontrolled residential combustion. The abatement technologies commonly used in industrial settings are not generally available for smaller residential heating and cooking appliances. However, the use of well-designed stoves with good operation can be effective in reducing chemicals listed in Annex C, with the important added benefit of improving indoor air quality.

Best available techniques include enclosed low emission burners with ducted flues and the use of dry, well-seasoned wood. For countries or regions where these fuels and appliances are not available, best available techniques and best environmental practices for residential combustion include ensuring separation of household waste from fuel to avoid burning of such waste in cooking and heating appliances. In all countries the use of treated wood or sea-salt laden driftwood and the use of plastics as a firelighter or fuel should be avoided.

Cooking and heating with wood is a common and significant practice in all countries of the world. Any action for reducing the emissions of chemicals listed in Annex C from residential combustion will also have to take into consideration local social, cultural and economic factors. Case studies from Australia and New Zealand are provided to highlight this.

D Fossil fuel-fired utility and industrial boilers

Summary

Utility and industrial boilers are facilities designed to burn fuel to heat water or to produce steam for use in electricity generation or in industrial processes. The volumetric concentrations of chemicals listed in Annex C of the Stockholm Convention in the emissions from fossil fuel-fired boilers are generally very low. However, the total mass emissions from the boiler sector may be significant because of the scale of fossil fuel combustion, in terms of both tonnage and distribution, for electricity generation and heat or steam production.

Measures that can be taken to decrease the formation and release of chemicals listed in Annex C include: maintenance of efficient combustion conditions within the boiler and ensuring sufficient time is available to allow complete combustion to occur; undertaking measures to ensure fuel is not contaminated with PCB, HCB or chlorine, and is low in other components known to act as catalysts in the formation of PCDD and PCDF; use of appropriate gas-cleaning methods to lower emissions that may contain entrained pollutants; and appropriate strategies for disposal, storage or ongoing use of collected ash.

Emission levels associated with best available techniques can be significantly lower than 0.1ng I-TEQ/Nm^3 (oxygen content: 6% for solid fuels; 3% for liquid fuels).

E Firing installations for wood and other biomass fuels

Summary

The main purpose of firing installations for wood and other biomass fuels is energy conversion. Large-scale installations for firing wood and other biomass fuels mainly use fluidized bed combustion and grate furnaces. Technologies for small-scale plants include underfeed furnaces and cyclone suspension furnaces. Recovery boilers in the pulp and paper industry apply specific combustion conditions. Technology selection is related to fuel properties and required thermal capacity.

Chemicals listed in Annex C of the Stockholm Convention can result from the firing of wood and other biomass fuels, particularly in the case of fuel contamination. For biomass-fired plants, particularly wood-fired installations, emission levels associated with best available techniques are generally below 0.1 ng I-TEQ/Nm^3. Among the primary measures, control of fuel quality is a key issue (including exclusion of treated wood). Control measures for non-contaminated biomass include optimized combustion techniques and dust removal. Straw combustion increases fouling of surfaces and requires combustion techniques that are not sensitive to the slagging of ashes.

Combustion of contaminated biomass, such as wood waste, should be avoided in these installations. Fly ash (especially the finest fraction) from biomass combustion has to be landfilled due to its high heavy metal content. In many countries (including in the European Union), wood treated with chlorinated compounds or heavy metals is regarded as waste and falls within the scope of waste incineration directives or regulations.

Other environmental benefits that accrue from applying best available techniques and best environmental practices include resource conservation and avoidance of carbon dioxide emissions originating from fossil fuels (in the case of substitution).

F Specific chemical production processes releasing chemicals listed in Annex C

Summary

This section focuses on processes for the manufacture of industrial chemicals that could theoretically give rise to persistent organic pollutants (particularly those chemicals listed in Annex C of the Stockholm Convention). Most of the processes described share common steps, including chlorination of organic or inorganic raw materials, purification of the products, separation of product streams (usually by distillation), destruction of high-molecular-weight side products and recycle or sale of hydrogen chloride. Efficient separation and destruction of chlorinated organic side products, which may include persistent organic pollutants, is key to best available techniques applicable to these processes, as is the associated guidance for any incorporated incineration processes. For certain products, modernized manufacturing processes that reduce formation of persistent organic pollutants are also presented. A range of performance standards associated with best available techniques are provided relevant to the individual processes

G Crematoria

Summary

From early history to the present day cremation has been a religiously and culturally important and accepted practice used by many cultures and countries as a way of dealing with the death of human beings. In many cases, cremation is integral to the religious and funeral practices of a particular country or culture; in others, it is a voluntary alternative to burial. These guidelines are not an attempt to redefine these practices or to demean their significance for the people involved. For those countries where cremation is practised and in keeping with the provisions of the Stockholm Convention, these guidelines seek to provide approaches that minimize or eliminate the formation and release of chemicals listed in Annex C of the Convention during the process of cremation.

The formation and release of PCDD and PCDF, HCB and PCB from crematoria is possible due to the presence of these chlorinated materials, precursors and chlorine in the cadavers and in some co-combusted plastics. Measures to minimize formation and release of chemicals listed in Annex C would include the avoidance of chlorinated material, the design of crematoria to deliver a minimum furnace temperature of 850° C, a 2-second residence time for the combustion gases and sufficient air to ensure combustion. Larger new crematoria should also be fitted with air pollution control equipment to minimize emission of sulphur dioxide, hydrogen chloride, carbon monoxide, volatile organic compounds, particulate matter and persistent organic pollutants. A performance level of < 0.1 ng I-TEQ/Nm^3 for PCDD/PCDF is associated with best available techniques.

H Motor vehicles, particularly those burning leaded gasoline

Summary

The major fuels used in motor vehicle transportation are gasoline and diesel. Liquefied petroleum gas, vegetable oil-based and other biofuels, and alcohol-oil mixtures are gaining importance.

PCDD and PCDF have been found in the emissions from motor vehicles fuelled with gasoline or diesel. The higher concentrations identified in emissions from vehicles run on leaded gasoline are due to the presence of chlorinated and brominated scavengers in the fuel.

As alternatives to leaded gasoline, the following fuels may be considered: unleaded gasoline (best when equipped with catalyst); diesel (best when equipped with diesel oxidation catalyst and particulate filter); liquefied petroleum gas; compressed natural gas; propane/butane gas; biofuels; and alcohol-oil mixtures.

Best available techniques include banning of halogenated scavengers, and fitting motor vehicles with an oxidation catalyst or particulate filter.

There are no measured data available for biofuels, alcohol-oil mixtures or liquefied petroleum gas, and no data for 2-stroke engines.

I Destruction of animal carcasses

Summary

The formation and emission of PCDD, PCDF, PCB and HCB from animal carcass incinerators is due to the presence of these chlorinated materials, precursors and chlorine in the carcasses or in some plastics that can be co-incinerated with animal carcasses and by-products. Measures that can be taken to decrease the formation and release of persistent organic pollutants include the avoidance of co-incineration with other wastes, the requirement for a minimum furnace temperature of 850° C, a 2-second residence time for the combustion gases and sufficient excess air to ensure combustion. Larger facilities (> 50 kg/h) should be fitted with air pollution control equipment to minimize emissions of sulphur dioxide, hydrogen chloride, carbon monoxide, volatile organic compounds, particulate matter and persistent organic pollutants. A performance level associated with best available techniques of < 0.1 ng I-TEQ/Nm^3 can be achieved for PCDD/PCDF.

Other methods of disposal, such as burial, landfill or composting, are not considered to contribute significantly to emissions of chemicals listed in Annex C, although environmental, public health, nuisance and animal health issues should be considered. Alkaline hydrolysis digestion is a further technique for the destruction of animal carcasses.

J Textile and leather dyeing and finishing

Summary

Contamination with PCDD and PCDF has been found in both textile and leather products. The occurrence of PCDD/PCDF in the textile and leather industries is due to use of chlorinated chemicals, especially pentachlorophenol and chloronitrofen, to protect the raw material (e.g. cotton, wool or other fibres, leather); and use of dioxin-contaminated dyestuffs (e.g. dioxazines or phthalocyanines). Smaller quantities of PCDD/PCDF may be formed during finishing, and during incineration of process-generated sludge.

Alternatives to the above-listed dye pigments exist and those listed should not be applied.

Possible alternatives to pentachlorophenol and chloronitrofen include 2-(thiocyanomethylthio) benzothiazole (TCMTB); *o*-phenylphenol (oPP); 4-chloro-3-methylphenol (CMK); and 2-*n*-octyl-4-isothiazolin-3-one (OIT).

As regards best available techniques, the most efficient primary measure to prevent contamination of textiles and leather goods with PCDD/PCDF would be not to use dioxin-contaminated biocides and dyestuffs in the production chains. Also, if any of the above-mentioned chemicals are being used, preference should be given to batches containing low concentration (e.g. distilled or otherwise purified chemicals). To the extent possible, burning of textile, upholstery, leather products and carpet should be avoided to prevent PCDD/PCDF formation.

In order to prevent or minimize formation and release of PCDD/PCDF when burning sludge from wastewater treatment and flotation, best available techniques should be applied as described in section VI.D of the present guidelines (industrial boilers). However, other environmentally sound techniques should also be explored.

K Shredder plants for the treatment of end-of-life vehicles

Summary

Shredder plants for treatment of end-of-life vehicles are lbisted in Annex C of the Stockholm Convention as a source that has the potential to form and release chemicals listed in Annex C. Shredders are large-scale machines equipped inside with one or more anvils or breaker bars and lined with alloy steel wear plates. An electric motor drives the rotor with the free-swinging alloy steel hammers. Beneath the shredder is a vibratory pan, which receives the shredded material discharged through the grates. Typically a ferrous metal stream is produced, which is relatively clean and consists of small (50 mm) pieces of steel and a “fluff” stream, which contains the fragments of non-ferrous metals and other materials that entered the shredder (also known as fragmentizer).

Very few data of stack emission measurements at shredder plants are available. However, the results of some studies have shown levels of dioxin compounds greater than 0.1 ng I-TEQ/m^3. At present there is not sufficient evidence that in the (mechanical) shredding of vehicles, household electrical equipment or other electrical appliances new formation occurs of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) or polychlorinated biphenyls (PCB). The data available indicate that the PCDD/PCDF and PCB released from shredder plants are from industrial, intentional production and have been introduced with oils, dielectric fluids, and other materials contained in these vehicles or consumer goods and which are simply set free through this mechanical process.

In any case, measures to prevent accidental fires (which could result in the formation of chemicals listed in Annex C) should be in place at shredder plants. Shredder light fluff consists of flammable plastic films and fibrous dust, which forces a careful plant operation for the prevention of accidental fire. Systems for dust suppression (e.g. wet shredding) or dust collection (e.g. cyclones, venture scrubbers or baghouse) are normally installed on shredder plants for the treatment of end-of-life vehicles. Dust suppression or collection systems would help to reduce potential emission of persistent organic pollutants. To improve emission control of the dust, fine dry residues should be stored in such a way that dispersion is minimized. Other sources of dioxin precursors that may result in the formation of PCDD/PCDF when burnt include PCB-containing condensers, PCB- or chlorobenzene-contaminated waste oils or textiles, and polymers containing brominated flame retardants (formation of polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans (PBDF) as contaminants).

L. Smouldering of copper cables

Summary

Scrap copper is often recovered by open burning of plastic coatings from electrical cable and wiring. Chemicals listed in Annex C of the Stockholm Convention are probably formed from plastic and trace oils with copper as a catalyst at smouldering temperatures between 250° and 500° C.

Best available techniques include mechanical cable chopping, stripping or high-temperature incineration > 850° C. A consideration is to set premium pricing for unstripped cables and wiring and encourage sending the feed material to copper smelters using best available techniques for treatment.

Performance levels associated with best available techniques are not applicable, as the smouldering process is not a best available technique or best environmental practice and should not be practisedcopper cables.

.M. Waste oil refineries

Summary

Waste oil refineries are listed in Annex C of the Stockholm Convention as a source that has the potential to form and release chemicals listed in Annex C.

For the purpose of this guidance section, waste oils (or used oils) are defined as any petroleum-based, synthetic, or plant- or animal-based oil that has been used. Waste oils may originate from two large sources: industrial waste oils, and vegetable and animal waste oils. Among the industrial waste oils, three main oil streams can be identified: industrial oil (e.g. hydraulic oil, engine lubricant, cutting oil); garage or workshop oil; and transformer oil.

Waste oils have been found to be contaminated with polychlorinated dibenzo-p-dioxins,, polychlorinated dibenzofurans and polychlorinated biphenyls.. At present there is no available evidence that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans or polychlorinated biphenyls, are newly formed in waste oil refineries. The data available indicate that the polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans or polychlorinated biphenyls released from waste oil refineries or waste oil handling and management plants are from industrial, intentional production of polychlorinated biphenyls or chlorobenzenes that are present in the waste oils either by contamination in the synthesis process (of these chemicals) or have become contaminated during the use phase or earlier recycling processes. In this sense, waste oil refineries represent a distribution source of chemicals listed in Annex C rather than a formation source.

According to available information, waste oil management options include reuse or regeneration; thermal cracking; and incineration or use as fuel. It should be noted that dumping and open burning are also practised in many countries.

For information on waste oil disposal in incinerators or on use as fuel, the relevant sections of this guidance document should be consulted (sections V.A, waste incinerators; V.B, cement kilns firing hazardous waste; VI.A, open burning of waste; VI.C, residential combustion sources; and VI.D, fossil fuel-fired utility and industrial boilers).

Section V

Guidance/guidelines by source category: Source categories in Part II of Annex C

Part II Source category (a): Waste incinerators

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V.A Waste incinerators

(i) Municipal solid waste, hazardous waste and sewage sludge

Summary

Waste incinerators are identified in the Stockholm Convention as having the potential for comparatively high formation and release of chemicals listed in Annex C to the environment.

The potential purposes of waste incineration include volume reduction, energy recovery, destruction or at least minimization of hazardous constituents, disinfection and the recovery of some residues.

When considering proposals to construct new waste incinerators, priority consideration should be given to alternatives such as activities to minimize the generation of waste, including resource recovery, reuse, recycling, waste separation and promoting products that generate less waste. Priority consideration should also be given to approaches that prevent the formation and release of persistent organic pollutants.

The environmentally sound design and operation of waste incinerators requires the use of both best available techniques and best environmental practices (which are to some extent overlapping) to prevent or minimize the formation and release of chemicals listed in Annex C.

Best environmental practices for waste incineration include appropriate off site procedures (such as overall waste management and consideration of environmental impacts of siting) and on site procedures (such as waste inspection, proper waste handling, incinerator operation and management practices and handling of residues).

Best available techniques for waste incineration include appropriate selection of site; waste input and control; techniques for combustion, flue gas, solid residue and effluent treatment.

To achieve best results for environmental protection as a whole it is essential to coordinate the waste incineration process with upstream activities (e.g. waste management techniques) and downstream activities (e.g. disposal of solid residues from waste incineration).

Releases of chemicals listed in Annex C from municipal solid waste incinerators designed and operated according to best available techniques and best environmental practices occur mainly via fly ash, bottom ash and filter cake from wastewater treatment. Therefore it is of major importance to provide for a safe sink of these waste types, for example by pretreatment and final disposal in dedicated landfills, which are designed and operated according to best available techniques.

With a suitable combination of primary and secondary measures, PCDD/PCDF performance levels in air emissions no higher than 0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluents, are associated with PCDD/PCDF concentration levels well below 0.1 ng I-TEQ/l.

1. Introduction

Waste incinerators are identified in the Stockholm Convention as having the potential for comparatively high formation and release to the environment of chemicals listed in Annex C of the Convention. Also, co-incineration of waste can be a source of releases of chemicals listed in Annex C.

This section deals only with the dedicated incineration of wastes and not with other situations where waste is thermally treated, for example co-incineration processes such as cement kilns and large combustion plants, which are dealt with in the sections relating to those processes.

When considering proposals to construct new waste disposal facilities, the Stockholm Convention advises Parties to give priority consideration to:

- Alternatives such as activities to minimize the generation of municipal waste, including resource recovery, reuse, recycling, waste separation and promoting products that generate less waste, when considering proposals to construct new waste disposal facilities (Stockholm Convention, Annex C, Part V, section A, subparagraph (f)), and to;
- Approaches that will prevent the formation and release of chemicals listed in Annex C.

Waste management considerations, which are described in section III.C (ii) of the present guidelines, and the alternative approaches outlined in subsection 6 below, can be taken into account as part of overall waste prevention and control strategies.

2. Process description

Incineration is used as a treatment for a very wide range of wastes. Incineration itself is commonly only one part of a complex waste treatment system that altogether provides for the overall management of the broad range of wastes that arise in society (for consideration of cross-cutting issues related to waste incineration and management see section III.C of the present guidelines).

The objective of waste incineration is to treat wastes so as to reduce their volume and hazard, whilst capturing (and thus concentrating) or destroying potentially harmful substances that are, or may be, released during incineration. Incineration processes can also provide a means to enable recovery of the energy, mineral or chemical content from waste.

Incinerators come in a variety of furnace types and sizes as well as combinations of pre- and post-combustion treatment. There is also considerable overlap among the designs of choice for municipal solid waste, hazardous waste and sewage sludge incineration.

Incinerators are usually designed for full oxidative combustion over a general temperature range of 850º–1,400º C. This may include temperatures at which calcinations and melting may also occur. Gasification and pyrolysis represent alternative thermal treatments that restrict the amount of primary combustion air to convert waste into process gas, which may be used as a chemical feedstock or incinerated with energy recovery. However, compared to incineration, application of these systems is low and operational difficulties are reported at some installations.

Waste incinerator installations can be characterized by the following: waste delivery, storage, pretreatment, incineration/energy recovery, flue gas cleaning, solid residue management, and wastewater treatment. The nature of the input waste will have a significant bearing on how each component is designed and operated.

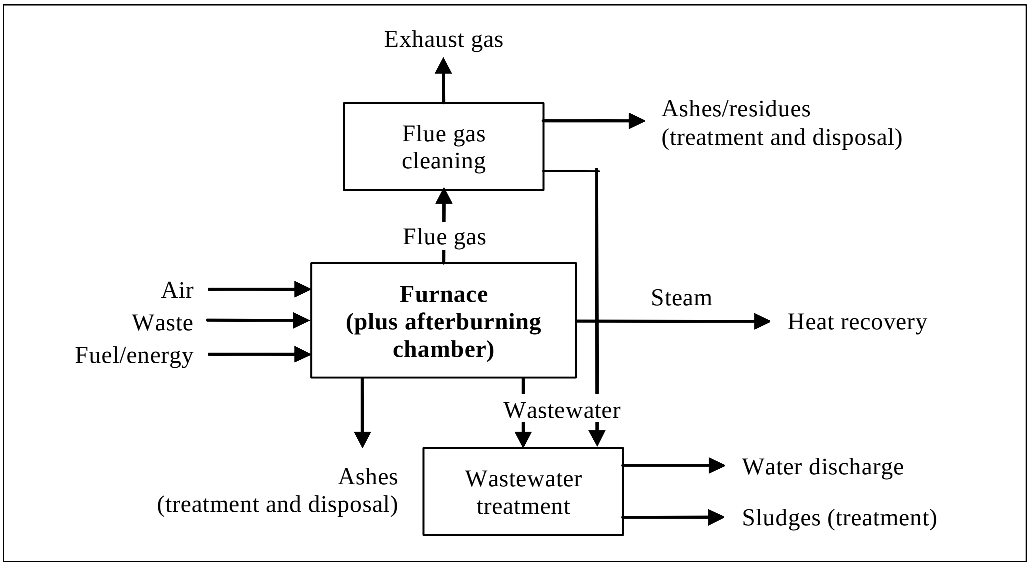
Waste is generally a highly heterogeneous material, consisting essentially of organic substances, minerals, metals and water. During incineration, flue gases are created that will contain the majority of the available fuel energy as heat.

In fully oxidative incineration the main constituents of the flue gas are water vapour, nitrogen, carbon dioxide and oxygen. Depending on the composition of the material incinerated , operating conditions and the flue gas cleaning system installed, acid gases (sulphur oxides, nitrogen oxides, hydrogen chloride), particulate matter (including particle-bound metals), and a wide range of volatile organic compounds, as well as volatile metals (such as mercury) are emitted. Incineration of municipal solid waste and hazardous waste have also been shown to lead to the unintentional formation and release of the persistent organic pollutants (PCDD/PCDF, PCB, HCB). In addition it has the potential to release polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans (PBDF). Formation is normally substantially increased in units that are poorly designed or operated.

Depending on the combustion temperatures during the main stages of incineration, volatile metals and inorganic compounds (e.g. salts) are totally or partly evaporated. These substances are transferred from the input waste to both the flue gas and the fly ash it contains. A mineral residue fly ash (dust) and heavier solid ash (bottom ash) are created. The proportions of solid residue vary greatly according to the waste type and detailed process design.

Other releases are residues from flue gas treatment and polishing, filter cake from wastewater treatment, salts and releases of substances into wastewater.

Figure 1: Presents a simplified flow scheme of an incinerator



2.1 Municipal solid waste incineration

Although in many areas landfilling of the non-recycled waste remains the principal means for the disposal of municipal solid waste, incineration and the subsequent landfilling of residues has become a common practice in many developed and industrializing countries. (For considerations of the waste hierarchy and recycling of waste see section III.C (ii)).

The European Council Directive on the landfill of waste (1999/31/EC) requires Member States to set up a national strategy for the implementation of the reduction of biodegradable waste going to landfills. This strategy should include measures to achieve the targets by means of, in particular, recycling, composting, biogas production and material or energy recovery.

Municipal solid waste incineration is commonly accompanied by the recovery of some energy (“waste to energy”) in the form of steam and/or the generation of electricity. Incinerators can also be designed to accommodate processed forms of municipal solid waste derived fuels, as well as co-firing with fossil fuels. Municipal waste incinerators can range in size from small package units processing single batches of only a few tons per day to very large units with continuous daily feed capacities in excess of a thousand tons. The capital investment costs of such facilities capable of meeting standards that may be considered best available techniques is normally in the range of millions to hundreds of millions of US$.

The primary benefits of municipal solid waste incineration are the destruction of organic (including toxic) materials, the reduction in the volume of the waste and the concentration of pollutants (e.g.

heavy metals) into comparatively small quantities of ashes, thus generating safe sinks if properly disposed of. The recovered energy can be an important additional benefit.

Large municipal waste incinerators are major industrial facilities and have the potential to be significant sources of environmental pollution (See Section 2).

2.1.1 Operational considerations for municipal solid waste incinerators

In many municipal solid waste incinerators other waste fractions such as bulky waste, (e.g. from sorting plants), sewage sludge or the high calorific fraction from waste pretreatment (e.g. from shredder plants) are also incinerated. These wastes have to be carefully evaluated prior to incineration to ascertain whether the waste incineration plant (including flue gas treatment, wastewater and residue treatment) is designed to handle these types of waste and whether it can do so without risk of harm to human health or the environment. Some important parameters are chlorine and bromine content, aluminium content, heavy metal content, calorific content and burnout behaviour. High concentration of bromine may lead to formation of brominated compounds such as polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans PBDF. Neglecting the limits of the incineration plant will result in operational problems (e.g. the necessity of repeated shutdowns due to cleaning of the grate or heat exchangers) or in a bad environmental performance (e.g. high emissions into water, high leachability of fly ash).

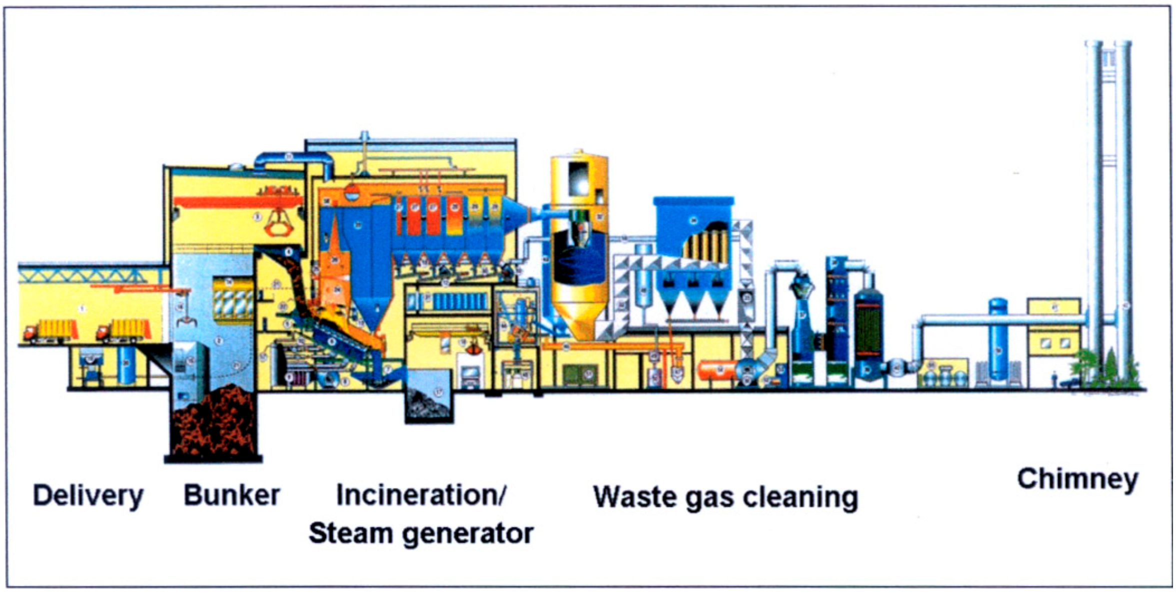
Figure 2 shows the typical layout of a large municipal solid waste incinerator.

2.1.2 Delivery, storage and pretreatment of municipal solid waste

Waste may be delivered to the incinerator by truck, by barge or rail. Recycling or source separation programmes upstream of waste delivery can significantly influence the efficiency of processing. Removing glass and metals prior to incineration will increase the per unit energy value of the waste. However, in some plants metals are separated from bottom ash after incineration. Recycling paper, cardboard and plastics will reduce the energy value of the waste but may also reduce available chlorine. Separating bulky wastes reduces the need for removal or shredding on site.

In addition to waste separation, pretreatment of mass burn municipal solid waste may include crushing and shredding to facilitate handling and homogeneity. Bunker storage areas are normally covered to protect against additional moisture and the facility is typically designed to draw combustion air through the bunker to reduce odour.

Figure 2. Typical municipal solid waste incinerator



Source: European Commission 2006.

2.1.3 Municipal solid waste incinerator designs

Municipal solid waste can be incinerated in several combustion systems including travelling grate, rotary kilns, and fluidized beds. In the United States and in Asia modular incinerators, which burn waste without preprocessing, are also in use. Fluidized bed technology requires municipal solid waste to be of a certain particle size range – this usually requires some degree of pretreatment and the selective collection of the waste. Combustion capacities of municipal solid waste incinerators typically range from 90 to 2,700 tons of municipal solid waste per day (modular configurations: 4 to 270 tons per day).

Other processes have been developed that are based on the decoupling of the phases that also take place in an incinerator: drying, volatilization, pyrolysis, carbonization and oxidation of the waste. Gasification using gasifying agents such as steam, air, oxides of carbon or oxygen is also applied. These processes aim to reduce flue gas volumes and associated flue gas treatment costs. Many of these developments have met technical and economic problems when scaled up to commercial, industrial sizes, and are therefore pursued no longer. Some are used on a commercial basis (e.g. in Japan) and others are being tested in demonstration plants throughout Europe, but still have only a small share of the overall treatment capacity when compared to incineration.

2.2 Hazardous waste incineration

Incineration and other forms of thermal treatment also represent options for the treatment of hazardous waste. Hazardous wastes are distinguished from other wastes by their listing in waste statutes and regulations or by exhibiting hazardous properties. In the United States, for example, a waste may be considered hazardous if it is shown to be ignitable, corrosive, reactive or toxic. Mixtures of hazardous wastes with other wastes may also be considered hazardous.

Because of the higher potential hazard of dealing with such wastes and the uncertainty often associated with their composition, special procedures for transportation, handling, storage, monitoring and control are required. Special handling may also be necessary for any residues remaining after treatment.

The most common combustion technology in hazardous waste incineration is the rotary kiln. Facilities in the merchant sector range in size from 82 to 270 tons per day waste throughput (European Commission 2006). Certain hazardous wastes, particularly spent solvents, are also burnt as fuel in cement kilns. This latter application is covered under section V.B. of the present guidelines.

Similar to the incineration of municipal solid waste, hazardous waste incineration offers the benefits of destruction of organic (including toxic) materials, of volume reduction and concentration of pollutants into relatively small quantities of ashes, and , less frequently, energy recovery.

Hazardous waste incinerators have the potential to be significant sources of environmental pollution (see section 2).

Hazardous waste is normally incinerated in two types of facilities:

- Merchant plants, which provide commercial, off-site, waste treatment services. These incinerators handle a variety of waste streams and can compete internationally for business;[1]
- Dedicated or captive hazardous waste incinerators, which are typically located at large industrial facilities and process waste streams generated at the site, for example an incinerator at a chemical manufacturing plant treating chlorinated wastes to recover hydrogen chloride (HCl).

Solid residues from hazardous waste incinerators are similar to those of municipal solid waste incinerators with the exception of slag resulting from rotary kiln incineration.

2.2.1 Design and operation of hazardous waste incinerators

For the incineration of hazardous waste rotary kilns are most commonly used (Figure 3), but grate incinerators (including co-firing with other wastes) are also sometimes applied to solid wastes, and fluidized bed incinerators to some pretreated materials. Static furnaces are also widely applied at on-site facilities at chemical plants.

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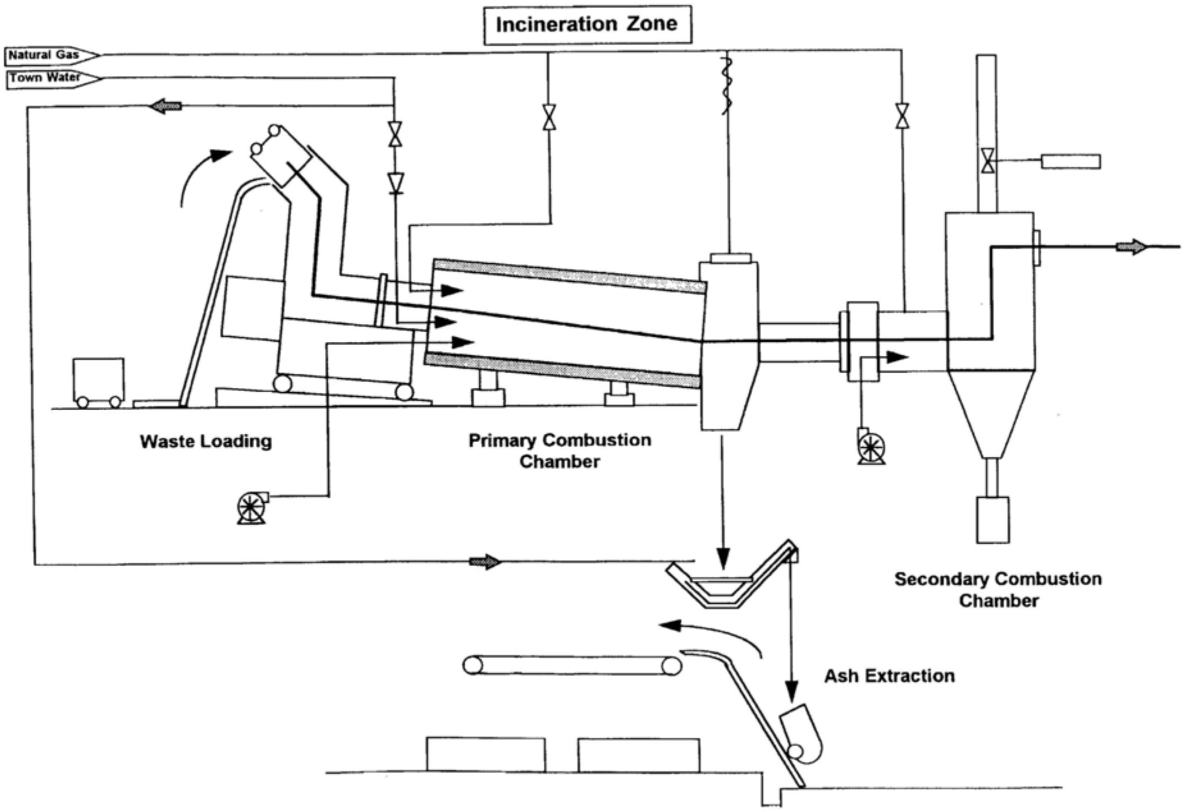
[1] Note the requirements of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal regarding the shipment of hazardous wastes.

Figure3. Schematic of a rotary kiln incineration system



Due to the hazardous (and often uncertain) composition of the incoming waste streams, there is a greater emphasis on acceptance criteria, storage, handling and pretreatment than with municipal solid waste. For low-energy-value wastes, auxiliary fuels may be required.

In a rotary kiln solid, sludge, containerized or pumpable waste is introduced at the upper end of the inclined drum. Temperatures in the kiln usually range between 850º C (500º C when used as a gasifier) and 1,450º C (as a high-temperature ash melting kiln). The slow rotation of the drum allows a residence time of 30 to 90 minutes. Temperatures in the range of 850º–1,000º C can be considered adequate for destruction of non-halogenated hazardous waste, while 1,100º–1,200º C is considered adequate for breaking down halogenated hazardous compounds, i.e. PCDD/PCDF, PCB and HCB.

The secondary combustion chamber following the kiln allows the oxidation of the combustion gases. Liquid wastes or auxiliary fuels may be injected here along with secondary air to maintain a minimum residence time of 2 seconds and temperatures in the range of 850º–1,100º C, effectively breaking down most remaining organic compounds (requirements for combustion conditions are prescribed e.g. in the EU-Directive 2000/76/EC on the Incineration of Waste).

Hazardous waste is also incinerated in cement kilns. This application is addressed in section V.B of the present guidelines.

2.2.2 Delivery, storage and pretreatment of hazardous waste

Before accepting a hazardous waste for treatment, merchant incinerators must assess and characterize the material. Documentation by the producer is routinely required, including the origin of the waste, its code or other designation, the identification of responsible persons and the presence of particular hazardous materials. The waste must also be properly packaged to avoid the possibility of reaction and emissions during transport.

Storage at the incinerator site will depend on the nature and physical properties of the waste. Solid hazardous waste is typically stored in bunkers constructed to prevent leakage into any environmental media and enclosed to allow the removal of bunker air to the combustion process. Liquid wastes are stored in tank farms, often under inert gas atmosphere (for example N_2), and transported to the incinerator by pipeline. Some wastes may be fed directly to the incinerator in their transport containers. Pumps, pipelines and other equipment that may come into contact with the wastes must be corrosion proof and accessible for cleaning and sampling.

Pretreatment operations may include neutralization, drainage or solidification of the waste. Shredders and mechanical mixers may also be used to process containers or to blend wastes for more efficient combustion.

2.3 Sewage sludge incineration

Domestic sewage sludge is disposed of in a number of ways, including application on agricultural land after pre-treatment, surface disposal (e.g. landscaping), incineration, co-disposal with municipal solid waste and co-incineration. The incineration of sewage sludge is practised in several countries, either alone or through co-incineration in municipal solid waste incinerators or in other combustion plants (e.g. coal-fired power plants, cement kilns). The effective disposal of sewage sludge by this process depends on a number of factors. These include whether the sewage is mixed with industrial waste streams (which can increase heavy metal loadings), location (coastal locations can result in salt water intrusion), pretreatment (or the lack thereof), and weather (rainfall dilution) (European Commission 2006).

The incineration of sewage sludge presents some differences from the incineration of municipal solid waste and hazardous waste. The variability of moisture content, energy value, and possible mixture with other wastes (e.g. industrial waste if sewage systems are interconnected) require special considerations in handling and pretreatment.

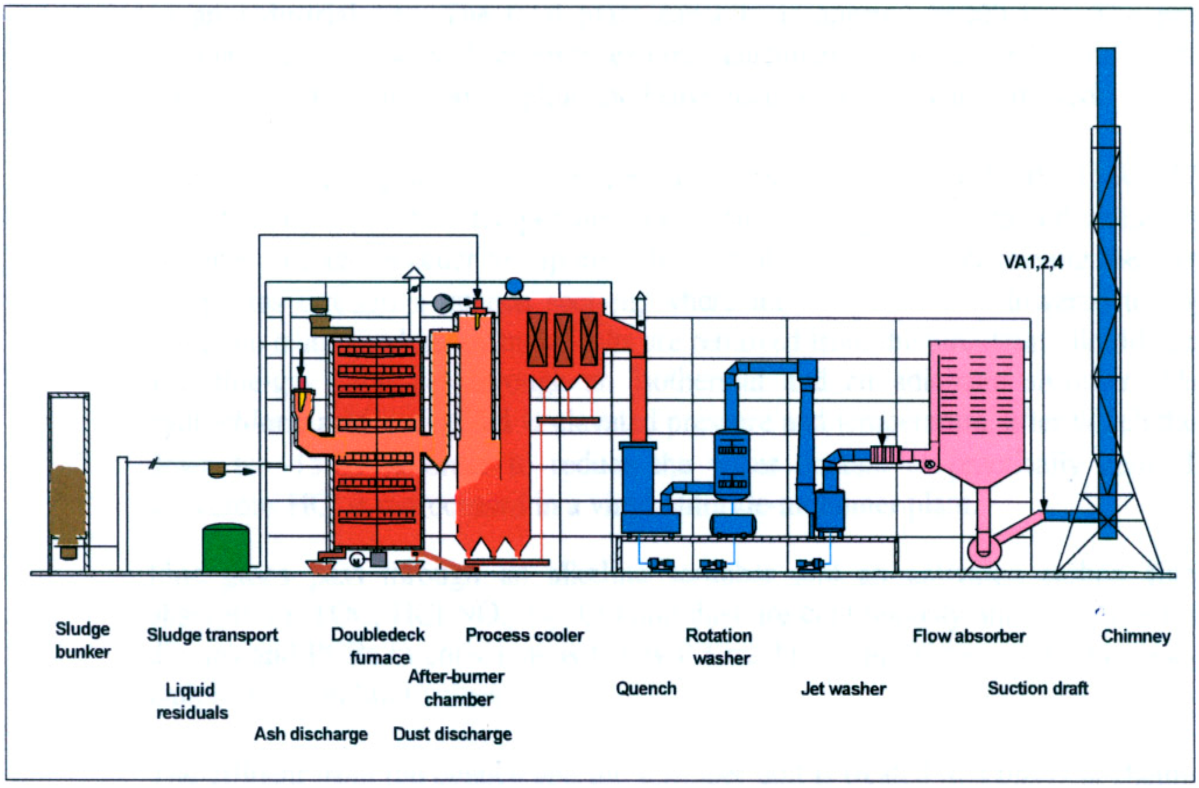
Pretreatment, especially dewatering and drying, is particularly important in preparing sludge for incineration. Drying reduces the volume of the sludge and increases the heat energy of the product. Moisture removal to at least 35% dry solids is normally required to provide the necessary heat energy for autothermal incineration. Further drying may be necessary if co-incineration with municipal solid waste is envisioned.

As with municipal solid waste and hazardous waste incinerators, pollutants and chemicals listed in Annex C and their precursor compounds are available in the inputs to sewage sludge incinerators and have resulted in the formation and release of these substances into air, water and residues/waste (See Section 2). Solid residues from sewage sludge incineration are mainly fly ash and bed ash (from fluidized bed incineration) and residues from flue gas treatment (see description of municipal solid waste incineration).

2.3.1 Design and operation of sewage sludge incinerators

A typical sewage sludge incinerator may process as much as 80,000 tons of sewage sludge (35% dry solids) per year. The incineration technologies of choice for sewage sludge are the multiple hearth (Figure 3) and fluidized bed furnace systems, although rotary kilns are also used in smaller applications.

Figure 4. Example of a multiple hearth sewage sludge incinerator



Source: European Commission 2006.

Depending on the percentage of dry solids (dryness), an auxiliary fuel, usually heating oil or natural gas, is provided. The preferred operating temperatures are in the range of 850º–950º C with a 2-second residence time, although some fluidized bed facilities are able to operate at a temperature as low as 820º C without deterioration in performance. Operation at or above 980º C can cause ash to fuse (European Commission 2006).

Sewage sludge is co-incinerated with municipal solid waste in both fluidized bed and mass burn (grated) incinerators. In the latter case, a ratio of 1:3 (sludge to waste) is typical, with dried sludge introduced into the incineration chamber as a dust or drained sludge applied to the grate through sprinklers. In some cases, drained or dried sludge may be mixed with municipal solid waste in the bunker or hopper before being charged to the incinerator. The feeding methods represent a significant proportion of the additional capital investment required for co-incineration.

2.3.2 Pretreatment of sewage sludge

Some pretreatment of sludge may occur before delivery to an incineration facility. This may include screening, anaerobic and aerobic digestion, and the addition of treatment chemicals.

Physical dewatering reduces sludge volume and increases heating value. Mechanical dewatering processes include decanters, centrifuges, belt filter and chamber filter presses. Conditioners (for example, flocking agents) are often added before dewatering to facilitate drainage. Mechanical dewatering can routinely achieve 20–35% dry solids (European Commission 2006).

Drying introduces heat to further dewater and condition the sludge. Heat for drying at the incineration facility is often provided by the incineration process itself. Drying processes can be direct (sludge contacts thermal carrier) or indirect (for example, heat supplied by steam plant). In direct drying the vapour and gas mixture must be subsequently cleaned.

Autothermal (self-sustaining) incineration of sludge requires 35% dry solids. Although mechanical dewatering can reach this threshold, additional drying of sludge to as much as 80–95% dry solids may be employed to increase the heat value. Co-incineration with municipal solid waste generally requires additional sludge drying.

3. Sources of formation of chemicals listed in Annex C

For formation mechanisms of chemicals listed in Annex C of the Stockholm Convention refer to section III.C (i) of the present guidelines.

Chemicals listed in Annex C are released into the air, into water (when wet flue gas cleaning systems are installed or when residues are washed by liquids to remove some toxic substances) and by solid residues.

Solid residues from municipal solid waste incineration are mainly bottom ash, boiler ash and fly ash. Solid residues from hazardous waste incinerators are similar to those of municipal solid waste incinerators with the exception of slag resulting from rotary kiln incineration. Solid residues from sewage sludge incineration are mainly fly ash and bed ash (from fluidized bed incineration) and residues from flue gas treatment (see description of municipal solid waste incineration).

In addition residues arise from flue gas treatment that show different characteristics depending on the systems (dry, semi-wet, wet) installed. When wet systems are applied filter cake from wastewater treatment and gypsum will also accumulate. Furthermore residues from air polishing have to be considered.

Options for treatment of the air polishing residues depend on the adsorbent used (activated carbon, coke, lime, sodium bicarbonate, zeolite). The residue of (activated) carbon from fixed bed reactors is sometimes permitted to be incinerated in the waste incineration plant itself, if certain process conditions are fulfilled. The residue of entrained bed systems can also be incinerated, if the applied adsorbent is activated carbon or oven cokes only. If a mixture of other reagents and activated carbon is used, the residue is generally sent for external treatment or disposal, since there might be risks of corrosion.

In many countries waste fractions generated by waste incineration plants are classified as hazardous waste, with the exception of gypsum from flue gas desulphurization and ferrous and non-ferrous metal scrap. As an example Austrian law requires that if the limit for PCDD/PCDF (100 ng I-TEQ/kg) in the wastes is exceeded, then the wastes must be disposed of in an environmentally sound manner. This means in most cases landfilling in specially engineered landfills (following pretreatment) or underground storage. Furthermore, according to Austrian law, formation and dispersion of dust from these wastes must be prevented during transport and intermediate storage (Austrian Waste Incineration Ordinance, Fed. Law Gazette Nr. II 389/2002).

Table 1 illustrates the relative solid residue masses for a typical municipal solid waste incinerator.

Table 1. Waste and solid residues from municipal solid waste incineration

Types of waste	Specific mass, dry (kg/t of waste)
Slag/ash (including grate siftings/riddlings)	200–350
Dust from boiler and dedusting	20–40
Residues from flue gas cleaning without filter dust:	
Wet sorption[a]	8–15
Semi-wet sorption	15–35
Dry sorption	7–45
Residues from flue gas cleaning and filter dust:	
Wet sorption[a]	30–50
Semi-wet sorption	40–65
Dry sorption	32–80
Loaded activated carbon	0.5–1

a. Wet sorption residues have a specific dryness (e.g. 40–50% dry solids) (74, TWG Comments, 2004).

Source: Umweltbundesamt Deutschland 2001

Typical concentrations of organic compounds in ashes from modern waste incineration plants are given in Table 2.

Table 2. Concentration ranges of organic compounds in ashes from modern facilities

Parameter	Bottom ash (ng/kg)	Boiler ash (ng/kg)	Fly ash (ng/kg)
PCDD/F (I-TEQ)	< 1–10	20–500	200–10,000
PCB	< 0.005–0.05	0.004–0.05	10,000–250,000
PCBz[a]	< 0.002–0.05	200,000–1,000,000	100,000–4,000,000
PCPh[b]	< 0.002–0.05	20,000–500,000	50,000–10,000,000
PAH[c]	< 0.005–0.01	10,000–300,000	50,000–2,000,000

a. PCBz: polychlorinated benzenes.

b. PCPh: polychlorinated phenols.

c. PAH: polycyclic aromatic hydrocarbons.

Source: European Commission 2006.

Emissions to air from waste incineration plants depend to a large extent on the firing conditions and the design and operating conditions of the flue gas treatment systems. PCDD/PCDF emissions from most modern waste incineration plants using best available techniques are in the range of 0.0008–0.05 ng/ I-TEQ/ Nm^3; (see Stubenvoll, Böhmer et al. 2002). However, emissions can be higher than 150 ng/ I-TEQ/ Nm^3 in the case of badly designed and operated plants.

PCDD/PCDF emissions to water only occur where wet systems are applied for flue gas treatment. Modern wastewater treatment plants include steps such as neutralization, precipitation, flocculation and activated coke filters to remove organic substances. Generally emissions from these plants are in the range of 0.01–0.3 ng/ I-TEQ/ l (e.g. in the Waste Incineration Directive of the European Council, an PCDD/PCDF emission limit value (ELV) of 0.3 ng/ I-TEQ/ l is prescribed).

Typical concentrations of PCDD/PCDF found in the waste itself are reported to be in the range of 50–250 ng I-TEQ /kg for municipal solid waste, up to 10,000 ng/kg I-TEQ for hazardous waste and 8.5–73 ng/kg I-TEQ for sewage sludge (European Commission 2006).

Table 3 gives an estimation of PCDD/PCDF (I-TEQ) releases into different media based on typical parameters of municipal solid waste incinerators designed and operated according to best available techniques (for parameters see Stubenvoll, Böhmer et al. 2002 and European Commission 2006).

Table 3. Estimation of releases of PCDD/PCDF into different media from municipal waste incinerators

Medium	Accumulation per t of treated waste	Unit	Average concentration	Unit	Specific release (µg/t waste)
Bottom ash	220	kg	46	ng I-TEQ /kg	10.12
Fly ash	20	kg	2,950	ng I-TEQ /kg	59
Filter cake	1	kg	4,000	ng I-TEQ/kg	4
Wastewater	450	l	0.3	ng I-TEQ /l	0.135
Air	5,000	Nm^3	0.02	ng I-TEQ/ Nm^3	0.1
Total release					**73.355**

Source: Stubenvoll, Böhmer et al. 2002 and European Commission 2006

From the data presented in Table 3 it becomes clear that dioxins and furans are mainly released by solid waste from incineration. Filter cake (e.g. by underground storage) and fly ash have to be disposed of in dedicated landfills in most countries (sometimes after pretreatment) whereas bottom ash is used in some countries (e.g. for road construction), usually after pretreatment.

Provided that the total content and the leaching rate of persistent organic pollutants from ashes and other wastes from waste incineration is low (this can be achieved e.g. by pretreatment) the specially engineered landfills – if designed and operated according to best available techniques – can be regarded as final sinks for hazardous substances, so that the risk of further release of and re-exposure to these chemicals is strongly reduced. In this case emissions from modern waste incineration plants are very low.

4. Alternatives to the incineration of municipal solid waste, hazardous waste and sewage sludge

For an overview of waste management considerations see section III.C (ii) of the present guidelines.

In addition to urging Parties to give priority to approaches that promote recycling and recovery of waste and minimize waste generation, the Stockholm Convention stresses the importance of considering alternative disposal and treatment options that may avoid the formation and release of chemicals listed in Annex C. Examples of such alternatives, including emerging technologies, are listed below.

For municipal waste, possible alternatives to incineration are:

- Zero waste management strategies, which aim to eliminate the generation of waste through the application of a variety of measures, including legislative and economic instruments;
- Waste minimization, source separation and recycling to reduce the waste volume requiring final disposal;
- Composting, which reduces waste volume by biological decomposition;
- Mechanical biological treatment, which reduces waste volume by mechanical and biological means and generates residues requiring further management;

- High-temperature melting, which uses thermal means to reduce waste volume and encapsulates residues requiring further management.
- Specially engineered landfill, which contains and isolates wastes (including effective capturing and burning of formed methane with energy recovery or at least flaring if the latter technique is not applicable);

For hazardous waste, possible alternatives to incineration include:

- Waste minimization and source separation with final disposal by other techniques or to appropriate landfill;

For POPs wastes, possible alternatives to incineration are listed in the Basel Technical Guidelines (Basel Convention Technical Guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs); 2005)

- Gas phase chemical reduction;
- Base catalysed decomposition;
- Sodium reduction;
- Supercritical water oxidation.

For non-contaminated sewage sludge, possible alternatives to incineration are disposal to landfill or landspreading, which avoid formation of chemicals listed in Annex C. Though it is noted that any persistent organic pollutants and other hazardous substances present in such sludges may be released to the environment through this latter approach. For land application, non-contaminated sludge should ideally be collected separately.

Further work is needed by the international community to test and verify technologies such as those listed above. Work is also needed to promote additional innovation in this important field.

5. Best environmental practices for waste incineration

Well-maintained facilities, well-trained operators, a well-informed public, and constant attention to the process are all important factors in minimizing the formation and release of chemicals listed in Annex C from the incineration of waste. In addition, effective waste management strategies (for example, waste minimization, source separation and recycling), by altering the volume and character of the incoming waste, can also significantly impact releases.

It should be mentioned here that due to the unclear definition of what constitutes best environmental practices there is some overlap between the descriptions of best environmental practices and best available techniques. Some practices listed in this subsection on best environmental practices may also be a prerequisite for operation of a plant using best available techniques.

In this subsection best environmental practices for operation of a waste incinerator are described. Relevant practices that should be applied before the waste reaches the incineration plants are described elsewhere in this document (see for example section III.C on cross-cutting considerations).

5.1 Waste management practices

Waste management considerations, which are described in section III.C (ii) of the present guidelines, and the alternative approaches outlined in subsection 6 below, must be taken into account as part of overall waste prevention and control strategies.

5.1.1 Waste minimization

Reducing the overall mass of wastes that have to be disposed of by any means serves to reduce both the releases and residues from incinerators. Diversion of biodegradables to composting and initiatives to reduce the amount of packaging materials entering the waste stream can significantly affect waste volumes. Responsibility for waste minimization lies only to a minor extent with the operator of a waste incineration plant. However, coordination and harmonization of relevant activities on different organizational levels (e.g. operator, local, regional or national level) is of major importance for protection of the environment as a whole.

5.1.2 Source separation and recycling

Kerbside or centralized sorting and collection of recyclable materials (for example, aluminium and other metals, glass, paper, recyclable plastics, and construction and demolition waste) also reduces waste volume, saves valuable resources and removes some non-combustibles. Responsibility for these activities must be coordinated between relevant levels.

5.1.3 Waste inspection and characterization

A thorough knowledge of the characteristics and attributes of the incoming waste is essential. The characteristics of a particular waste stream may vary significantly from country to country and region to region. If certain wastes or waste constituents are considered inappropriate for incineration, procedures should be in place for detecting and separating these materials in the waste stream or residues. Checking, sampling and analyses should be performed. This is particularly true for hazardous wastes. Manifests and audit trails are important to maintain and they should be kept updated. Table 5 illustrates some of the techniques applicable to the different types of waste.

5.1.4 Removal of non-combustibles at the incinerator

The removal of both ferrous and non-ferrous metals on site is a common practice at municipal solid waste incinerators.

5.1.5 Proper handling, storage and pre-treatment

Proper handling, particularly of hazardous waste, is essential. Appropriate sorting and segregation should be undertaken to enable safe processing (Table 5).

Storage areas must be properly sealed with controlled drainage and weatherproofing. Fire detection and control systems for these areas should also be considered along with adequate capacity to retain contaminated fire water onsite. Storage and handling areas should be designed to prevent contamination of environmental media and to facilitate clean-up in the event of spills or leakage. Odours and release of volatile persistent organic pollutants to environmental media can be minimized by using bunker air for the combustion process. In the case of sewage sludge, pre-treatment must ensure that adequate drying and conditioning has been performed.

Table 4. Examples of inspection techniques

Waste type	Techniques	Comments
Mixed municipal wastes	Visual inspection in bunker Spot checking of individual deliveries by separate offloading Weighing the waste as delivered Radioactive detection	Industrial and commercial loads may have elevated risks
Pretreated municipal wastes and refuse-derived fuels	Visual inspection Periodic sampling and analysis for key properties or substances	
Hazardous wastes	Visual inspection Sampling/analysis of all bulk tankers Random checking of drummed loads Unpacking and checking of packaged loads Assessment of combustion parameters Blending tests on liquid wastes prior to storage	Extensive and effective procedures are particularly important for this sector. Plants receiving monostreams may be able to adopt

	Control of flashpoint for wastes in the bunker Screening of waste input for elemental composition, for example by EDXRF[a]	more simplified procedures
Sewage sludges	Periodic sampling and analysis for key properties and substances Checking for stones/metals prior to drying stages Process control to adapt to sludge variation	

a. EDXRF: energy dispersive X-ray fluorescence (spectrometer).

Source: European Commission 2006.

Table 5. Examples of segregation techniques

Waste type	Segregation techniques
Mixed municipal wastes	Segregation is not routinely applied unless various distinct waste streams are received, when these can be mixed in the bunker Bulky items requiring pretreatment can be segregated Emergency segregation areas for rejected waste
Pretreated municipal wastes and refuse-derived fuels	Segregation not routinely applied Emergency segregation areas for rejected waste
Hazardous wastes	Extensive procedures required to separate chemically incompatible materials (examples given as follows): Water from phosphides Water from isocyanates Water from alkaline materials Cyanide from acids Flammable materials from oxidizing agents Maintain separation of presegregated packed delivered wastes
Sewage sludges	Wastes generally well mixed before delivery to plant Some industrial streams may be separately delivered and require segregation for blending

Source: European Commission 2006.

5.1.6 Minimizing storage times

Although having a constant supply of waste is important for continuous operation and stable firing conditions in large municipal solid waste incinerators, stored wastes are unlikely to improve with age. Minimizing the storage period will help prevent putrefaction and unwanted reactions, and the deterioration of containers and labelling. Managing deliveries and communicating with suppliers will help ensure that reasonable storage times (e.g. four to seven days for municipal solid waste) are not exceeded.

5.1.7 Establishing quality requirements for waste-fed facilities

Operators must be able to accurately predict the heating value and other attributes of the waste being combusted in order to ensure that the design parameters of the incinerator are being met. This can be done using the results from a feed monitoring programme of key contaminants and parameters where sampling and analysis frequencies and rigour would increase as feed variability increases.

5.1.8 Waste loading

For facilities that accept heterogeneous municipal solid waste, proper mixing and loading of the feed hopper is critical. Loading crane operators must have both the experience and the appropriate vantage point to be able to select the appropriate mix of waste types to keep the incinerator performing at peak efficiency.

5.2 Incinerator operating and management practices

5.2.1 Ensuring good combustion

To achieve optimal prevention of formation, and capture, of chemicals listed in Annex C, proper care and control of both burn and exhaust parameters are necessary. In continuous feed units, the timing of waste introduction, control of burn conditions and post-burn management are important considerations (see subsection 6 below).

5.2.2 Avoiding cold starts, upsets and shutdowns

These events are normally characterized by poor combustion, and consequently create the conditions for formation of chemicals listed in Annex C. For smaller, modular incinerators operating in batch mode, start-up and shutdown may be daily occurrences. Preheating the incinerator and initial co-firing with a clean fossil fuel will allow efficient combustion temperatures to be reached more quickly. Wherever possible, however, continuous operation should be the practice of choice. Independent of the operation mode waste should be fed into the combustion system only when the required temperature (e.g. above 850° C) is reached. Upsets can be minimised through periodic inspection and preventive maintenance. Incinerator operators should not feed the waste during filter bypass (“dump stack”) operations or during severe combustion upsets.

5.2.3 Regular facility inspections and maintenance

Routine inspections by the operator and periodic inspections by the relevant authority of the furnace and air pollution control devices should be conducted to ensure system integrity and the proper performance of the incinerator and its components.

5.2.4 Monitoring

High-efficiency combustion is facilitated by establishing a monitoring regime of key operating parameters, such as carbon monoxide (CO), volumetric flow rate, temperature and oxygen content. Low CO is associated with higher combustion efficiency in terms of the burnout of the municipal solid waste. Generally, if the CO concentration is low by volume (for example, < 50 parts per million or 30 mg/m^3) in the stack flue gases, this provides a general indication that high combustion efficiency is being maintained within the combustion chamber. Good combustion efficiency is related to the minimization of the formation of PCDD/PCDF within the incinerator, and the combustion temperature in the chamber should therefore be recorded.

Carbon monoxide, oxygen in the flue gas, particulate matter, hydrogen chloride (HCl), sulphur dioxide (SO_2), nitrogen oxides (NO_x), hydrogen fluoride (HF), airflows and temperatures, pressure drops, and pH in the flue gas should all be routinely monitored. These measurements reflect combustion conditions and give a general indication of the potential for formation and release of chemicals listed in Annex C. Periodic or semi-continuous measurement (continuous sampling and periodic analysis) of PCDD/PCDF in the flue gas can help the operator to ensure that releases are minimized and the incinerator is operating properly.

In Japan, simplified measurement methods by bioassay are approved as official standard methods for periodical measuring of dioxins from waste incineration plants with capacity less than 2 tons/hour (see also section III.C (vi))

5.2.5 Handling of residues

Bottom and fly ash from the incinerator must be handled, transported and disposed of in an environmentally sound manner. This includes the separate management of bottom ash from fly ash and other flue gas treatment residues in order to avoid contamination of the bottom ash and thereby improve the potential for bottom ash recovery. Covered hauling and dedicated landfills are a common practice for managing these residues.

Particularly if reuse of the residues is contemplated, an evaluation of the content and potential environmental mobility of heavy metals and chemicals listed in Annex C is required, and guidelines adopted by the Basel Convention and subsequently adopted by the Conference of the Parties of the Stockholm Convention should be followed. Periodic analysis of the ash can also serve as an indicator of incinerator performance or the introduction of non-permitted wastes.

Scrubber effluents, including the filter cake from wet flue gas cleaning, is regarded as hazardous waste in many countries and must be treated and disposed of in an environmentally sound manner (e.g. stabilisation prior to disposal in specially engineered landfills).

5.2.6 Operator training

Regular training of personnel is essential for good operation of waste incinerators. In the United States, for example, training and certification of operators is provided by the American Society of Mechanical Engineers (see also section III.C (v) of the present guidelines).

5.2.7 Maintaining public awareness and communication

Creating and maintaining public goodwill towards a waste incineration project is critical to the success of the venture. Outreach should begin as early in the planning of the project as possible. The public and citizens' advocacy groups will have understandable concerns about the construction and operation of a facility and dealing with these openly and honestly will help prevent misinformation and misunderstanding.

Effective practices for improving public awareness and involvement include: placing advance notices in newspapers; distributing information to area households; soliciting comment on design and operational options; providing information displays in public spaces; maintaining pollutant release and transfer registers; and holding frequent public meetings and discussion forums.

Authorities and proposers of incineration projects should engage with all stakeholders including the public interest groups by: holding regular consultation meetings with concerned citizens; providing days for public visitation; posting release and operational data to the Internet; and displaying real-time data on operations and releases at the facility site. Consultations with the public must be transparent, meaningful and sincere if they are to be effective.

6. Best available techniques for incineration

In addition to applying best environmental practices to the incineration of municipal solid waste, hazardous waste and sewage sludge, there is a variety of demonstrated combustion engineering, flue gas cleaning and residue management techniques that are available for preventing the formation or minimizing the releases of chemicals listed in Annex C. For a detailed analysis of what represents best available techniques for waste incineration reference should be made to the European Commission BAT Reference (BREF) Document on waste incineration (European Commission 2006).

There are also non-incineration and emerging technology options (see section III.C (ii) of the present guidelines) that may represent feasible and environmentally sound alternatives to incineration. The purpose of this subsection, however, is to identify the best techniques applicable to the process of incineration. Best available techniques for incineration include the design, operation and maintenance of a waste incineration plant that effectively minimizes the formation and release of chemicals listed in Annex C.

When considering the best available techniques described here for waste incineration, it is important to consider that the optimal solution for a particular type of incineration installation varies according to local conditions. The best available techniques provided here are not intended as a checklist indicating the best local solution, as this would require the consideration of local conditions to a degree that cannot be described in a document dealing with best available techniques in general. Hence, the simple combination of the individual elements described here as best available techniques, without consideration of local conditions, is not likely to give the optimized local solution in relation to the environment as a whole (European Commission 2006).

With a suitable combination of primary and secondary measures, PCDD/PCDF performance levels in air emissions no higher than 0. 1–0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluent, are associated with PCDD/PCDF concentration levels of well below 0.1 ng I-TEQ/l.

As an illustrative example of a multimedia guideline, Japan established in 1997 a future target for the total amount of PCDD/PCDF released, including not only PCDD/PCDF contained in emission gas but also those contained in bottom ash and fly ash, of 5 µg I-TEQ/ton-waste (see subsection 3, Table 3 above for comparison).

It should be mentioned that most of the conclusions on best available techniques drawn in this chapter are taken from the European Commission BREF Document on waste incineration (European Commission 2006). There are many waste incinerator plants worldwide that are designed and operated according to most of the parameters defining best available techniques and that meet the associated emission levels.

6.1 Site selection

For waste incineration, the local factors to be taken into account may, amongst others, include:

- Local environmental drivers, for example background environmental quality may influence the required local performance in respect of releases from the installation, or availability of certain resources;
- The particular nature of the waste(s) that arise locally and the impact of the waste management infrastructure upon the type and nature of waste arriving at the installation;
- The cost and technical possibility of implementing a particular technique in relation to its potential advantages – this is of particular relevance when considering the performance of existing installations;
- The availability, degree of utilization and price of options for the recovery and disposal of residues produced at the installation;
- The availability of users and price received for recovered energy;
- Local economic, market and political factors that may influence the tolerability of the higher gate fees that may accompany the addition of certain technological options.

6.2 Best available techniques for waste input and control

- Maintain the site in a generally tidy and clean state;
- Establish and maintain quality controls over the waste input, according to the types of waste that may be received at the installation. This includes:
    - Establish process input limitations and identify key risks;
    - Communicate with waste suppliers to improve incoming waste quality control;
    - Control waste feed quality on the incinerator site;
    - Check, sample and test incoming wastes;
    - Employ detectors for radioactive materials.

6.3 Best available techniques for combustion

Optimal burn conditions involve:

- Mixing of fuel and air to minimize the existence of long-lived, fuel-rich pockets of combustion products;
- Attainment of sufficiently high temperatures in the presence of oxygen for the destruction of hydrocarbon species;
- Prevention of quench zones or low-temperature pathways that will allow partially reacted fuel to exit the combustion chamber.

Proper management of time, temperature and turbulence (the “3 Ts”), as well as oxygen (airflow), by means of incinerator design and operation will help to ensure the above conditions. Temperatures at or above 850° C (e. g. for waste with content of halogenated organic substances, expressed as chlorine, > 1% above 1,100° C) are required for complete combustion in most technologies. Turbulence, through the mixing of fuel and air, helps prevent cold spots in the burn chamber and the build-up of carbon, which can reduce combustion efficiency. The recommended residence time in the secondary combustion chamber in the primary furnace is at least 2 seconds at 6% oxygen.

6.3.1 General combustion techniques

1. Ensure design of furnace is appropriately matched to characteristics of the waste to be processed.
2. Maintain temperatures in the gas phase combustion zones in the optimal range for completing oxidation of the waste (for example, 850º–950º C in grated municipal solid waste incinerators, 1,100º–1,200º C when chlorine content of waste is high).
3. Provide for sufficient residence time (e.g. at least 2 seconds at 6% Oxygen) and turbulent mixing in the combustion chamber(s) to complete incineration.
4. Preheat primary and secondary air to assist combustion.
5. Use continuous rather than batch processing wherever possible to minimize start-up and shutdown releases.
6. Establish systems to monitor critical combustion parameters such as temperature, pressure drop, levels of CO, CO_2 and O_2 and, where applicable , grate speed.
7. Provide for control interventions to adjust waste feed, grate speed, and temperature, volume and distribution of primary and secondary air.
8. Install automatic auxiliary burners to maintain optimal temperatures in the combustion chamber(s).
9. Use air from bunker and storage facilities as combustion air.
10. Install system that automatically stops waste feeding when combustion parameters are not appropriate.

6.3.2 Municipal solid waste incineration techniques

1. Mass burn (moving grate) incinerators are well demonstrated in the combustion of heterogeneous municipal solid waste and have a long operational history.
2. Water-cooled grated incinerators have the added advantages of better combustion control and the ability to process municipal solid waste with higher heat content.
3. Rotary kilns with grates can accept heterogeneous municipal solid waste but a lower throughput than the mass burn or moving grate furnaces.
4. Static grated furnaces with transport systems (for example, rams) have fewer moving parts but waste may require more pretreatment (i.e., shredding, separation).
5. Modular designs with secondary combustion chambers are well demonstrated for smaller applications. Depending on size, some of these units may require batch operation.

6. Fluidized bed furnaces and spreader/stoker furnaces are well demonstrated for finely divided, consistent wastes such as refuse-derived fuel.

6.3.3 Hazardous waste incineration techniques

1. Rotary kilns are well demonstrated for the incineration of hazardous waste and can accept liquids and pastes as well as solids.
2. Water-cooled kilns can be operated at higher temperatures and allow acceptance of wastes with higher energy values.
3. The applicability of waste heat recovery boilers should be considered carefully, particularly with regard to the possibility of PCDD/PCDF reformation.
4. Waste consistency (and combustion) can be improved by shredding drums and other packaged hazardous wastes.
5. A feed equalization system (for example, screw conveyors that can crush and provide a constant amount of solid hazardous waste to the furnace) will help ensure a continuous, controlled feed to the kiln and maintenance of uniform combustion conditions.

6.3.4 Sewage sludge incineration techniques

1. Fluidized bed incinerators are well demonstrated for thermal treatment of sewage sludge.
2. Circulating fluid bed furnaces allow greater fuel flexibility than bubbling beds, but require cyclones to conserve bed material.
3. Care must be exercised with bubbling bed units to avoid clogging.
4. The use of heat recovered from the process to aid sludge drying will reduce the need for auxiliary fuel.
5. Supply technologies are important in the co-incineration of sewage sludge in municipal solid waste incinerators. Demonstrated techniques include: dried sludge blown in as dust; drained sludge supplied through sprinklers and distributed and mixed on the grate; and drained or dried sludge mixed with municipal solid waste and fed together (European Commission 2006).[2]

6.4 Best available techniques for flue gas treatment

The type and order of treatment processes applied to the flue gases once they leave the incineration chamber is important, both for optimal operation of the devices and for the overall cost-effectiveness of the installation. Waste incineration parameters that affect the selection of techniques include: waste type, composition, and variability; type of combustion process; flue gas flow and temperature; and the need for, and availability of, wastewater treatment. The following treatment techniques have direct or indirect impacts on preventing the formation and minimizing the release of chemicals listed in Annex C. Best available techniques involve applying the most suitable combination of flue gas cleaning systems.

6.4.1 Dust (particulate matter) removal techniques

1. Dust removal from the flue gases is essential for all incinerator operations.
2. Electrostatic precipitators and fabric filters have demonstrated effectiveness as capture techniques for particulate matter in incinerator flue gases. For a comparison of the primary dust removal systems see Table 3 in section III.C (iv) of the present guidelines.
3. Cyclones and multicyclones are less efficient in dust removal and should only be used in a pre-dedusting step to remove coarser particles from the flue gases and reduce dust loads on

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[2] Additional information on the comparison of combustion techniques among furnace types may be found in Annex I.

downstream treatment devices. Preseparation of coarse particles will decrease the amount of fly ash contaminated with high loads of persistent organic pollutants.

4. The collection efficiency of electrostatic precipitators is reduced as electrical resistivity of the dust increases. This may be a consideration in situations where waste composition varies rapidly (e.g. hazardous waste incinerators).
5. Electrostatic precipitators and fabric filters should be operated below 200º C to minimize formation of PCDD/PCDF and other chemicals listed in Annex C.
6. Wet electrostatic precipitators can capture very small particle sizes but require effluent treatment and are usually employed following dedusting.
7. Fabric filters (bag filters) are widely applied in waste incineration and have the added advantage, when coupled with semi-dry sorbent injection (spray drying), of providing additional filtration and reactive surface on the filter cake.
8. Pressure drop across fabric filters and flue gas temperature (if a scrubbing system is used upstream) should be monitored to ensure filter cake is in place and bags are not leaking or being wetted. A bag leak detection system using a triboelectric detector represents one option for monitoring fabric filter performance.
9. Fabric filters are subject to water damage and corrosion and gas streams must be maintained above the dew point (130º–140º C) to prevent these effects. Some filter materials are more resistant to damage. For an outline of filter material choices and attributes see Table 2 in section III.C (iv) of the present guidelines.

6.4.2 Acid gas removal techniques

1. Wet scrubbers have the highest removal efficiencies for soluble acid gases among the demonstrated techniques where pH of scrubber water is a function of removal efficiency. Solid particles in scrubber water may also cause interaction with PCDD/PCDF in the mobile gas stream, thus influencing the reliability of the relationship between results obtained from periodic stack gas monitoring and plant destruction performance.
2. Pre-dedusting of the gas stream may be necessary to prevent clogging of the scrubber, unless scrubber capacity is sufficiently large.
3. The use of carbon-impregnated materials, activated carbon, or coke in scrubber packing materials can achieve a 70% reduction in PCDD/PCDF across the scrubber (European Commission 2006) but this may not be reflected in overall releases.
4. Spray dryers (semi-wet scrubbing) also provide high removal efficiencies and have the advantage of not requiring subsequent effluent treatment. In addition to the alkaline reagents added for acid gas removal, activated carbon injection is also effective in removing PCDD/PCDF as well as mercury. Spray dry scrubbing systems also typically achieve 93% SO_2 and 98% HCl control.
5. Spray dryers, as noted above, are often deployed upstream of fabric filters. The filters provide for capture of the reagents and reaction products as well as offering an additional reactive surface on the filter cake.
6. Inlet temperature to the fabric filter in such combinations is important. Temperatures above 130º–140º C are normally required to prevent condensation and corrosion of the bags.
7. With regards to acid gas removal, dry scrubbing systems cannot reach the efficiency of wet or semi-wet (spray dry) scrubbers without significantly increasing the amount of reagent/sorbent. Increased reagent use adds to the volume of fly ash.

6.4.3 Flue gas polishing techniques

1. Additional dust removal may be appropriate before cleaned flue gases are sent to the stack. Techniques for the polishing of flue gas include fabric filters, wet electrostatic precipitators and venturi scrubbers.
2. Double filtration (filters in series) can routinely achieve collection efficiencies for dust at or below 1 mg/m^3.
3. The additional benefits of these techniques may be small, and the cost-effectiveness disproportionate, if effective upstream techniques are already being applied.
4. Flue gas polishing may have greatest utility at large installations and in further cleaning of gas streams prior to selective catalytic reactions.
5. Adsorption can be achieved by activated carbon injection, in static beds or by use of carbon impregnated materials.

6.4.4 Nitrogen oxides (NO_x) removal techniques using a catalyst

1. Although the primary role of selective catalytic reaction is to reduce NO_x emissions, this technique can also destroy gas phase chemicals listed in Annex C (for example, PCDD/PCDF) with an efficiency of 98–99.5% (European Commission 2006).
2. Flue gases may have to be reheated to the 250º–400º C required for proper operation of the catalyst.
3. Performance of selective catalytic reaction systems improves with upstream flue gas polishing. These systems are installed after dedusting and acid gas removal.
4. The significant cost (capital and energy) of selective catalytic reaction is more easily borne by large facilities with higher gas flow rates and economies of scale.

6.5 Management techniques for solid residues

Wastes and residues from incineration include various types of ash (e.g. bottom ash, boiler ash, fly ash) and residues from other flue gas treatment processes (such as gypsum from wet scrubbers), including liquid effluents in the case of wet scrubbing systems.

Dry and semi-wet scrubbers generally produce greater amounts of solid waste than wet scrubbers. Furthermore this waste can contain fly ash (if it is not separated efficiently), heavy metals (especially mercury) and unreacted sorbent.

Because constituents of concern may vary considerably, maintaining the separation of residues for treatment, management and disposal is in general appropriate. The presence and concentration of chemicals listed in Annex C in these residues (if separately treated) is a function of their presence in the incoming waste, survival or formation in the incineration process, and formation and capture during flue gas treatment. Techniques that may be considered are listed in detail in the Basel Technical Guidelines, chapter IV, G 3, and also in section III C. (iv) - chapters 2.1.2 and 2.2. It will be necessary to establish case by case, which of these techniques may be considered as best available techniques and best environmental practices.

6.5.1 Bottom and boiler ash treatment techniques

Bottom ash from incinerators designed and operated according to best available techniques (i.e., incinerators showing a good burnout behaviour) tends to have a very low content of chemicals listed in Annex C, in the same order of magnitude as background concentrations in urban soils (i.e., < 1–10 ng I-TEQ /kg ash). Boiler ash levels tend to be higher (20–500 ng I-TEQ /kg ash) but both are well below the average concentrations found in fly ash (European Commission 2006).

Because of the differences in pollutant concentration, the mixing of bottom ash with fly ash will contaminate the former and is forbidden in many countries. Separate collection and storage of these residues provides operators with more options for disposal.

Bottom ash (or slag from fluidized bed incinerators) is disposed of in landfills in many countries but may be reused in construction and road-building material following pretreatment. Prior to such use, however, an assessment of content and leachability should be conducted and upper levels of persistent organic pollutants, heavy metals and other parameters have to be defined.

Pretreatment techniques include dry, wet and thermal treatment as well as screening and crushing and separation of metals.

Leachability of chemicals listed in Annex C is known to increase with increasing pH and humic (presence of organic matter) conditions. This would suggest that disposal in lined and dedicated landfills is preferable to mixed waste facilities.

6.5.2 Management techniques for flue gas treatment residues

Unlike bottom ash, air pollution control device residuals, including fly ash and scrubber sludges, contain relatively high concentrations of heavy metals, organic pollutants (including PCDD/PCDF), chlorides and sulphides. Separate removal of fly ash and residues from flue gas cleaning stages (e.g. those for acid gas and dioxin removal) prevents mixing of low contaminated waste fractions with highly contaminated ones.

Whenever bottom ash is to be further used (e.g. as construction material) mixing with other flue gas treatment residues is not a best available technique.

Fly ash is disposed of in dedicated landfills in many countries. However, pre-treatment is likely to be required for this to constitute BAT. (See also section III. C (iv) - chapters 2.1.2 and 2.2 on Cross-cutting Issues).

6.6 Best available techniques for effluent treatment

Process wastewater in incineration arises mainly from the use of wet scrubbing technologies. The need for and treatment of wastewater can be alleviated by the use of dry and semi-wet systems.

Best available techniques for wastewater treatment include optimization of the recirculation and reuse of wastewater arising on the site within the installation, the use of separate systems for the treatment of wastewater with different level of contamination, use of physico-chemical treatment of the scrubber effluents and removal of ammonia if necessary. For the removal of organic compounds activated coke filters and carbon-impregnated polymers are used.

With a combination of suitable treatment techniques (See also chapter on Cross-cutting issues) PCDD/PCDF levels in the treated wastewater will be in the range of < 0.01–0.1 ng I-TEQ/l (European Commission 2006).

6.7 Impact of best available techniques and best environmental practices on other pollutants

The description of techniques and practices in this provisional guidance is primarily focused on their demonstrated effectiveness in the prevention, minimization or reduction of the formation and release of chemicals listed in Annex C. Many of these practices also serve to reduce releases of other pollutants, and some may be primarily designed for this purpose (e.g. source separation of metals and other non-combustibles from waste streams, selective catalytic reduction for NO_x control, acid gas controls for reducing SO_2, carbon adsorption for mercury control). Some that may have been designed for the capture of other pollutants (e.g. higher inlet temperature electrostatic precipitators) have had to be redesigned or replaced to avoid increasing formation and release of chemicals listed in Annex C.

In the final analysis, what constitutes best available techniques and best environmental practices for waste incineration is broader than the impact on chemicals listed in Annex C alone, involving all aspects of the incineration, energy recovery, flue gas treatment, wastewater treatment and residue treatment process. The great majority of these, however, are complementary with the aims of preventing or reducing releases of the chemicals listed in Annex C (for consideration of co-benefits see section III.C (iii) of the present guidelines).

6.8 New and significantly modified incinerators

The Stockholm Convention (Annex C, Part V, section B, subparagraph (b)) states that before Parties proceed with proposals to construct or significantly modify sources that release chemicals listed in Annex C, they should give “priority consideration” to “alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release” of these compounds. In cases where such consideration results in a determination to proceed with construction or modification, the Convention provides a set of general reduction measures for consideration. While these general measures have been incorporated into the preceding discussion of best available techniques and best environmental practices for these categories, there are additional factors that will be important in deciding whether it is feasible to construct or modify a waste incinerator. The direct and indirect effects on human health and the environment should be addressed by performing an appropriate environmental impact assessment. Additional factors are listed below:

6.8.1 Additional factors in the siting of new municipal solid waste incinerators

1. Is there an accurate prediction of the nature and volume of non-recyclable municipal solid waste generation in the area to be served?
2. Will the supply allow for continuous operation of the incinerator?
3. Does this prediction include appropriate waste minimization, recycling and recovery programmes?
4. Is the transportation infrastructure sufficient to support collection and hauling?
5. Has the likelihood of intra- or inter-State restrictions on waste transportation been investigated?
6. Are there available markets for any on-site separated materials?
7. Are there available markets for excess steam or electricity generated on site?
8. Are there environmentally sound options for the treatment and disposal of residues?

6.8.2 Additional factors in the siting of new hazardous waste incinerators

1. Is there an accurate prediction of the nature and volume of hazardous waste generation in the area to be served?
2. Will the supply allow for continuous operation of the incinerator?
3. Is the infrastructure sufficient to support transportation needs?
4. If international transport is envisioned, are the necessary agreements in place to allow transfer across borders?
5. Have the necessary agreements been made with suppliers to ensure safe packaging and handling?
6. Are there available markets for excess steam or electricity generated on site?
7. Are there environmentally sound options available for the treatment and disposal of residues?

6.8.3 Additional factors in the siting of new sewage sludge incinerators

1. Is there an accurate prediction of the nature and volume of sewage sludge generation in the area to be served?
2. Will the supply allow for continuous operation of the incinerator?
3. Has it been determined whether the sewage sludge in the service area is mixed with industrial or other wastes?

4. Is it intended to co-incinerate the sewage sludge with municipal solid waste or as a supplemental fuel in a utility generating facility?
5. Are there available markets for excess steam or electricity generated on site?
6. Are there environmentally sound options available for the treatment and disposal of residues?

6.9 Modification of existing waste incinerators

Significant modifications to an existing waste incinerator may be considered for several reasons. These could include an expansion of capacity, the necessity of major repairs, enhancements to improve combustion efficiency and energy recovery, and the retrofitting of air pollution control and wastewater treatment devices. Many waste incineration plants have already been retrofitted with such devices, greatly improving their environmental performance. Before undertaking such a modification, in addition to the “priority consideration” noted above, the following factors will be important to consider:

1. How will the modification affect the potential releases of chemicals listed in Annex C?
2. If the modification is the addition of an air pollution control device, is it designed properly for the facility?
3. Is there sufficient space to install and operate it according to best available techniques? For example, available space may dictate the retrofit of double filtration (filters in series, though not necessarily adjacent) rather than an alternative scrubbing system.
4. Will the retrofitted device operate in concert with the existing air pollution and wastewater control devices to minimize releases?

The costs of making modifications to an existing facility depend on the plant-specific situation and may exceed similar changes at a new installation by 25–50% (European Commission 2006). Factors influencing this increase include the additional engineering necessary, the removal and disposal of replaced equipment, reconfiguring connections, and losses in productivity with down time.

7. Performance levels associated with best aavailable techniques

With a suitable combination of primary and secondary measures, PCDD/PCDF performance levels in air emissions no higher than 0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluent, are associated with PCDD/PCDF concentration levels well below 0.1 ng I-TEQ/l.

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(ii) Medical waste

Summary

Incineration of medical waste (infectious health-care waste, biological health-care waste and sharps in dedicated waste incineration plants is performed in order to minimize chemical, biological and physical risks, and to reduce the volume of waste as a pretreatment step to environmentally sound landfilling.

If medical waste is incinerated in conditions that do not constitute best available techniques or best environmental practices, there is potential for the release of PCDD and PCDF in relatively high concentrations. For small medical waste incinerators, application of best available techniques is often difficult, given the high costs associated with building, operating, maintaining and monitoring such facilities.

Possible alternatives to incineration are sterilization (steam, advanced steam, dry heat), microwave treatment, alkaline hydrolysis, biological treatment or in certain cases landfilling. The most important step in managing medical waste is segregating different types of waste at the source. As between 75% and 90% of waste in hospitals is comparable to municipal solid waste, segregation greatly reduces the volume of medical waste. Effective waste management, including waste minimization and segregation at the source, is essential.

Appropriate treatment of bottom ashes and residues from flue gas cleaning is essential for the reduction of PCDD/PCDF releases into the environment. The use of best available techniques in incinerators will also reduce emissions of hydrochloric acid and metals (in particular mercury) and will also, in effect, reduce subsequent releases from residues disposed of into landfills.

With regard to incineration, primary measures alone will significantly reduce emission of the chemicals listed in Annex C of the Stockholm Convention. However, implementation of best available techniques requires both primary and secondary measures. .

With a suitable combination of primary and secondary measures, PCDD/PCDF emission levels in air emissions no higher than 0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluents, are associated with PCDD/PCDF concentration levels well below 0.1 ng I-TEQ/l.

1. Introduction

This section addresses best available techniques and best environmental practices in the (thermal) treatment of medical waste (referred to here as “health-care waste”), because the Stockholm Convention lists medical waste incinerators as a Part II source category that can result in significant emission of chemicals listed in Annex C of the Convention.

This section is concerned almost exclusively with infectious health-care waste. When wastes comparable to domestic waste are properly segregated from infectious wastes they can be dealt with by the municipal waste disposal mechanisms. However, in the absence of effective waste segregation practices and the management and training systems required to maintain them, the total quantity of potentially infectious waste requiring treatment rises dramatically.

Other possible techniques for treating health-care waste, for example the sterilization of infectious waste, do not result in emissions of chemicals listed in Annex C. The advantages, drawbacks and applicability of these techniques are already described elsewhere and are not repeated in detail here.

2. Health-care waste categories

Hospitals generate large amounts of waste that fall into different categories. Health-care waste can also originate from other sources, such as emergency medical care services, transfusion or dialysis centres, laboratories, animal research and blood banks. Between 75% and 90% of the waste produced is non-risk or general health-care waste, which is comparable to domestic waste. It comes mostly from the administrative and housekeeping functions of health-care establishments and may also include waste generated during maintenance of health-care premises. The remaining 10–25% of health-care waste is regarded as hazardous and may create a variety of health risks. Less than 10% of this waste is of an infectious nature. Other types of waste include toxic chemicals, cytotoxic drugs, and flammable and radioactive wastes.

Different types of health-care waste can be classified as follows:

1. Infectious health-care waste (hazardous);
2. Sharps (hazardous);
3. Anatomical and pathological waste (body parts, etc.);
4. Chemical, toxic or pharmaceutical waste, including cytotoxic drugs (antineoplastics) (mostly hazardous);
5. Radioactive waste;
6. General non-infectious waste (e.g. glass, paper, packaging material, food).

For the purpose of these guidelines, the following definitions are taken from *Technical Guidelines on the Environmentally Sound Management of Biomedical and Health-Care Waste* (Basel Convention Secretariat 2002).

2.1 Infectious health-care waste[1]

Infectious health-care waste includes discarded materials or equipment contaminated with blood and its derivatives, and other body fluids or excreta from infected patients with hazardous communicable diseases. It also includes contaminated waste from patients known to have blood-borne infections undergoing haemodialysis (e.g. dialysis equipment such as tubing and filters, disposable sheets, linen, aprons, gloves or laboratory coats contaminated with blood); and laboratory waste (cultures and stocks with any viable biological agents artificially cultivated to significantly elevated numbers, including dishes and devices used to transfer, inoculate and mix cultures of infectious agents and infected animals from laboratories).

2.2 Biological health-care waste

Biological health-care waste includes all body parts and other anatomical waste, including blood and biological fluids and pathological waste that is recognizable by the public or the health-care staff and that demand, for ethical reasons, special disposal requirements.

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[1] The interpretation of the definition of infectious health-care waste varies according to national circumstances, policies and regulations. International organizations (WHO, the United Nations, etc.) have specific interpretations of the definition. Infectiousness is one of the hazardous characteristics listed in Annex III to the Basel Convention and defined under class H6.2.

2.3 Sharps

Included in this category are all biomedical and health-care wastes with sharps or pointed parts able to cause an injury or invasion of the skin barrier of the human body. Sharps from infected patients with hazardous communicable diseases or from isolated wards, or other pointed parts contaminated with the above-mentioned laboratory waste, must be categorized as infectious waste.

3. Alternative techniques for new and existing sources

3.1 New sources

When deciding on methods of waste treatment from health-care activities, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of chemicals listed in Annex C.

Due to the high investment, operational, maintenance and monitoring costs of waste incinerators using best available techniques, economical and effective plant operation is seldom achieved, especially for small hospital incinerators. This is also indicated by the fact that many small plants have been shut down instead of being retrofitted.

Therefore, in many cases on-site steam sterilization and other forms of non-combustion health-care waste treatment techniques may be preferred. In other cases, centralized waste treatment facilities are preferred to decentralized on-site treatment of health-care waste. The treatment of medical waste should then be an integral part of a country or region’s waste management plan.

3.2 Existing sources

Due to the poor design, operation, equipment and monitoring of many existing small hospital incinerators these installations cannot be regarded as employing best available techniques. A medical waste incinerator without sophisticated pollution abatement devices releases a wide variety of pollutants, including PCDD/PCDF, metals (such as lead, mercury and cadmium), particulate matter, acid gases (hydrogen chloride (HCl) and sulphur dioxide (SO_2)), carbon monoxide (CO) and nitrogen oxides (NO_x). These emissions have serious adverse consequences on worker safety, public health and the environment.

The cost of retrofitting old plants is a key factor in the consideration of medical waste disposal. In evaluating the costs of an incineration unit employing best available techniques, decision makers should take into account several factors, including: capital and operating costs of the incinerator plus scrubber and other pollution control devices; the cost of secondary chamber retrofits for old incinerators; the costs of periodic stack testing, continuous monitoring, operator training and qualification; and the costs of maintenance and repair, especially in relation to refractory wear or failure.

As a consequence, the shutdown of existing inappropriate plants has to be considered along with the introduction of alternative techniques for waste treatment or the transfer of waste to centralized health care waste treatment facilities.

3.3 Alternative techniques

The following alternative techniques do not result in the formation and release of chemicals listed in Annex C and should therefore be given priority consideration for their ultimate elimination. However, they might have advantages and drawbacks in other respects. For more information on these techniques see Basel Convention Secretariat 2002.

The following methods are suitable for infectious and biological waste and sharps and are widely applied.[2] The establishment of an effective waste management programme, as described in subsection

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[2] Cost data on the various techniques can be obtained from *Non-Incineration Medical Waste Treatment Technologies*, chapter 11 (Health Care Without Harm 2001).

4 of the present section, is essential for all the techniques described below. Hazardous chemical waste, chemotherapeutic waste, volatile organic compounds, mercury and radioactive waste should not be fed into the systems described here, as this would result in the release of toxic substances into air, condensate or into the treated waste.

Alternative techniques such as sterilization techniques, microwave treatment, alkaline hydrolysis and biological treatment still require final disposal in sanitary landfills.

Workers should be provided with training in such skills as the proper handling of waste and equipment operation and maintenance. Another issue relates to occupational exposure to the chemical disinfectant itself through fugitive emissions, accidental leaks or spills from storage containers, discharges from the treatment unit or volatilized chemicals from treated waste or liquid effluent. Chemical disinfectants are sometimes stored in concentrated form, thus increasing the hazards.

Since chemical processes usually require shredding, the release of pathogens through aerosol formation may be a concern. Chemical-based technologies commonly operate as closed systems or under negative pressure passing their air exhaust through HEPA (high efficiency particulate absorbing) and other filters.

Health care facilities should consider the following factors when selecting a non-incineration technology (Health Care Without Harm Europe 2004):

- Regulatory acceptance;
- Throughput capacity;
- Types of waste treated;
- Microbial inactivation efficacy;
- Environmental emissions and waste residues;
- Space requirements;
- Utility and other installation requirements;
- Waste reduction;
- Occupational safety and health;
- Noise;
- Odour;
- Automation;
- Reliability;
- Level of commercialization;
- Background of the technology manufacturer or vendor;
- Cost;
- Community and staff acceptance.

3.3.1 Steam sterilization

Steam sterilizing or autoclaving is the exposure of waste to saturated steam under pressure in a pressure vessel or autoclave. The technology does not render waste unrecognizable and does not reduce the waste volume unless a shredder or grinder is added. If waste streams are not properly segregated to prevent hazardous chemicals (e.g. antineoplastic drugs or heavy metals such as mercury) from being fed into the treatment chamber, toxic contaminants will be released into the air, condensate, or in the treated waste. Offensive odours containing low levels of alcohol, phenols, aldehydes, and other organic compounds can be generated but can be minimized by proper air handling equipment (e.g. by particulate and carbon filters). More independent emission tests of autoclaves operating under typical conditions would be useful.

Autoclaves are available in a wide range of sizes, from units that treat a few kilograms per cycle to several tons per cycle. Capital costs are relatively low compared to other alternative techniques. Autoclaves have to be inspected at least annually to determine if there are any significant changes from the previous temperature-time profiles, vacuum and steam pressure readings.

The treatment cycle (minimum requirement is 121° C for 30 minutes) is determined by the ability of the heat to penetrate the waste load. Some types of waste or loading configurations that create barriers to heat transfer require longer exposure times and/or higher temperatures. The proper level of disinfection has to be controlled by appropriate means (e.g. test strips, microbiological tests).

3.3.2 Advanced steam sterilization systems

Advanced autoclaves or advanced steam sterilization systems combine steam treatment with prevacuuming and various kinds of mechanical processing before, during and after steam treatment. Many of the advanced systems also include automated waste feed systems; post-treatment vacuum/dehydration; cooling of treated waste; and high-efficiency particulate air filtration and/or carbon filters to remove odours.

Advanced systems with internal shredders or grinders are capable of treating sharps waste as well as pathological waste, including anatomical parts. Drawbacks include the relatively higher capital costs, and the noise generation and higher maintenance costs associated with the shredders and other mechanical devices.

As with steam sterilization, advanced steam sterilization requires proper waste segregation to avoid releases of hazardous substances into different media (see Figure 1 below).

3.3.3 Microwave treatment

Microwave disinfection is essentially also a steam-based process since disinfection occurs through the action of moist heat and steam generated by microwave energy. Microwave units with internal shredders can treat pathological waste and are routinely used to treat sharps waste. Drawbacks are the relatively high capital costs, noise generation from the shredder and the possibility of offensive odours. Offensive odours containing low levels of alcohol, phenols, aldehydes, and other organic compounds can be generated but can be minimized by proper air handling equipment (e.g. by particulate and carbon filters).

3.3.4 Dry heat sterilization

Dry heat sterilization is the exposure of the waste to heat at a temperature and for a time sufficient to ensure sterilization of the entire waste load. As a general rule, dry heat processes use higher temperatures and longer exposure times than steam-based processes. Internal shredding is usually included (for reduction of waste volume). The technology is simple, automated and easy to use.

Volatile and semi-volatile organic compounds, chemotherapeutic wastes, mercury, other hazardous chemical wastes, and radiological wastes should not be treated in a dry heat system. Offensive odours can occur, which are removed in some systems with high-efficiency particulate air or carbon filters. The hot air from the chamber is cooled in a venturi scrubber, which also removes particulates.

3.3.5 Alkaline hydrolysis

Alkaline hydrolysis (or heated alkali digestion) is another chemical process used for the breakdown of organic materials. The same process can degrade bulk chemotherapeutic agents, formaldehyde, fixatives and other toxic chemicals. A typical process uses a sealed stainless steel tank, where waste is mixed with alkali heated to around 110° to 150° C. Depending on the amount of waste, alkali concentration and temperature, the process of digestion can take 3 to 8 hours. Commercial systems are highly automated. Treatment of waste and liquids from alkaline hydrolysis may be necessary.

3.3.6 Biological treatment

Biological treatment involves the use of micro-organisms or biochemicals to decompose the waste. These include the use of enzymes and aerobic or anaerobic digestion. Preferably treatment should take place in a closed system. Offensive odours may result from the application of anaerobic treatment.

3.3.7 Specially engineered landfill

(a) Infectious wastes (i.e. Infectious health-care waste, sharps anatomical and pathological wastes):

Such wastes should not be disposed of to landfill. However, if sterilized they may be regarded as general noninfectious waste and either landfilled or treated in accordance with Section V.A.(i) above (except for sharps, which must also be considered in the light of their physical characteristics).

(b) Chemical, toxic and pharmaceutical wastes and general wastes:

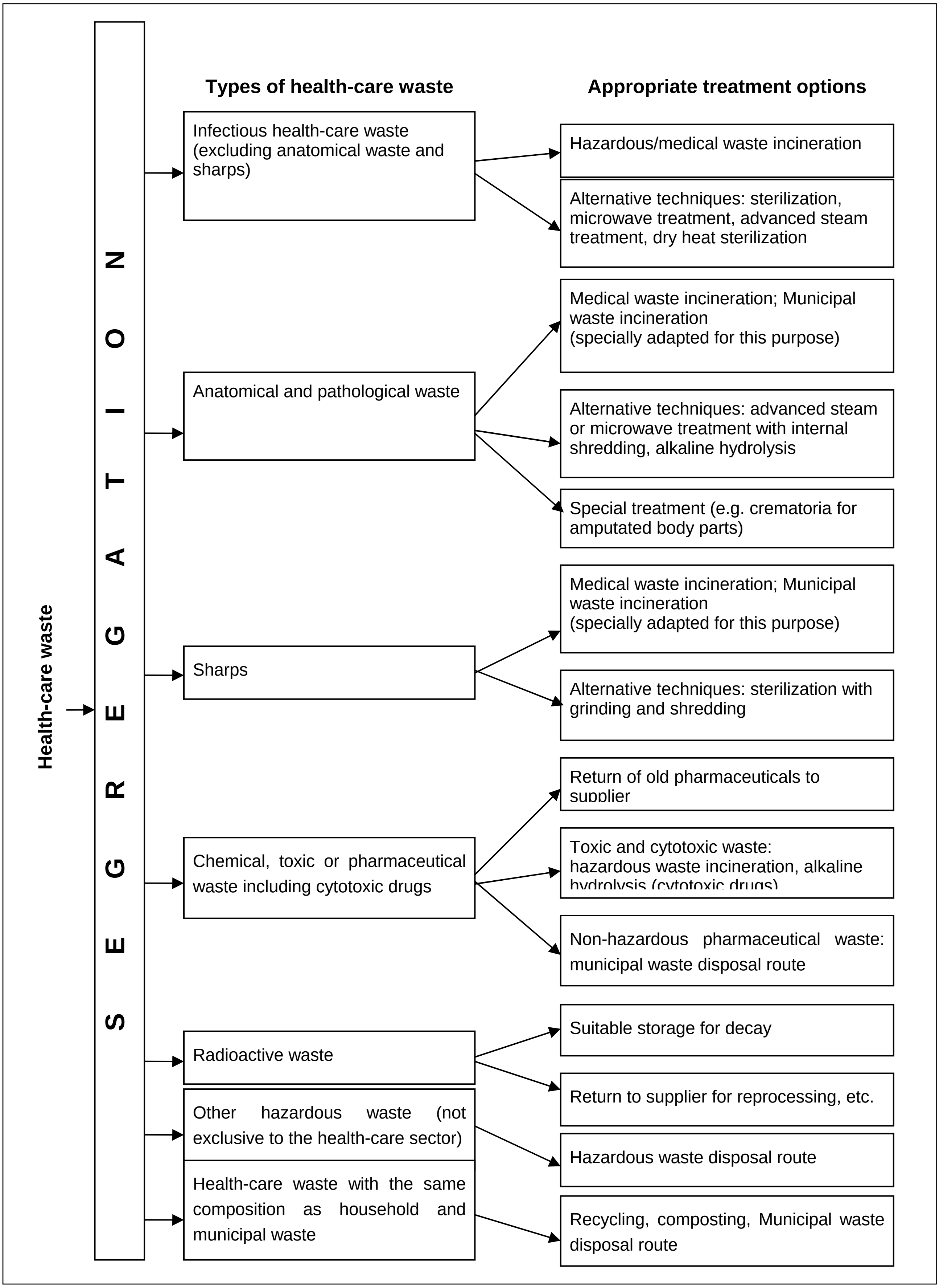
A specially engineered landfill may be an option for such wastes but careful attention must be given to their individual physical and chemical characteristics.

(c) Radioactive wastes:

This waste should not be landfilled.

Figure 1 (Basel Convention Secretariat 2002, chapter 2, Figure 2, adapted) shows into which waste fractions the health-care waste should be segregated and suggests treatment options for these fractions.

Figure 1. Segregation and treatment options for health-care waste



4. Best environmental practices for health-care waste management

Each hospital should develop a waste management plan that provides for thorough segregation and treatment of waste. This can lower the costs of the ultimate disposal. A waste management plan of one hospital can also include treatment of certain fractions of waste from other hospitals to lower costs and to increase the environmental performance of overall waste management.

The main aims of hospital waste management are:

- Minimizing risk for personnel, the general public and the environment;
- Minimizing the amounts of waste being generated;
- Providing for segregation and separation of wastes;
- Designation of deposit areas in the wards;
- Establishment of safe routes for the transportation of the waste;
- Establishment of a safe and proper area for temporary storage;
- Environmentally sound waste treatment and disposal.

Under the framework of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal, *Technical Guidelines on the Environmentally Sound Management of Biomedical and Health-Care Waste* has been published (Basel Convention Secretariat 2002). Use and application of these guidelines, which provide detailed information on the hazards of health-care waste, safe management of health-care waste, the proper segregation and collection of wastes, treatment and disposal methods, and capacity-building, is strongly advised.

In the establishment of a proper health-care waste management plan it is necessary to:

- Characterize the nature and amount of the different waste fractions;
- Identify options to avoid or reduce waste generation (purchasing policies that avoid unnecessary packaging, optimized package sizes, stock keeping, evaluation of work processes, reuse of supplies and equipment where safe and feasible);
- Establish training and management systems to assure effective segregation and handling of infectious, toxic and ordinary wastes;
- Specify suitable containers for collection, storage and transport;
- Lay down the responsibilities of the personnel;
- Describe the appropriate treatment options for the different waste fractions;
- Provide for proper documentation and control of waste disposal;
- Describe the transport of the waste fraction to the final disposal location and the type of final treatment;
- Calculate the costs for the different activities.

Prior to efficient and state-of-the-art treatment and disposal a number of practices are considered necessary. The practices described below can be directly linked to the reduction and avoidance of chemicals listed in Annex C but represent general principles that can influence the generation of waste fractions and contribute to the safety of personnel, the public and the environment.

For more detailed information ample material concerning health-care waste management is available from different sources (Basel Convention Secretariat 2002; WHO 2000; Health Care Without Harm Europe 2004).In this document only a brief overview of common best practices is given.

4.1 Source reduction

Source reduction means minimizing or eliminating the generation of waste at the source itself. Source reduction should have a higher priority than recycling or reuse. Medical staff, waste managers and product standardization committees should be aware of what proportions of the waste stream are generated by the products they buy. Indeed, the close involvement of purchasing staff is critical to the effectiveness of any source reduction scheme. Steps should be taken to reduce at source regulated medical waste, hazardous waste, low-level radioactive waste, as well as regular trash. Some specific source reduction techniques include (bearing in mind that alternative products have to meet the relevant requirements in terms of hygiene and patient safety):

- Material elimination, change or product substitution;
- Technology or process change;
- Preferential purchasing;
- Good operating practice.

4.2 Segregation

Above all, segregation is the key to effective health-care waste management. It ensures that correct disposal routes are taken. Wastes should be separated according to the treatment options suggested. Segregation should be carried out under the supervision of the waste producer and as close as possible to the source, that is, in the ward, at the bedside, in the theatre, in the laboratory, in the delivery room, etc., and must be carried out by the person generating the waste, for example the nurse, the doctor or the specialist, in order to secure the waste immediately and to avoid dangerous secondary sorting.

4.3 Resource recovery and recycling

Specific examples of means recovery and reuse of materials from the waste stream include:

- Recycling newspapers, packaging material, office paper, glass, aluminium cans, construction debris, and other recyclables;
- Purchasing products made of post-consumer recycled material;
- Composting organic food waste;
- Recovering silver from photographic chemicals.

4.4 Training of personnel

Personnel should receive thorough instructions about:

- Risks connected with health-care waste;
- Classification and codes of the different waste fractions and their classification criteria;
- Costs of waste treatment;
- Waste management processes from generation to disposal;
- Operation and maintenance of waste treatment facilities;
- Responsibilities;
- Effects of mistakes and mismanagement.

4.5 Collection at the site of waste generation

- Provide colour-coded containers at or near the points of generation for segregation of the different waste types
- Proper packaging of the waste: either solid containers or plastic bags placed within a rigid or semi-rigid container should be used for non-sharps infectious waste. The plastic bags should be impervious to moisture, and have strength sufficient to resist tearing or bursting when used under normal conditions. Containers for sharps waste should be rigid, puncture resistant and leak proof. The containers may be recyclable (metal or autoclavable plastic) or single use (thick cardboard or plastic). Sharps containers should have a closing lid;
- Proper labelling of waste containers e.g. as infectious or cytotoxic;
- Containers should not be more than three quarters full;
- Highly infectious waste should, whenever possible, be sterilized immediately by autoclaving. It therefore needs to be packaged in bags that are compatible with the proposed treatment process.

4.6 Transport to the intermediate storage area

- Once the primary containers are full they must be taken to an intermediate storage area;
- Establish a designated storage area following the WHO recommendations where access is only allowed for authorized personnel;
- Personnel handling the waste must wear protective clothing (gloves, shoes) during collection, transportation and storage;
- Clear transport routes and times;
- No compaction of containers containing sharps or other infectious waste should take place;
- No manual sorting of infectious waste fractions.

5. Applied techniques for the incineration of health-care waste

5.1 Process description

Open burning of health-care wastes should not be carried out. Incineration is an important method for the treatment and decontamination of biomedical and health-care waste. This subsection gives guidance on the incineration of the following (mostly) hazardous waste fractions: infectious health-care waste, biological health-care waste and sharps.

Incineration is a high-temperature (850º to 1,100º C) dry oxidation process that reduces organic and combustible waste to inorganic, incombustible matter and results in a very significant reduction of waste volume and weight.

Pyrolysis is a process of smouldering whereby thermal conversion occurs in an oxygen-deficient atmosphere at a temperature between 500° and 600° C.

Incineration or pyrolysis should only be carried out in well-designed operated and maintained plants. The system should be designed to cope with the specific characteristics of hazardous health-care waste (high water content, high plastic content). As the following technologies are rather sophisticated only hazardous waste fractions should be burnt in these plants. Other health-care waste that is similar to municipal waste should be segregated in advance and be subject to different waste treatment technologies.

If infectious waste is not burnt immediately (during 48 hours) it must be deposited in a cooled storage room (10° C maximum). Working and storage areas should be designed to facilitate disinfection.

An incineration plant basically consists of the following units (Figure 2):

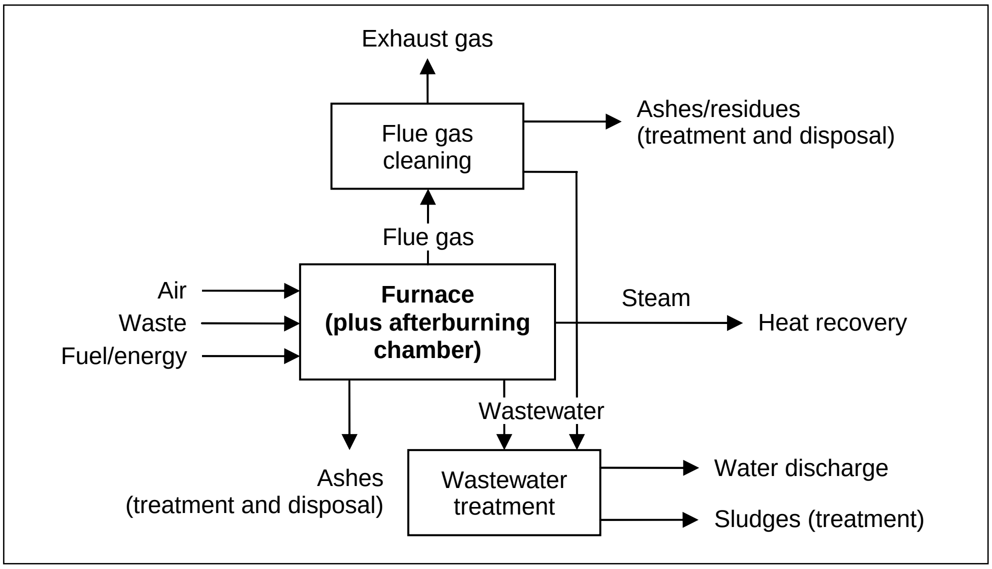
- Furnace or kiln;
- Afterburning chamber;
- Dry, wet and/or catalytic flue gas cleaning devices (including adsorption techniques);
- Wastewater treatment plant (in case wet systems are used for flue gas treatment).

The following technologies are considered best available techniques for the thermal treatment of health-care waste:

- Pyrolytic treatment or gasification of wastes;
- Rotary kiln;
- Grate incinerator specially adapted for infectious health-care waste (municipal waste disposal line);
- Fluidized bed incinerator;
- Modular systems.

Single-chamber, drum and brick incinerators are not considered best available techniques.

Figure 2. Simplified flow scheme of an incinerator



5.2 Thermal treatment techniques

5.2.1 Pyrolysis plants

Pyrolysis plants with afterburning chambers are usually small plants operating in a discontinuous mode. Health-care waste is packed in barrels or bags for charging. Larger plants should be equipped with automatic loading devices. At plants with degassing or gasification systems, drying, degassing and gasification take place in a reactor prior to combustion.

Waste is introduced discontinuously into a distillation chamber, which is heated up to a sufficient temperature to distil the waste. Gases leaving the distillation chamber are mixed with a continuous airflow in the afterburning chamber and held at a temperature of about 900° C by co-firing of supplementary fuel. Combustion gases leaving the afterburning chamber are cooled in a downstream hot water boiler and routed to a flue gas cleaning system. The boiler converts water into steam. The steam can be used to produce electricity to run a hospital, homes or businesses. In order to ensure sufficient burnout of the ash it is fired with gas burners before it is discharged from the distillation chamber. At small plants fluctuations in throughput and variations in combusted waste content are compensated by the auxiliary fuels.

In pyrolysis plants the dust content of flue gases is small compared to conventional combustion systems. However, there is great demand for additional fuels, so that consequently high volumes of flue gas are formed.

Typical capacities (on-site treatment): 200 kg to 10 tons per day.

5.2.2 Rotary kiln

Another technology used is the rotary kiln (see also section V.A (i), paragraph 2.2 of the present guidelines). The combustion of health-care waste can be performed in either small rotary kilns (for example, in the hospital) or, more commonly, in larger plants used for the combustion of several hazardous waste fractions.

Wastes are delivered by crane from the bunker into the waste chute, which is located in front of the firing chamber. In most cases a sluice is integrated into the chute where waste can directly be fed into the rotary kiln. Highly viscous and liquid wastes can be inserted through the front wall of the rotary kiln. As a result of the slope and the rotation of the rotary kiln, wastes are transported and circulated, which leads to intensive contact with primary air that flows through the rotary kiln. In contrast to grate firings rotary kilns are closed systems. Therefore liquid and highly viscous materials can also be inserted. Exhaust gases coming out of the rotary kiln are treated in an afterburning chamber. In order to ensure the high temperatures necessary for complete destruction of organic compounds (850°–1,100° C, depending on the waste) afterburning chambers are equipped with burners that automatically start when the temperature falls below the given value.

At the end of the rotary kiln slag, either sintered or melted, arises. By dropping this into the water of the deslagging unit, granulated slag is formed. When the slag is sintered, this part of the plant is similar to that of a grate firing system. Rotary kilns and afterburning chambers are in most cases constructed as adiabatic, ceramic-lined combustion chambers. After the combustion chamber flue gases pass a void zone until a temperature of about 700° C is reached. Subsequently heating bundles such as evaporators, superheaters and feed water preheaters are arranged. The waste heat boiler and energy supply system is comparable to that of grate firing systems.

Incinerator capacities: 0.5 to 3 tons per hour (for health-care waste incineration).

5.2.3 Grate incinerator

Incineration of health-care waste in municipal waste incinerators requires special adaptations. If infectious health-care waste is to be burnt in a municipal waste incinerator it has to be disinfected and sterilized beforehand or fed into the incinerator in appropriate containers by automatic loading. Previous mixing of infectious waste with other waste types and direct handling has to be avoided. See section V.A (i) of the present guidelines for further information about municipal waste incineration.

5.2.4 Fluidized bed incinerator

Fluidized bed incinerators are widely applied to the incineration of finely divided wastes such as refuse-derived fuel and sewage sludge. The method has been used for decades, mainly for the combustion of homogeneous fuels. The fluidized bed incinerator is a lined combustion chamber in the form of a vertical cylinder. In the lower section, a bed of inert material (e.g. sand or ash) on a grate or distribution plate is fluidized with air. The waste for incineration is continuously fed into the fluidized sand bed from the top or side.

Preheated air is introduced into the combustion chamber via openings in the bed plate, forming a fluidized bed with the sand contained in the combustion chamber. The waste is fed to the reactor via a pump, a star feeder or a screw-tube conveyor. In the fluidized bed drying, volatilization, ignition and combustion take place. The temperature in the free space above the bed (the freeboard) is generally between 850° and 950° C. Above the fluidized bed material, the freeboard is designed to allow retention of the gases in a combustion zone. In the bed itself the temperature is lower, and may be around 650° C. Because of the well-mixed nature of the reactor, fluidized bed incineration systems generally have a uniform distribution of temperatures and oxygen, which results in stable operation. For heterogeneous wastes, fluidized bed combustion requires a preparatory process step for the waste so that it conforms to size specifications. For some waste this may be achieved by a combination of selective collection of wastes or pretreatment, such as shredding. Some types of fluidized beds (for example, the rotating fluidized bed) can receive larger particle size wastes than others. Where this is the case the waste may only require a rough size reduction, or none at all.

5.2.5 Modular systems

Modular systems are a general type of (municipal solid) waste incinerator used widely in the United States of America, Europe and Asia. Modular incinerators consist of two vertically mounted combustion chambers (a primary and secondary chamber). In modular configurations combustion capacity typically ranges from 1 to 270 tons per day. There are two major types of modular systems, excess air and starved air:

- The modular excess air system consists of a primary and a secondary combustion chamber, both of which operate with air levels in excess of stoichiometric requirements (i.e., 100–250% excess air);
- In the starved (or controlled) air type of modular system, air is supplied to the primary chamber at substoichiometric levels. The products of incomplete combustion entrain in the combustion gases that are formed in the primary combustion chamber and then pass into a secondary combustion chamber. Excess air is added to the secondary chamber, and combustion is completed by elevated temperatures sustained with auxiliary fuel (usually natural gas). The high, uniform temperature of the secondary chamber, combined with the turbulent mixing of the combustion gases, favours low levels of particulate matter and organic contaminants being formed and emitted.

5.3 Flue gas cleaning

Flue gases from incinerators contain fly ash (particulates) contaminated with metals, PCDD/PCDF, thermally resistant organic compounds, and gases such as nitrogen oxides, sulphur oxides, carbon oxides and hydrogen halides. Flue gases resulting from uncontrolled batch mode (no flue gas cleaning) will contain around 2,000 ng I-TEQ/m³ (UNEP 2005).[3]

Appropriate flue gas cleaning measures have to be combined in a suitable manner to ensure the application of best available techniques (see section III.C (iv) and also V.A. (i) 6.4 of the present guidelines).

5.4 Fly and bottom ash treatment, wastewater treatment

The main waste fractions are fly ash, slag, filter cake from the wastewater treatment, gypsum and spent activated carbon. These wastes are predominantly hazardous wastes and have to be disposed of in safe landfills. Landfilling in proper double-walled containers, solidification and subsequent landfilling, and thermal post-treatment are the most common methods (see also section V.A (i), subsection 5 of the present guidelines).

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[3] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

6. Best available techniques and summary of best environmental practices

In addition to applying best environmental practices to the incineration of medical waste there is a variety of demonstrated combustion engineering, flue gas cleaning and residue management techniques that are available for preventing the formation or minimizing the releases of chemicals listed in Annex C. For a detailed analysis of what represents best available techniques for waste incineration reference should be made to the European Commission BAT Reference (BREF) Document on waste incineration (European Commission 2006).

There are also non-incineration technology options (see section III.C (ii) of the present guidelines) that may represent feasible and environmentally sound alternatives to incineration. The purpose of this subsection, however, is to identify the best techniques applicable to the process of incineration. Best available techniques for incineration include the design, operation and maintenance of a waste incineration plant that effectively minimizes the formation and release of chemicals listed in Annex C.

When considering the best available techniques described here for waste incineration, it is important to consider that the optimal solution for a particular type of incineration installation varies according to local conditions. The best available techniques provided here are not intended as a checklist indicating the best local solution, as this would require the consideration of local conditions to a degree that cannot be described in a document dealing with best available techniques in general. Hence, the simple combination of the individual elements described here as best available techniques, without consideration of local conditions, is not likely to give the optimized local solution in relation to the environment as a whole (European Commission 2006).

The use of best available techniques in incinerators will also reduce emissions of hydrochloric acid and metals (in particular mercury). Appropriate treatment of bottom ashes and residues from flue gas cleaning is essential for the reduction of PCDD/PCDF releases into the environment and will reduce subsequent releases from residues disposed of into landfills.

With regard to incineration, primary measures alone will significantly reduce emission of the chemicals listed in Annex C of the Stockholm Convention. However, implementation of best available techniques requires both primary and secondary measures. With a suitable combination of primary and secondary measures, PCDD/PCDF performance levels in air emissions no higher than 0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluents, are associated with PCDD/PCDF concentration levels well below 0.1 ng I-TEQ.

A summary of what constitutes best environmental practice and best available techniques for medical waste incineration is presented in the tables below.

Table 1. General guidance

Measure	Description	Considerations	Other comments
Segregation of waste	Clear classification, segregation at source of health-care waste from other waste and within the health-care waste category to minimize the amount of waste to be treated		Can be directly effective for reduction of chemicals listed in Annex C but part of an integrated concept for the management of waste
Alternative processes	In particular, if performance requirements cannot be met by the	Alternative processes to incineration of infectious	

Measure	Description	Considerations	Other comments
	existing or planned facility, priority consideration should be given to alternative processes with potentially less environmental impacts than waste incineration	health-care waste include: • Steam sterilization • Advanced steam sterilization • Microwave treatment • Dry heat sterilization • Biological treatment • Alkaline hydrolysis • Landfill	

Table 2. Health-care waste incineration: Firing technologies representing best available techniques

Technology	Considerations	Other comments
Pyrolysis plants	Suitable for smaller plants (200 kg/day to 10 tons/day) and on-site treatment	High investment and maintenance costs, well-trained personnel required
Rotary kiln	Suitable for medium-sized plants (0.5–3 tons/hour)	Use of water cooling for rotary kilns, high investment and maintenance costs, well-trained personnel required, high energy consumption
Incinerator with grate (municipal waste incinerator)		Use of water cooling for grates, incineration in municipal waste incinerators requires special adaptations for health-care waste (e.g. automatic loading), no previous mixing or direct handling of infectious health-care waste
Fluidized bed incinerator		
Modular systems	Ranges from 1 to 270 tons per day	

Table 3. Health-care waste incineration: General measures

Management options	Release characteristics	Other considerations
No burning of waste unless specific measures for reduction of chemicals listed in Annex C are taken (both primary and secondary measures, as appropriate; see Tables 5 and 6))	Possible releases of Annex C compounds and volatile metals	Be aware of possible halogen content in the waste and take the appropriate primary and secondary measures (see Table 5 and 6). Be aware of possible heavy metal content in the waste and take appropriate secondary measures (see Table 6).
Appropriate transport, storage and security of health-care waste according to the needs of types of waste	Not directly effective for reduction of chemicals listed in Annex C but part of an	

Management options	**Release characteristics**	**Other considerations**
	integrated concept for the management of waste	
Location of the plant: Centralized incineration units are preferred to decentralized on-site treatment of hazardous health-care waste		
Incineration of health-care waste only in dedicated plants or in larger incinerators for hazardous waste		The characteristics of health-care waste (high water and plastics content) require special equipment
If a dedicated health-care waste incinerator is not used a separate charging system for infectious waste should be applied	Not directly effective for reduction of chemicals listed in Annex C but part of an integrated concept for the management of waste	
Do not burn radioactive waste	Not effective for reduction of chemicals listed in Annex C	

Table 4. Health-care waste incineration: Organizational measures

Measure	Considerations
• Well-trained personnel • Operation and monitoring of the incinerator by periodic maintenance (cleaning of combustion chamber, declogging of air inflows and fuel burners, personnel should wear protective clothing) • Regular and/or continuous measurement of the relevant pollutants • Development of environmental monitoring (establishing standard monitoring protocols) • Development and implementation of audit and reporting systems • General infrastructure, paving, ventilation • Environmental impact assessment, public hearings and community input prior to siting of new incinerators	Operation of incinerators requires qualified incinerator operators. It should be remembered that qualified operators should be available for the whole operating period of the incinerator (i.e. 20 and more years as a rule). The availability of such operators in certain regions should be verified before purchasing high-technology incinerators. If qualified operators are not available, health-care establishments should either resort to alternative health-care waste disinfection technologies or contract the incineration out through a regional facility. In a similar way long-term contracts should be signed about issues such as maintenance and repair, retrofitting (if necessary) and final treatment and disposal of solid residues generated by incineration.

Table 5. Primary measures and process optimization to reduce PCDD/PCDF emissions

Management options for optimization of combustion conditions	Other considerations
Introduction of the waste into the combustion chamber only at temperatures of 850° C; plants should have and operate an automatic system to prevent waste feed before the appropriate temperature is reached	Retrofitting of the whole process needed
Installation of auxiliary burners (for start-up and close-down operations)	
In general, avoidance of starts and stops of the incineration process	
Avoidance of temperatures below 850° C and cold regions in flue gas	
Sufficient oxygen content; control of oxygen input depending on the heating value and consistency of feed material	At oxygen content: 6% vol.
Sufficient residence time (minimum 2 sec.) in a secondary combustion chamber after the last injection of air and temperature above 850° C (1,100° C for highly chlorinated wastes, i.e. wastes with more than 1% halogenated organic substances) and 6% O_2	Sufficient residence time is required especially because of the plastic and water content of the waste
High turbulence of exhaust gases and reduction of air excess: e.g. injection of secondary air or recirculated flue gas, preheating of the air streams, regulated air inflow	Optimized air inflow contributes to higher temperatures
(Online) monitoring for combustion control (temperature, oxygen content, CO, dust), operation and regulation of the incineration from a central console	

Table 6. Secondary measures

Management options	Release characteristics	Applicability	Other considerations
Dedusting			
Avoiding particle deposition by soot cleaners, mechanical rappers, sonic or steam soot blowers, frequent cleaning of sections that are passed by flue gas at the critical temperature range			Steam soot blowing can increase PCDD/PCDF formation rates
Effective dust removal by the following measures:	< 10 % remaining emission in comparison to uncontrolled mode	Medium	Removal of PCDD/PCDF adsorbed onto particles
Fabric filters	1–0.1% remaining emission	Higher	Use at temperatures < 260° C (depending on material)
Ceramic filters			Emerging technique;Use at temperatures 800°–1,000° C, not common for waste incinerators
Cyclones (only for precleaning of flue gases)	Low efficiency	Medium	Only efficient for larger particles
Electrostatic precipitation	Medium efficiency		Use at a temperature of 450° C; promotion of de novo synthesis of PCDD/PCDF possible, low efficiency for fine particles, higher NO_x emissions, reduction of heat recovery
High-performance adsorption unit with added activated charcoal particles (electrodynamic venturi)			For fine dust removal
Reduction of emissions of chemicals listed in Annex C by:			
Catalytic oxidation	High efficiency (< 0.1 ng TEQ/m^3)	High investment, low operating costs	Only for gaseous compounds, previous removal of heavy metals and dust necessary, additional NO_x reduction if NH_3 is added; high space demand, catalysts can be reprocessed by manufacturers in most cases, overheating when too much CO present, higher energy consumption due to reheating of flue gas; no solid residues
Gas quenching			Not common in waste incinerators
Fabric filter coated with catalyst	High efficiency (< 0.1 ng TEQ/m^3)		e.g. made from PTFE, with parallel dedusting, lower contamination of filter dusts because of PCDD/PCDF destruction at the catalytic surface
Different types of wet and dry adsorption			

methods with mixtures of activated charcoal, open hearth coke, lime and limestone solutions in fixed bed, moving bed and fluidized bed reactors:			
Fixed bed reactor, adsorption with activated charcoal or open hearth coke	< 0.1 ng TEQ/m^3	High investment, medium operating costs	High demand of space, disposal of solid residues from flue gas cleaning (= hazardous waste) necessary, permanent monitoring of CO necessary, increase of dust emissions due to aggregation with coal particles possible, consumption of open hearth coke in comparison with activated charcoal 2 to 5 times higher, incineration of used adsorption agent in the plant possible, fire/explosion risk
Entrained flow or circulating fluidized bed reactor with added activated coke/lime or limestone and subsequent fabric filter	< 0.1 ng TEQ/m^3	Low investment, medium operating costs	Not common for plants burning exclusively health-care waste, disposal of solid residues from flue gas cleaning (= hazardous waste) necessary, fire/explosion risk
Appropriate fly and bottom ash and wastewater treatment: • Disposal in safe landfills (e.g. underground disposal) • Catalytic treatment of fabric filter dusts under conditions of low temperatures and lack of oxygen • Scrubbing of fabric filter dusts by the 3-R process (extraction of heavy metals by acids) • Combustion for destruction of organic matter (e.g. rotary kiln, Hagenmeier-Trommel) with subsequent fabric filter, scrubber • Vitrification of fabric filter dusts or other immobilization methods (e.g. solidification with cement) and subsequent landfilling • Application of plasma technology (emerging technique)			Sludges from wastewater treatment and from cooling of fly ash are hazardous waste. Flue gas can be lead back into the combustion chamber of the incinerator

7. Performance levels associated with best available techniques

With a suitable combination of primary and secondary measures, PCDD/PCDF performance levels in air emissions no higher than 0.1 ng I-TEQ/Nm^3 (at 11% O_2) are associated with best available techniques. It is further noted that under normal operating conditions emissions lower than this level can be achieved with a well designed waste incineration plant.

Best available techniques for discharges of waste water from effluent treatment plants, receiving flue gas treatment scrubber effluents, are associated with PCDD/PCDF concentration levels well below 0.1 ng I-TEQ/l.

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Part II Source category (b): Cement kilns firing hazardous waste

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B. Cement kilns firing hazardous waste

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V.B. Cement kilns firing hazardous waste

Summary

The main purpose of cement kilns is clinker production. Firing wastes in cement kilns aims at energy recovery and substitution of fossil fuels or substitution of minerals. In some cases hazardous wastes are disposed of in these installations.

The manufacturing process includes the decomposition of calcium carbonate ($CaCO_3$) at about 900° C to calcium oxide (CaO, lime) (calcination) followed by the clinkering process at about 1450C° in a rotary kiln. The clinker is then ground together with gypsum and other additives to produce cement. According to the physical and chemical conditions the main process routes for the manufacture of cementare termed dry, wet, semi-dry and semi-wet.

The combustion process in the kiln, has the potential to result in the formation and subsequent release of chemicals listed in Annex C of the Stockholm Convention. In addition, releases from storage sites may occur.

Well-designed process conditions, and the installation of appropriate primary measures, should enable cement kilns firing hazardous waste to be operated in such a manner that the formation and release of chemicals listed in Annex C can be minimized sufficiently to achieve concentrations of PCDD and PCDF in flue gases of < 0.1 ng I-TEQ/Nm^3 (oxygen content 10%), depending on such factors as the use of clean fuels, waste feeding, temperature and dust removal. Where necessary, additional secondary measures to reduce such emissions should be applied.

Many data on PCDD/PCDF emissions to air are available

PCDD/PCDF releases via cement kiln dust and possibly clinker have been reported and are currently under further investigation. Data on PCB and HCB releases are still scarce

The performance level associated with best available techniques and best environmental practice for control of PCDD/PCDF in flue gases is < 0.1 ng I-TEQ/Nm^3 with reference conditions of 273 K, 101.3 kPa, 10% O_2 and a dry gas basis.

Preamble

The following draft guidelines provide guidance on best available techniques and guidance on best environmental practices for cement kilns firing hazardous waste relevant to Article 5 and Annex C, Part II of the Convention. Waste may be co-processed in cement kilns either as alternative fuel or for destruction purposes. Therefore this section also considers the requirements of Article 6 of the Convention regarding destruction of wastes containing persistent organic pollutants.

In this section consideration is also given to the *General Technical Guidelines for the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with Persistent Organic Pollutants (POPs)* developed by the Parties to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal (Basel Convention Secretariat 2005). Those guidelines give guidance on the best available techniques to be applied to the destruction or irreversible transformation of persistent organic pollutants and identify cement kiln co-incineration as a process that can be used for such destruction and irreversible transformation of persistent organic pollutants in waste.

Destruction and co-incineration of wastes and hazardous wastes in cement kilns also fall within the scope of this section. It should be kept in mind when reading these guidelines that stringent definitions of the terms “waste” and “hazardous waste” do not currently exist. In the context of this guideline the term “waste” is used independent of its calorific value or its potential to substitute mineral resources.

This section addresses the issues arising from source categories in Annex C part II b: cement kilns firing hazardous wastes; and in the case of co-incineration in cement kilns of municipal wastes or sewage sludge, source category part II a.

1. Introduction

1.1 Cement industry in general

Global production of cement has consistently risen in past years, and this trend is forecast to continue. According to investigations by the cement industry, worldwide cement production in 2003 was 1,940 million tons, increasing from an estimated 1,690 million tons in 2001 and 1,660 million tons in 2002. A large part of the production is based on dry processes (de Bas 2002; DFIU/IFARE 2002).

Over the last years there has been a steady annual increase of an estimated 3.6% due to the strong demand in developing countries and countries with economies in transition. At present, of total global output, Europe has a share of 14.4%, United States of America 4.7%, rest of America 6.6%, Asia 67.5% (China 41.9%), Africa 4.1% and the rest of the world 2.7%. Cement consumption globally was estimated to be an average 260 kg per capita in 2004 (Cembureau 2004).

Cement production in Europe amounts to about 190 million tons per year. More than 75% of this output is based on dry processes, due to the increased adoption of these more energy-efficient processes for new and expanding facilities in recent years; 16% is based on semi-dry or semi-wet processes and 6% on wet processes. The typical capacity of a new European kiln is 3,000 tons of clinker per day (Wulf-Schnabel and Lohse 1999).

The Chinese cement industry produced 1, 038 million tons of cement in 2005 (808 kg per capita; 45.4% of world production)[1]. Approximately 60% was produced in 4,000 vertical shaft kilns (Karstensen 2006a).

In the United States the average kiln produces 468,000 tons per year (2002 figures). Currently, about 81% of the cement produced in the United States is manufactured using dry process technology (Portland Cement Association website).

Traditionally, the primary fuel used in cement kilns is coal. A wide range of other fuels is or has been also used, including petroleum coke, natural gas and oil (European Commission 2001). In Europe the specific energy consumption of the cement industry has been reduced by about 30% over the past 20 years (equivalent to approximately 11 million tons of coal per year) (Cembureau 2004). It is not uncommon for kilns to be capable of multifuelling and for fuels to be changed from time to time based on the prevailing costs of different fuels.

1.2 Firing of waste in cement kilns

In addition to conventional fuels mentioned in section 1.1, the cement industry uses various types of waste as a fuel. In the European cement industry the consumption of waste as a fuel amounts to about 6 million tons, which corresponds to a thermal substitution rate of 18% (Cembureau 2004).

Furthermore, cement kilns can contribute to the destruction of waste, including hazardous waste, some with little or no useful energy or mineral content. This may be done at the request of national governments or in response to local demand. In a well-controlled facility high destruction efficiency of organic compounds present in such wastes can be achieved.

This co-processing of hazardous waste can only be done if certain requirements with respect to input control (for example of heavy metal content, heating value, ash content, chlorine content), process control and emission control are met, as outlined below.

However, it must be reiterated that cement kilns are primarily production processes for clinker, and not all operating conditions that may produce satisfactory clinker product are ideal for the destruction

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[1] Communication of CEMBUREAU (2006).

of wastes; for example, cement kilns tend to operate at lower exhaust oxygen levels and more elevated carbon monoxide levels than well-operated incinerators. Destruction of organic wastes requires not only high temperature and long residence time, but also the availability of adequate oxygen and sufficient mixing between the organic compounds intended for destruction and the oxygen. Conditions can arise where wastes are not destroyed adequately if waste is not introduced properly to the kiln or available oxygen levels are too low. Good design and operation are critical to the use of cement kilns for this application.

It should be emphasized that this activity is distinct from fuel or raw material substitution in the process. Cement kilns have been used in this way for many years in countries such as Japan, Norway and Switzerland, where there is little space for landfill sites. More recently, modern kilns have been used for waste destruction in some developing countries where the lack of existing waste disposal and incineration infrastructure means that kilns are the most economical and readily available option. This section aims to give guidance with respect to environmental issues that may arise in such instances. Even where good waste disposal infrastructure exists, it may be useful to supplement local capacity through use of cement kilns.

Application of approaches involving waste management, such as recycling or reprocessing, is preferable to disposal by landfill or dumping or destruction of waste in cement kilns. A case-by-case evaluation should be carried out in the context of an overall waste management strategy (see section III C (ii)).

In exceptional cases cement kilns can be used for the safe disposal of wastes that have little calorific or mineral value and do not contribute to the clinker production process. For this type of treatment, regulatory authorities and cement plant operators must come to individual agreements on a case-by-case basis.

Where cement kilns are used for the destruction of wastes, alternative disposal routes should be carefully assessed. Waste destruction in cement kilns must meet strict environmental, health and safety standards, and must not impair the quality of the final product. In countries where stringent requirements for the final product do not exist it is more important to require application of best available techniques and best environmental practices for those installations co-incinerating wastes. The process must be precisely controlled when destroying such wastes, and emissions regularly measured.

2. Links to other relevant information

Comprehensive background information on cement kiln operation in general and on the firing of waste in cement kilns can be found in:

European Commission.2001. *Reference Document on the Best Available Techniques in the Cement and Lime Manufacturing Industries*. BAT Reference Document (BREF). European IPPC Bureau, Seville, Spain[2].(http://eippcb.jrc.es/pages/FActivities.htm)

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CSI (Cement Sustainability Initiative). 2006. *Guidelines for the Selection and Use of Fuels and Raw Materials in the Cement Manufacturing Process: Fuels and Raw Materials*. World Business Council for Sustainable Development, Geneva, Switzerland.
(http://www.wbcsdcement.org/pdf/tf2/tf2_guidelines.pdf)

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[2] This Reference Document is currently (2006) under revision.

2.1 General waste management considerations (Section III.C (ii))

Society can manage wastes in a number of ways, depending on their physical and chemical nature, and on the economic, social, and environmental context in which they are produced. Some of these are listed below. Specific decisions will always be influenced by local circumstances such as the availability of waste treatment facilities, alternative markets for materials, and the infrastructure available to safely collect, manage and transport waste materials (CSI 2005). Section III C (ii) of these Guidelines, shows a hierarchy of decision-making for waste management.

2.2 Other options for treatment of waste

The use of cement kilns for the treatment of waste should be considered only as part of the general context of waste management options in a hierarchy such as that illustrated above. Waste incineration is also an option for disposal of wastes and the guidelines for best available techniques and best environmental practices for this source category should be considered when cement kilns are used in this application.

2.3 Basel Technical Guidelines

Technical Guidelines developed by the Basel Convention have to be given careful consideration as they provide guidance on best available techniques to be applied to the destruction or irreversible transformation of persistent organic pollutants as wastes.

3. Cement production processes

In this guideline the description of the cement production process is limited to the various rotary kiln process routes. It has to be kept in mind that in China most cement is produced in vertical shaft kilns which show low energy efficiency and poor environmental performance (H. Klee, World Business Council for Sustainable Development, personal communication 2004). Therefore, vertical shaft kilns should not be considered as an option for best available techniques..

3.1 General principles

The basic chemistry of the cement manufacturing process begins with the decomposition of calcium carbonate ($CaCO_3$) at about 900° C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO_2); this process is known as calcination. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically 1,400°–1,500° C) with silica, alumina and ferrous oxide to form the silicates, aluminates and ferrites of calcium that comprise the Portland clinker. This clinker is then ground together with gypsum and other additives to produce cement. Figure 1 identifies the principal processes and system boundaries of cement production.

3.2 Preparation of raw materials

Preparation of the raw material is of great importance to the subsequent kiln system both in getting the chemistry of the raw feed right and in ensuring that the feed is sufficiently fine. Accurate metering and proportioning of the mill feed components by weight is important for achieving a consistent chemical composition. This is essential for steady kiln operation and a high-quality product.

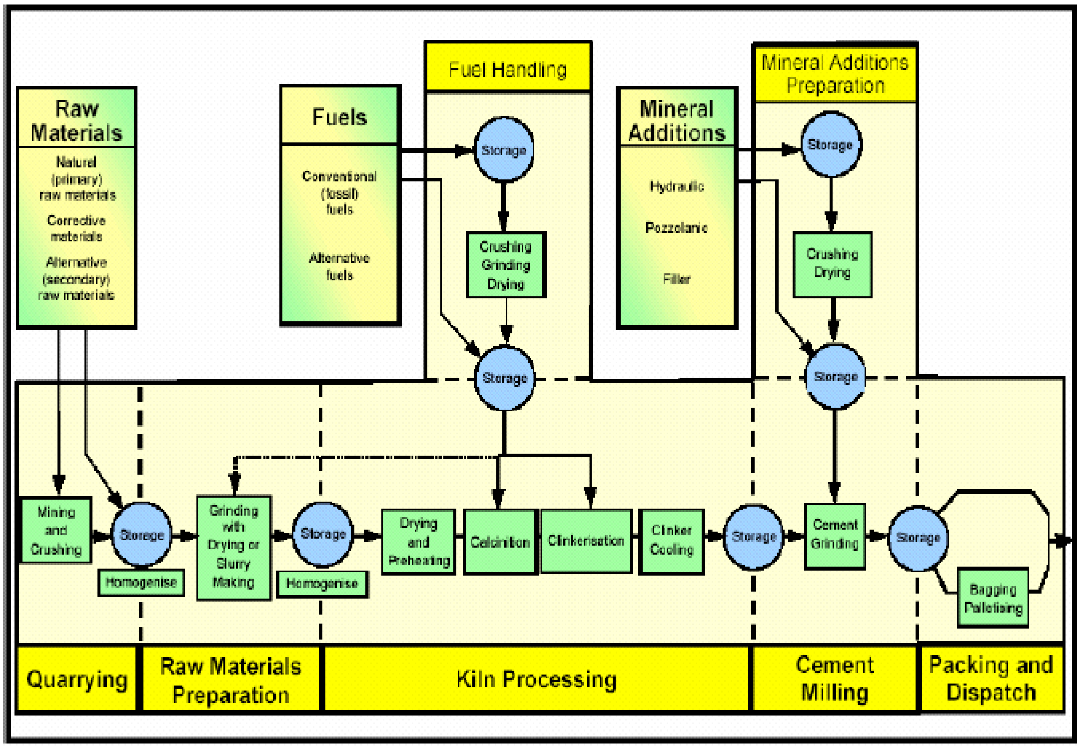
Solid fuel preparation (crushing, grinding and drying) is usually carried out on site.

The raw materials, in controlled proportions, are ground and mixed together to form a homogeneous blend with the required chemical composition. For dry and semi-dry kiln systems, the raw material components are ground and dried to a fine powder, making use mainly of the kiln exhaust gases and/or cooler exhaust air. For raw materials with a relatively high moisture content, and for start up procedures, an auxiliary furnace may be needed to provide additional heat.

Wet grinding is used only in combination with a wet or semi-wet kiln system. The raw material components are ground with added water to form a slurry. The wet process is normally preferred whenever the raw material has a moisture content of more than 20% by weight.

(European Commission 2001)

Figure 1. Process identification and system boundaries of cement production



3.3 The rotary kiln processes

The raw feed material, known as raw meal, raw mix, slurry (with a wet process) or kiln feed, is heated in a kiln, typically a large, inclined, rotating cylindrical steel furnace (rotary kiln). Kilns are operated in a countercurrent configuration. Gases and solids flow in opposite directions through the kiln, providing for more efficient heat transfer. The raw meal is fed at the upper or cold end of the rotary kiln, and the slope and rotation cause the meal to move toward the lower or hot end. The kiln is fired at the hot end, usually with coal or petroleum coke as the primary fuel. As the meal moves through the kiln and is heated, it undergoes drying and pyroprocessing reactions to form the clinker, which consists of lumps of fused, incombustible material. There are several ways of introducing the fuels (both fossil and alternative) into the kiln. This is described in more detail in paragraph 4.1 below.

The clinker leaves the hot end of the kiln at a temperature of about 1,000° C. It falls into a clinker cooler, typically a moving grate through which cooling air is blown.

Various process routes for the manufacture of cement can be followed during the pyroprocessing step to accomplish the required physical and chemical transformations. They vary with respect to equipment design, method of operation and fuel consumption.

3.3.1 The dry process

In the dry process, the raw materials are ground and dried to raw meal in the form of a flowable powder. The dry raw meal is fed to the preheater or precalciner kiln or, more rarely, to a long dry kiln. The energy efficiency of the kiln is higher if the raw meal is preheated before it enters the kiln.

3.3.1.1 The preheater dry process

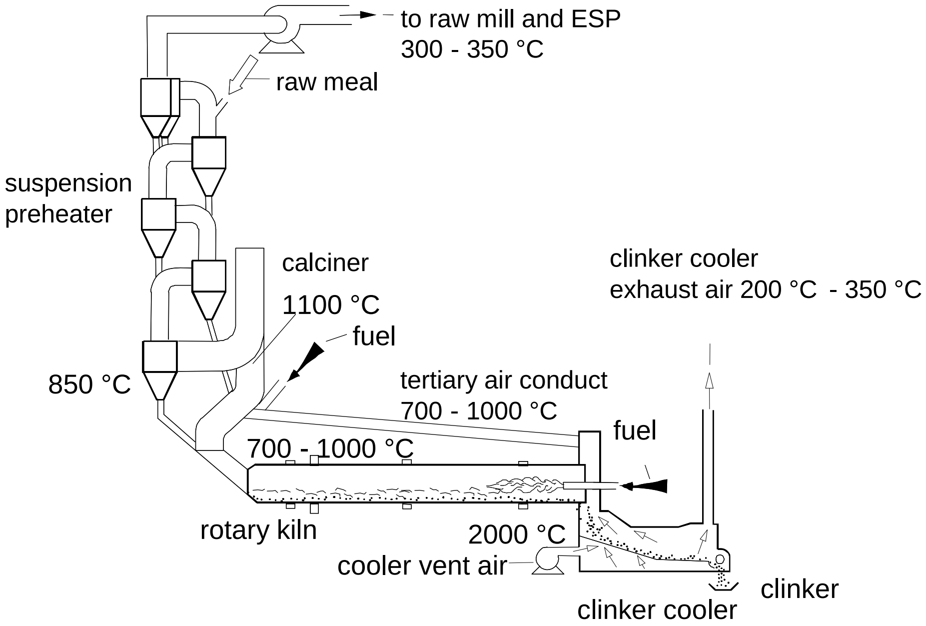
In this process preheaters are used to increase the thermal efficiency. A raw meal preheater consists of a vertical tower containing a series of cyclone-type vessels. Raw meal is introduced at the top of the tower. Hot kiln exhaust gases pass countercurrent through the downward moving meal to heat the meal prior to introduction into the kiln. The meal is separated from the kiln flue gases in the cyclone, and then dropped into the next stage. Because the meal enters the kiln at a higher temperature than with conventional long dry kilns, the length of the preheater kiln is shorter.

With preheater systems, it is sometimes necessary to remove undesirable components, such as certain alkali constituents, through an alkali bypass system located between the feed end of the rotary kiln and the preheater tower. Otherwise, these alkali constituents may accumulate in the kiln, and removal of the scale that deposits on vessel walls is difficult and may require kiln shutdown. This problem can be reduced by withdrawing a portion of the gases with a high alkali content. If this alkali bypass has a separate exhaust stack it can be expected to carry and release the same pollutants as the kiln exhaust.

3.3.1.2 The preheater/precalciner dry process

This process is similar to the preheater dry process, with the addition of an auxiliary firing system to increase the raw materials temperature prior to introduction into the kiln (Figure 2). A precalciner combustion vessel is added to the bottom of the preheater tower. The primary advantage of using the precalciner is that it increases the production capacity of the kiln, as only the clinker burning is performed there. Use of the precalciner also increases the kiln refractory lifetime due to reduced thermal load on the burning zone. This configuration may also require a bypass system for alkali control, which, if released from a separate exhaust stack, can be expected to carry and release the same pollutants as the kiln exhaust.

Figure2. Rotary kiln with suspension preheater and calciner



Note: ESP = electrostatic precipitator (dust collection device).

3.3.2 The semi-dry process

In the semi-dry process dry raw meal is pelletized with 12–14% water and fed into a grate preheater before the kiln or to a long kiln equipped with crosses, on which the pellets are dried and partially calcined by hot kiln exhaust gases before being fed to the rotary kiln.

3.3.3 The semi-wet process

In the semi-wet process the raw materials (often with high moisture content) are ground in water to form a pumpable slurry, which is then dewatered in filter presses. The filter cake is extruded into pellets and fed either to a grate preheater or directly to a filter cake dryer for raw meal production.

3.3.4 The wet process

In the wet process, the raw materials (often with high moisture content) are ground in water to form a pumpable slurry. The slurry is either fed directly into the kiln or first to a slurry dryer. The wet process is an older process used in the case of wet grinding of raw materials. It results in a higher energy demand compared to the dry process because of water evaporation from the slurry.

3.4 The cement grinding process

The clinker is ground with gypsum and other additives, usually in a ball mill, to produce the final product – cement. The cement is conveyed from the finish cement mill to large, vertical storage silos in the dispatch or shipping department. Cement is withdrawn from the cement storage silos by a variety of extracting devices and conveyed to loading stations in the plant or directly to transport vehicles.

3.5 Emission control

In general, modern cement kilns are equipped with either electrostatic precipitators or fabric filters, or both, for particulate matter control. In some cases, the flue gases are cooled prior to the dry air pollution control device. Acid gas pollution control devices have not been used at cement kilns as the raw materials are highly alkaline and provide a significant degree of acid gas control (Karstensen 2006b), although there are a number of kilns equipped with wet scrubbers, if the sulphur content of the raw meal is high.

Techniques for reduction of NO_x are mainly primary integrated methods like flame cooling, burner design, staged combustion or selective non-catalytic reduction by ammonia injection.

4. Burning

4.1 Operation with conventional fuels

Conventional fuels used in cement plants are fossil fuels such as coal, lignite, fuel oil or natural gas. These fuels can be used singly or in combination, in which case a minimum quality (in terms of heating value, heavy metal or sulphur content) must be ensured. Some of the fossil fuels (e.g. coal) are ground in mills before they are injected.

For smooth kiln operation, the production of a homogeneous clinker and complete combustion, some important criteria have to be considered for conditioning of the fuels. The oxidation of the fuel constituents occurs more quickly when the fuels are well mixed and the specific surface is larger. In the case of liquid fuel, injection has to be as smooth as possible. In the case of solid fuels, thorough mixing with other fuels used at the same time is required. This is not necessarily required as long as the material is homogenous and highly uniform.

A cement plant consumes 3,000 to 6,500 MJ (electricity and transport not included) per ton of clinker produced, depending on the raw materials and the process used. Most cement kilns today use coal and petroleum coke as primary fuels, and to a lesser extent natural gas and fuel oil. As well as providing energy, some of these fuels burn to leave fuel ash containing silica and alumina compounds (and other trace elements). These combine with the raw materials in the kiln, contributing to the structure of the clinker and forming part of the final product. Energy use typically accounts for 30–40% of the production costs. The different types of fuels, in decreasing order of importance, are:

- Pulverized coal and petroleum coke (petcoke);
- (Heavy) fuel oil;
- Natural gas.

Potential feed points for supplying fuel to the kiln system are via:

- The main burner at the rotary kiln outlet end;
- A feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
- Secondary burners to the riser duct;
- Precalciner burners to the precalciner;
- A feed chute to the precalciner/preheater (for lump fuel);
- A mid-kiln valve in the case of long wet and dry kilns (for lump fuel).

Depending on operational conditions – explicitly in the case of improper operation of the installation – significant emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) can occur. In proper operation the release of PCDD/PCDF should be well below 0.1 ng TEQ/m3.

4.2 Firing of waste or hazardous waste

The selection of wastes and materials is driven by a number of additional interrelated considerations, including:

- Impact on CO2 emissions and fuel consumption;
- Impact on fuel cost;
- Impact on other emissions such as NOx, SO2, particulates, other persistent organic pollutants, heavy metals, CO, organic substances;
- Impact on mining and quarry activity;
- Stability of kiln operation (affected by parameters such as heating value and water content);
- Impact of product quality (e.g. restriction of the chlorine content in cement: < 0.1%).

The requirements of product quality, particularly the restriction of the chlorine content of cement to 0.1%, limits firing options, and the chlorine input has to be monitored.

4.2.1 Examples of waste and alternative fuels

The substitution of fossil fuels with alternatives is a well-developed practice in a number of countries. Some countries have been using wastes as alternative fuels for almost 30 years, and some national governments actively promote this approach, provided that stringent requirements with regard to input, process and emission control are met. However, some stakeholders and other jurisdictions have viewed the practice in the same light as incineration. In the countries where this practice is well established, consideration has been given to the types of materials best suited to use in cement kilns (CSI 2005), which may include:

- Used tyres;
- Meat, bonemeal and animal fat;
- Plastics;
- Impregnated sawdust;
- Wood, paper, cardboard, packaging waste;

- Sludge (paper fibre, sewage);
- Agricultural and organic waste;
- Shale, oil shales;
- Coal slurries;
- Distillation residues;
- Fine fractions of coal or coke /anodes/chemical cokes;
- Waste oils, oiled water;
- Spent solvents.

It is important to control waste parameters (e.g. heat value, water content, ash content, content of chlorine, content of heavy metals).

4.2.2 Negative waste list

Co-processing should only be applied if not just one but all tangible preconditions and requirements of environmental, health and safety, socio-economic and operational criteria are fulfilled. As a consequence not all waste materials are suitable for co-processing. The following is a list of waste not recommended for co-processing in cement plants:

- Nuclear waste;
- Electronic waste;
- Explosives;
- Mineral acids;
- Asbestos-containing waste;
- High-concentration cyanide waste;
- Infectious medical waste;
- Chemical or biological weapons destined for destruction;
- Entire batteries;
- Unsorted municipal garbage and other waste of unknown composition.

Electronic waste is composed of computer and accessories, entertainment electronics, communication electronics, toys and also white goods such as kitchen devices or medical apparatus. The average composition shows that electronic waste contains, on the one hand, substances harmful to health and the environment such as Cl, Br, P, Cd, Ni, Hg, PCB and brominated flame retardants in high concentrations, often higher than threshold limit values. On the other hand, electronic waste contains such a high scarce precious metal content that all efforts have to be undertaken to recycle it. Co-processing of the plastic parts of electronic waste would be an interesting option, but requires disassembling and segregation first (after Holcim, 2006).

The list outlined above is not an exhaustive list. In general, wastes with a low heat value and a very high heavy metal content are not suitable for being inserted into a cement kiln. Municipal solid waste should not be co-incinerated in cement kilns due to its unpredictable composition and its characteristics. Furthermore, individual companies may exclude additional materials, depending on local circumstances.

4.2.3 Considerations for selection of wastes

The selection of wastes is a complex process and is influenced by many factors, such as kiln operation, the nature of the waste itself, the general impact on the environment, the desired clinker quality and the probability of the formation and release of chemicals listed in Annex C of the

Stockholm Convention and other releases into the environment. The operator should develop a fuels evaluation and acceptance procedure. Based on this procedure an assessment is carried out of the effect of the fuel on plant emissions and the potential need for new equipment or procedures to ensure that there is no negative impact on the environment.

The variables that should be considered when selecting fuels and raw materials include (CSI 2005):

4.2.3.1 Kiln operation

- Chlorine, sulphur, and alkali content: These may build up in the kiln system, leading to accumulation, clogging and unstable operation; excess in chlorine or alkali may produce cement kiln dust or bypass dust (and may require installation of a bypass), which must be removed, recycled or disposed of responsibly;
- Water content: High water content may reduce the productivity and efficiency of the kiln system;
- Heat value (fuel): The heat value is the key parameter for the energy provided to the process;
- Ash content: The ash content affects the chemical composition of the cement and may require an adjustment of the composition of the raw materials mix;
- Additional factors are relevant, such as treatment capacity and volume of waste gas;
- Stability of operation (e.g. CO peaks) and the state (liquid, solid), preparation (shredded, milled) and homogeneity of the waste.

4.2.3.2 Clinker and cement quality

- Phosphate content: This influences setting time;
- Chlorine, sulphur, and alkali content: These affect overall product quality;
- Thallium and chromium: in relation to cement kiln dust and cement quality and possible allergic reactions in sensitive users.

4.2.3.3 Atmospheric pollutant emissions other than chemicals listed in Annex C

- High sulphur contents in raw materials and inserted fuels and wastes: These may result in the release of SO_2;
- Control of exhaust: Where an alkali bypass system is installed, appropriate control of the exhaust to atmosphere also needs to be provided on the bypass exhaust similar to that mandated for the main exhaust stack;
- Chlorides in raw materials or fuels: These may combine with alkalis also present in the feed to form fine particulate matter composed of chlorides of those alkalis, which can be difficult to control; in some cases chlorides have combined with ammonia present in the limestone feed to produce highly visible detached plumes of fine particulate composed mainly of ammonium chloride;
- Metals in fuel or raw material: Raw materials and fuels will always contain metals in varying concentrations. The behaviour of these metals in the burning process is dependent on their volatility. Nonvolatile metal compounds remain within the process and exit the kiln as part of the cement clinker composition. Semi-volatile metal compounds are partly taken into the gas phase at sintering temperatures to condense on the raw material in cooler parts of the kiln system. This leads to a cyclic effect within the kiln system (internal cycles) which builds up to the point where an equilibrium is established and maintained between input and output via the cement clinker. Volatile metal compounds condense on raw material particles at lower temperatures and potentially form internal or external cycles, if not emitted with the flue gas of the kiln. Thallium and mercury and their compounds are particularly easily volatilised and to a lesser extent so are cadmium, lead, selenium and their compounds. (European Commission 2001).

- The metal concentration in cement kiln dust depends on the feedstock and recirculation in the kiln system. In particular, the use of coal and waste fuels may increase the input of metals into the process. Dust control devices can only capture the particle-bound fraction of heavy metals. The retention rate for the gaseous fraction of volatile metals such as mercury is low. Such inputs into the kiln system should therefore be limited. This needs to be taken into account as soon as wastes containing volatile heavy metals such as mercury, lead or cadmium are co-incinerated. Wood treated with copper, chromium, arsenic etc. also requires special consideration with regard to the efficiency of the flue gas cleaning system.
- The choice of fuels can also affect greenhouse gas emissions. For example, substituting fossil fuels by biomass results in a decrease of net CO_2 emissions;
- Wastes may influence NO_x emissions, depending on their composition and water content.

4.2.4 Analysis of input streams

The kiln operators should develop criteria for acceptance of raw materials including wastes and should carry out an ongoing evaluation procedure that includes the following features:

- Name and address of the deliverer/supplier, origin of the waste, volume, water and ash content, calorific value, concentration of chlorides, fluorides, sulphur and heavy metals;
- Each material supplier should be required to provide, initially and periodically thereafter, representative samples of the fuel, which will be used to evaluate the fuel before it is delivered to the plant;
- The supplier should also be required to include a datasheet detailing the chemical and physical properties of the fuel being supplied, and information on relevant health, safety and environmental considerations during transport, handling and use;
- The sample’s physical and chemical characteristics should be tested and checked against specifications.

A clear system for the management of quality assurance and quality control has to be implemented, including periodic sampling and analysis of the materials actually delivered to the plant and verification that levels of contaminants of concern remain within the established specifications.

4.2.5 Pretreatment and storage for use of waste as alternative fuel

The storage requirements for waste depend on the type of materials. In general, care has to be taken to minimize emissions of pollutants, and to address technical and hygienic concerns.

As regards initial storage, materials strongly contaminated (e.g. with substantial biologic content) and high moisture (up to 40%) need to be stored in specially designed containers due to hygienic concerns. Animal meal has to be conditioned in absolutely closed systems. It is supplied in containers, and the material is conveyed either pneumatically or by mechanical equipment into storage. Liquid waste (waste oil, solvents) needs to be stored in special containers designed to resist leakage and explosion hazards. Special security precautions have to be developed and implemented (taking into account, for example, risk of explosion).

Intermediate storage at the conditioning plant aims at checking the quality of the waste-derived fuels after the preparation process. Here, containers are normally used.

Initial storage and preparation of different types of waste for use as fuel is usually performed outside the cement plant by the supplier or by waste treatment specialist organizations. Such centralized solutions can be of benefit to kiln operators, whose primary task is to produce clinker for cement production. However, due diligence mandates that such fuels should be subjected to quality assurance measures by the receiving facility. This means only the separated and pretreated waste fractions need to be stored at the cement plant and then proportioned for feeding to the cement kiln. Since supplies of waste suitable for use as fuel tend to be variable whilst waste material markets are rapidly developing, it is advisable to design storage and preparation plants as multipurpose (Karstensen 2006b). Measures have been initiated (2003) in the European Union to standardize solid recovered fuels derived from non-hazardous waste.

Mixing of waste with the aim of meeting certain requirements, but resulting in concealment of environmental impact by dilution of concentrations, cannot be considered as acceptable practice.

4.2.6 Destruction efficiency

The co-processing of hazardous waste can only be done if certain requirements with respect to input control, process control and emission control are met. One of these process parameters is the oxygen content in the exhaust gases. Destruction of organic wastes requires not only high temperature and long residence time, but also the availability of adequate oxygen, proper introduction into the kiln of the organic compounds intended for destruction, and sufficient mixing of the compounds and the oxygen. Good design and operation are crucial to the use of cement kilns for this application.

Many cement kilns co-process waste commercially (i.e., they accept waste from off-site generators), in most cases for use as a fuel substitute in the production of Portland cement clinker. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. For long kilns, this means that the solid waste is introduced mid-kiln, and for preheater/precalciner kilns it is introduced onto the feed shelf in the high-temperature section.

In the case of hazardous wastes, complete destruction of combustible toxic compounds such as halogenated organic substances has to be ensured. Wastes that are fed through the main burner will be destroyed in the primary burning zone at a flame temperature of > 1,800° C. Waste fed to a secondary burner, preheater or precalciner will be exposed to lower temperatures, though expected burning zone temperatures in the precalciner are typically > 1,000° C.

Volatile components in material that is fed at the upper end of the rotary kiln or as lump fuel can evaporate or evolve by pyrolysis and be released from the stack without being combusted, since kiln operation is countercurrent. Batch wastes injected at mid or feed-end locations do not experience the same exceptionally elevated temperatures as do liquid wastes introduced at the hot end. In some situations, volatile organic compounds may be released from the charge so rapidly that they are not able to mix with oxygen and ignite before they cool below a critical temperature, forming products of incomplete combustion. CO sensors installed for process control can detect incomplete combustion and allow corrective measures to be undertaken.

The hazardous waste used as a fuel by the cement industry consists mainly of organic material, but may also contain varying amounts of metal components. To determine whether or not a cement kiln can burn hazardous waste fuel effectively, the fate of the organic constituents must be determined.

Testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of combusting wastes in cement kilns was first considered. The destruction and removal efficiency for chemicals such as methylene chloride, carbon tetrachloride, trichlorobenzene, trichloroethane and polychlorinated biphenyls (PCB) has typically been measured at 99.995% and better (Karstensen 2006b).

The potential use of cement kilns to incinerate wastes containing PCB has been investigated in many countries. The destruction and removal efficiencies determined from several trial burns indicate that well-designed and operated cement kilns are effective at destroying PCB. A destruction and removal efficiency of 99.9999% is required by several jurisdictions (e.g. United States Toxic Substances Control Act, Canadian Federal Mobile PCB Treatment and Destruction Regulations) for the incineration of these compounds, which could be used as an indicative best available technique standard.

5. Process inputs and outputs

5.1 General outputs

The main environmental issues associated with cement production are emissions to air, energy use, and soil and groundwater contamination from the handling and storage of waste cement kiln dust.

Wastewater discharges are usually limited to surface run-off and cooling water and generally do not contribute substantially to water pollution.

Primary process outputs of cement production are:

- Product: Clinker, which is ground and then mixed with other ingredients to produce cement;
- Kiln exhaust gas: Typical kiln exhaust gas volumes range between 1,700 and 2,500 m^3/Mg of clinker (cubic metres per metric ton of clinker; reference conditions 101.3 kPa, 273 K, dry gas basis) for all types of kilns. Suspension preheater and precalciner kiln systems normally have exhaust gas volumes around 2,000 m^3/Mg of clinker (dry gas, 101.3 kPa, 273 K);
- Cement kiln dust (collected in the air pollution control equipment): In the United States, some 64% of cement kiln dust is recycled back into the kiln and the remainder, which is generated at the rate of about 40 kg/ton of clinker, is primarily buried in landfills (WISE 2002; EPA 2000). Holcim, one of the world’s largest cement producers, sold or landfilled 29 kg of cement kiln dust per ton of clinker in 2001 (Holcim website);
- Recycling cement kiln dust to the kiln generally results in a gradual increase in the alkali content of generated dust, which may lead to damage to kiln linings, produce inferior cement and increase both stack particle emissions (EPA 1998b) and the amount of cement kiln dust that must be disposed of and the resulting air emissions due to its handling and disposal (EPA 1998a). In Europe cement kiln dust is usually circulated back to the kiln feed material or added directly to the product cement (Lohse and Wulf-Schnabel 1996). The build up of alkalis in the kiln system may be avoided by either removal of the collected kiln dust or by using an alkali bypass system. For preheater and precalciner kilns, this is sometimes accomplished by alkali bypass systems at the preheater tower that removes alkalis from the kiln system;
- Alkali bypass exhaust gas: At facilities equipped with an alkali bypass, the alkali bypass gases can be released either from a separate exhaust stack or from the main kiln stack. According to the United States Environmental Protection Agency, the pollutants in this gas stream are similar to those in the main kiln exhaust gases and similar pollution abatement equipment and monitoring is required (EPA 1999). An alkali bypass ratio of more than 10% is commonly required for alkali removal (Sutou, Harada and Ueno 2001). However, a bypass ratio of 30% has also been reported (Holsiepe, Shenk and Keefe 2001).

5.2 Energy use

The cement industry is an energy-intensive industry where energy typically accounts for 30–40% of operating costs (i.e., excluding capital costs). A cement plant consumes 3,000 to 6,500 MJ of fuel per ton of clinker produced. This large range of energy demand covers all kinds of cement kilns.

The theoretical energy use for the burning process (involving chemical reactions) is about 1,700 to 1,800 MJ per ton of clinker. The actual fuel energy use for different kiln systems is in the following ranges (MJ per ton of clinker)[3]:

- 3,000–3,800 for dry process, multistage cyclone preheater and precalciner kilns;
- 3,100–4,200 for dry process rotary kilns equipped with cyclone preheaters;
- 3,300–4,500 for semi-dry/semi-wet processes (Lepol kiln);
- Up to 5,000 for dry process long kilns;
- 5,000–6,000 for wet process long kilns;
- 3,100 to > 6,500 for shaft kilns and for special cements.

The electricity demand is about 90–130 kWh per ton of cement (European Commission 2001).

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[3] CEMBUREAU contribution to Cement & Lime BREF Revision Energy Efficiency; 15 May 2006

To optimize the input of energy in existing kiln systems it is possible to change the configuration of the kiln to a short dry process kiln with multistage preheating and precalcination. This is usually only feasible as part of a major upgrade with an attendant increase of production.

Electrical energy use can be minimized through the installation of power management systems and the utilization of energy-efficient equipment such as high-pressure grinding rolls for clinker communition and variable speed drives for fans.

Energy efficiency will generally be decreased by the addition of most types of end-of-pipe abatement, since their operation usually requires an increment in electrical energy use. Some of the reduction techniques described below will have a positive effect on energy use, for example process control optimization.

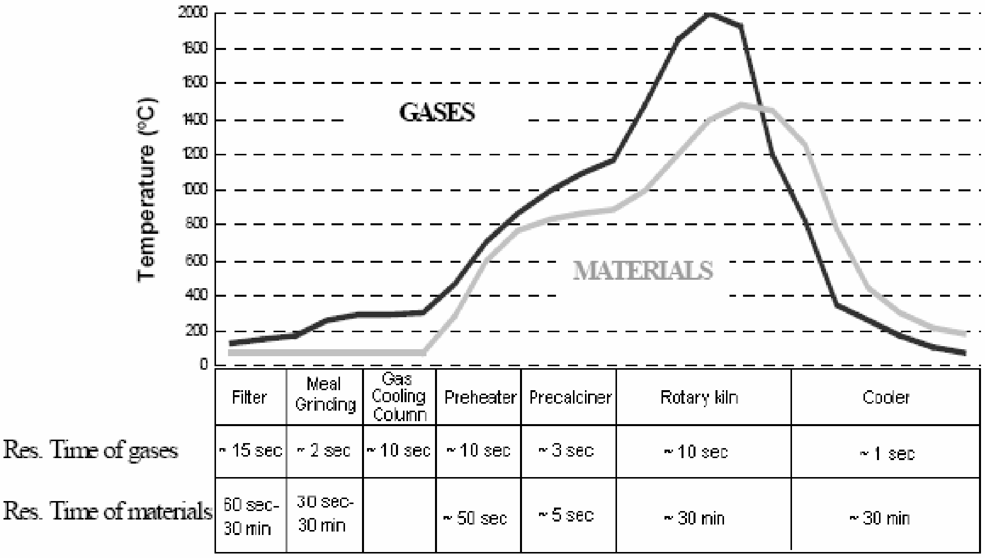
Current estimates suggest that the cement industry can increase its energy efficiency by 0.5–2% per year by replacing old or outdated equipment. If new dry process plants replace older wet process units, significant energy efficiency gains are possible (CSI 2005).

5.3 Emissions of PCDD/PCDF

5.3.1 Formation of PCDD/PCDF

Any chlorine input in the presence of organic material may potentially cause the formation of PCDD and PCDF in heat (combustion) processes. PCDD/PCDF can be formed by the de novo synthesis mechanism in or after the preheater and in the air pollution control device if chlorine and hydrocarbon precursors are available in sufficient quantities in the temperature range 200º C to 450º C. A graph of the temperature profile for gases and materials and their typical residence times in each stage of a clinker kiln with cyclonic preheater and precalciner is shown in Figure 4 (Fabrellas et al. 2004).

Figure 3. Temperature profile and typical residence time stages of clinker kiln with cyclonic preheater and precalciner



	Filter	Meal Grinding	Gas Cooling Column	Preheater	Precalciner	Rotary kiln	Cooler
Res. Time of gases	~ 15 sec	~ 2 sec	~ 10 sec	~ 10 sec	~ 3 sec	~ 10 sec	~ 1 sec
Res. Time of materials	60 sec- 30 min	30 sec- 30 min		~ 50 sec	~ 5 sec	~ 30 min	~ 30 min

Source: Fabrellas et al. 2004.

5.3.2 Studies on emissions of PCDD/PCDF into air

A comprehensive survey of PCDD/PCDF emissions from cement kilns in developed and developing countries is given in (Karstensen 2006). The data represents more than 2200 measurements in kilns with and without the firing of a wide range of waste materials and covering the period from early 1990'ies until recently. Table 1 summarizes the results of the PCDD/PCDF measurements; some examples are described in more detail hereunder.

Table 1. Summary of PCDD/PCDF measurement data

Country or company	Use of alternative fuel and raw materials?	Concentration, in ng I-TEQ/m^3, of PCDD/PCDF[a]	Number of measurements	Emission factor µg I-TEQ/ton cement[a]
Australia	Yes	0.001–0.07	55	0.0032–0.216
Belgium	Yes	< 0.1	23	
Canada	Yes	0.0054–0.057	30	
Chile	Yes	0.0030–0.0194	5	
Colombia	Yes	0.00023–0.0031	3	
Denmark	Yes	< 0.0006–0.0027	?	
Egypt	Yes	< 0.001	3	
Europe	Yes	< 0.001–0.163	230	< 0.001–5
Germany 1989–1996	Yes	0.02	> 150	
Germany 2001	Yes	< 0.065	106	
Holcim 2001	Yes	0.0001–0.2395	71	0.104 (clinker)
Holcim 2002	Yes	0.0001–0.292	82	0.073 (clinker)
Holcim 2003	Yes	0.0003–0.169	91	0.058 (clinker)
Heidelberg	Yes	0.0003–0.44	> 170	
Japan	Yes	0–0.126	164	
Lafarge	Yes	0.003–0.231	64	
Mexico	Yes	0.0005–0.024	3	
Norway	Yes	0.02–0.13	> 20	0.04–0.40
Philippines	Yes	0.0059–0.013	5	
Poland	Yes	0.009–0.0819	7	
Portugal		0.0006–0.0009	4	
RMC	Yes	0.0014–0.0688	13	
Siam Cement Co.	Yes	0.0006–0.022	4	
South Africa	(Yes)	0.00053–0.001	2	
Spain	Yes	0.00695	89	0.014464
Spain Cemex	Yes	0.0013–0.016	5	
Spain Cimpor	Yes	0.00039–0.039	8	
Taiheiyo	Yes	0.011	67	
Thailand	Yes	0.0001–0.018	12	0.00024–0.0045
UK	Yes	0.012–0.423	14	< 0.025–1.2
Uniland		0.002–0.006	2	0.005–0.011
USA[b]	Yes	0.004– ~ 50	~ 750	< 0.216–16.7
Venezuela	Yes	0.0001–0.007	5	
Vietnam		0.0095–0.014	3	

a. The numbers are either given as a range or as the mean value, and refer to 10 or 11% O_2, depending on national regulations.

b. The high numbers from the United States relate to measurements obtained in the 1990s; the number of measurements is approximate.

Source: Karstensen 2006b.

In a recent survey performed by Cembureau, PCDD and PCDF measurements from 110 cement kilns in 10 countries were presented. The countries covered by the survey were Czech Republic, Denmark, France, Germany, Hungary, Italy, the Netherlands, Norway, Spain and the United Kingdom. The average concentration, taking into account all of the data in this dataset, was 0.016 ng I-TEQ/m^3. The range between the lowest and highest concentrations measured was < 0.001 to 0.163 ng I-TEQ/m^3 (Karstensen 2006b). All measurements were expressed corrected to standard conditions (dry gas, 273 K, 101.3 kPa and 10% O_2).

The Holcim Cement Company operates cement kilns worldwide. A recent report from Holcim gives average PCDD/PCDF values for 2001 and 2002 as 0.041 ng TEQ/Nm^3 (71 kilns) and 0.030 ng TEQ/Nm^3 (82 kilns) respectively. Of these measurements, 120 were from countries within the Organisation for Economic Co-operation and Development (OECD), with an average value of 0.0307 ng TEQ/Nm^3; the minimum and maximum values measured were 0.0001 and 0.292 ng TEQ/Nm^3 respectively, with nine long wet kilns being above 0.1 ng TEQ/Nm^3. For the 29 measurements from non-OECD countries, the average value was 0.0146 ng TEQ/Nm^3; the minimum and maximum values measured were 0.0002 and 0.074 ng TEQ/Nm^3 respectively, with no measurements being above 0.1 ng TEQ/Nm^3 (Karstensen 2006b). Table 1 above summarizes the results of the PCDD/PCDF measurements.

Experience has shown that, with relatively high temperatures in the electrostatic precipitator and the use of raw material with high organic content, high levels of emissions of chemicals listed in Annex C are possible.

PCDD/PCDF emissions in 2004 from a long dry kiln in the UK reached 136 ng TEQ/m^3 and averaged more 50 ng TEQ/m^3 over the year with total emissions of more than 40 g TEQ. The kiln, now closed, was operating with relatively high temperatures in the electrostatic precipitator and used raw material with high organic content together with waste pulverised fuel ashes[4] .

Data from several kilns in the United States show PCDD/PCDF emissions of 1.76 ng I-TEQ/m^3 when operating their air pollution control devices in the range of 200°–230° C.[5] Tests in the United States also indicated higher emissions for some kilns where hazardous wastes were fired.

In both the United States and German studies, a positive correlation was identified between PCDD emission concentration and electrostatic precipitator/stack temperature. In the United States tests, at one facility the electrostatic precipitator temperature recorded was between 255° C and 400° C. The PCDD emissions were highest at 400° C, and decreased fiftyfold at 255° C. This behaviour was observed generally across the set of facilities tested. At temperatures lower than 250° C at the electrostatic precipitator/stack inlet there was no correlation between temperature and PCDD emissions. This is consistent with known mechanisms of PCDD formation within municipal waste incinerator systems (Karstensen 2006b).

More detailed investigations have suggested that – provided combustion is good – the main controlling factor for the level of chemicals listed in Annex C in stack gas is the operating temperature of the dust collection device in the gas cleaning system. Plants equipped with electrostatic precipitators operating at lower temperatures (200° C or less) appear to have low emission concentrations whether or not they use waste (UNEP 2003).

The possible effect of feeding different wastes to the lower-temperature preheater/precalciner was investigated by Lafarge and results are presented in Table 2. Wastes injected at mid or feed-end locations do not experience the same elevated temperatures and long residence times as wastes introduced at the hot end. The observed concentration level of PCDD/PCDF was low in all measurements (Karstensen 2006b).

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[4] Communication by IPEN

[5] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, paragraph 3 of the present guidelines.

Table 2. Feeding of wastes to the preheater/precalciner and influence on PCDD/PCDF emissions

Plant	Year	Type of alternative fuel	PCDD/PCDF emissions in ng I-TEQ/Nm^3
1	2002	Animal meal, plastics and textiles	0.0025
2	2002	Animal meal and impregnated sawdust	0.0033
3	2002	Coal, plastic and tyres	0.0021 & 0.0041
4	2002	Tyres	0.002 & 0.006
5	2002	Petcoke, plastic and waste oil	0.001
6	2002	Petcoke, sunflower shells and waste oil	0.012
7	2002	Tyre chips	0.004 & 0.021
8	2002	Solvents	0.07
9	2002	Impregnated saw dust and solvents	0.00003 & 0.00145
10	2002	Solvents	0.00029 & 0.00057
11	2002	Sludge	< 0.011
12	2002	Car waste and sludge	0.0036 & 0.07 & 0.0032

The reported data indicate that cement kilns can comply with an emission level of 0.1 ng I-TEQ/Nm^3, which is the limit value in several Western European countries' legislation on hazardous waste incineration plants.

5.3.4 Study on releases of PCDD/PCDF through solids

Since the data for stack emissions from cement kilns indicate that well-designed, well-operated facilities can achieve very low exhaust gas concentrations of PCDD/PCDF, it can also be expected that such facilities will have low levels in cement kiln dust recovered from the air pollution control system. The same factors that contribute to low levels remaining in the exhaust to atmosphere argue for low concentrations in the collected solid material. The two main solid materials produced in cement production are cement clinker from the cooler and dust materials trapped in the air pollution control devices.

New analyses of solid materials have been gathered from cement companies participating in the Cement Sustainability Initiative (CSI) (Karstensen 2006b). Eight CSI companies reported the PCDD/PCDF concentration in cement clinker dust in 2005. Ninety samples showed an average value of 6.7 ng I-TEQ/kg, seemingly strongly influenced by a few high-level samples. The highest concentration reported was 96 ng I-TEQ/kg.

Eight CSI companies reported the PCDD/PCDF concentration in 57 clinker samples in 2005. The average value of all samples was 1.24 ng I-TEQ/kg. The clinker samples came from wet and dry suspension preheater kilns. The highest concentration reported was 13 ng I-TEQ/kg.

Two CSI companies reported the PCDD/PCDF concentration in 11 kiln feed samples in 2005, consisting of raw meal, pellets, and slurry and raw material components. The average value of these samples was 1.4 ng I-TEQ/kg. The kiln feed samples came from wet and dry suspension preheater kilns. The highest concentration reported was 7.1 ng I-TEQ/kg.

5.4 Releases of PCB and HCB

Hexachlorobenzene (HCB) and PCB have not been the subject of regulatory monitoring in cement plants to date. Most measurements that have taken place have not detected HCB emissions. As regards PCB_6 emissions, 40 measurements carried out in 13 kilns in Germany in 2001 revealed a maximum concentration of 0.4 µg PCB /Nm^3; in nine of the 40 measurements, no PCB were detected.

From Vietnam co-incineration of pesticides has shown emissions of dioxin like PCB of 0.001 ng TEQ/m^3 and HCB emissions below the detection limit of 31 ng/m^3 (Karstensen 2006b).

6. Best available techniques and best environmental practices

The following paragraphs summarize best available techniques and best environmental practices for cement kilns firing hazardous waste.

6.1 General measures for management

6.1.1 Legal aspects

An appropriate legislative and regulatory framework has to be in place to ensure enforcement and to guarantee a high level of environmental protection.

Furthermore, an established waste management regime that emphasizes the waste management hierarchy illustrated in Section III C (ii) on waste management should be established before or in parallel with the formal designation of cement kilns as sanctioned recipients of hazardous wastes, whether as waste-derived fuels or as wastes for disposal. All relevant authorities need to be involved during the permitting process, and in this regard, among other actions, the cement plant operator should:

- Establish and maintain credibility through open, consistent, responsive and ongoing communication with authorities and the public;
- Provide all necessary information to ensure that authorities are able to evaluate the safety and environmental impacts of the processing of hazardous waste;
- Establish community advisory panels early in the planning process;
- The Holcim and the CSI guidelines represent good guidance on BEP in relation to the section.

6.1.2 Environmental aspects

Co- incineration of hazardous wastes should only be performed if the cement kiln operates according to the best available techniques described in these guidelines. If certain provisions for waste quality and waste feeding are met the co-processing of waste will not change the emissions from a cement kiln stack significantly. However, some fuels may contain metals with a high volatility, such as mercury, which has a poor trapping coefficient. To control mercury emissions, it can therefore be necessary to limit mercury inputs into the kiln system. Alternative fuels have to undergo a rigorous acceptance and inspection procedure before being used.

Emission monitoring is obligatory in order to demonstrate compliance with existing laws, regulations and agreements.

6.1.3 Operational aspects

Operators need to ensure that only hazardous waste originating from trustworthy parties will be accepted, considering the integrity of all participants throughout the supply chain. The traceability of the wastes needs to be ensured prior to reception by the facility, with deliveries of unsuitable wastes refused.

Materials transport, handling and storage must be effectively monitored, and full compliance with existing regulatory requirements must be assured. This includes analysis and reporting of parameters such as the heating value, water content, heavy metal content, ash content, sulphur content and chlorine content. Also retained samples should be stored for a certain period of time.

6.1.4 Health and safety aspects

The suitability of the production site must be assessed to avoid risks associated with location (proximity to human habitation, potential impact of releases, logistics, transport) and infrastructure (potential releases of vapours and odours or possibility of leaks that might release hazardous waste or other substances of concern into environmental media, requiring control through application of technical solutions).

Adequate documentation and information on safe waste-derived fuel handling, operating procedures and emergency contingency measures are mandatory. Facility management staff must ensure an informed workforce through openness and transparency about health and safety measures and standards. It is essential that employees, regulatory authorities and local emergency response officials (e.g. fire departments) have such information well before firing of wastes, including hazardous waste, begins in a cement kiln facility.

6.1.5 Communication issues and social responsibility

In the interest of openness and transparency, the cement kiln operator planning to handle and co-incinerate waste, including hazardous or waste-derived fuel, must provide all necessary information to allow stakeholders to understand the purpose of the use of hazardous waste in the cement kiln, and to make them aware of the measures that will be implemented to avoid adverse impacts on the public and the environment, the functions of the parties involved and decision-making procedures. In summary, the following general management aspects should be taken into account:

- General infrastructure, paving, ventilation;
- Good site and facility housekeeping;
- General control and monitoring of basic performance parameters;
- Control and abatement of air emissions (NO_x, SO_2, particles, metals);
- Development of environmental monitoring (establishing standard monitoring protocols);
- Development of audit and reporting systems;
- Implementation of specific permit and audit systems for use of wastes and alternative fuels;
- Demonstration by emission monitoring that a facility can achieve a given emission limit value;
- Occupational health and safety provisions: Cement kilns fired with wastes and alternative fuels need to have appropriate practices to protect workers handling those materials during the feeding process;
- Sufficient qualification and training of staff.

6.2 Specific measures

For new plants and major upgrades, best available techniques for the production of cement clinker are considered to be a dry process kiln with multistage preheating and precalcination. For existing installations, varying degrees of reconstruction may be needed.[6]

6.2.1 Primary measures and process optimization

6.2.1.1 Process optimization

- Ensure rapid cooling of exhaust gases to a temperature lower than 200° C.
- Characterize the parameters that correspond to good operation and use these as a basis to improve other operational performance. Having characterized good kiln operating parameters,

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[6] The dry process is only appropriate in the case of limestone as a raw material feed. It is possible to utilize preheater/precalciner technology to process chalk, with the chalk slurry dried in a flash dryer at the front end of the process.

establish reference data by adding controlled doses of waste, and assess what are the changes and required controls and practices to control emissions;

- Manage the kiln process to achieve and maintain stable operating conditions, i.e. by optimizing process control (including implementing computer-based automatic control systems) and using modern, gravimetric solid fuel feed systems;
- Minimize fuel energy use by employing preheating and precalcination to the extent possible considering the existing kiln system configuration; and use of modern clinker coolers, enabling maximum heat recovery from the exhaust gas.

Control of chemicals listed in Annex C: Indirect measures for control of chemicals listed in Annex C are an important element of an integrated emission control strategy. Such measures are generally applicable and are relatively simple to implement technically.

6.2.1.2 Hazardous waste preparation

Pretreatment of waste, including hazardous waste, for the purpose of providing a more homogeneous feed and thus more stable combustion conditions may, depending on the nature of the waste-derived fuel, involve drying, shredding, mixing or grinding (see also section 3.4). It is important to give close scrutiny to:

- Good maintenance, housekeeping and procedures appropriate to the safe acceptance, handling and storage of wastes as they arrive at the site, and appropriately designed interim storage facilities taking into account the hazards and characteristics of each waste;
- Good maintenance, housekeeping and operating procedures and appropriately designed storage facilities for the alternative fuel.

These measures are not necessarily specific for control of chemicals to be eliminated and reduced by Annex C, but are essential elements of an integrated emission control strategy.

6.2.1.3 Input controls

- Consistent long-term supply of a given waste or alternative fuel (e.g. a supply of a month or more) is required in order to maintain stable conditions during operation;
- Substances entering the kiln should be carefully selected and controlled; specifications should be set based on product/process or emission considerations and monitored;
- Continuous supply of alternative fuels with specification of heavy metals, chlorine, sulphur;
- Waste-derived fuel should never be used during start-up and shutdown.
- The feeding of raw mix containing waste with organic compounds that could act as precursor should be avoided;
- Halogenated waste should be fed through the main burner.
- In general, waste should be fed through either the main burner or the secondary burner for preheater/precalciner kilns. For the secondary burner it should be ensured that the combustion zone temperature is maintained > 850° C for a sufficient residence time(2 s);
- Waste feed containing organic compounds that could act as precursor should not be fed as part of the raw mix;
- Waste-derived fuel should never be used during start-up and shutdown.

Control of chemicals listed in Annex C: Indirect measures for control of such chemicals are an important element of an integrated emission control strategy. Such measures are generally applicable and are generally simple to implement technically.

6.2.1.4 Stabilization of process parameters

It is important for combustion and process stability to ensure:

- Consistency in fuel characteristics (both alternative and fossil);
- Consistency in fuel supply rate or frequency of introduction of batch-charged materials;
- That adequate excess oxygen is supplied to achieve good combustion;
- That concentrations of CO in exhaust gases are monitored and do not exceed pre-established levels reflecting poor combustion conditions.

Control of chemicals listed in Annex C: Indirect measures for control of such chemicals are an important element of an integrated emission control strategy. Such measures are generally applicable and help ensure stable operating conditions.

6.2.1.5 Process modification

The off-gas dust (also known as cement kiln dust) must be managed carefully. In many cases it may be fed back into the kiln to the extent that it can be demonstrated to be practicable and to avoid excessive emissions of volatile metals and alkali salts. Where this recycle stream can be maximized it will reduce issues related to disposal of the dust. Dust that cannot be recycled must be managed in a manner demonstrated to be safe. Depending upon the level of contaminants of concern (e.g. heavy metals, persistent organic pollutants), this material can in some cases be considered hazardous waste and may then require the special handling and disposal measures mandated by such a determination.

Control of chemicals listed in Annex C: Indirect measures for control of such chemicals are an important element of an integrated emission control strategy.

6.2.1.6 Summary of primary measures

In general, the primary measures mentioned above are sufficient to achieve an emission level below 0.1 ng I-TEQ/Nm^3 in flue gases for new and existing installations. Where all of these options do not lead to performance down to 0.1 ng I-TEQ/Nm^3, secondary measures may be considered, as described below.

6.2.2 Secondary measures

The secondary measures cited below are usually installed for the purpose of controlling pollutants, other than unintentionally formed persistent organic pollutants, but they may also lead to a simultaneous reduction in emissions of chemicals listed in Annex C.

6.2.2.1 Further improvement of dust abatement and recirculation of dust

These measures will not reduce levels of chemicals listed in Annex C present in the gas phase in the exhaust to any appreciable extent. As a result, the effectiveness of this strategy will generally decrease with increasing temperature of the particulate collection system. Changing from no recirculation of cement kiln dust to full recirculation will change its chemical composition over time, increasing the alkali content and leading to operating issues; a certain fraction of the collected dust must be disposed of and where high recirculation rates are practised the dust is likely to be enriched in semi-volatile and volatile heavy metals, mandating careful handling procedures and safe disposal at a facility designed to treat or contain hazardous wastes. General applicability; moderate technical construction requirements; good capture of the fraction of chemicals listed in Annex C which are bound to particles.

Rotary kilns are generally equipped with electrostatic precipitators, on account of the relatively high exhaust gas temperatures. Fabric filters are also used, particularly on preheater kilns, where exhaust gas temperatures are lower.

Shaft kilns are usually fitted with fabric filters. Wet scrubbers are sometimes used. Lime grinding plants use fabric filters to collect the product and dedust the conveying air. Hydrating plants, with exhaust gases saturated with water vapour at about 90° C, are generally fitted with wet scrubbers, although fabric filters are increasingly being used where the feed lime has a high reactivity.

Information from the European Union (European Commission 2001) indicates that particulate matter from point sources can be effectively removed by application of:

- Electrostatic precipitators with fast measuring and control equipment to minimize the number of CO trips;
- Fabric filters with multiple compartments and burst bag detectors.

The emission level associated with these best available techniques is 20–30 mg dust/m^3 on a daily average basis. This emission level can be achieved by electrostatic precipitators or fabric filters at the various types of installations in the cement industry.

6.2.2.2 Activated carbon injection

Where fabric filters are used for particulate control purposes, it is possible to inject powdered activated carbon upstream of the fabric filter and achieve very good removal of metals and organic compounds. Pollutants are collected by adsorption on the surface of the carbon both as it is dispersed in the exhaust stream, and as the exhaust passes through the filter cake formed on the inside of the fabric filter bags. A low operating temperature is critical to successful application of this technique, since at temperatures within the range for de novo synthesis (250º–400º C) activated carbon could serve as a carbon source for PCDD/PCDF formation. Activated carbon also performs better at adsorbing metals and PCDD/PCDF at temperatures below 200º C. At the same time, the temperature must be maintained above the dew point for the exhaust gases in order to avoid condensation and blinding of the bags. An operating temperature in the vicinity of 160º C is generally used, although with careful monitoring somewhat lower values may be achieved. Temperature control is usually achieved by evaporative cooling and carbon is typically injected in or just downstream of the evaporative cooler. It should be noted that if cement kiln dust is to be recycled to the kiln this technique may not be highly effective for mercury emission control, as collected mercury will be re-released in the kiln and the cement kiln dust bleed stream for disposal may need to be a large fraction of the total in order to achieve positive control.

This technique has general applicability for control of Annex C chemicals, with very good (> 90%) capture expected when operating temperatures are optimized properly; it has low to moderate technical construction requirements and is better suited to retrofit situations than the following two options.

6.2.2.3 Activated carbon filter

This measure has high removal efficiency for certain pollutants (> 90% generally; > 99% for some compounds). Pollutants such as sulphur dioxide (SO_2), organic compounds, metals, ammonia (NH_3), ammonium (NH_4^+) compounds, hydrogen chloride (HCl), hydrogen fluoride (HF) and residual dust (after an electrostatic precipitator or fabric filter) may be removed from exhaust gases that have been treated in an activated carbon bed. The only activated carbon filter installed at a cement works in Europe is that at Siggenthal, Switzerland. The Siggenthal kiln is a four-stage cyclone preheater kiln with a capacity of 2,000 tons of clinker per day. Measurements show high removal efficiencies for SO_2, metals and PCDD/PCDF (European Commission 2001).

Control of chemicals listed in Annex C: General applicability; demanding technical construction.

6.2.2.4 Selective catalytic reduction

In general, selective catalytic reduction installations are applied for NO_x control. The process reduces NO and NO_2 to N_2 using NH_3 as a reducing agent in the presence of an appropriate catalyst at a temperature range of about 300°–400° C, which would require heating of the exhaust gases from a typical cement kiln. Only a subset of the catalysts capable of reducing nitrogen oxides are also suited to the destruction of Annex C pollutants such as PCDD/PCDF. To date, selective catalytic reduction for NO_X control has only been tested on preheater and semi-dry (Lepol) kiln systems, but it may be applicable to other kiln systems as well (European Commission 2001). Its relatively high capital cost, along with significant energy costs for reheat of the exhaust gases in order to use it, make this solution appear unlikely to be economically favourable in general application. The first full-scale plant (Solnhofer Zementwerke) has been in operation since the end of 1999 (IPTS 2004).

Control of chemicals listed in Annex C: Demanding technical construction and capital/operating costs; expected excellent control of chemicals listed in Annex C by appropriately selected catalysts.

6.2.2.5 Activated carbon injection, an emerging technology

It is possible to inject powdered activated carbon upstream of the dust collecting filter, which may achieve efficient removal of metals and organic compounds. However, the following remarks should be made:

- A low operating temperature to < 160° C is critical to successful application of this technique;
- At the same time, the temperature must be maintained above the acid dew point to avoid condensation or corrosion;
- If cement kiln dust is to be recycled to the kiln, which is usually the case, this technique will not be effective for mercury emission control, as collected mercury will once again be re-released in the kiln;
- This carbon injection technology has not been demonstrated for the control of PCDD/PCDF emission from cement kilns and has only been applied in municipal waste incinerators.

7. Performance requirements based on best available techniques

Performance requirements based on best available techniques for control of PCDD/PCDF in flue gases should be < 0.1 ng I-TEQ/Nm^3 with reference conditions of 273 K, 101.3 kPa, 11% O_2 and a dry gas basis.

8. Monitoring of pollutant emissions and operation parameters

To control kiln process, continuous measurement is recommended for the following parameters (European Commission 2001):

- Pressure;
- Temperature;
- O_2 content;
- NO_x;
- CO, and possibly when the SO_x concentration is high;
- SO_2 (a technique is being developed to optimize CO with NO_x and SO_2).

Above these parameters control of mercury (if mercury content in the waste is high) should be ensured.

To accurately quantify the emissions, continuous measurement is best available technique for the following parameters (these may need to be measured again if their levels can change after the point where they are measured to be used for control):

- Exhaust volume (can be calculated but the process is regarded by some as complicated);
- Humidity;
- Temperature at particulate matter control device inlet;
- Dust/particulate matter;
- O_2;
- NO_x;

- Dust;
- SO_2;
- CO.

Regular periodical monitoring is best available technique for the following substances:

- Metals and their compounds;
- Total organic carbon/organic components;
- HCl, HF;
- NH_3;
- PCDD/PCDF.

Measurements of the following may be required occasionally under special operating conditions:

- Destruction and removal efficiency, in the case of destruction of persistent organic pollutants in cement kilns;
- Benzene, toluene, xylene;
- Polycyclic aromatic hydrocarbons;
- Other organic pollutants (principal organic hazardous constituents, e.g. chlorobenzenes, PCB including coplanar congeners, chloronaphthalenes).

It is especially important to measure metals when wastes with higher metal content are used as raw materials or fuels.

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Part II Source category (c): Production of pulp using elemental chlorine or chemicals generating elemental chlorine

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V. C. Production of pulp using elemental chlorine or chemicals generating elemental chlorine

Summary

The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, deknotting, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing.

Of the chemicals listed in Annex C of the Stockholm Convention, only PCDD and PCDF have been identified as being produced during the production of pulp using elemental chlorine. Of the 17 PCDD/PCDF congeners with chlorine in the 2,3,7 and 8 positions, only two congeners – namely 2,3,7,8-TCDD and 2,3,7,8-TCDF – have been identified as potentially being produced during chemical pulp bleaching using chlorine. Most of the formation of the 2,3,7,8-TCDD and 2,3,7,8-TCDF is generated in the C-stage of bleaching via the reaction of chlorine with precursors of TCDD and TCDF. HCB and PCB are not formed during pulp bleaching.

As a summary, the following primary measures can be taken for decreasing or eliminating the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in wood and non-wood bleaching processes: eliminate elemental chlorine by replacing it with chlorine dioxide (elemental chlorine-free bleaching) or in some cases with totally chlorine-free processes; reduce application of elemental chlorine by decreasing chlorine multiple or increasing the substitution of chlorine dioxide for molecular chlorine; minimize precursors such as dibenzo-p-dioxin and dibenzofuran entering the bleach plant by using precursor-free additives and thorough washing; maximize knot removal; and eliminate pulping of furnish contaminated with polychlorinated phenols.

1. Introduction

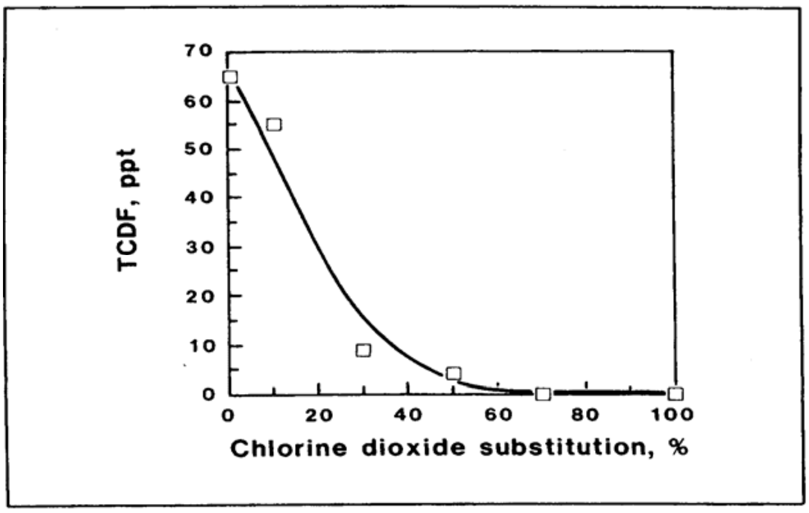
The following draft guidelines provide guidance on best available techniques and best environmental practices for chemical pulp bleaching using elemental chlorine or chemicals generating elemental chlorine. Within a pulp bleaching plant, PCDD/PCDF may be released at several stages in the process: in the effluent discharged to water or land; from emissions to air from the recovery boilers (reference to section VI.E.); and residues sent to landfill (reference to section III.C. (ii) of the present guidelines).

The chemicals listed in Annex C of the Stockholm Convention include polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB). Of these, neither HCB nor PCB is or has been unintentionally produced during chemical pulp bleaching. Furthermore, of the 17 PCDD/PCDF congeners with chlorine in the 2,3,7 and 8 positions and which are considered to express dioxin-like toxicity, only two, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), have been identified as potentially being produced during chemical pulp bleaching. Therefore any best available techniques and best environmental practices in the context of chemical pulp bleaching using elemental chlorine or chemicals generating elemental chlorine should be directed at reduction and elimination of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The adsorbable organic halogen (AOX) compounds do not correlate with dioxins or furans and are therefore not discussed here.

In the mid-1980s the discovery of dioxins and furans in effluents from pulp mills using chlorine and hypochlorite in their bleaching sequences prompted extensive research into how to reduce or eliminate their formation. The intense international research showed that the principle mechanism for formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF is the chlorination of the precursor compounds dibenzodioxin (DBD) and dibenzofuran (DBF) present in the unbleached pulp via aromatic electrophilic substitution. The formation of 2,3,7,8-TCDF will be reduced by increasing chlorine dioxide substitution, as shown in Figure 1. The use of molecular chlorine in bleaching has been largely replaced by chlorine dioxide (ECF, elemental chlorine-free) and other oxygen-based chemicals such as molecular oxide, peroxide and ozone (TCF, totally chorine-free).

Over 80% of all chemical pulp comes from the kraft process (Gullichsen and Fogelholm 2000). However, over 10% of world pulp production is made from non-wood fibres and in some countries, for example China and India, it is the dominant fibre source. In China, over 24 % of the pulp used in the paper industry is produced from wheat straws, reed, bamboo other and non-wood sources, whereas in Western countries the use of non-wood sources is currently very small. The average plant processing non-wood raw material is about one fifth of that in world. In 1998, 107 Nordic paper and board mills produced 25 million tons of products, while about 6,000 Chinese mills produced 28 million tons (Edelmann et al. 2000). In 2005 about 3600 Chinese mills produced 56 million tons of paper and board (2005 annual report of China paper industry).

Figure 1. Elimination of 2,3,7,8-TCDF with increasing substitution of chlorine dioxide for chlorine



1.1 Raw materials

Pulp and paper are manufactured from wood-based materials and from many kinds of non-wood materials, such as straw, bagasse, bamboo, reeds and kenaf. At present, wood provides over 90% of the world’s virgin fibre requirement while non-wood sources provide the remainder. In 2005, the production of wood-based chemical pulps was about 126 million tons and the production of non-woods 17 million tons (statistics from *FAOSTAT*). Non-wood pulps are mainly produced in developing countries, but for many reasons non-wood pulp fibres are gaining new interest in Eastern and Western Europe as well as in North America (Paavilainen 1998).

Wood and the main non-wood materials used in papermaking represent a complex mixture of the same substances – cellulose (40–45%), hemicelluloses (25–35%), lignin (20–30%) and extractives (2–15%). Most ligno-cellulosic and cellulosic materials of fibrous structure may be processed into various grades of papers and paperboard. Fibres from different raw materials are, however, dissimilar. They differ considerably in their morphological and chemical characteristics, which make them suitable for varying grades of final products (Paavilainen 1998). Wheat or rice straw is the most commonly used non-wood fibre raw material. Straw yields short-fibre pulp, which is similar to hardwood pulp. The high silica content is typical of non-wood materials (Myréen 2000).

1.2 Technology and final product

Pulping and bleaching technology must be matched with the quality and characteristics of the pulp and paper grades to be produced. No single pulping or bleaching process can produce pulp suitable for all uses. For instance, newsprint is a high-volume product of moderate strength, opacity and printability, and it has a relatively short life. Therefore, a high yield of pulp at the expense of maximum achievable strength and brightness can be manufactured from the raw materials, and there is a lower bleaching requirement due to the natural brightness of the pulps. On the other hand, packaging papers need strength if they are to be usable: here it is necessary to accept a lower yield via a different manufacturing route in order to obtain this strength, but once again the bleaching requirement may be low. The level of delignification and bleaching applied needs to be high in the case of writing and printing papers as well as outer packaging boards – their brightness and durability need to last for years without yellowing. The amount of effort required in bleaching can therefore vary widely.

2. Process description

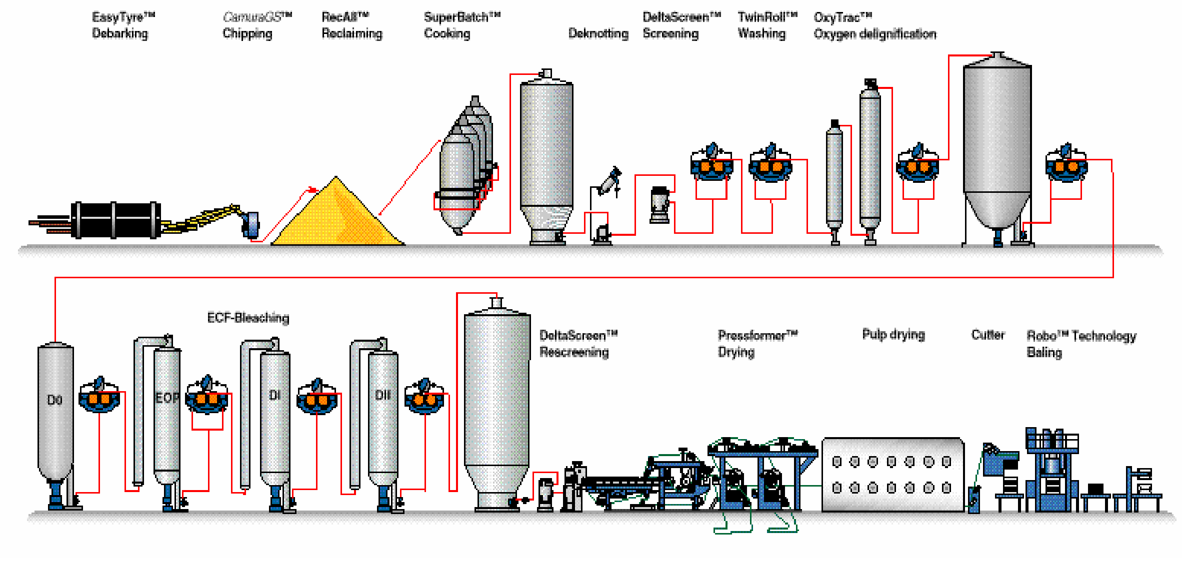
2.1 Pulping methods applied

The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, deknotting, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing.

The manufacture of pulp utilizes mechanical, thermomechanical, chemimechanical and chemical methods. Mechanical pulping processes use grinding for logs and disc refiners for chips. In these processes, mechanical shear forces are used to pull the fibres apart, and the majority of the lignin remains with the fibres, although there is still some significant dissolution of organics. The first step is followed by secondary disc refining and direct supply to a paper machine. Mechanical pulps can often be used without bleaching, but where brightening is applied it is achieved using compounds such as dithionite or peroxides (Gullichsen and Fogelholm 2000).

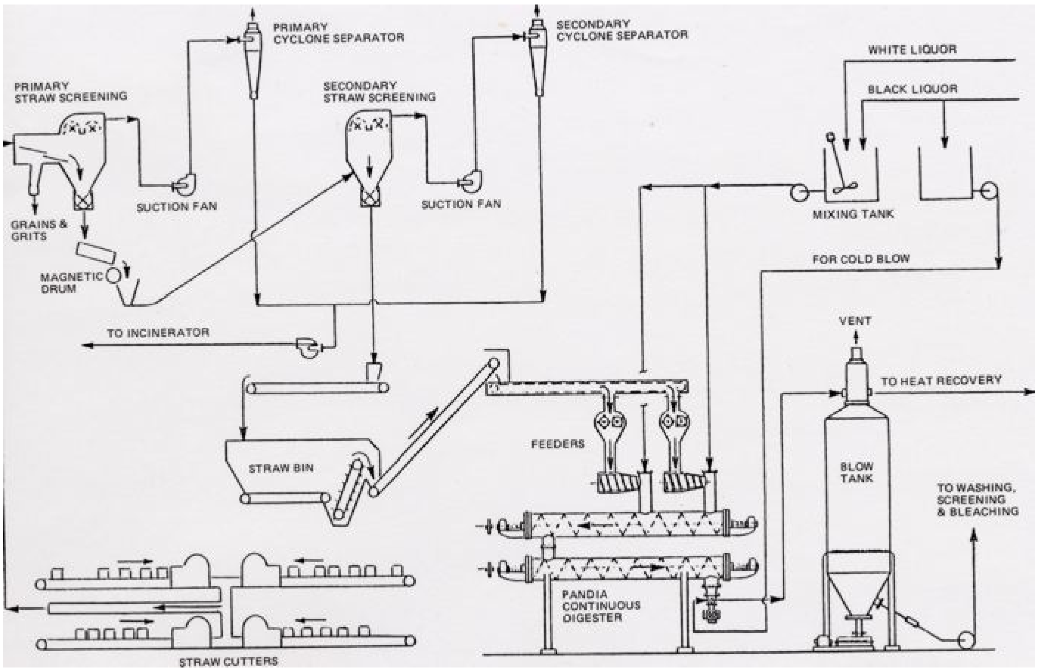
Lignin binds the fibres in the wood structure. In chemical pulping, the release of fibres is facilitated by chemicals that dissolve lignin. The lignin and many other organic substances are thus put into solution. This occurs in pressure vessels, called digesters, which are heated, pressurized vertical stationary vessels for wood-based raw material. Spherical rotary digesters or tumbling cylindrical digesters are used in batch pulping systems in various chemical processes for non-woods. In Figures 2 and 3, typical flow diagrams for wood-based and non-wood-based processes are presented. The residual lignin in fibres is removed by bleaching with chemical reagents. Some attempts to use enzymes have been introduced to enhance the effect of chemicals. Loss of yield, impacts on fibre properties and increased costs set limits to wider use of enzymes.

Figure 2. Typical flow diagram for modern kraft pulping process with ECF bleaching



Source: Metso Automation Inc.

Figure 3. Typical flow diagram for wheat straw pulping using the Pandia continuous digester system



Source: Kocurek 1983.

The main chemical, semi-chemical and chemimechanical pulping techniques are as follows:

- Sulphate (kraft) uses a mixture of sodium hydroxide and sodium sulphide under alkaline conditions to dissolve the lignin from wood and most non-wood fibres (chemical method);
- Sulphite: Acid bisulphite, bisulphite, alkaline and neutral sulphite methods (Ca, Mg, NH4, Na); different bases, including anthraquinone, under a range of pH, to dissolve the lignin; most wood fibres (chemical and semi-chemical methods);

- Lime, lime-soda: In particular, non-wood fibres;
- Cold soda uses sodium hydroxide pretreatment at ambient temperatures, alone or with sodium carbonate: In particular, hardwood and non-wood fibres (semi-chemical);
- Soda anthraquinone (AQ): Sodium hydroxide alone or with sodium carbonate and a catalyst anthraquinone; hardwood and non-wood fibres (chemical, similar to kraft but without sulphur), reduced odour;
- Organosolv methods: Wood and non-wood applications, some proven at mill scale but only one process is available commercially.

The kraft or sulphate process is the dominating pulping process worldwide, constituting 84% of the world's chemical pulp production and 63% of total chemical and mechanical pulp production.

Non-wood pulps are almost exclusively produced using chemical and semi-chemical processes. Of the chemical pulping methods applied to non-wood materials, the soda process is the most important, followed by the kraft process and the neutral sulphite process. Mills based on traditional lime and lime-soda processes are still in operation (Edelman et al. 2000; *Proceedings* 1992). Many new processes for non-wood pulping are under investigation.

2.1.1 The kraft (sulphate) pulping process

The kraft process uses a sodium-based alkaline pulping solution consisting of sodium sulphide (Na_2S) and sodium hydroxide (NaOH). The fibres are liberated in the cooking plant by dissolving the lignin and part of the hemicellulose in the cooking chemical solution (white liquor). Used cooking liquor (black liquor) is recovered to generate white liquor for the first pulping step. At mills with chemical recovery, most of the dissolved wood substances are combusted, and the wastewater mainly contains the organics in condensates and, at bleached mills, the substances dissolved during bleaching and the residues of the bleaching chemicals. Many small mills do not recover the liquor.

The recovery of non-wood fibre liquors is problematic due to the high silica content of fibre materials and rapid increase of the liquor viscosity during evaporation, as well as difficulties in achieving high solids content in the concentrated liquor fed to the recovery system. However, this area of recovery technology is currently receiving considerable attention with some claims for viable processes.

2.1.2 Lime and soda processes

These are processes that use simple alkaline cooking liquors in a similar process to kraft pulping but without the use of sulphur compounds. At mills with no chemical recovery, all the dissolved wood substances and pulping and bleaching chemicals remain in the wastewater, apart from the volatiles incidentally released to the atmosphere. The delignification ability is inadequate for producing wood-based pulps with low yield and high brightness. Its application to non-wood pulps is widespread, and it is also used with oxygen for straw pulping. In the soda process, the chemistry is simplified, as there is no added sulphur to form undesirable by-products, and the hydroxide can be recovered by lime causticization of the sodium carbonate smelt. After cooking, pulps that are not to be bleached are refined to separate the fibres.

2.1.3 Sulphite pulping processes

The sulphite pulping process is based on aqueous sulphur dioxide and a base – calcium, sodium, magnesium or ammonium. This method is losing its importance and only 10% of the world's pulp is produced with this method. Alkaline sulphite mills for non-wood fibres are often operated as a batch process, and chemical recovery is generally not practised at such mills due to their small size and the complexity of chemical recovery from what is normally a sodium-based process. Compared to kraft pulps, sulphite pulps are relatively bright and are also relatively easy to bleach with oxygen-based chemicals, such as peroxides.

2.1.4 Solvent-based processes

Solvent-based pulping processes can be used for both wood and non-wood raw materials. These organosolv pulping processes use the following solvents, amongst others: formic acid, peroxyformic acid, acetic acid, ethanol, methanol and acetone (Rousu and Antila 2002; Laxén and Halttunen 1992; Stern 2003; Edelman et al. 2000). Most alcohol and acidic cooking methods are sulphur-free processes and they produce readily bleachable pulp. Some solvent-based cooking methods are better suited for hardwood (e.g. Alcell) and some for both hardwood and softwood raw materials (e.g. NAEM, Organocell, Acetocell, Formacell and ASAM). However, none of these suggested techniques has been proven to be feasible in commercial operation, and the pilot production lines have been shut down. The applicability of solvent-based pulping for non-wood material has been studied (e.g. Alcell, Milox, Chempolis). When compared to traditional kraft non-wood pulping some laboratory-scale experiments show that the yield of the non-wood organosolv pulps is higher using ethanol-soda, ASAM and Organocell processes (Shatalov and Pereira 2005). The pilot-scale processes of Milox, Formacell, and ASAM produce pulps that are best for bleachability (Gullichsen and Fogelholm 2000).

2.2 Bleaching

Bleaching after pulping is a chemical process applied to pulps in order to increase their brightness. To reach the required brightness level, bleaching should be performed by removing the residual lignin of chemical pulps (delignifying or lignin-removing bleaching). All lignin cannot be removed selectively enough in a single bleaching stage, but pulp is usually bleached in three to six stages. The first two stages primarily release and extract lignin, and the subsequent stages remove the lignin residues and finish the product. These bleaching sequences are applied to maximize the bleaching effect of each component. Water is used to perform intermediate washes to remove extracted waste from the pulp (Gullichsen and Fogelholm 2000; Stenius 2000). The commonly applied chemical treatments in bleaching, and their abbreviated designations, are shown in Table 1.

Table 1. Commonly applied chemical treatments in bleaching

Treatment	Abbreviation	Description
Chlorination	C	Reaction with elemental chlorine in acidic medium
Alkaline extraction	E	Dissolution of reaction products with NaOH
Hypochlorite	H	Reaction with hypochlorite in alkaline medium
Chlorine dioxide	D	Reaction with chlorine dioxide (ClO_2)
Chlorine and chlorine dioxide	CD	Chlorine dioxide is added in chlorine stage
Oxygen	O	Reaction with molecular oxygen at high pressure in alkaline medium
Extraction with oxygen	EO	Alkaline extraction with oxygen
Peroxide	P	Reaction with hydrogen peroxide (H_2O_2) in alkaline medium
Chelating	Q	Reaction with chelating agent EDTA or DTPA in acidic medium for removal of metals
Ozone	Z	Ozone using gaseous ozone (O_3)

If molecular chlorine and hypochlorite are excluded, the term applied for the bleaching sequence is chlorine dioxide bleaching or elemental chlorine-free (ECF) bleaching. If the sequence only uses oxygen-based chemicals, such as oxygen, ozone, alkaline or acidic peroxide, the terms oxygen chemical bleaching or totally chlorine-free (TCF) bleaching can be used.

For softwood kraft pulps, a number of bleach sequences utilizing four to six stages are commonly used to achieve full-bleach brightness (level 89–91%). Bleaching sequences (full brightness) like CEHDED and CEDED were in operation in the 1960s and 1970s. Sequences more typical of modern mills are OD(EOP)D, OD(EOP)DP, Q(PO)DD, Q(PO)(DQ)(PO) and (Z(EO))DD (full brightness).

With an oxygen delignification stage or reinforced extraction stage, the bleaching sequences could be as follows: O(D+C)(EO)D; O(CD)EDED; and O(D)(EO)DED.

Hardwoods are easier to bleach due to their lower lignin content. Furthermore, less bleaching effort is required for sulphite pulps due to higher prebleach brightness.

For both non-wood and wood raw material, the pulping process removes some of the lignin. After pulping a variety of chemicals and catalysts can be used to remove lignin. Traditionally these chemicals have included gaseous chlorine and chlorine dioxide. For non-wood pulps, one-stage hypochlorite bleaching or conventional four-stage bleaching (CEHH, CEHD) is still very commonly used, depending on the final brightness requirements (Zheng et al. 1997). More recently, pressurized oxygen, ozone and hydrogen peroxide have been employed (Stern 2003).

2.2.1 Bleaching with elemental chlorine and hypochlorous acid

Elemental chlorine and hypochlorous acid are electrophilic bleaching chemical agents that react with all unsaturated structures, namely lignin structures; with polysaccharide degradation products, such as hexenuronic acid; and with extractive structures that contain carbon-carbon double bonds. These electrophilic bleaching agents are able to react with different unsubstituted aromatic carbon atoms in lignin to:

a. Chlorinate (when the carbon is not bonded with an oxygen atom); or

b. Chlorinate and depolymerize (via displacement of an α-hydroxyl group); or

c. Merely depolymerize without chlorination (via hydroxylation).

These chlorination or depolymerization reactions make lignin alkaline soluble, and it can be removed from pulp in the alkaline bleaching stages of the bleaching sequence.

2.2.2 Formation of 2,3,7,8-TCDD/TCDF

Most of the formation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is generated in the C-stage via the reaction of chlorine with the precursor of TCDD, namely dibenzo-p-dioxin (DBD), and with the precursor of TCDF, which is unchlorinated dibenzofuran (DBF). When these precursors are chlorinated, the key reaction is electrophilic aromatic substitution. The rate of this reaction will depend both on the concentration of the precursor and the concentration of chlorine. The levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF are not determined by the content of the lignin in pulp (Berry et al. 1989).

The chlorination of non-aromatic structures, such as hexenuronic acid, does not lead to the formation of polychlorinated aromatic degradation products.

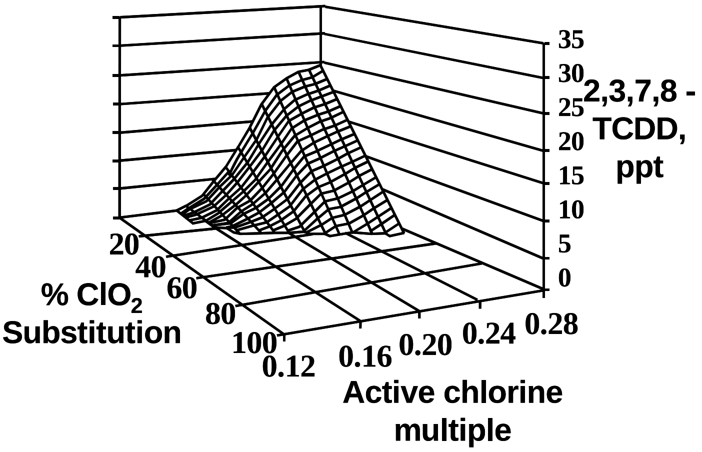
The unchlorinated dioxin precursors are prevalent in certain mineral oils, which are part of some defoamer formulations used in the pulp and paper industry and are the major source of precursors. Wood itself may act as the source of dioxin precursor. Compression wood in particular contains higher concentrations of precursors than normal wood. The compression of wood also entails higher levels of coumaryl-type lignin, which may be a source of DBD- and DBF-like precursors.

2.2.3 Elimination mechanisms for 2,3,7,8-TCDD/TCDF

Preventing the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the bleaching can be achieved mainly by using totally chlorine-free bleaching method and virtual elimination can be achieved by decreasing the amount of chlorine used in the first bleaching stage. This can be accomplished by reducing the atomic chlorine multiple by improving washing prior to chlorination, by using an oxygen and peroxide-reinforced extraction stage, and by increasing ClO_2 substitution (Rappe et al. 1989; Tana and Lehtinen 1996). The formation of 2,3,7,8-TCDF and 2,3,7,8-TCDD will be reduced by increasing ClO_2 substitution, as demonstrated in Figures 1 and 4. When the ClO_2 substitution level is higher than 85%, 2,3,7,8-TCDF and 2,3,7,8-TCDD can be virtually eliminated.

The summary effect of active chlorine multiple[1] and the ClO_2 substitution level can be seen in Figure 4. The level of dioxin formation under these conditions, i.e., high active chlorine multiple and low ClO_2 substitution, is expected to vary, depending on the DBD content of the brownstock.

Figure 4. Effect of active chlorine multiple and chlorine dioxide substitution level on 2,3,7,8-TCDD formation



Elemental chlorine can be completely replaced by ClO_2 (elemental chlorine-free bleaching). In this process ClO_2 is usually the main bleaching agent. The elemental chlorine can be replaced with ClO_2 in the first bleaching stage because the ClO_2 per chlorine atom has fivefold oxidation power compared with chlorine and it has practically the same selective lignin removal properties. Reinforcing the alkaline extraction stages in bleaching with oxygen and/or hydrogen peroxide results in an enhanced oxidizing bleaching effect, which reduces the residual lignin content of the pulp before the final ClO_2 bleaching stages. Increasing the degree of ClO_2 substitution decreases the formation of chlorinated organic substances and eliminates the formation of dioxins and furans. The increased substitution of chlorine by ClO_2 generally requires modifications in the bleaching process and also expansion of the on-site chlorine dioxide plant.

The elemental chlorine-free bleaching process is different for softwood and hardwood, and in existing mills the possibilities of the concept are tied to the current bleaching process. Generally, to reach a certain brightness target hardwood requires fewer chemicals than softwood, which usually means that the number of bleaching stages can be reduced. Over the years the dosage of chlorine dioxide has decreased in hardwood bleaching by one-third as it has been substituted by oxygen-based chemicals. Examples for light elemental chlorine-free bleaching sequences are (DZ)(EOP)D, (DQ)(PO) and D(EOP)D(PO). These can be applied for both hardwood and softwood, depending on the brightness target (European Commission 2000).[2]

Small amounts of chlorine are formed as a by-product in chlorine dioxide generation systems. Part of this molecular chlorine impurity will be present when chlorine dioxide is used as a bleaching reagent. There are several chlorine dioxide preparation processes available producing different amounts of elemental chlorine as by-product. Therefore a careful selection of the chlorine dioxide generation method will decrease the formation of molecular chlorine impurities and the unintentional formation of dioxins.

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[1] The term active chlorine multiple means the amount of active or equivalent chlorine expressed as a percentage on oven dry unbleached pulp divided by the unbleached pulp kappa number.

[2] See Table 1 for designations.

Elemental chlorine-free pulp (kraft pulp) bleached with ClO_2 holds the predominant position within the industry, accounting for roughly three-quarters of the bleached pulp produced worldwide.

3. Best available techniques for production of pulp using elemental chlorine

3.1 Primary measures

The principal best available techniques for minimizing or eliminating the formation of 2,3,7,8-TCDD/TCDF in wood and non-wood bleaching processes are as follows:

- Reduction of the application of elemental chlorine by decreasing the multiple or increasing the substitution of ClO_2 for molecular chlorine;
- Elimination of elemental chlorine by replacing it with ClO_2 (elemental chlorine-free bleaching) or with chlorine-free chemicals;
- Utilization of DBD- and DBF-free defoamers;
- Prevention of using non-wood raw material (reeds) that are contaminated or potentially contaminated by PCDD/PCDF as impurities in sodium pentachlorophenolate (Zheng 1997)
- Effective brownstock washing to enable the reduction of chlorine multiple;
- Maximization of knot and dirt removal to enable the reduction of chlorine multiple;
- Elimination of the pulping of furnish contaminated with polychlorinated phenols.

3.2 Secondary measures

The following general measures are suggested:

- Substitution: The identification and substitution of potentially harmful substances with less harmful alternatives. Use of a detailed inventory of raw materials used, chemical composition, quantities, fate and environmental impact;
- Investment planning/cycles: Coordination of process improvements to reduce technical bottleneck delays in the introduction of better techniques;
- Training, education and motivation of personnel: Training staff can be a very cost-effective way of reducing discharges of harmful substances;
- Process control monitoring and optimization: To be able to reduce different pollutants simultaneously and to maintain low releases, improved process control is required, including raw materials specification and monitoring of raw materials for precursor materials;
- Adequate maintenance: To maintain the efficiency of the process and the associated abatement techniques at a high level, sufficient maintenance has to be ensured;
- Environmental management system: A system that clearly defines the responsibilities for environmentally relevant aspects in a mill. It raises awareness and includes goals and measures, process and job instructions, checklists and other relevant documentation, and incorporation of environmental issues into process change controls;
- Development of environmental monitoring and standard monitoring protocols, including release monitoring for new facilities.

4. Alternatives

4.1 Totally chlorine-free bleaching for kraft pulp

The totally chlorine-free (TCF) process developed rapidly in the 1990s but has gradually lost its attraction because of its weaknesses in fibre characteristics, lower pulp yield and higher energy consumption. The elemental chlorine-free (ECF) process has taken over as the leading bleaching method. Some TCF processes have started to lose their shares in the market and a number of TCF mills are converting to ECF pulp production. The operating costs of TCF pulping are usually higher than those of ECF pulping due to the higher chemical costs required to reach the same level of pulp brightness.

TCF bleaching is a bleaching process carried out without any chlorine-containing chemicals. In this process, hydrogen peroxide together with ozone or peracetic acid are the most commonly used chemicals. Ozone has become the most common complement to peroxide in TCF bleaching sequences. The main purpose of using ozone is to provide more delignification power. Provided that the pulp has a low enough kappa number[3] after extended cooking and oxygen delignification and that transition metals (e.g. Mn_2^+) have been removed in the necessary chelating stages (Q-stages), it is possible to attain full market brightness with peroxide as a the sole bleaching chemical.

Examples for different TCF bleaching sequences are listed below:

Softwood	**Hardwood**
Q(EP)(EP)(EP)	QPZP
Q(OP)(ZQ)(PO)	Q(OP)(ZQ)(PO)
Q(EOP)Q(PO)	Q(EOP)Q(PO)
Q(OP)ZQ(PO)	Q(OP)ZQ(PO)

Notes:
Q = Acid stage where chelating agent EDTA or DTPA has been used for removal of metals.
EP = Extraction stage using NaOH with subsequent addition of H_2O_2 solution as a reinforcing agent.
EOP = Alkaline extraction bleaching stage using sodium hydroxide with subsequent addition of oxygen and hydrogen peroxide solution as a reinforcing agent.
EO = Extraction stage using NaOH with subsequent addition of gaseous oxygen as a reinforcing agent.
P = Alkaline stage with H_2O_2 as liquid.
Z = Ozone bleaching using gaseous O_3.
PO = Pressurized peroxide bleaching.

The trends of total chemical pulp production in the world are demonstrated in Figure 5. TCF kraft and sulphite pulp accounts for less than 5% of production and is primarily produced in Northern and Central Europe.

Figure 5. Trends in bleached chemical pulp production: World, excluding China and India.

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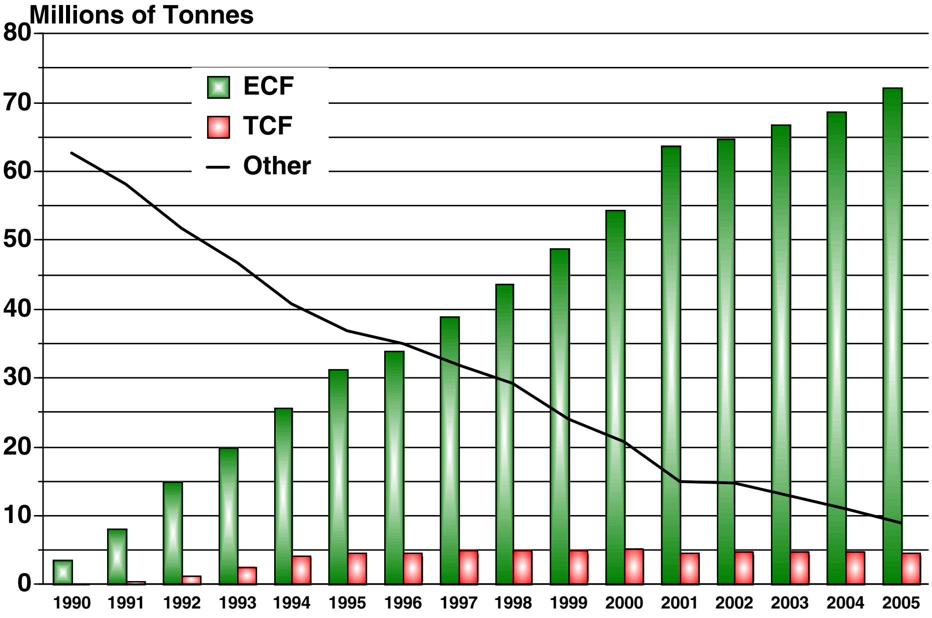
[3] The kappa number is an indirect measure of the residual lignin content in a pulp measured via the consumption of an oxidant chemical (for example, potassium permanganate).



Note: “Other” refers to pulp bleached with some molecular chlorine.

4.2 TCF bleaching for non-wood pulp

Because of their poor bleachability, non-wood pulps cannot be satisfactorily bleached without chlorine chemicals if the traditional alkaline non-wood process is used. Non-wood materials also contain notable amounts of metal ions, including potassium, calcium, manganese, copper and iron. When the pulp is bleached without chlorine chemicals the transition elements form radicals, which react unselectively with the pulp, causing a loss of yield and strength properties. Chelates are often added in the initial stages of bleaching to reduce the quantity of metals in the fibre. Furthermore, bleaching is accompanied by the formation of oxalic acid. Calcium reacts with oxalic acid into calcium oxalate, which deposits easily. Due to this, TCF bleaching is not viable in traditional alkaline non-wood processes. There is continuous research on TCF bleaching in solvent-based processes.

5. Achievable performance levels associated with best available techniques and best environmental practices

When the ClO_2 substitution level is higher than 85% in traditional bleaching, or if ECF bleaching or TCF bleaching is used, emissions of 2,3,7,8-TCDF and 2,3,7,8-TCDD to water are lower than the limit of quantification using EPA Method 1613,(refer to table 2.).

5.1 Performance reporting

Performance reporting is recommended as described in section III.C (vi) of the present guidelines.

Where emissions testing is not possible (for example, analytical capacity is not readily available), the use of PCDD/PCDF release factors associated with a similar mill type and operation is suggested as an interim performance reporting requirement until such time as annual emissions testing and analysis is available. Emission factors for releases of PCDD/PCDF from mills are presented in section 6.7.1 of the UNEP *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases* (UNEP 2003).

5.2 Performance standards

Table 2 summarizes the existing performance standards applied to pulp mills.

Table 2. Summary of existing performance standards applied to pulp mills

New plant	2,3,7,8-TCDD/TCDF pg/l to water	2,3,7,8-TCDD/TCDF ng/kg to sludge	Defoamers DBD and DBF mg/kg
Canada – Federal[a]	Lower than quantification level in treated final effluent		DBD < 10 DBF < 40
USA kraft and soda[b]	2,3,7,8-TCDD < 10 2,3,7,8-TCDF ≤ 31.9 in bleach plant effluent	10/100	
USA ammonium-based and speciality sulphite[b]	2,3,7,8-TCDD < 10 2,3,7,8-TCDF < 10 in bleach plant effluent		
Australia[c]	2,3,7,8-TCDD < 15 in treated final effluent		
Tasmania, Australia[d]	2,3,7,8-TCDD < 10 in treated final effluent		
Japan[e]	< 10 pg TEQ/L		

Sources:

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b. United States Congress, Office of Technology Assessment. 1989. *Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp*. OTA-BP-O-54. United States Government Printing Office, Washington, D.C. govinfo.library.unt.edu/ota/Ota_2/DATA/1989/8931.PDF.

c. Government of Australia. 1990. *Bleaching and the Environment*. Industry Commission, Pulp and Paper: Report No. 1. Australian Government Publishing Service, Canberra. www.pc.gov.au/ic/inquiry/01pulp/finalreport/01pulp.pdf.

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Part II Source category (d):
Thermal processes in the metallurgical industry

Table of contents

V.D Thermal processes in the metallurgical industry

(i) Secondary copper production

Summary

Secondary copper smelting involves copper production from sources that may include copper scrap, sludge, computer and electronic scrap, and drosses from refineries. Processes involved in copper production are feed pretreatment, smelting, alloying and casting. Factors that may give rise to chemicals listed in Annex C of the Stockholm Convention include the presence of catalytic metals (of which copper is a highly effective example); organic materials in feed such as oils, plastics and coatings; incomplete combustion of fuel; and temperatures between 250° and 500° C.

Best available techniques include presorting, cleaning feed materials, maintaining temperatures above 850° C, utilizing afterburners with rapid quenching, activated carbon adsorption and fabric filter dedusting.

Performance levels associated with best available techniques and best environmental practices for secondary copper smelters: < 0.5 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

1. Process description

Secondary copper smelting involves pyrometallurgical processes dependent on the copper content of the feed material, size distribution and other constituents. Feed sources are copper scrap, sludge, computer scrap, drosses from refineries and semi-finished products. These materials may contain organic materials like coatings or oil, and installations take this into account by using de-oiling and decoating methods or by correct design of the furnace and abatement system (European Commission 2001, p. 201–202). Copper can be infinitely recycled without loss of its intrinsic properties.

The quoted material that follows is from *Secondary Copper Smelting, Refining and Alloying*, a report of the Environmental Protection Agency of the United States of America (EPA 1995).

> “Secondary copper recovery is divided into 4 separate operations: scrap pretreatment, smelting, alloying, and casting. Pretreatment includes the cleaning and consolidation of scrap in preparation for smelting. Smelting consists of heating and treating the scrap for separation and purification of specific metals. Alloying involves the addition of 1 or more other metals to copper to obtain desirable qualities characteristic of the combination of metals.
>
> Scrap pretreatment may be achieved through manual, mechanical, pyrometallurgical, or hydrometallurgical methods. Manual and mechanical methods include sorting, stripping, shredding, and magnetic separation. Pyrometallurgical pretreatment may include sweating (the separation of different metals by slowly staging furnace air temperatures to liquefy each metal separately), burning insulation from copper wire, and drying in rotary kilns to volatilize oil and other organic compounds. Hydrometallurgical pretreatment methods include flotation and leaching to recover copper from slag. Leaching with sulphuric acid is used to recover copper from slime, a byproduct of electrolytic refining.
>
> Smelting of low-grade copper scrap begins with melting in either a blast or a rotary furnace, resulting in slag and impure copper. If a blast furnace is used, this copper is charged to a converter, where the purity is increased to about 80 to 90 percent, and then to a reverberatory furnace, where copper of about 99 percent purity is achieved. In these fire-refining furnaces, flux is added to the copper and air is blown upward through the mixture to oxidize impurities.
>
> These impurities are then removed as slag. Then, by reducing the furnace atmosphere, cuprous oxide (CuO) is converted to copper. Fire-refined copper is cast into anodes, which are used during electrolysis. The anodes are submerged in a sulphuric acid solution containing copper

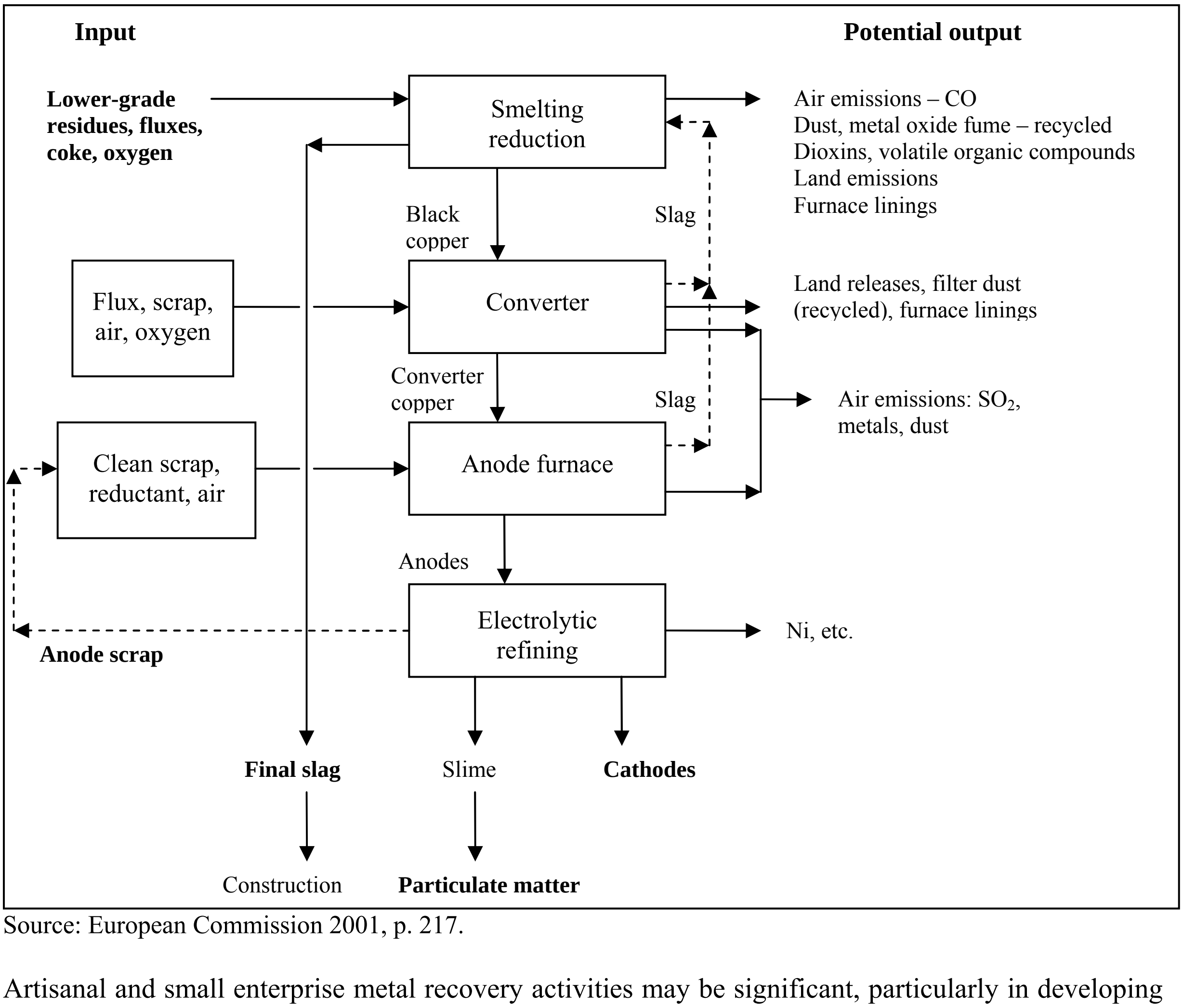
sulphate. As copper is dissolved from the anodes, it deposits on the cathode. Then the cathode copper, which is as much as 99.99 percent pure, is extracted and recast. The blast furnace and converter may be omitted from the process if average copper content of the scrap being used is greater than about 90 percent.

In alloying, copper-containing scrap is charged to a melting furnace along with 1 or more other metals such as tin, zinc, silver, lead, aluminium, or nickel. Fluxes are added to remove impurities and to protect the melt against oxidation by air. Air or pure oxygen may be blown through the melt to adjust the composition by oxidizing excess zinc. The alloying process is, to some extent, mutually exclusive of the smelting and refining processes described above that lead to relatively pure copper.

The final recovery process step is the casting of alloyed or refined metal products. The molten metal is poured into moulds from ladles or small pots serving as surge hoppers and flow regulators. The resulting products include shot, wire bar, anodes, cathodes, ingots, or other cast shapes."

Figure 1 presents the process in diagrammatic form.

Figure 1. Secondary copper smelting



Source: European Commission 2001, p. 217.

Artisanal and small enterprise metal recovery activities may be significant, particularly in developing countries and countries with economies in transition. These activities may contribute significantly to pollution and have negative health impacts. For example, artisanal zinc smelting is an important atmospheric mercury emission source. The technique used to smelt both zinc and mercury is simple; the ores are heated in a furnace for a few hours, and zinc metal and liquid mercury are produced. In many cases there are no pollution control devices employed at all during the melting process. Other metals that are known to be produced by artisanal and small enterprise metal recovery activities include antimony, iron, lead, manganese, tin, tungsten, gold, silver, copper and aluminium.

These are not considered best available techniques or best environmental practices. However, as a minimum, appropriate ventilation and material handling should be carried out.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

The formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is probably due to the presence of carbon, oxygen, chlorine precursors (from feeds and fuels) and highly potent copper catalyst from plastics and trace oils in the feed material in a system that can provide ideal formation conditions of temperatures between 200°–450° C, high levels of particulate and long residence times. As copper is the most efficient metal to catalyse PCDD/PCDF formation, copper smelting is a particular concern.

2.1 General information on emissions from secondary copper smelters

Airborne pollutant emissions include nitrogen oxides (NO_x), carbon monoxide (CO), dust and metal compounds, organic carbon compounds and persistent organic pollutants. Off-gases usually contain little or no sulphur dioxide (SO_2), provided sulphidic material is avoided. Scrap treatment and smelting generate the largest quantity of atmospheric emissions. Dust and metal compounds are emitted from most stages of the process and are more prone to fugitive emissions during charging and tapping cycles. Particulate matter may be removed from collected and cooled combustion gases by electrostatic precipitators or fabric filters. Fume collection hoods are used during the conversion and refining stages due to the batch process, which prevents a sealed atmosphere. NO_x is minimized in low-NO_x burners, while CO is burnt in hydrocarbon afterburners. Burner control systems are monitored to minimize CO generation during smelting (European Commission 2001, p. 218–229).

2.2 Emissions of PCDD/PCDF to air

PCDD/PCDF are formed during base metal smelting through incomplete combustion or by de novo synthesis when organic compounds, such as oils and plastics, and a source of chlorine atoms are present in the feed material. Secondary feed often consists of contaminated scrap.

The process is described in European Commission 2001, p. 133:

> “PCDD/PCDF or their precursors may be present in some raw materials and there is a possibility of de novo synthesis in furnaces or abatement systems. PCDD/PCDF are easily adsorbed onto solid matter and may be collected by all environmental media as dust, scrubber solids and filter dust.
>
> The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reductants, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically bound chlorine in the temperature range of 250 to 500° C to produce PCDD/PCDF. This process is known as de novo synthesis and is catalysed by the presence of metals such as copper or iron.
>
> Although PCDD/PCDF are destroyed at high temperature (above 850° C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled through the ‘reformation window’. This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimize the residence time in the window is practised to prevent de novo synthesis.”

2.3 Releases to other media

Process, surface and cooling water can be contaminated by suspended solids, metal compounds and oils, as well as by chemicals listed in Annex C of the Stockholm Convention. Most process and cooling water is recycled. Wastewater treatment methods should be used before discharge. By-products and residues are often recycled in the process as these contain recoverable quantities of copper and other non-ferrous metals. Waste material generally consists of acid slimes, which are disposed of on site. Care must be taken to ensure the proper disposal of slimes and pollution control residues in order to minimize exposure of the environment to copper and dioxins. Any transfer to another process should be carefully evaluated for the need to abate and control releases of chemicals listed in Annex C.

3. Recommended processes

Process design and configuration is influenced by the variation in feed material and quality control. Processes considered as best available techniques for smelting and reduction include the blast furnace, the mini-smelter (totally enclosed), the top-blown rotary furnace, the sealed submerged electric arc furnace, and ISA smelt. The top-blown rotary furnace (totally enclosed) and Pierce-Smith converter are best available techniques for converting. The submerged electric arc furnace is sealed and is cleaner than other designs if the gas extraction system is adequately designed and sized.

The use of blast furnaces for scrap melting is becoming less common due to difficulties in economically preventing pollution, and shaft furnaces without a coal/coke feed are increasingly being used instead.

Clean copper scrap devoid of organic contamination can be processed using the reverberatory hearth furnace, the hearth shaft furnace or Contimelt process. These are considered to be best available techniques in configurations with suitable gas collection and abatement systems.

No information is available on alternative processes to smelting for secondary copper processing.

4. Primary and secondary measures

Primary and secondary measures for PCDD/PCDF reduction and elimination are discussed below.

4.1 Primary measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of persistent organic pollutants. Possible measures include:

4.1.1 Presorting of feed material

The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of chemicals listed in Annex C during incomplete combustion or by de novo synthesis. Feed material should be classified according to composition and possible contaminants. Storage, handling and pretreatment techniques will be determined by feed size distribution and contamination.

Methods to be considered are (European Commission 2001, p. 232):

- Oil removal from feed (for example, thermal decoating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas);
- Use of milling and grinding techniques with good dust extraction and abatement. The resulting particles can be treated to recover valuable metals using density or pneumatic separation;
- Elimination of plastic by stripping cable insulation (for example, possible cryogenic techniques to make plastics friable and easily separable);
- Sufficient blending of material to provide a homogeneous feed in order to promote steady-state conditions.

Additional techniques for oil removal are solvent use and caustic scrubbing. Cryogenic stripping can be used to remove cable coatings.

Washing with an aqueous solution of detergents is a potential additional technique for oil removal. In this way, contaminating oil can also be recovered.

4.1.2 Effective process control

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation, such as maintaining furnace temperature above 850° C to destroy PCDD/PCDF. Ideally, PCDD/PCDF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still ongoing for applications to other sources. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas composition and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF emissions.

4.2 Secondary measures

Secondary measures are pollution control techniques. These methods do not eliminate the generation of contaminants, but serve as a means to contain, prevent or reduce emissions.

4.2.1 Fume and gas collection

Air emissions should be controlled at all stages of the process, from material handling, smelting and material transfer points, to limit potential emissions of chemicals listed in Annex C. Sealed furnaces are essential to contain fugitive emissions while permitting heat recovery and collecting off-gases for process recycling. Proper design of hooding and ductwork is essential to trap fumes. Furnace or reactor enclosures may be necessary. If primary extraction and enclosure of fumes is not possible, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged. Roofline collection of fume should be avoided due to high energy requirements. The use of intelligent damper controls can improve fume capture, reducing fan sizes and associated costs. Sealed charging cars or skips used with a reverberatory furnace can significantly reduce fugitive emissions to air by containing emissions during charging (European Commission 2001, p. 187–188).

4.2.2 High-efficiency dust removal

The smelting process generates large quantities of particulate matter with high surface area on which chemicals listed in Annex C can form and adsorb. These dusts with their associated metal compounds should be removed to reduce emissions of chemicals listed in Annex C. Fabric filters are the most effective technique, although wet or dry scrubbers and ceramic filters can also be considered. Collected dust must be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals.

Fabric filter operations should be constantly monitored by devices to detect bag failure. Other relevant technology developments include online cleaning methods and use of catalytic coatings to destroy PCDD/PCDF (European Commission 2001, p. 139–140).

4.2.3 Afterburners and quenching

Afterburners (used post-combustion) should be operated at a minimum temperature of 950° C to ensure full combustion of organic compounds (Hübner et al. 2000). This stage is to be followed by rapid quenching of hot gases to temperatures below 250° C. Oxygen injection in the upper portion of the furnace will also promote complete combustion (European Commission 2001, p. 189). Further information on optimal temperature is provided in Section I.

It has been observed that PCDD/PCDF are formed, on a net basis, in the temperature range of 250° to 500° C. They are destroyed above 850° C in the presence of oxygen. However, de novo synthesis remains possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace if the necessary precursors and metal catalysts are still present. Proper operation of cooling systems to minimize the time during which exhaust gases are within the de novo synthesis temperature range should be implemented (European Commission 2001, p. 133).

4.2.4 Adsorption on activated carbon

Activated carbon treatment should be considered for removal of chemicals listed in Annex C from smelter off-gases. Activated carbon possesses a large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or by injection of carbon particulate into the gas stream followed by removal as a filter dust using high-efficiency dust removal systems such as fabric filters.

5. Emerging research

Catalytic oxidation is an emerging technology used in waste incinerators to reduce PCDD/PCDF emissions. This process should be considered by secondary base metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators. However, catalytic oxidation can be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process.

Catalytic oxidation processes organic compounds into water, carbon dioxide (CO_2) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370° to 450° C. In comparison, incineration occurs typically at 980° C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and > 99% efficiency. Particulate matter should be removed from exhaust gases prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and CO_2 are released to the air after cooling (Parvesse 2001).

Fabric filters used for dust removal can also be treated with a catalytic coating to promote oxidation of organic compounds at elevated temperature.

6. Summary of measures

Table 1. Measures for recommended processes for new secondary copper smelters

Measure	Description	Considerations	Other comments
Recommended processes	Various recommended smelting processes should be considered for new facilities	Processes to consider include: • Blast furnace, mini-smelter, top-blown rotary furnace, sealed submerged electric arc furnace, ISA smelt, and the Pierce-Smith converter • Reverberatory hearth furnace, hearth shaft furnace and Contimelt process to treat clean copper scrap devoid of organic contamination	These are considered to be best available techniques in configuration with suitable gas collection and abatement. The submerged electric arc furnace is sealed and can be cleaner than other designs if the gas extraction system is adequately designed and sized

Table 2. Summary of primary and secondary measures for secondary copper smelters

Measure	Description	Considerations	Other comments
Primary measures			
Presorting of feed material	The presence of oils, plastics, organic materials and chlorine compounds in	Processes to consider include: • Strict control over materials	Thermal decoating and de-oiling processes for oil removal should be

Measure	Description	Considerations	Other comments
	the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de novo synthesis	sources • Oil removal from feed material • Use of milling and grinding techniques with good dust extraction and abatement • Elimination of plastic by stripping cable insulation	followed by afterburning to destroy any organic material in the off-gas
Effective process control	Good combustion. Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to minimizing generation of chemicals listed in Annex C	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas composition and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF	Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (for example, waste incineration), but research is still ongoing for applications to other sources
Secondary measures			
Fume and gas collection	Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions	Processes to consider include: • Sealed furnaces to contain fugitive emissions while permitting heat recovery and collecting off-gases. Furnace or reactor enclosures may be necessary • Proper design of hooding and ductwork to trap fumes	Roofline collection of fume is to be avoided due to high energy requirements
High-efficiency dust removal	Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions	Processes to consider include: • Fabric filters (most effective method) • Wet/dry scrubbers and ceramic filters	Dust removal is to be followed by afterburners and quenching. Collected dust must be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals
Afterburners and quenching	Afterburners should be used at temperatures > 950° C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250° C	Considerations include: • PCDD/PCDF formation at 250°–500° C, and destruction > 850° C with O_2 • Requirement for sufficient O_2 in the upper region of the furnace for complete combustion • Need for proper design of cooling systems to minimize reformation time	De novo synthesis is still possible as the gases are cooled through the reformation window

Measure	Description	Considerations	Other comments
Adsorption on activated carbon	Activated carbon treatment should be considered as this material possesses large surface area on which PCDD/PCDF can be adsorbed from smelter off-gases	Processes to consider include: • Treatment with activated carbon using fixed or moving bed reactors • Injection of powdered carbon into the gas stream followed by removal as a filter dust	Lime/carbon mixtures can also be used
Emerging research			
Catalytic oxidation	Catalytic oxidation is an emerging technology for sources in this sector (demonstrated technology for incinerator applications) which should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, CO_2 and hydrochloric acid using a precious metal catalyst	Considerations include: • Process efficiency for the vapour phase of contaminants • Hydrochloric acid treatment using scrubbers while water and CO_2 are released to the air after cooling • Complexity, sensitivity to flue gas conditions and high cost	Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and > 99% efficiency. Particulate matter should be removed from exhaust gases prior to catalytic oxidation for optimum efficiency

7. Performance levels associated with best available techniques and best environmental practices

The achievable performance level[1] for emissions of PCDD/PCDF from secondary copper smelters is < 0.5 ng I-TEQ/Nm^{3} (1) (at operating oxygen concentrations).

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[1] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^{3} = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, paragraph 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.

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(ii) Sinter plants in the iron and steel industry

Summary

Sinter plants in the iron and steel industry are a pretreatment step in the production of iron whereby fine particles of iron ores and, in some plants, secondary iron oxide wastes (collected dusts, mill scale) are agglomerated by combustion. Sintering involves the heating of fine iron ore with flux and coke fines or coal to produce a semi-molten mass that solidifies into porous pieces of sinter with the size and strength characteristics necessary for feeding into the blast furnace.

Chemicals listed in Annex C appear to be formed in the iron sintering process mainly via de novo synthesis. PCDF generally dominate in the waste gas from sinter plants. The PCDD/PCDF formation mechanism appears to start in the upper regions of the sinter bed shortly after ignition, and then the dioxins, furans and other compounds condense on cooler burden beneath as the sinter layer advances along the sinter strand towards the burn-through point.

Primary measures identified to prevent or minimize the formation of PCDD/PCDF during iron sintering include the stable and consistent operation of the sinter plant, continuous parameter monitoring, recirculation of waste gases, minimization of feed materials contaminated with persistent organic pollutants or contaminants leading to formation of such pollutants, and feed material preparation.

Secondary measures identified to control or reduce releases of PCDD/PCDF from iron sintering include adsorption/absorption (for example, activated carbon injection), suppression of formation using urea addition, and high-efficiency dedusting, as well as fine wet scrubbing of waste gases combined with effective treatment of the scrubber wastewaters and disposal of wastewater sludge in a secure landfill.

Performance levels associated with best available techniques and best environmental practices for an iron sintering plant operating according to best available techniques: < 0.2 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

1. Process description

Iron sintering plants may be used in the manufacture of iron and steel, often in integrated steel mills. The sintering process is a pretreatment step in the production of iron whereby fine particles of iron ores and, in some plants, secondary iron oxide wastes (collected dusts, mill scale) are agglomerated by combustion. The sinter feed materials and rations, as well as the amount of sinter that is used in a blast furnace, vary; typically a greater proportion of the furnace feed would be sinter in Europe compared to North American practice. Agglomeration of the fines is necessary to enable the passage of hot gases during the subsequent blast furnace operation (UNEP 2003, p. 60).

Sintering involves the heating of fine iron ore with flux and coke fines or coal to produce a semi-molten mass that solidifies into porous pieces of sinter with the size and strength characteristics necessary for feeding into the blast furnace. Moistened feed is delivered as a layer onto a continuously moving grate or strand. The surface is ignited with gas burners at the start of the strand and air is drawn through the moving bed, causing the fuel to burn. Strand velocity and gas flow are controlled to ensure that burn-through (i.e., the point at which the burning fuel layer reaches the base of the strand) occurs just prior to the sinter being discharged. The solidified sinter is then broken into pieces in a crusher and is air cooled. Product outside the required size range is screened out, oversize material is recrushed, and undersize material is recycled back to the process. Sinter plants that are located in a steel plant recycle iron ore fines from the raw material storage and handling operations and from waste iron oxides from steel plant operations and environmental control systems. Iron ore may also be processed in on-site sinter plants (Environment Canada 2001, p. 18).

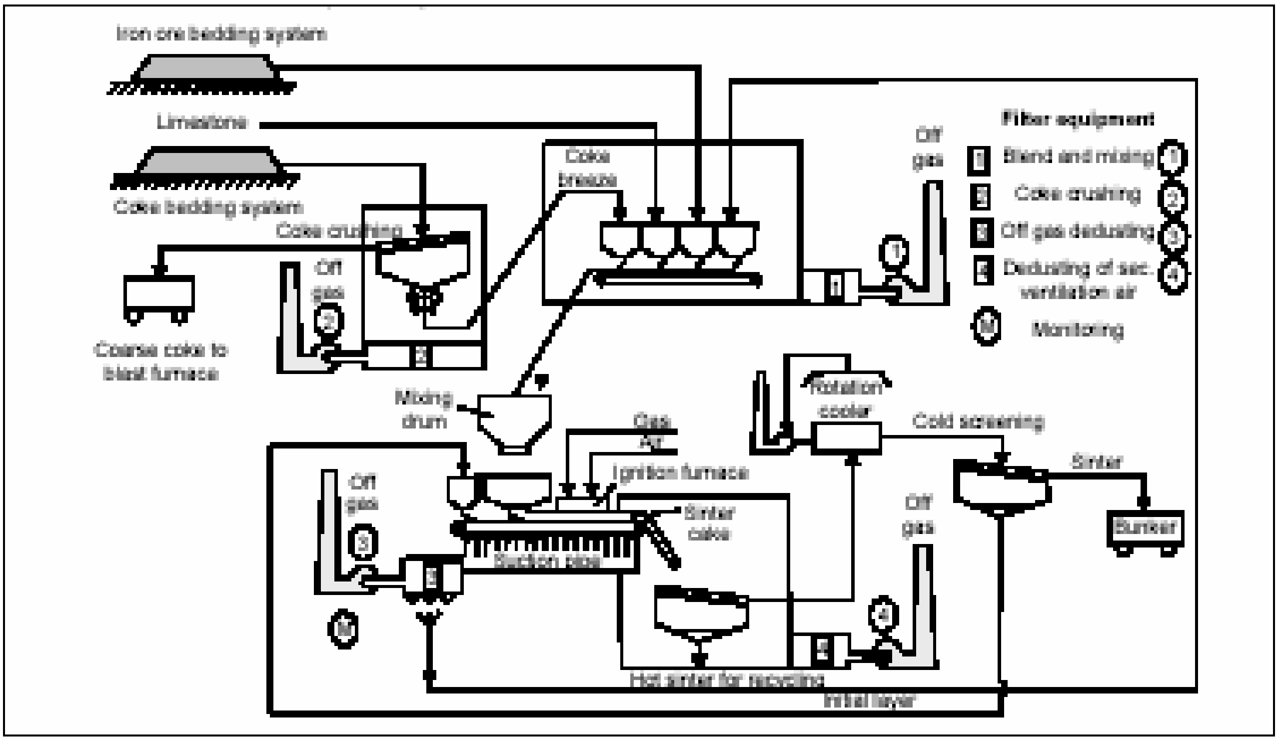
A blast furnace is a vertical furnace using tuyeres to blast heated or cold air into the furnace burden to smelt the contents. Sinter is charged into the top of the blast furnace in alternating layers with coke.

The flexibility of the sintering process permits conversion of a variety of materials, including iron ore fines, captured dusts, ore concentrates, and other iron-bearing materials of small particle size (e.g. mill scale) into a clinker-like agglomerate (Lankford et al. 1985, p. 305–306). The types and amounts of materials that are recycled can vary widely; this may be a significant factor in determining formation and release of chemicals listed in Annex C of the Stockholm Convention.

Waste gases are usually treated for dust removal in electrostatic precipitators; more recently, fabric filters and (less commonly) wet scrubbers have been used. Any of these may be preceded by a cyclone or other inertial removal device in order to reduce the loading to the final particulate collection device.

Figure 1 provides a schematic of an iron sintering plant

Figure 1. Process diagram of a sinter plant



Source: United Kingdom Environment Agency, 2001

2. Sources of chemicals listed in Annex C of the Stockholm Convention

As regards emissions of chemicals listed in Annex C of the Stockholm Convention, iron sintering has been identified as a source of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The formation and release of hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) have yet to be fully assessed.

2.1 Releases to air

2.1.1 General information on emissions from iron sintering plants

The following information is drawn from Environment Canada 2001, p. 23–25.

> “Emissions from the sintering process arise primarily from materials-handling operations, which result in airborne dust, and from the combustion reaction on the strand. Combustion gases from the latter source contain dust entrained directly from the strand along with products of combustion such as CO, CO_2, SO_x, NO_x, and particulate matter. The concentrations of these substances vary with the quality of the fuel and raw materials used and combustion conditions. Atmospheric emissions also include volatile organic compounds (VOCs) formed from volatile material in the coke breeze, oily mill scale, etc., and dioxins and furans, formed from organic material under certain operating conditions. Metals are volatilized from the raw materials used, and acid vapours are formed from the halides present in the raw materials.
>
> Combustion gases are most often cleaned in electrostatic precipitators (ESPs), which significantly reduce dust emissions but have minimal effect on the gaseous emissions. Water scrubbers, which are sometimes used for sinter plants, may have lower particulate collection efficiency than ESPs but higher collection efficiency for gaseous emissions. Significant amounts of oil in the raw material feed may create explosive conditions in the ESP. Sinter crushing and screening emissions are usually controlled by ESPs or fabric filters. Wastewater discharges, including runoff from the materials storage areas, are treated in a wastewater treatment plant that may also be used to treat blast furnace wastewater.
>
> Solid wastes include refractories and sludge generated by the treatment of emission control system water in cases where a wet emission control system is used. Undersize sinter is recycled to the sinter strand.”

2.1.2 Emissions of PCDD and PCDF

The processes by which PCDD/PCDF are formed are complex. PCDD/PCDF appear to be formed in the iron sintering process via de novo synthesis. PCDF generally dominate in the waste gas from sinter plants (William Lemmon and Associates Ltd. 2004, p. 20–21).

The PCDD/PCDF formation mechanism appears to start in the upper regions of the sinter bed shortly after ignition, and then the dioxin/furan and other compounds condense on cooler burden beneath as the sinter layer advances along the sinter strand towards the burn-through point. The process of volatilization and condensation continues until the temperature of the cooler burden beneath rises sufficiently to prevent condensation and the PCDD/PCDF exit with the flue gas. This appears to increase rapidly and peak just before burn-through and then decrease rapidly to a minimum. This is supported by the dioxin/furan profile compared to the temperature profile along the sinter strand in several studies.

The quantity of PCDD and PCDF formed has been shown to increase with increasing carbon and chlorine content. Carbon and chloride are present in some of the sinter feed materials typically processed through a sinter plant.

2.1.3 Research findings of interest

It appears that the composition of the feed mixture has an impact on the formation of PCDD/PCDF, i.e., increased chlorine content can result in increased PCDD/PCDF formation and the form of the carbon source appears to be more significant than simply the amount of carbon. The replacement of coke as a fuel with anthracite coal appears to reduce PCDD/PCDF concentration.

The form of the solid fuel (another potential carbon source) has also been noted to impact furan emissions. Changing between coal, graphite, and activated coke in a Japanese laboratory research programme reduced pentachlorinated dibenzofuran emissions by approximately 90%.

The operating parameters of the sintering process appear to have an impact on the formation of PCDD/PCDF (William Lemmon and Associates Ltd. 2004).

2.2 Releases to other media

No information has been identified on releases of chemicals listed in Annex C from iron sintering operations to other media such as through wastewater or collected dusts.

3. Alternatives

In accordance with the Stockholm Convention, when consideration is being given to proposals for construction of a new iron sintering plant, consideration should be given to alternative processes, techniques or practices that have similar usefulness but avoid the formation and release of chemicals listed in Annex C. With respect to iron sintering, careful consideration should be given to the benefits of sintering in recycling iron wastes and the need for sintering in traditional iron and steel making processes using coke and blast furnaces, and the various stages of existing steel production and product mixes. For any alternative processes the environmental advantages and disadvantages of these alternatives should also be carefully assessed. A comprehensive review of alternative ironmaking processes is provided by Lockheed Martin Energy Systems, 2000 and Augerman, 2004.

Alternative processes to iron sintering include:

3.1 Direct reduction

This technique, also known as direct reduction iron or hot briquetted iron, processes iron ore to produce a direct reduced iron product that can be used as a feed material to steel-manufacturing electric arc furnaces, iron-making blast furnaces, or steel-making basic oxygen furnaces. Natural gas is reformed to make hydrogen and carbon dioxide, where hydrogen is the reductant used to produce the direct reduced iron. The availability and cost of natural gas will impact the feasibility of using this technique.

Two new direct reduction processes for iron ore fines, Circored® and Circofer®, are available. Both processes use a two-stage configuration, combining a circulating fluidized bed with a bubbling fluidized bed. The Circored process uses hydrogen as reductant. The first-of-its-kind Circored plant was built in Trinidad for the production of 500,000 tons per year of hot briquetted iron and commissioned in 1999. In the Circofer process, coal is used as reductant. In some direct reduction process systems (e.g. Fastmet®), various carbon sources can be used as the reductant. Examples of carbon sources that may be used include coal, coke breeze and carbon-bearing steel mill wastes (blast furnace dust, sludge, basic oxygen furnace dust, mill scale, electric arc furnace dust, sinter dust). These processes convert iron oxide pellet feed, oxide fines or steel mill wastes into metallic iron, and produces a direct reduced iron product suitable for use in a blast furnace.

An innovative air-based direct smelting technology, called the HIsmelt iron-making process, has been developed recently. The process takes place under pressure within a vertical smelt reduction vessel that has a refractory lined hearth and a water-cooled topspace. The biggest advantage of the process to iron makers is that it produces hot metal without the need for coke ovens and sinter plants.

Other patented technologies such as Tecnored® are reported by Lockheed Martin Energy Systems, 2000.

3.2 Direct smelting

Direct smelting replaces the traditional combination of sinter plant, coke oven and blast furnace to produce molten iron. A number of direct smelting processes are evolving and are at various stages of development and commercialization.

4. Primary and secondary measures

Primary and secondary measures for reducing emissions of PCDD and PCDF from iron sintering processes are outlined below. Much of this material has been drawn from William Lemmon and Associates Ltd. 2004.

The extent of emission reduction possible with implementation of primary measures only is not fully understood and may well be plant specific.

A review of experiences of sinter plant waste gas cleaning by European industry is presented by the Nordic Council et al., June 2006. A review of experiences by Nordic facilities is included in a general best available techniques review by Norden 2006.

4.1 Primary measures

Primary measures are understood to be pollution prevention measures that will prevent or minimize the formation and release of chemicals listed in Annex C. These are sometimes referred to as process optimization or integration measures. Pollution prevention is defined as: "The use of processes, practices, materials, products or energy that avoid or minimize the creation of pollutants and waste, and reduce overall risk to human health or the environment" (see section III.B of the present guidelines).

Primary measures have been identified that may assist in preventing and minimizing the formation and release of chemicals listed in Annex C. Plant-specific emission reductions associated with implementation of the following primary measures only are not known and would need to be assessed. It is recommended that the following measures be implemented together with appropriate secondary measures to ensure the greatest minimization and reduction of emissions possible. Identified primary measures include the following:

4.1.1 Stable and consistent operation of the sinter strand

Research has shown that PCDD/PCDF are formed in the sinter bed itself, probably just ahead of the flame front as the hot gases are drawn through the bed. Disruptions to the flame front (i.e., non-steady-state conditions) have been shown to result in higher PCDD/PCDF emissions.

Sinter strands should be operated to maintain consistent and stable process conditions (i.e., steady-state operations, minimization of process upsets) in order to minimize the formation and release of PCDD, PCDF and other pollutants. Operating conditions requiring consistent management include strand speed, bed composition (consistent blending of revert materials, minimization of chloride input), bed height, use of additives (for example, addition of burnt lime may help reduce PCDD/PCDF formation), minimization of oil content in mill scale, minimization of air in-leakage through the strand, ductwork and off-gas conditioning systems, and minimization of strand stoppages. This approach will also result in beneficial operating performance improvements (e.g. productivity, sinter quality, energy efficiency) (European Commission 2000, p. 47; IPPC 2001, p. 39).

4.1.2 Continuous parameter monitoring

A continuous parameter monitoring system should be employed to ensure optimum operation of the sinter strand and off-gas conditioning systems. Various parameters are measured during emission testing to determine the correlation between the parameter value and the stack emissions. The identified parameters are then continuously monitored and compared to the optimum parameter values. Variances in parameter values can be alarmed and corrective action taken to maintain optimum operation of the sinter strand and emission control system.

Operating parameters to monitor may include damper settings, pressure drop, scrubber water flow rate, average opacity and strand speed.

Operators of iron sintering plants should prepare a site-specific monitoring plan for the continuous parameter monitoring system that addresses installation, performance, operation and maintenance, quality assurance and record keeping, and reporting procedures. Operators should keep records documenting conformance with the identified monitoring requirements and the operation and maintenance plan (EPA 2003).

4.1.3 Recirculation of off-gases

Recycling of sinter off-gas (waste gas) has been shown to minimize pollutant emissions, and reduce the amount of off-gas requiring end-of-pipe treatment. Recirculation of part of the off-gas from the entire sinter strand, or sectional recirculation of off-gas, can minimize formation and release of pollutants. For further information on this technique see ECSC 2003 and European Commission 2000, p. 56–62.

Recycling of iron sintering off-gases can reduce emissions of PCDD/PCDF, NO_x and SO_2. However, this option can also lead to reduced production, can affect sinter quality and may result in increased workplace dust exposure and maintenance requirements. Any such measure needs to be carefully implemented taking into account its potential to impact other aspects of plant operation.

4.1.4 Feed material selection

Unwanted substances should be minimized in the feed to the sinter strand. Unwanted substances include persistent organic pollutants and other substances associated with the formation of PCDD/PCDF, HCB and PCB (e.g. chlorine/chlorides, carbon, precursors and oils). Poor control over inputs can also affect the operation of the blast furnace.

A review of feed inputs should be conducted to determine their composition, structure and concentration of substances associated with persistent organic pollutants and their formation. Options to eliminate or reduce the unwanted substances in the feed material should be identified. For example:

- Removal of the contaminant from the material (e.g. de-oiling of mill scales);
- Substitution of the material (e.g. replacement of coke breeze with anthracite);
- Avoidance of the use of the contaminated material (e.g. avoid processing electrostatic precipitator sinter dusts, which have been shown to increase PCDD/PCDF formation and release) (Kasai et al. 2001);
- Specification of limits on permissible concentrations of unwanted substances (e.g. oil content in feed should be limited to less than 0.02%) (EPA 2003).

Documented procedures should be developed and implemented to carry out the appropriate changes.

4.1.5 Feed material preparation

Fine feed materials (for example, collected dusts) should be adequately agglomerated before they are placed on the sinter strand and feed materials should be intimately mixed or blended. These measures will minimize formation and entrainment of pollutants in the waste gas, and will also minimize fugitive emissions.

4.1.6 Urea injection

Tests using urea injection to suppress formation of dioxins and furans have been conducted at an iron sintering plant in the United Kingdom. Controlled quantities of urea prills were added to the sinter strand. This technique is thought to prevent or reduce both PCDD/PCDF and sulphur dioxide emissions. The trials indicated that PCDD/PCDF formation was reduced by approximately 50%. It is estimated that a 50% reduction in PCDD/PCDF would achieve a 0.5 ng I-TEQ/m^3 emission concentration. Capital costs are estimated at UK£0.5 million to £1 million per plant (approximately US$0.9 million to $1.8 million) (Entec UK Ltd. 2003, p. D10–D20).

A number of European sinter facilities have tested urea addition and reported that PCDD/PDFF emission could be reduced by 50% by addition of small quantities of urea into the sinter mix (Hartig, Steden and Lin, 2005). However it was also reported that there were additional emissions of dust, NOx and NH3 in the cleaned waste gases (presumably using the existing air pollution prevention and control systems). Also, while significant reductions of SO2 were found in some facilities, other facilities indicated that ammonia compounds may adulterate SO2 results by using conventional measurement methods. It was not reported, however, if these trials tried to optimize and modify air pollution prevention and control systems for various pollutants. As of December 2005 it was reported that no member of the European industry association was using urea addition in their current operations at that time

At Canada's only sinter plant, operated by Stelco Inc. in Hamilton, Ontario, trials have been completed using a new similar process in order to reduce dioxin emissions. Stelco found that sealing the furnace to reduce the amount of oxygen and adding a small amount of urea interfered with the chemical reaction that produces dioxins, resulting in reduced emissions. This new process configuration, combined with air-scrubbing systems, released 177 pg/m^3 of dioxins in a test. This result surpasses the 2005 Canada-wide standard limit of 500 pg/Rm^3 and is below the 200 pg/Rm^3 limit for 2010. It also represents a 93% reduction from the 1998 measured levels of 2,700 pg/Rm^3. The improvement clearly does not depend on scrubbing dioxins out of the stack gases, but is thought to result from "true pollution prevention", as chlorine is needed to produce dioxins and the urea releases ammonia, which captures chlorides in the dust, reducing its availability for dioxin formation (*Hamilton Spectator* 1 March 2006).

4.2 Secondary measures

Secondary measures are understood to be pollution control technologies or techniques, sometimes described as end-of-pipe treatments.

Primary measures identified earlier should be implemented together with appropriate secondary measures to ensure the greatest minimization and reduction of emissions possible. Measures that have been shown to effectively minimize and reduce PCDD and PCDF emissions include:

4.2.1 Removal techniques

4.2.1.1 Adsorption/absorption and high-efficiency dedusting

This technique involves sorption of PCDD/PCDF to a material such as activated carbon, together with effective particulate matter (dedusting) control.

For regenerative activated carbon technology an electrostatic precipitator is used to reduce dust concentration in the off-gases prior to entry to the activated carbon unit (William Lemmon and Associates Ltd. 2004). The waste gas passes through a slowly moving bed of char granules, which acts as a filter/adsorption medium. The used char is discharged and transferred to a regenerator, where it is heated to elevated temperatures. PCDD/PCDF adsorbed to the char are decomposed and destroyed within the inert atmosphere of the regenerator. This technique has been shown to reduce emissions to 0.1 to < 0.3 ng I-TEQ/m^3.

Another sorption technique is the use of lignite or activated carbon injection, together with a fabric filter. PCDD/PCDF are sorbed onto the injected material, and the material is collected in the fabric filter. Along with good operation of the sinter strand, this technique is associated with PCDD/PCDF emission concentrations ranging from 0.1 to 0.5 ng I-TEQ/m^3 (IPPC 2001, p. 135).

In principle it should be possible to inject carbon into the gas stream ahead of existing dust collectors such as electrostatic precipitators and fabric filters in the same manner that some incinerators control emissions of persistent organic pollutants, and there has been some success with this technique for iron sintering in Belgium. Capital costs for adding carbon to existing equipment would be much less than for adding a regenerative active carbon system.

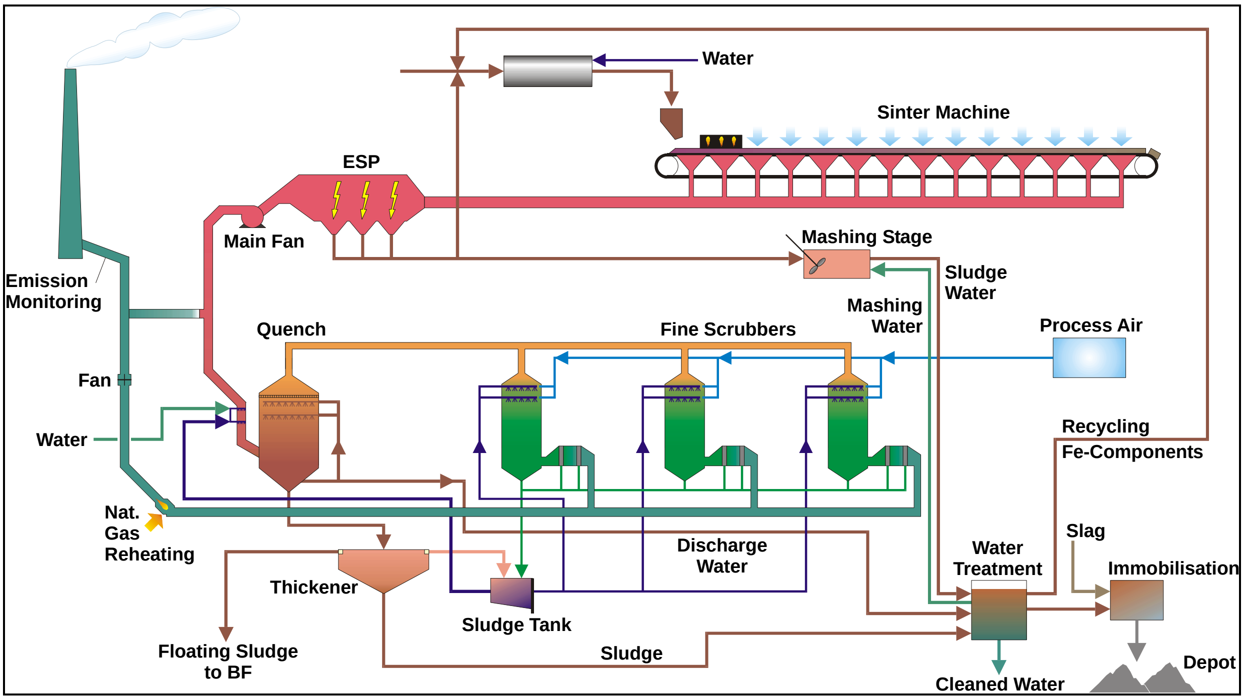
4.2.1.2 Fine wet scrubbing system

The Airfine scrubbing system, shown in Figure 2, developed by Voest Alpine Industries (Austria), has been shown to effectively reduce emission concentrations to 0.2 to 0.4 ng I-TEQ/m^3. The scrubbing system uses a countercurrent flow of water against the rising waste gas to scrub out coarse particles and gaseous components (for example, sulphur dioxide (SO_2)), and to quench the waste gas. (An electrostatic precipitator may also be used upstream for preliminary dedusting.) Caustic soda may be added to improve SO_2 absorption. A fine scrubber, the main feature of the system, follows, employing high-pressure mist jet co-current with the gas flow to remove impurities. Dual flow nozzles eject water and compressed air (creating microscopic droplets) to remove fine dust particles, PCDD and

PCDF (William Lemmon and Associates Ltd. 2004, p. 29–30; European Commission 2000, p. 72–74).

This technique should be combined with effective treatment of the scrubber wastewaters and wastewater sludge should be disposed of in a secure landfill (European Commission 2000). The application of this technique should be considered cautiously with respect to its suitability for each site.

Figure 2. Process diagram of a sinter plant using a web scrubbing system



Source: Hofstadler et al. 2003.

4.2.2 General measures

The following measures can assist in minimizing pollutant emissions, but should be combined with other measures (e.g. adsorption/absorption, recirculation of off-gases) for effective control of PCDD/PCDF formation and release.

4.2.2.1 Removal of particulate matter from sinter off-gases

It has been suggested that effective removal of dust can help reduce emissions of PCDD and PCDF. Fine particles in the sinter off-gas have an extremely large surface area for adsorption and condensation of gaseous pollutants, including PCDD and PCDF (Hofstadler et al. 2003). The best available technique for removal of particulate matter is the use of fabric filters. Fabric filters used at sinter plants are associated with particulate matter emission concentrations of < 10 to < 30 mg/m^3 (UNECE 1998; IPPC 2001, p. 131).

Other particulate control options that are commonly used for sinter plant off-gases include electrostatic precipitators and occasionally wet scrubbers, though their particulate removal efficiencies are not as high as for fabric filters. Good performance of electrostatic precipitators and high-efficiency wet gas scrubbers is associated with particulate matter concentrations of < 30 to 50 mg/m^3 (IPPC 2001; William Lemmon and Associates Ltd. 2004, p. 26; UNECE 1998).

Adequately sized capture and particulate emission controls for both the feed and discharge ends should be required and put in place.

Fabric filters can also be fitted downstream of electrostatic precipitators, allowing separate collection and use of the dusts they collect.

4.2.2.2 Hooding of the sinter strand

Hooding of the sinter strand reduces fugitive emissions from the process, and enables use of other techniques, such as waste gas recirculation.

5. Emerging research

Selective catalytic reduction has been used for controlling NO_x emissions from a number of industrial processes, including iron sintering. Modified selective catalytic reduction technology (i.e., increased reactive area) and select catalytic processes have been shown to decompose PCDD and PCDF contained in off-gases, probably through catalytic oxidation reactions. This may be considered an emerging technique with potential for reducing emissions of persistent organic pollutants from iron sintering plants and other applications.

A study investigating stack emissions from four sinter plants noted lower concentrations of PCDD/PCDF (0.995–2.06 ng I-TEQ/Nm^3) in the stack gases of sinter plants with selective catalytic reduction than a sinter plant without (3.10 ng I-TEQ/Nm^3), and that the PCDD/PCDF degree of chlorination was lower for plants with selective catalytic reduction. It was concluded that selective catalytic reduction did indeed decompose PCDD/PCDF, but would not necessarily be sufficient as a stand-alone PCDD/PCDF destruction technology to meet stringent emission limits. Add-on techniques (for example, activated carbon injection) may be required (Wang et al. 2003, p. 1123–1129).

Catalytic oxidation can, subject to catalyst selection, be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process. Further study of the use of selective catalytic reduction and other catalytic oxidation techniques at iron sintering applications is needed to determine its value and effectiveness in destroying and reducing PCDD/PCDF released from this source.

6. Summary of measures

Tables 1 and 2 present a summary of the measures discussed in previous sections.

Table 1. Alternatives and requirements for new iron sintering plants

Measure	**Description**	**Considerations**	**Other comments**
Alternative processes	Priority consideration should be given to alternative processes with potentially less environmental impacts than traditional iron sintering	Examples include: • Pelletization plants • Direct reduction of iron (Fastmet®, Circored® and Circofer®) • Direct smelting	
Performance requirements	New iron sintering plants should be permitted to achieve stringent performance and reporting requirements associated with best available techniques	Consideration should be given to the primary and secondary measures listed in Table 2 below	Performance levels associated with BAT and BEPare: < 0.2 ng I-TEQ/Nm^3 for PCDD/PCDF and may be as low as<0.1ng I-TEQ/N

Table 2. Summary of primary and secondary measures for iron sintering plants

Measure	**Description**	**Considerations**	**Other comments**
Primary measures			
Stable and consistent operation of the sinter plant	The sinter strand should be operated to maintain stable consistent operating conditions (steady-state conditions, minimization of process upsets) to minimize formation of PCDD, PCDF and other pollutants	Conditions to optimize operation of the strand include: • Minimization of stoppages • Consistent strand speed • Bed composition • Bed height • Additives (e.g. burnt lime) • Minimization of oil content • Minimization of air in-leakage	This approach will have co-benefits such as increased productivity, increased sinter quality and improved energy efficiency. Impact on chemicals listed in Annex C would need to be assessed on a plant-specific basis
Continuous parameter monitoring	A continuous parameter monitoring system should be employed to ensure optimum operation of the sinter strand and off-gas conditioning systems. Operators should prepare a site-specific monitoring plan for the continuous parameter monitoring system and keep records that document conformance with the plan	Correlations between parameter values and stack emissions (stable operation) should be established. Parameters are then continuously monitored in comparison to optimum values. System can be alarmed and corrective action taken when significant deviations occur	
Recirculation of waste gases	Waste gases may be recycled back to the sinter strand to minimize pollutant emissions and reduce the amount of off-gas requiring end-of-pipe treatment	Recirculation of the waste gases can entail recycling of part of the off-gas from the entire sinter strand, or sectional recirculation of off-gas	This technique will result in only a modest reduction of PCDD/PCDF but can have significant impacts on other operational parameters and should be carefully assessed
Feed material selection: Minimization of feed materials contaminated with persistent organic pollutants or leading to their formation	A review of feed materials and identification of alternative inputs and/or procedures to minimize unwanted inputs should be conducted. Documented procedures should be developed and implemented to carry out the appropriate changes	Examples include: • Removal of the contaminant from the material (e.g. de-oiling of mill scales) • Substitution of the material (e.g. replacement of coke breeze with anthracite) • Avoid use of the material (e.g. collected sinter electrostatic precipitator dust)	Plant-specific assessment may be needed

Measure	Description	Considerations	Other comments
		- Specification of limits on permissible concentrations of unwanted substances (e.g. oil content in feed should be limited to less than 0.02%)	
Feed material preparation	Fine material (e.g. collected dusts) should be agglomerated before being placed on the sinter strand. Feed materials should be intimately mixed before placement on the sinter strand		These measures will help reduce entrainment of pollutants in the waste gas, and minimize fugitive emissions
Urea addition	Controlled quantities of urea prills are added to feed mix on the sinter strand; this technique is thought to prevent or reduce both PCDD/PCDF and sulphur dioxide emissions	Need to seal the strand to reduce the amount of oxygen (ammonia acts as a reducing agent; excess oxygen as an oxidant). Recommended for use combined with air-scrubbing systems to remove nitrogenous gaseous emissions	
Secondary measures			
The following secondary measures can effectively reduce emissions of PCDD/PCDF and should be considered as examples of best available techniques:			
Adsorption/ absorption and high-efficiency dedusting	Use of this technique should include an adsorption stage together with high-efficiency particulate control as key components of the off-gas conditioning system	The following adsorption techniques have been demonstrated: - Injection of carbon with collection on electrostatic precipitators - Regenerative activated carbon technology whereby off-gases are first cleaned by electrostatic precipitator, and passed through moving adsorption bed (char) to both adsorb PCDD/PCDF and to filter particulates. Adsorptive material is then regenerated - Injection of activated carbon, lignite or other similar adsorptive material into the gas stream followed by fabric filter dedusting	These techniques are associated with the following emission concentration levels: < 0.3 ng I-TEQ/m^3; 0.1 to 0.5 ng I-TEQ/m^3. Cost-effectiveness of different carbon-based adsorption systems needs to be assessed carefully; in-flight injection would probably be much less expensive than regenerative carbon bed systems

Measure	Description	Considerations	Other comments
Fine wet scrubbing of waste gases	Use of this technique should include a preliminary countercurrent wet scrubber to quench gases and remove larger particles, followed by a fine scrubber using high pressure mist jet co-current with off-gases to remove fine particles and impurities		The fine wet scrubbing system under the trade name Airfine®, as developed by Voest Alpine Industries, has been shown to reduce emission concentrations to 0.2 to 0.4 ng I-TEQ/m^3. However application should be considered cautiously for each site.
The following secondary measures should not be considered best available techniques on their own. For effective minimization and reduction of PCDD, PCDF and other persistent organic pollutants, these measures should be employed in concert with other identified measures:			
Removal of particulate matter from waste gases	Waste gases should be treated using high-efficiency techniques, as this can help minimize PCDD/PCDF emissions. A recommended best available technique for particulate control is the use of fabric filters. Feed and discharge ends of the sinter strand should be adequately hooded and controlled to capture and mitigate fugitive emissions	Fabric filters have been shown to reduce sinter off-gas particulate emissions to < 10 to < 30 mg/m^3	Other particulate control techniques used include electrostatic precipitators and high-efficiency scrubbers. Good performance of these technologies is associated with particulate concentrations of < 30 to 50 mg/m$^{3.}$ Lower particulate emissions (and associated Dioxins and Furans) may be achieved with fabric filters <5 to 20 mg/m3
Hooding of the sinter strand	The sinter strand should be hooded to minimize fugitive process emissions		Hooding of the strand will enable use of other measures, such as waste gas recirculation

7. Performance levels associated with BAT and BEP

Performance levels associated with BAT and BEP for emissions of PCDD/PCDF from iron sintering plants are <0.2 ng I.TEQ/Mm^3 (at operating oxygen concentrations).

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(iii) Secondary aluminium production

Summary

Secondary aluminium smelting involves the production of aluminium from used aluminium products or process waste to recover metals by pretreatment, smelting and refining.

Fuels, fluxes and alloys are used, while magnesium removal is practised by the addition of chlorine, aluminium chloride or chlorinated organics. Chemicals listed in Annex C of the Stockholm Convention probably result from demagging additions, incomplete combustion, organics in the feed, chlorine compounds and formation in the system at temperatures between 250° and 500° C.

Best available techniques include high-temperature advanced furnaces, oil- and chlorine-free feeds (if alternatives are available), afterburners with rapid quench, activated carbon adsorption and dedusting fabric filters, as well as avoiding the use of hexachloroethane for the removal of magnesium from the melt (demagging) and maintaining careful control over demagging in general.

Performance levels associated with best available techniques and best environmental practices for secondary aluminium smelters: < 0.5 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

1. Process description

Processes used in secondary aluminium smelting are dependent on feed material. Pretreatment, furnace type and fluxes used will vary with each installation. Production processes involve scrap pretreatment and smelting/refining. Pretreatment methods include mechanical, pyrometallurgical and hydrometallurgical cleaning. Smelting is conducted using reverberatory or rotary furnaces. Induction furnaces may also be used to smelt the cleaner aluminium feed materials.

Reverberatory furnaces consist of two sections: a smelting chamber heated by a heavy oil burner and an open well where aluminium scraps of various sizes are supplied. Rotary furnaces consist of a horizontal cylindrical shell mounted on rollers and lined with refractory material. The furnace is fired from one end, usually using gas or oil as the fuel.

Feed consists of process scrap, used beverage cans, foils, extrusions, commercial scraps, turnings and old rolled or cast metal. Skimmings from the secondary smelting process are also recycled as feed. Presorting of scrap into desired alloy groups can reduce processing time. Scrap is often contaminated with oil or coatings, which must be removed to reduce emissions and improve melting rate (European Commission 2001, p. 279). Salt slag is treated to recover the salt, which is reutilized as flux in rotary furnaces. The residue from the salt slag treatment has a high aluminium oxide (Al_2O_3) content and can be recycled using the Bayer process or used as an additive in the cement industry.

The following summary of the process is drawn from EPA 1994:

> "Most secondary aluminium recovery facilities use batch processing in smelting and refining operations. The melting furnace is used to melt the scrap, and remove impurities and entrained gases. The molten aluminium is then pumped into a holding furnace. Holding furnaces are better suited for final alloying, and for making any additional adjustments necessary to ensure that the aluminium meets product specifications. Pouring takes place from holding furnaces, either into molds or as feedstock for continuous casters.
>
> Smelting and refining operations can involve the following steps: charging, melting, fluxing, demagging, degassing, alloying, skimming, and pouring. Charging consists of placing

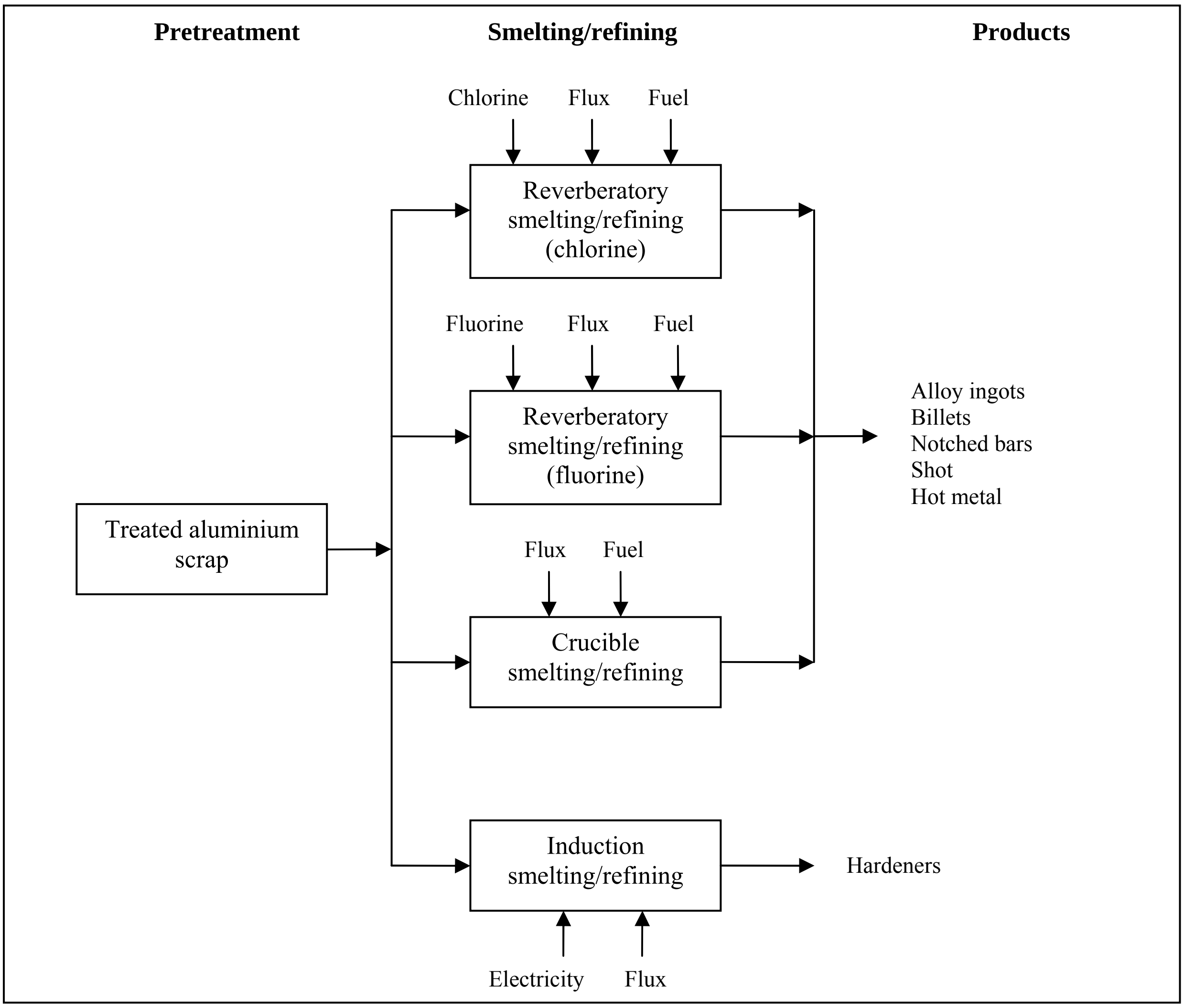
pretreated aluminium scrap into a melted aluminium pool (heel) that is maintained in melting furnaces. The scrap, mixed with flux material, is normally placed into the furnace charging well, where heat from the molten aluminium surrounding the scrap causes it to melt by conduction. Flux materials combine with contaminates and float to the surface of the aluminium, trapping impurities and providing a barrier (up to 6 inches thick) that reduces oxidation of the melted aluminium. To minimize aluminium oxidation (melt loss), mechanical methods are used to submerge scrap into the heel as quickly as possible.

Demagging reduces the magnesium content of the molten charge. In the past, when demagging with liquid chlorine, chlorine was injected under pressure to react with magnesium as the chlorine bubbled to the surface. The pressurized chlorine was released through carbon lances directed under the heel surface, resulting in high chlorine emissions. A more recent chlorine aluminium demagging process has replaced the carbon lance procedure. Chlorine gas is metered into the circulation pump discharge pipe. It is anticipated that reductions of chlorine emissions (in the form of chloride compounds) will be reported in the future. Other chlorinating agents or fluxes, such as anhydrous aluminium chloride or chlorinated organics, are used in demagging operations.

Degassing is a process used to remove gases entrained in molten aluminium. High-pressure inert gases are released below the molten surface to violently agitate the melt. This agitation causes the entrained gases to rise to the surface to be absorbed in the floating flux.

Alloying combines aluminium with an alloying agent in order to change its strength and ductility. The skimming operation physically removes contaminated semisolid fluxes (dross, slag, or skimmings) by ladling them from the surface of the melt.”

Figure 1. Secondary aluminium smelting



Source: EPA 1994.

Artisanal and other small-scale aluminium recovery processes are used in a number of countries. Achievable performance limits are not applicable to artisanal and small-scale aluminium recovery processes as the processes used cannot be considered best available techniques or best environmental practices and ideally would not be practised at all. Sometimes largely unsorted scrap is melted in a small crucible or furnace housed in a building or a roofed space, most often inadequately ventilated. This device may be fired with charcoal, oil, waste oil or coal, depending on economic factors and the local fuel supply situation. In larger furnaces, the melt may be treated with fluxes and degasifying chemicals to improve the quality of the molten metal. Artisanal and other small-scale aluminium recovery processes may release many chemicals into the environment, including persistent organic pollutants. These processes should be discouraged in favour of using the proper air pollution controls on larger-scale secondary aluminium smelting operations.

However, where artisanal and other small-scale aluminium recovery processes are practised, certain measures can be put in place in order to reduce the amount of pollutants released into the environment. Measures to reduce emissions of persistent organic pollutants and other pollutants from artisanal processes include presorting of scrap material, selecting a better fuel supply (oil or gas fuels instead of coal), adequate ventilation, filtration of exhaust gases, proper management of wastes and proper choice of degasifiers. These measures can be achieved by education and outreach programmes working with craft groups and town authorities.

Effective presorting can lead to significant reductions in releases of persistent organic pollutants. Manual scrap sorting, rather than mechanical sorting, is feasible in some economies, depending on the balance between labour costs and capital availability. Proper training and supervision can make manual scrap sorting highly effective, and has the potential to lead to improvements in energy consumption and product quality and a reduction in the amount of slag to be disposed of. The drying of feed materials and prewarming of refractories, while using more fuel, reduces hydrogen production in the melt and so can improve product quality without use of chemicals.

Adequate ventilation of the workplace will reduce workplace exposure. Extraction of fumes and off-gases through a chimney and hood enclosure around the crucible by providing natural draught will aid ventilation and provide some dispersion but will not reduce emissions except by improving the quality of combustion. Heating with oil or gas fuels reduces the amount of persistent organic pollutants formed.

In larger facilities, ducting exhaust gases and fitting pollution controls may be feasible. Filters, dry scrubbers or wet scrubbers for particle abatement can be effective at pollution control but require a reliable electricity supply to power the fans. Wet scrubbers require appropriate arrangements for the collection, treatment and safe disposal of effluent. All pollution control systems require appropriate residue handling arrangements and disposal routes to be in place before installation. If effluent treatment is not in place then dry air pollution control devices should be preferred. However, storage of fine particulate matter is demanding in many environments and appropriate storage and waste arrangements are required for the captured material until a safe disposal route is identified. Co-location of facilities and regional cooperation to manage and dispose of wastes would be beneficial.

The use of hexachloroethane as a degasifier for reducing melts has been thought to lead to significant release of persistent organic pollutants. The use of potassium fluoride or potassium aluminium fluoride as a degassing agent has proved successful in some larger plants. Other large plants have successfully used chlorine as a degasifier. At these locations appropriate handling and safety arrangements are in place, including appropriately trained staff.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

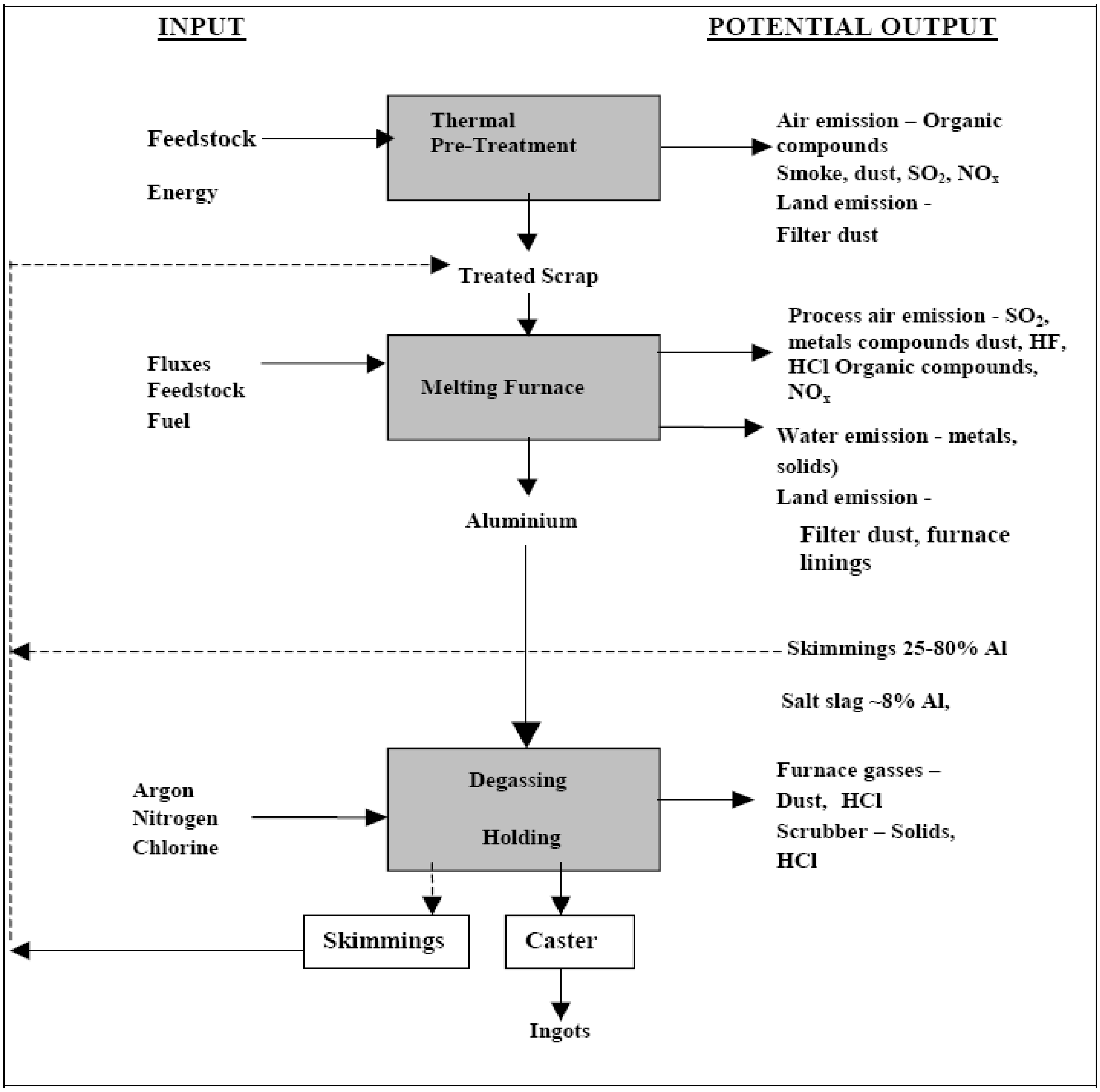
The generation of chemicals listed in Annex C of the Stockholm Convention is probable due to incomplete combustion and addition of contaminants in the feed, and from chemical additions for demagging combined with process conditions favourable to formation of persistent organic pollutants.

2.1 General information on emissions from secondary aluminium smelters

Potential emissions to air include dust, metal compounds, chlorides, nitrogen oxides (NO_x), sulphur dioxide (SO_2) and organic compounds such as polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and carbon monoxide (CO). Ammonia can also be generated from the improper storage, treatment and transport of skimmings. Chlorine compounds can be removed using wet or dry scrubbers and their formation minimized by good control and the use of mixtures of chlorine and inert gases. Low-NO_x burners and low-sulphur fuels can be used to decrease emissions of NO_x and SO_2 (European Commission 2001, p. 294–300).

> "Afterburning is used to destroy organic materials that escape the combustion zone, while injection of treatment materials such as lime, sodium bicarbonate and carbon is also practised. Most installations then use (high-efficiency) bag filters or ceramic filters to remove dust and emissions can lie in the range 0.6 to 20 mg/Nm^3. A spark arrester or cooling chamber often precedes them to provide filter protection. Energy recovery can be practised, most commonly recuperative burners are used" (European Commission 2001).

Figure 2. Input and output from secondary aluminium production



Note: Smoke and dust can be associated with volatile organic compounds and dioxins (European Commission 2001).

2.2 Emissions of PCDD/PCDF to air

PCDD/PCDF are formed during aluminium smelting through incomplete combustion or by de novo synthesis when organic and chlorine compounds such as fluxes, hexachloroethane, chlorine, unburnt fuel, oils and plastics are present in the feed material. Secondary feed often consists of contaminated scrap.

> "The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reductants, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically bound chlorine in the temperature range of 250° to 500° C to produce PCDD/PCDF. This process is known as de novo synthesis and is catalysed by the presence of metals such as copper or iron.
>
> Although PCDD/PCDF are destroyed at high temperature (above 850° C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled through the "reformation window". This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the

> residence time in the window is practised to prevent de novo synthesis” (European Commission 2001, p. 133).
>
> “Poor combustion of fuel or the organic content of the feed material can result in the emission of organic materials. The provision of effective burner and furnace to controls is used to optimise combustion. Peak combustion rates from included organic materials need to be taken into account if they are fed to the furnace. It is reported that pre-cleaning of scrap removes much of the organic material and improves the melting rate. The use of chlorine mixtures for degassing and magnesium removal and the use of chlorides (salt flux) will provide a source of chlorine for the potential formation of PCDD/PCDF” (European Commission 2001, p. 297).

Based on information obtained from Japanese secondary aluminum operations, emissions have been found to vary according to the furnace type employed. The highest-emitting furnace type in this study was the open well reverberatory furnace. These units were found to average 0.38 ng I-TEQ/Nm^3. These results are believed to relate to the fact that this is the only furnace design that permits the introduction of large pieces of scrap material, and this material is often the most contaminated with organic compounds that may contribute to PCDD/PCDF formation (Government of Japan 2005).

2.3 Releases to other media

(European Commission 2001, p. 294–300)

> “Production of aluminium from secondary raw materials is essentially a dry process. Discharge of wastewater is usually limited to cooling water, which is often recirculated, and rainwater run-off from surfaces and roofs. The rainwater run-off can be contaminated by open storage of raw materials such as oily scrap and deposited solids.
>
> Salt slags arise when mixtures of sodium and potassium chloride are used to cover the molten metal to prevent oxidation, increase yield and increase thermal efficiency. These slags are generally produced in rotary furnaces and can have an environmental impact if they are deposited on land. Skimmings are used as a raw material in other parts of the secondary aluminium industry and are sometimes pretreated by milling and air classification to separate aluminium from aluminium oxide. Spent filters from metal treatment are usually disposed of. In some cases when sodium bicarbonate is used for gas cleaning, solid residues can be recovered with the salt flux. Alternatively filter dust can be treated thermally to destroy dioxins. Furnace linings and dust can be recovered in the salt slag treatment processes or disposed.”

3. Recommended processes

Process design and configuration is influenced by the variations in feed material and quality control. Processes considered as best available practices are the reverberatory furnace, rotary and tilting rotary furnaces, the induction furnace and the Meltower shaft furnace. All techniques should be applied in conjunction with suitable gas collection and abatement systems.

No information is available on alternative processes to smelting for secondary aluminium processing.

4. Primary and secondary measures

Primary and secondary measures for PCDD/PCDF reduction and elimination are discussed below.

4.1 Primary measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of persistent organic pollutants. Possible measures include:

4.1.1 Presorting of feed material

The presence of oils, organic materials including plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de novo synthesis. Sorting of feed material should be conducted prior to smelting to suit furnace type and abatement and to permit the transfer of unsuitable raw materials to other facilities better suited for their treatment. This will prevent or minimize the use of chloride salt fluxes during smelting.

Scrap material should be cleaned of oils, paints and plastics during pretreatment. The removal of organic and chlorine compounds will reduce the potential for PCDD/PCDF formation. Methods used include the swarf centrifuge, swarf drying or other thermal decoating techniques. Thermal decoating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas (European Commission 2001, p. 310).

Scrap sorting using laser and eddy current technology is being tested. These methods could provide more efficient selection of materials for recycling and the ability to produce desired alloys in recycling plants (European Commission 2001, p. 294–300).

4.1.2 Effective process control

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation, such as maintaining furnace temperature above 850° C to destroy PCDD/PCDF. Ideally, PCDD/PCDF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF.

4.1.3 Demagging

An essential measure to control chemicals listed in Annex C appears to be correct demagging (removal of magnesium from the melt). The use of hexachloroethane tablets has been shown to give rise to high releases of PCDD/PCDF and particularly hexachlorobenzene (HCB), and the practice has been banned in Europe. This is an important aspect of the process. The choice of a demagging approach requires careful assessment of the options since there are practical and health and safety considerations as well as environmental ones.

4.2 Secondary measures

Secondary measures are pollution control techniques. These methods do not eliminate the generation of contaminants, but serve as a means to contain and prevent emissions.

4.2.1 Fume and gas collection

Fume and off-gas collection should be implemented in the control of air emissions from all stages of the process. The use of sealed feeding systems and furnaces should be practised. Fugitive emissions should be controlled by maintaining negative air pressure within the furnace to prevent leaks. If a sealed unit is not possible, hooding should be used. Furnace or reactor enclosures may be necessary. Where primary extraction and enclosure of fumes is not practicable, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged (European Commission 2001, p. 187–188). Additional benefits of fume and off-gas collection from rooflines include reducing exposure of the workforce to fumes and heavy metals.

4.2.2 High-efficiency dust removal

Particulate matter generated during the smelting process should be removed as this material possesses a large surface area on which PCDD/PCDF, polychlorinated biphenyls (PCB) and HCB can adsorb. Proper isolation and disposal of these dusts will aid in PCDD/PCDF control. Collected particulate should be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals. Methods to consider are the use of fabric filters, wet and dry scrubbers and ceramic filters.

Scrubbing off-gases with sodium bicarbonate will remove chlorides produced by the salt flux, resulting in sodium chloride, which can then be removed by fabric filters to be recharged to the furnace. In addition, use of a catalytic coating on fabric filter bags could destroy PCDD/PCDF by oxidation while collecting particulate matter on which these contaminants have adsorbed (European Commission 2001, p. 294–300). Note that rapid cooling should be assured (see below) to ensure that formation does not take place in the dust abatement system.

4.2.3 Afterburners and quenching

Afterburners (post-combustion) should be used at a minimum temperature of 950° C to ensure full combustion of organic compounds (Hübner et al. 2000). This stage is to be followed by rapid quenching of hot gases to temperatures below 250° C. Oxygen injection in the upper portion of the furnace will promote complete combustion (European Commission 2001, p. 189).

It has been observed that PCDD/PCDF are formed in the temperature range of 250° to 500° C. They are destroyed above 850° C in the presence of oxygen. Yet, de novo synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Proper operation of cooling systems to minimize reformation time should be implemented (European Commission 2001, p. 133). A benefit of cooling the flue gases before scrubbbing would be reduced gas volume, hence reducing the size of abatement equipment, the duct size and the energy needs for gas movement.

4.2.4 Adsorption on activated carbon

Activated carbon treatment should be considered as this material is an ideal medium on which PCDD/PCDF can adsorb due to its large surface area. Off-gas treatment techniques include using fixed or moving bed reactors or injection of carbon into the gas stream followed by high-efficiency dust removal systems such as fabric filters. Lime/carbon mixtures can also be used.

4.2.5 Catalyst-coated filter

Japanese researchers have used a catalyst-coated filter on an experimental basis, and results are encouraging. This filter system consists of two filters, one to collect the soot and another coated with a catalyst to decompose dioxins and furans. The experimental work has demonstrated that the catalyst was effective at decomposing dioxins and furans at temperatures in the range of 180º to 200º C.

4.3 Best environmental practices

The following guidelines are derived from the Japan Aluminium Alloy Refiners Association (March 2004) and may be considered as best environmental practices:

Practical operation guidelines are presented below. The following main items are common to these guidelines:

- Do not purchase anything that is likely to generate smoke. Melt materials gradually;
- Perform smelting and combustion with no soot or smoke generation;
- Perfectly burn generated soot and smoke promptly;
- Quickly cool down exhaust gas at high or middle temperatures to 170° C or below;
- CO control in exhaust gas ($CO \leq 50$ ppm, air-fuel ratio management).

Operation guidelines:

1. Matters related to materials and scraps:
   - Reinforce sorting on and after accepting materials;
   - Sort and eliminate resin and oil;
   - Sort and eliminate foreign substances and resin after shredder processing;
   - Return materials where resin or oil is stuck. Do not accept them at discount prices.
2. At time of combustion and smelting at smelting chamber:

- Avoid turning the burner on and off as much as possible in order to reduce imperfect combustion and soot generation;
- Supply materials while the burner is on, and set generated smoke and soot in flame for secondary combustion.

3. At time of combustion and smelting in open well:

- Adjust the air-fuel ratio by measuring the CO and O_2 concentration in flue exhaust gas;
- In order to heat and burn smoke and soot generated from materials supplied to the open well, put the smoke and soot in burner flame;
- Adjust the supply of smelting materials according to the extent of smoke and flame (soot) generation:
  - Equalize the supply of burnable material (repetitively and little by little);
  - Keep the combustion space with no imperfect combustion;
  - Do not leak smoke from the exhaust gas hood;
- Maintain the performance of the dust collector (with regular inspection and bag replacement).

4. At time of demagnesium processing:

- Maintain the interval between the extinguishment of the burner and the start of chlorine processing, and between the completion of chlorine processing and burner ignition, for 5 to 10 minutes, while performing air suction (residual gas discharge);
- Make improvement in efficiency by an increase in the initial temperature of molten metal processing;
- Sort combined materials according to the quantity of Mg contained;
- Standardize the quantity of chlorine and that of flux used.

5. At time of drying turnings:

- Demand improvement in cut dust with excessive cutting oil (cutting oil with a high chlorine content);
- Reheat at high temperature, maintain the exhaust gas of the drying furnace, and quickly cool down the exhaust gas (i.e., keep good temperature control);
- Measure the CO concentration in exhaust gas regularly.

6. At time of paint removal and baking of can scraps (used beverage cans):

- Removal of foreign substances, such as resin and resin bags;
- Stable operation of the reheating furnace at constant circulation and exhaust gas temperature.

7. General:

- Maintenance and inspection of the capacity of the dust collector, bag replacement, shaking cycle, and suction pressure;
- Regular implementation of in-house environmental education for smelting workers;
- Targeting at the concentration of dioxins and furans in exhaust gas (< 1 ng I-TEQ/Nm^3) for existing facilities.

5. Emerging research

Catalytic oxidation is an emerging technology used in waste incinerators to eliminate PCDD/PCDF emissions. This process should be considered by secondary base metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators. However, catalytic oxidation can, subject to catalyst selection, be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process.

Catalytic oxidation processes organic compounds into water, carbon dioxide (CO_2) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction between 370° and 450° C, whereas incineration occurs typically at 980° C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be treated for particulate removal prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and CO_2 are released to the air after cooling (Parvesse 2001).

6. Summary of measures

Tables 1 and 2 present a summary of the measures discussed in previous sections.

Table 1. Measures for recommended processes for new secondary aluminium smelters

Measure	Description	Considerations	Other comments
Recommended processes	Various recommended smelting processes should be considered for new facilities	Processes to consider include reverberatory furnace, rotary and tilting rotary furnaces, induction furnace, and Meltower shaft furnace	All techniques should be applied in conjunction with suitable gas collection and abatement systems

Table 2. Summary of primary and secondary measures for secondary aluminium smelters

Measure	Description	Considerations	Other comments
Primary measures			
Presorting of feed material	The presence of oils, plastics and chlorine compounds in the feed material should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de novo synthesis	Processes to consider include: • Prevention or minimization of the use of chloride salts where possible • Cleaning scrap material of oils, paints and plastics during pretreatment • Using thermal decoating techniques such as the swarf centrifuge or swarf dryer	Sorting of feed material should be conducted prior to smelting to suit furnace type and abatement and to permit the transfer of unsuitable raw materials to other facilities better suited for their treatment. Thermal decoating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established optimum operating conditions for the reduction of PCDD/PCDF	Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field

Measure	**Description**	**Considerations**	**Other comments**
	generation		
Choice of demagging chemicals	Carefully consider choice of chemicals and control process to ensure that off-gases are treated	Hexachloroethane for demagging can lead to high releases of PCDD/PCDF and HCB (no information on PCB) but has significant process advantages	
Secondary measures			
Fume and gas collection	Effective fume and off-gas collection should be implemented in the capture of air emissions from all stages of the process	Processes to consider include: • Use of sealed feeding systems and furnaces • Control of fugitive emissions by maintaining negative air pressure within the furnace to prevent leaks • Use of hooding if a sealed unit is not possible • Use of furnace or reactor enclosures	Where primary extraction and enclosure of fumes is not practicable, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged
High-efficiency dust removal	Particulate matter generated during the smelting process should be removed as this material possesses large surface area on which PCDD/PCDF can adsorb. Proper isolation and disposal of these dusts will aid in PCDD/PCDF control	Processes to consider include: • Fabric filters, wet/dry scrubbers and ceramic filters • Catalytic coatings on fabric filter bags to destroy PCDD/PCDF by oxidation while collecting particulate matter on which these contaminants have adsorbed	Collected particulate should be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals
Afterburners and quenching	Afterburners should be used at temperatures > 950° C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250° C	Considerations include: • PCDD/PCDF formation at 250° to 500° C, and destruction > 850° C with O_2 • Requirement for sufficient O_2 in the upper region of the furnace for complete combustion • Need for proper design of cooling systems to minimize reformation time	De novo synthesis is still possible as the gases are cooled through the reformation window
Adsorption on activated carbon	Activated carbon treatment should be considered as this material is an ideal medium on which	Processes to consider include: • Treatment with activated carbon using fixed or moving bed reactors	Lime/carbon mixtures can also be used

Measure	Description	Considerations	Other comments
	PCDD/PCDF can adsorb due to its large surface area	• Injection of carbon into the gas stream followed by high-efficiency dedusting methods such as fabric filters	
Emerging research			
Catalytic oxidation	Catalytic oxidation is an emerging technology that should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, carbon dioxide (CO_2) and hydrochloric acid using a precious metal catalyst	Considerations include: • Process efficiency for the vapour phase of contaminants • Hydrochloric acid treatment using scrubbers while water and CO_2 are released to the air after cooling	Has been shown to reduce PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency. Off-gases should be dedusted prior to catalytic oxidation for optimum efficiency

7. Performance levels associated with best available techniques and best environmental practices

The performance levels associated with best available techniques and best environmental practices[2] for emissions of PCDD/PCDF from secondary aluminium smelters is < 0.5 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

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[2] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, paragraph 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.

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(iv) Secondary zinc production

Summary

Secondary zinc smelting involves the production of zinc from materials such as dusts from copper alloy production and electric arc steel making, and residues from steel scrap shredding and galvanizing processes.

Production processes include feed sorting, pretreatment cleaning, crushing, sweating furnaces to 364° C, melting furnaces, refining, distillation and alloying. Contaminants in the feed (including oils and plastics), poor combustion and temperatures between 250° and 500° C may give rise to chemicals listed in Annex C of the Stockholm Convention.

Best available techniques include feed cleaning, maintaining temperatures above 850° C, fume and gas collection, afterburners with quenching, activated carbon adsorption and fabric filter dedusting.

Performance levels associated with best available techniques and best environmental practices for secondary zinc smelters: < 0.5 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

1. Process description

Secondary zinc smelting involves the processing of zinc scrap from various sources. Feed material includes dusts from copper alloy production and electric arc steel making (both of which have the potential to be contaminated with chemicals listed in Annex C of the Stockholm Convention), residues from steel scrap shredding, and scrap from galvanizing processes. The process method is dependent on zinc purity, form and degree of contamination. Scrap is processed as zinc dust, oxides or slabs. The three general stages of production are pretreatment, melting and refining (EPA 1981).

During pretreatment scrap is sorted according to zinc content and processing requirements, cleaned, crushed and classified by size. A sweating furnace is used to heat the scrap to 364° C. At this temperature only zinc is melted, while other metals remain solid. The molten zinc is collected at the bottom of the sweat furnace and recovered. The leftover scrap is cooled, recovered and sold to other processors.

Pretreatment can involve leaching with sodium carbonate solution to convert dross and skimmings to zinc oxide, to be reduced to zinc metal. The zinc oxide product is refined at primary zinc smelters.

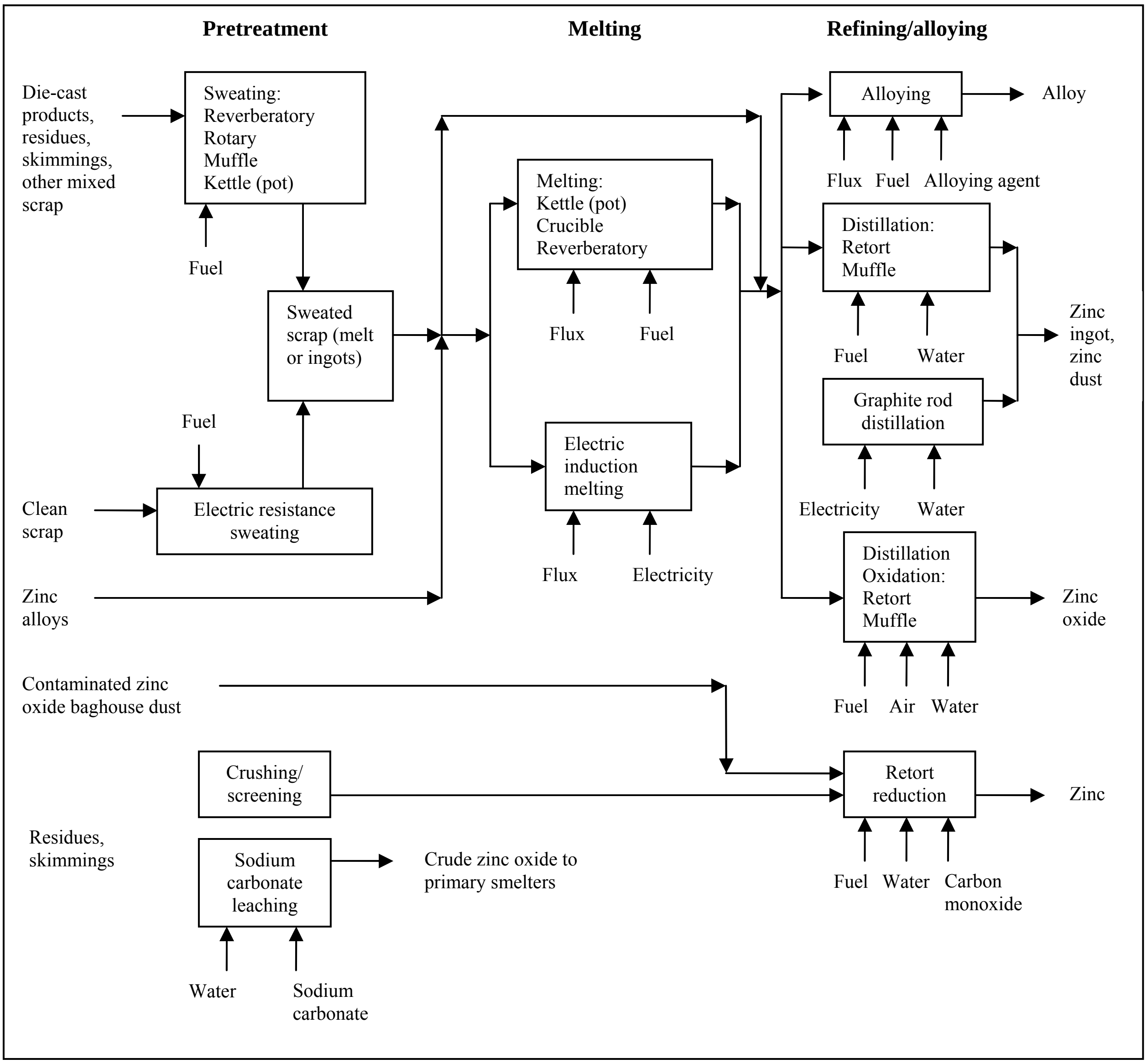
Melting processes use kettle, crucible, reverberatory, reduction and electric induction furnaces. Impurities are separated from molten zinc by flux materials. Agitation allows flux and impurities to float on the surface as dross, which can be skimmed off. The remaining zinc is poured into moulds or transferred in a molten state for refining. Alloys can be produced from pretreated scrap during sweating and melting.

Refining removes further impurities in clean zinc alloy scrap and in zinc vaporized during the melt phase in retort furnaces. Distillation involves vaporization of zinc at temperatures from 982° to 1,249° C in muffle or retort furnaces and condensation as zinc dust or liquid zinc. Several forms can be recovered depending on temperature, recovery time, absence or presence of oxygen and equipment used during zinc vapour condensation. Pot melting is a simple indirect heat melting operation whereby the final alloy cast into zinc alloy slabs is controlled by the scrap input into the pot. Distillation is not involved.

Final products from refining processes include zinc ingots, zinc dust, zinc oxide and zinc alloys. Figure 1 shows the production process in diagrammatic form.

Figure 1. Secondary zinc smelting

Source: EPA 1981.



Artisanal and small enterprise metal recovery activities may play a significant international role, in particular in developing countries and countries with economies in transition. These activities may contribute significantly to pollution and have negative health impacts. For example, artisanal zinc smelting is an important atmospheric mercury emission source. The techniques used to smelt both zinc and mercury are very simple. The ores are heated in a furnace for a few hours, and zinc metal and liquid mercury are produced. In many cases there are no pollution control devices employed at all during the melting process. Other metals that are known to be produced by artisanal and small enterprise metal recovery activities include antimony, iron, lead, manganese, tin, tungsten, gold, silver, copper and aluminum.

These are not considered best available techniques or best environmental practices. However, as a minimum, appropriate ventilation and material handling should be carried out.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

The formation of chemicals listed in Annex C of the Stockholm Convention (PCDD/PCDF being the most studied) can result from the presence of carbon and chlorine in regions of the process where temperatures are in the range 250° to 450° C. Note that the use of dusts from electric arc furnace and copper processes can also carry high levels of contamination into the process.

2.1 General information on emissions from secondary zinc smelters

Air emissions from secondary zinc smelting can escape as stack or fugitive emissions, depending on the facility age or technology. Main contaminants are sulphur dioxide (SO_2), other sulphur compounds and acid mists, nitrogen oxides (NO_x), metals (especially zinc) and their compounds, dusts and PCDD/PCDF. SO_2 is collected and processed into sulphuric acid in acid plants when processing secondary material with high sulphur content. Fugitive SO_2 emissions can be controlled by good extraction and sealing of furnaces. NO_x can be reduced using low-NO_x or oxy-fuel burners. Particulate matter is collected using high-efficiency dust removal methods such as fabric filters and returned to the process (European Commission 2001, p. 359–368).

2.2 Emissions of PCDD/PCDF to air

PCDD/PCDF may be formed during metals smelting through carry-over from contaminated feed (e.g. electric arc furnace dust), formation as a result of incomplete combustion, or by de novo synthesis from unburnt organics and chlorine compounds present in the downstream region as the gases cool.

> “The processing of impure scrap such as the non-metallic fraction from shredders is likely to involve production of pollutants including PCDD/PCDF. Relatively low temperatures are used to recover lead and zinc (340° and 440° C). Melting of zinc may occur with the addition of fluxes including zinc and magnesium chlorides” (UNEP 2003, p. 78).

The low temperatures used in zinc smelting fall directly within the 250° to 500° C range in which PCDD/PCDF are generated. The addition of chloride fluxes provides a chlorine source. Formation is possible in the combustion zone by incomplete combustion of organic compounds and in the off-gas treatment cooling section through de novo synthesis. PCDD/PCDF adsorb easily onto particulate matter such as dust, filter cake and scrubber products and can be discharged to the environment through air emissions, wastewater and residue disposal.

> “Although PCDD/PCDF are destroyed at high temperature (above 850° C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled through the ‘reformation window’. This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de novo synthesis” (European Commission 2001, p. 133).

A report prepared by the Government of Japan studied dioxin reduction technologies and their effects in secondary zinc production facilities of Japan. Various exhaust gas technologies were introduced in line with guidelines on best available techniques and best environmental practices at five existing facilities. Dioxin emissions were found to vary depending on the type of furnace employed. Dioxin discharge concentrations were found to range from 0.91 to 40 ng I-TEQ/Nm^3 before the introduction of the exhaust gas technologies, and from 0.32 to 11.7 ng I-TEQ/Nm^3 after their introduction. When a state-of-the-art two-step bag filter and two-step activated carbon injection system was introduced into the reduction furnace at one facility, dioxin concentration was reduced from 3.30 ng I-TEQ/Nm^3 to 0.49 ng I-TEQ/Nm^3 (Government of Japan 2005).

2.3 Releases to other media

Wastewater originates from process effluent, cooling water and run-off and is treated using wastewater treatment techniques. Process residues are recycled, treated using downstream methods to recover other metals, or safely disposed of. The use of wet scrubbing can lead to contaminated effluent as well as residues requiring treatment; dry particulate capture results in solid residues that may be contaminated. These residues require proper management to avoid releases.

3. Recommended processes

Variation in feed material and desired product quality influences process design and configuration. These processes should be applied in combination with good process control, gas collection and abatement systems. Processes considered to be best available techniques include: physical separation, melting and other high temperature treatment techniques followed by the removal of chlorides. (European Commission 2001, p.396)

No information is available on alternative processes to smelting for secondary zinc processing.

4. Primary and secondary measures

Primary and secondary measures of PCDD/PCDF reduction and elimination are discussed below.

4.1 Primary measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of persistent organic pollutants. Possible measures include:

4.1.1 Presorting of feed material

Contaminated feed such as dusts from electric arc furnace and copper processing may well contain elevated levels of PCDD/PCDF and other chemicals listed in Annex C. Consideration should be given to ensuring that any carry-over into the process will be effectively destroyed or captured and disposed of.

Impurities in the charge such as oils, paints and plastics in zinc scrap should be separated from the furnace feed to reduce the formation of PCDD/PCDF from the incomplete combustion of organic compounds or by de novo synthesis. However, the bulk of the organic material charged will come from the fuel added in many cases. Methods for feed storage, handling and pretreatment are influenced by material size distribution, contaminants and metal content.

Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics. Thermal decoating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas (European Commission 2001, p. 232).

4.1.2 Effective process control

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation, such as maintaining furnace temperature above 850° C to destroy PCDD/PCDF. Ideally, PCDD/PCDF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (for example, waste incineration), but research is still developing in this field. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF.

4.2 Secondary measures

Secondary measures are pollution control techniques to contain and prevent emissions. These methods do not prevent the formation of contaminants. Quenching may be used to reduce or virtually eliminate formation in the cooling zone and is a primary measure, although it may be implemented in conjunction with secondary measures.

4.2.1 Fume and gas collection

Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions.

> "The fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace [vacuum] that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment can be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. An [effective] fume collection system capable of targeting the fume extraction to the source and duration of any fume will consume less energy. Best available techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter." (European Commission 2001, p. 397).

4.2.2 High-efficiency dust removal

Dusts and metal compounds generated from the smelting process should be removed as this particulate matter possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions. Techniques to be considered are the use of fabric filters, wet and dry scrubbers and ceramic filters. Collected particulate matter is usually recycled in the furnace.

Fabric filters using high-performance materials are the most effective option. Innovations regarding this method include bag burst detection systems, online cleaning methods, and catalytic coatings to destroy PCDD/PCDF (European Commission 2001, p. 139–140).

4.2.3 Afterburners and quenching

Afterburners (post-combustion) should be used at a minimum temperature of 950° C to ensure full combustion of organic compounds (Hübner et al. 2000). This stage is to be followed by rapid quenching of hot gases to temperatures below 250° C. Oxygen injection in the upper portion of the furnace will promote complete combustion (European Commission 2001, p. 189).

It has been observed that PCDD/PCDF are formed in the temperature range of 250° to 500° C. These are destroyed above 850° C in the presence of oxygen. Yet, de novo synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Operation of cooling systems to minimize reformation time should be implemented (European Commission 2001, p. 133).

4.2.4 Adsorption on activated carbon

Activated carbon treatment should be considered for PCDD/PCDF removal from smelter off-gases. Activated carbon possesses large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or injection of carbon particulate into the gas stream followed by removal as a filter dust using high-efficiency dust removal systems such as fabric filters.

5. Emerging research

Catalytic oxidation is an emerging technology used in waste incinerators to eliminate PCDD/PCDF emissions. This process should be considered by secondary base metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators. Catalytic oxidation can, subject to catalyst selection, be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process.

Catalytic oxidation processes organic compounds into water, carbon dioxide (CO_2) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370° to 450° C. In comparison, incineration occurs typically at 980° C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be treated for particulate removal prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and CO_2 are released to the air after cooling (Parvesse 2001).

6. Summary of measures

Tables 1 and 2 present a summary of the measures discussed in previous sections.

Table 1. Measures for recommended processes for new secondary zinc smelters

Measure	**Description**	**Considerations**	**Other comments**
Recommended Processes	Various recommended smelting processes should be considered for new facilities	Processes to consider include: • Physical separation, melting and other high-temperature treatment techniques followed by the removal of chlorides • The use of Waelz kilns, cyclone- or converter-type furnaces to raise the temperature to volatilize the metals and then form the oxides that are then recovered from the gases in a filtration stage	These processes should be applied in combination with good process control, gas collection and abatement systems. Waelz kilns can be a major source of PCDD/PCDF (and other chemicals listed in Annex C) – control of their use and operation is key to reducing overall releases

Table 2. Summary of primary and secondary measures for secondary zinc smelters

Measure	**Description**	**Considerations**	**Other comments**
Primary measures			
Presorting of feed material	Electric arc furnace and copper processing dusts used as zinc-bearing feedstock may contain high levels of PCDD/PCDF (and other chemicals listed in Annex C). Oils and plastic in zinc scrap should be separated from the furnace feed to reduce the formation of PCDD/PCDF from incomplete combustion or by de novo synthesis	Processes to consider include: • Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics • Oil removal conducted through thermal decoating and de-oiling processes	Thermal decoating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls, after having	Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but

Measure	**Description**	**Considerations**	**Other comments**
	minimization of PCDD/PCDF generation	established optimum operating conditions for the reduction of PCDD/PCDF	research is still developing in this field
Secondary measures			
Fume and gas collection	Effective fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions	Processes to consider include: • Furnace-sealing systems to maintain a suitable furnace vacuum that avoids leaks and fugitive emissions • Use of hooding • Hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems	Best available techniques for gas and fume treatment systems are those that use cooling and heat recovery if practicable before a fabric filter except when carried out as part of the production of sulphuric acid
High-efficiency dust removal	Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions	Processes to consider include: • Use of fabric filters, wet/dry scrubbers and ceramic filters	Fabric filters using high-performance materials are the most effective option. Collected particulate matter should be recycled in the furnace
Afterburners and quenching	Afterburners should be used at temperatures > 950° C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250° C	Considerations include: • PCDD/PCDF formation at 250° to 500° C, and destruction > 850° C with O_2 • Requirement for sufficient O_2 in the upper region of the furnace for complete combustion • Need for proper design of cooling systems to minimize reformation time	De novo synthesis is still possible as the gases are cooled through the reformation window
Adsorption on activated carbon	Activated carbon treatment should be considered as this material is an ideal medium for adsorption of PCDD/PCDF due to its large surface area	Processes to consider include: • Treatment with activated carbon using fixed or moving bed reactors • Injection of carbon particulate into the gas stream followed by removal as a filter dust	Lime/carbon mixtures can also be used
Emerging research			
Catalytic oxidation	Catalytic oxidation is an emerging technology which should be	Considerations include: • Process efficiency for the vapour phase of	Catalytic oxidation has been shown to destroy PCDD/PCDF with

Measure	Description	Considerations	Other comments
	considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, CO_2 and hydrochloric acid using a precious metal catalyst	contaminants • Hydrochloric acid treatment using scrubbers while water and CO_2 are released to the air after cooling	shorter residence times, lower energy consumption and 99% efficiency. Off-gases should be treated for particulate removal prior to catalytic oxidation for optimum efficiency

7. Performance levels associated with best available techniques and best environmental practices

The performance levels associated with best available techniques and best environmental practices[3] for emissions of PCDD/PCDF from secondary zinc smelters is < 0.5 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

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[3] 1 ng (nanogram) = 1×10^{-12} kilogram (1×10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, paragraph 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.

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Section VI

Guidance/guidelines by source category: Source categories in Part III of Annex C

Part III Source category (a):
Open burning of waste,
including burning of landfill sites

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Figures

VI.A Open burning of waste, including burning of landfill sites

Summary

Open burning is an environmentally unacceptable process that generates chemicals listed in Annex C of the Stockholm Convention and numerous other pollutant products of incomplete combustion. Consistent with Annex C, Part V, section A, subparagraph (f) of the Stockholm Convention, the best guidance is to reduce the amount of material disposed of via this method with the goal of elimination altogether.

Other techniques which may effect improvement include, with respect to the materials burned: avoid including non-combustible materials, such as glass and bulk metals, wet waste and materials of low combustibility; avoid waste loads containing high chlorine content, whether inorganic chloride such as salt, or chlorinated organics such as PVC; and avoid materials containing catalytic metals such as copper, iron, chromium and aluminum, even in small amounts. Materials to be burned should be dry, homogeneous or well blended, and of low density, such as non-compacted waste.

With respect to the burning process, aims should include: supply sufficient air; maintain steady burning or rate of mass loss; minimize smouldering, possibly with direct extinguishment; and limit burning to small, actively turned, well-ventilated fires, rather than large poorly ventilated dumps or containers.

1. General guidance

Open burning covers a wide range of different uncontrolled waste combustion practices, including dump fires, pit burning, fires on plain soil and barrel burning. For people in many parts of the world, open burning is the cheapest, easiest, most sanitary means of volume reduction and disposal of combustible materials. This is especially true for people with no access to organized waste handling and who have been left to their own devices for materials disposal.

1.1 Public health threats of open burning

Current research indicates that open burning is a more serious threat to public health and the environment than previously thought. The low temperature burning and smouldering conditions typical of open burning promote the formation of many toxic and potentially harmful chemicals, including chemicals listed in Annex C of the Stockholm Convention. These compounds may form during open burning regardless of the composition of the material being burnt. The compounds produced from sources of open burning can travel long distances and deposit on soil, plants, and in water.

The remaining ash in the burn pile also contains pollutants, which can spread into the soil and water. Animals and fish ingest the pollutants and accumulate them in their tissues, while plants can absorb them through their leaf surfaces. When this contaminated food is eaten, the pollutants are passed on to humans. Additionally, smoke and particulates from open burning sources can trigger respiratory health problems, particularly among children, the elderly, and people with asthma or other respiratory diseases, and those with chronic heart or lung disease.

1.2 Status of open burning

While this document provides guidance for open burning practices, it recognizes the environmental harm resulting from open burning, and should not be taken as licence to continue the practice, which should be minimized and eliminated as soon as possible and wherever feasible. Open burning may still be a last resort where there are no alternative disposal or recovery methods due to inadequate infrastructure; where sanitary disposal is required to control disease or pests; or in the case of disaster or other emergency (Great Lakes Binational Toxics Strategy 2004). However, household wastes should never be burnt in indoor residential combustion devices such as stoves, fireplaces or furnaces (see section VI.C of the present guidelines).

Open burning of waste, including burning at landfill sites for volume reduction, is listed as an inadvertent source of persistent organic pollutants in Annex C, Part III of the Stockholm Convention. Most importantly, subparagraph (f) of Annex C, Part V, section A refers aspirationally to "… the aim of cessation of open and other uncontrolled burning of wastes, including the burning of landfill sites".

Although the Stockholm Convention is concerned with persistent organic pollutants such as polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) as products of incomplete combustion, open burning is responsible for generation of toxic by-products of combustion well beyond the named chemicals. Other by-products include polycyclic aromatic hydrocarbons, particulate matter, benzene and carbon monoxide. Regardless of specific chemistry, smoke and unpleasant odours always accompany open burning, and are at best a nuisance and at worst a health hazard. Elimination of the persistent organic pollutants listed in the Stockholm Convention would not sufficiently improve the emissions from open burning to make it an environmentally preferred means of waste disposal. It is imperative that the focus of implementation of the Stockholm Convention be on establishing alternatives to open burning rather than simply trying to improve a bad practice. Provision of this guidance should not be construed as acceptance or justification.

Efforts to reduce open burning should be promoted and such efforts should focus on government, private sector and civil society support of alternative end-of-life and waste management options. Government agencies in charge of public health policy and education should be as deeply involved as those responsible for waste policy. The Basel Convention Technical Guidelines offer basic guidance on alternatives to open burning and how to implement them (Basel Convention Secretariat 1994).

Countries should work diligently to establish and implement sound waste management practices, including resource use reduction, reuse, recycling, composting, modern sanitary landfilling and incineration using best available techniques. The Convention's implementation efforts and its financial mechanism could be used to support the establishment of model waste management systems as alternatives to open burning. In addition, educational programmes and materials designed to educate target audiences (e.g. the public, waste handlers) about the risks to human health and the environment occasioned by open burning should be considered as part of an overall effort towards continuous minimization (Canadian Centre for Pollution Prevention 2006; EPA 2006).

Many countries have formulated regulations and prohibitions covering various open burning practices (Government of New Zealand 2006). A number of these regulations contain specific guidance on categories mentioned in this section, including tyres and waste oil. Enforcement of such provisions depends on the public having access to acceptable waste collection and disposal options.

In this part of the guidance, a number of specific types of open burning are considered in generic categories, typically because means of reducing emissions of persistent organic pollutants in each category are similar (Lemieux, Lutes and Santoianni 2004). Accidental fires and intentional combustion of non-waste materials are not considered; however, they may also be sources of persistent organic pollutants. Parties to the Convention are urged to take steps to reduce accidental biomass burning of all types as well as accidental fires in residences, automobiles and places of business. Parties may wish to consider restrictions on fireworks or other recreational open combustion.

1.3 Scientific basis and general considerations

Waste composition varies by source. Domestic waste may contain more organic material; industrial waste may contain more metals and possibly organic chemicals. Some of the waste itself – even domestic waste such as clothing or leather – may contain persistent organic pollutants (UNEP 2003). Sections III.C (i) and (ii) of the present guidelines describe formation mechanisms of persistent organic pollutants and their relationship to materials that might be contained in waste. Subparagraph 1.3.1 below contains general guidance on materials and processes; subsections 2–4 contain further information on material composition for different types of waste.

Waste composition also varies among countries, and over time. Accurate waste composition data from each country will aid in overall waste management, increase the amount of material available for recycling or reuse and reduce the amount that is open burnt.

Figure 1. Animals grazing near open burning

Grazing animals may be adversely affected by open burning and may ingest harmful substances. Photo: Kenya POPs Office.

There are few data regarding generation of persistent organic pollutants from uncontrolled waste combustion. Most experimentation has been conducted on so-called barrel burning, but there are limited or no data on dump fires, open burning in pits or waste burning on soil.

The UNEP *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases* (UNEP 2003) provides a sound basis for calculating emissions of dioxins and furans. A number of parties who have completed their dioxin and furan inventories using the toolkit have found that open burning of waste is one of the four largest sources of dioxins and furans.

1.3.1 Burning process

In the short term, where there are not realistic means to eliminate all open burning, the best guidance is to reduce the amount of material disposed of via this method. This is consistent with the convention and its goal of elimination.

Other techniques that may effect improvement include the following (Gullett 2003):

With respect to the materials burnt:

- Avoid including non-combustible materials, such as glass and bulk metals, wet waste and materials of low combustibility;
- Avoid waste loads containing high chlorine and/or bromine content, whether inorganic such as salts, or halogenated organics such as PVC (Lemieux et al. 2003);[1]
- Avoid materials containing catalytic metals such as copper, iron, chromium and aluminum, even in small amounts;
- Materials to be burnt should be dry, homogeneous or well blended and of low density (e.g. non-compacted waste).

With respect to the burning process:

- Supply sufficient air;

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[1] "No distinction is observed in log (TEQ) for inorganic (7% Cl in $CaCl_2$) versus organic Cl sources (7% Cl in PVC)" (Lemieux et al. 2003).

- Maintain steady burning or rate of mass loss;
- Minimize smouldering, possibly with direct extinguishment. Smouldering is the phase of burning associated with the largest production of persistent organic pollutants (Lemieux et al. 2003);
- Limit burning to small, actively turned, well-ventilated fires, rather than fires in large poorly ventilated dumps or containers.

Figure 2. Typical mode of disposal of mixed waste through open burning

Potentially explosive items (e.g. aerosol cans, partially full containers of flammable liquids) and hazardous materials should be removed, especially those that should be destroyed using best available techniques described in other parts of the guidance (see section V.A (i), paragraph 2.2 of the present guidelines).

1.3.2 Handling after burning

Before burnt waste can be handled or covered, it must be completely extinguished. Failure to do this can potentially ignite uncontrolled burning over large areas or allow ongoing smouldering. Ash from mixed waste burning should be kept from forage areas, and landfilled rather than landspread.

1.3.3 Health and safety considerations

In addition to the aforementioned guidance, steps should be taken to mitigate exposure routes to dioxins and furans. As is widely recognized, most human exposure comes through the food chain. Thus, necessary burning sites should be located away from production of plants and animals for food. It is also good practice to locate combustion sites remote from the population or at the very least downwind of residential areas.

In addition to isolating citizens from the odour, nuisance and potential toxics exposure of open burning, in all cases, whether in a landfill or at a secluded facility, personnel tending the fires should position themselves upwind from any burning waste and be clear of the burning waste. Protective clothing such as gloves, boots and overalls, together with smoke masks and goggles, are advisable where possible.

1.3.4 Intermediate burning technologies and practices

Combustion devices, sometimes called “incinerators” by vendors, are sold for the purpose of burning refuse. In some cases these devices may be as simple as steel drums or barrels that contain the waste but do not constitute a best available technique for incineration. For the purposes of this guidance, open burning includes any form of combustion for waste disposal, whether in unconfined piles or confined in metal barrels or burners, that does not meet the standards for incineration (using best available techniques) of municipal, medical or hazardous waste, as defined by a Party.

Utility of these intermediate burning devices is limited by lack of data on generation of persistent organic pollutants. It is strongly recommended that manufacturers of these devices supply such data, specific to the waste for which they are intended.

2. Intentional biomass burning

2.1 Agricultural/crop residue and land clearing debris

2.1.1 Material composition

In general, this material is biomass: wood, grass and other vegetation. Depending on locality the material may include sisal, coffee husks, corn (maize) cobs and stalks, sugar cane or rice husks. The material may be composed of living plants, deadfalls or plant material that has been cut and dried. Intentional burning does not constitute well-controlled combustion despite the fact that the geographical boundaries of the material to be burnt may be well defined.

Biomass materials will vary in water content (live versus harvested material; wet versus dry season; low versus high humidity), fuel density (mass per hectare and degree of compaction or other measure) and species. Biomass materials vary naturally in chloride content and may have been treated with chemicals (chlorinated pesticides or fertilizers), metals capable of catalysing formation of persistent organic pollutants (copper, for example as copper chromium arsenate-treated wood) or inhibitors (sulphur, nitrogen-containing materials), all of which may impact generation of persistent organic pollutants, particularly dioxin and furans, during uncontrolled combustion (See paragraph 1.3 above on general process considerations). Some research on large-scale biomass burning has been published (Lobert et al. 1999; Nussbaumer and Hasler 1998; Gullett and Touati 2003; Gullett and Touati 2002).

2.1.2 Barriers to elimination; remedies or policy to remove barriers

Prescribed burning may be permitted by government for perceived economic benefit (cost reduction), perceived agricultural benefit (ash as soil adjuvant), risk prevention (e.g. to minimize bushfires in Australia), termite, reptile or other pest control, convenience or recreation. In each of these cases the government has the power to remove permission for such burning and to educate the public regarding the health risks of open burning, especially if it is conducted on a large scale. In some cases, as for termite control, open burning of biomass may be the least environmentally problematic approach. Cost and availability of alternative means of disposal or environmental management can be an overarching issue.

2.1.3 Strategies and policy instruments to avoid, reduce or divert waste

Where possible, machine harvesting paired with alternative, non-destructive uses for harvested materials can reduce the need for wholesale burning. In areas of livestock cultivation materials may be harvested for silage. Grass may be dried for hay; other crop waste may be processed for fodder, fermented, allowed to decompose in situ or composted; wood of sufficient quality may be harvested for timber; yard waste can be composted and utilized as soil amendment; some non-traditional biomass can be used as a raw material for paper. In most cases, these alternatives also require markets and infrastructure for economic feasibility.

Beneficial results can be obtained if agricultural vegetation residues are composted, especially in areas with poor soil. Zero burning techniques, as outlined by the Association of South-East Asian Nations, should be applied where applicable to the region and the crops (ASEAN Secretariat 2003). Reduction and elimination of persistent organic pollutants from open burning may provide an opportunity to reform agricultural practices.

2.1.4 Alternatives, barriers to use and policy instruments to remove barriers

Alternatives vary by situation. Barriers include lack of education, lack of government will to reduce dependence upon open burning to accomplish goals, and lack of alternative machinery or processes whereby open burning is an integral part of local agriculture. The sometimes high cost of alternatives in any form may be a barrier and, as with any reforms, economic instruments may be necessary or desirable to induce change. Demonstration projects and research in the regions may help understanding of the feasibility of alternatives.

2.1.5 Burning techniques and attributes, and means of improvement

Where open burning of biomass is permitted by government policy the process improvements noted in the general guidance should be implemented. Careful planning of prescribed burns modulated by weather conditions will allow greater control and the potential exposure of air pollutants to downwind populations should be minimized. After the fires, residue management may be an issue.

Application of chemicals in agriculture and forestry should be minimized consistent with local needs and good management. Where mechanical clearing and alternative use of harvested material is possible, incidental burns can be avoided; however, in certain local situations prescribed small burns may have a place in an overall land management scheme if used to prevent more devastating inadvertent burning with concomitant larger emissions of persistent organic pollutants. Recognizing that control of prescribed burns can be lost, fire abatement procedures (training, equipment, planning), infrastructure (access, roads) and management planning are all reasonable secondary support measures.

3. Open burning of mixed consumer waste

3.1 Household waste, landfill/dump fires, industrial non-hazardous waste

3.1.1 Material composition

Household waste and the composition of landfills and dumps may be qualitatively very similar. They differ importantly where modulated by programmes (such as recycling, scavenging, composting or other segregation) that remove specific streams from waste between collection point and repository. Non-hazardous waste may arise from commercial establishments such as shops, restaurants and light manufacturing. It will differ according to the exact commercial source but may contain many of the same materials found in household waste.

Open burning of waste has been the topic of significant study (Lemieux et al. 2003). However, there seem to be very few data regarding dump fires and persistent organic pollutants (Lemieux, Lutes and Santoianni 2004). Waste composition studies show variation in waste among countries and especially between developed and developing countries. In developing countries as much as 50% of waste composition may be putrescibles such as kitchen waste. In developed countries, more convenience packaging and electronics may be found unless these materials have been removed by other end-of-life systems. Significant differences may also exist between urban and rural waste and among wastes from different regions, regardless of development. In general, household waste streams and landfill waste will contain paper, plastic, organics such as food refuse, glass, metal, wood, leather and miscellaneous other materials. Under poorly controlled conditions, household hazardous waste such as cleaners, paints and solvents may find its way into a non-hazardous-rated landfill or dump.

Moreover, negative management approaches will change the composition and performance of a landfill or dump. In a modern, compartmentalized landfill, daily cover consisting of soil or clay will be added to the refuse to reduce not only the moisture content of the landfill but also the likelihood of spontaneous ignition. A traditional dump, by comparison, is rarely well organized and is more likely to burn spontaneously.

All disposal sites will generate some combustible gas (e.g. methane) from anaerobic degradation of organic materials contained within. Unless this gas is controlled it constitutes a highly combustible fuel for either spontaneous or illicit anthropogenic ignition. It is also a potent greenhouse gas. Methane collection systems have been designed and implemented as part of modern landfill technology, both for reasons of safety and potential energy recovery.

3.1.2 Barriers to elimination; remedies or policy to remove barriers

3.1.2.1 Household waste

Household waste will be burnt in the open where cost, convenience or local custom and social acceptability make that option attractive to individuals or groups of citizens. In cases where people live far outside municipal governance, options for waste disposal will undoubtedly be ad hoc. Without appropriate systems in place waste disposal may be ad hoc even within municipal governance.

In order to eliminate open burning, reasonable alternatives must exist and the public must be educated regarding their availability as well as the consequences of open burning.

Figure 3. Centralized sorting of waste for reuse and recycle

At-source or centralized collection, recycling, transport or other disposal must be made affordable, convenient and effective. Landfills must be designed and operated according to modern standards (Hickman and Eldredge 2004). If combustion is to be used, incineration using best available techniques, with energy recovery, is strongly preferable.

Governments must accept responsibility to create waste reclamation and disposal systems as a public utility or service. Countries and municipalities must then have the will to mandate an end to waste burning and accept the responsibility for enforcement of those laws. Additionally, where modern landfilling is an option, waste management plans and regulations must include provisions for establishing new landfills so as to maintain disposal capacity.

Simply accepting the responsibility for providing waste management systems may not in itself mean the end of open burning. Waste could be collected and deposited in landfills or dumps, which can themselves be sites for open burning. Policies and practices must be developed and applied to these centralized services. Spontaneous ignition and combustion can be reduced by collection of landfill gas or regulations requiring modern landfill construction techniques along with the permanent closing of obsolete dumps.

3.1.2.2 Accidental anthropogenic combustion

Accidental anthropogenic combustion in dumps can be reduced by prohibiting, licensing or limiting access to landfills and dumps. In many cases fires are set by scavengers living and working in these areas. Fires, accidental or intentional, can ignite discarded materials or landfill gas. Authorities must accept responsibility and enact regulations organizing scavenging activities, providing safe conditions for workers and limiting access to and overt residence on landfills.

3.1.2.3 Intentional anthropogenic combustion

Intentional anthropogenic combustion, that is, burning dump contents for volume reduction, must be prohibited by authorities. In order to avoid the need for dump burning sufficient planning must be given to landfill size, space, location and management, as well as to waste reduction and elimination programmes so as to obviate the need.

Waste management is a system. Where the system works to make final disposal of true waste a collective responsibility rather than an individual responsibility, direct economic costs may rise, but in general environmental costs and impacts will fall.

3.1.3 Strategies and policy instruments to avoid, reduce or divert waste

3.1.3.1 Source reduction

Careful study of local waste composition may lead to specific programmes for reduction of large volume streams. As an example, in certain cases bulk purchase of products can reduce the need for individual product packaging. This and other strategies may be modulated by population density.

3.1.3.2 Composting

Where significant fractions of household waste will biodegrade, and where the population density will allow it, municipalities should provide education on cost- and space-effective composting. Included in this strategy is appropriate diversion of organic waste to animal feed or other similar productive use, modulated by a concern for spread of disease. Education must include means for vermin and disease vector control. Some organic wastes may contain persistent organic pollutants or materials that could be converted to persistent organic pollutants under composting conditions, and they should be treated separately in order to guarantee high-quality compost with low content of such pollutants (EPA 2005). In some cases, composting can be enhanced by substitution of certain biodegradable materials for alternatives.

3.1.3.3 Reuse

Where parts or entire devices can be recovered, washed, repaired or reclaimed as fabricated articles the need for disposal can be reduced. In many cases, involvement of labour in such reclamation and value creation can be more cost-effective and economically beneficial than the purchase of new devices.

3.1.3.4 Recycling

Many waste streams contain valuable, reclaimable items. Metals, glass, clean dry paper, corrugated board, cloth, plastics and wood are recyclable streams. Depending on the situation, centralized collection and recycling infrastructure can be cost effective. In other situations, simply providing a safe staging area at a disposal site and encouraging the development of markets for recycled materials can facilitate recovery by scavengers. This can greatly support employment creation, conservation of resources and poverty reduction strategies.

3.1.3.5 Incineration

In some situations incineration using best available techniques, especially with energy recovery, and open burning may coexist. Where they do, incineration is preferable to open burning, but may not be the only alternative. Authorities must take care to understand specific local barriers to the elimination of open burning in favour of less environmentally burdensome disposal, including source reduction, reuse, recycling and incineration using best available techniques. Collection and cost may be one such barrier; however, incineration using best available techniques, when coupled with energy recovery, may mitigate that cost and provide significant energy benefit.

3.1.3.6 Modern landfill

Given the differences between modern engineered landfills and unorganized dumps, modern landfill construction with collection of gas and leachate, and appropriate opportunity for recycling and reuse, is preferable to open burning. As noted above, authorities will need to accept that education and cost-effective waste disposal options must be provided if open burning is to be eliminated.

Modern landfills differ from dumps in many ways. As engineered constructions, they are typically safer, more sanitary and less prone to anthropogenic combustion. They also require active management and security measures to exclude unauthorized people (e.g. scavengers) and may be relatively more expensive than open burning or low-tech dumping.

Policies that prohibit disposal of hazardous industrial and infectious wastes in the normal waste stream will enhance the safety of the municipal disposal system. Governments can encourage effective use of alternative methods listed above by implementing legal restrictions on open burning; mandates for composting, recycling or recovery; taxes on excessive waste placed into the disposal system; or institution of lower-cost and more convenient resource management systems.

3.1.4 Alternatives, barriers to use and policy instruments to remove barriers

Strategies for waste reduction and available alternatives to open burning are largely the same.

3.1.5 Burning techniques and attributes, and means of improvement

Where none of the previously mentioned alternatives are feasible or when alternatives cannot be implemented in a timely fashion, governments may wish to educate citizens on ways to reduce the impacts of open burning. Those process improvements have been outlined in the general guidance.

3.2 Construction, demolition and post-disaster debris

3.2.1 Material composition

3.2.1.1 Construction waste

Construction waste will consist of the usual materials of construction and potentially the packaging in which the materials are brought to the site (e.g. pallets and sacks). Materials of construction of buildings vary by size, type and geographical location. Types of buildings, whether commercial, office, or residential, will differ significantly between developed and developing countries and among regions. Common combustible materials of construction include wood, paper and other cellulosics, asphalt, paint and various plastics. Metal contamination of combustibles is not unknown.

3.2.1.2 Demolition waste

Demolition waste, particularly post-disaster debris, will contain other occupant belongings. These materials also vary with the type of building, geography and development of the economy. Partially burnt remains of a fire in an industrial operation may also qualify as post-disaster debris or hazardous waste.

For dwellings, this similarity will be to household waste, and will be greater in developing countries; in developed countries there will be a greater proportion of fabric (clothes), foam (furniture), rigid plastics (appliances) and fibre (carpeting).

For commercial buildings the contents will be representative of the business and will include furnishings and fibre similar to those in dwellings, as well as electronics and volumes of paper (offices) or concentrations of products for sale.

3.2.2 Barriers to elimination; remedies or policy to remove barriers

Intentional combustion of waste derived from construction or demolition is a matter of low cost and convenience at the job site. It is done due to sanitary needs, the cost of removal, the inconvenience of on-site burial or unavailability of alternatives. While it is a poor practice and should be avoided under any but the worst circumstances regarding public health, the intentional combustion of post-disaster debris is known due to unavailability of alternatives, desire to avoid massive use of landfill space or for convenience in clearing areas after earthquake (Nakao et al. 1997). The issue, nominally, is cost, whether expressed as direct cost or the cost of development or use of other disposal means.

3.2.3 Strategies and policy instruments to avoid, reduce or divert waste

Clean, uncontaminated construction waste can be collected and sorted with usable materials diverted to other construction, shredding for mulch and material recycling. Demolition, when done as disassembly, can yield many fixtures suitable for resale and reuse. Materials from demolition that cannot be reused or reprocessed can be separated and disposed of, much as construction wastes.

While in theory the strategies used for treatment of construction and demolition waste can also be used for post-disaster debris, the scale can be enormously different. After a disaster there may be no choice but to move material to a landfill site, allowing scavenging as usual or conducting recovery operations there. Landfilling without scavenging or incineration using best available techniques may be the best options in an emergency, depending on exact circumstances.

Governments can, and some do, prohibit the open burning of construction and demolition debris. Where there is poor waste management infrastructure, many of the same instruments used in the recovery of household waste may be useful for construction and demolition materials.

3.2.4 Alternatives, barriers to use and policy instruments to remove barriers

As outlined above, the alternatives for waste disposal on construction and demolition sites are collection, separation, disassembly, resale, reuse and recycling. These processes can be economically viable or can be made so by changes in laws or regulations governing disposal of these materials. Such instruments include bans on open burning, removal of taxes and other financial barriers on landfill disposal of construction and demolition material, or economic instruments promoting recycling or reuse. In many cases, the resale of building fixtures is encouraged and economically viable; this is particularly true in developing countries.

Additionally, contracts for construction can be written to specify removal of debris as a responsibility of the contractor. Acceptable means of disposal can also be specified by contract.

3.2.5 Burning techniques and attributes, and means of improvement

For these materials the same general guidance holds as outlined elsewhere in the document. Open burning should be a last resort and should actively exclude materials that do not burn well or at all.

4. Open burning of specific materials and miscellaneous

4.1 Agricultural plastic

4.1.1 Material composition

Agricultural film is usually made from polyethylene due to cost but ethylene-vinyl acetate copolymer (EVA) is also often used. PVC has been used previously, but appears to be less common today. Among other uses, agricultural film is used for covering fields in early season to warm the ground; as bale wrap; as bags for silage, fertilizer or agricultural chemicals; and as greenhouse film. Some specialty suppliers offer material specified to be degradable, though this requirement is not universal.

Rigid plastic containers of pesticides or other agricultural chemicals may be found as well. Bags are usually low-density polyethylene; bottles, drums and tubs are usually high-density polyethylene, a multilayer polyethylene, or a polyethylene container whose interior surface has been treated to reduce interaction with the product contents. One report discusses experiments burning bags containing residual pesticide but finds PCDD/PCDF only “at very low levels”, and blanks for both air emissions and solid residual (Oberacker et al. 1992). Following published procedures for rinsing containers and treating the rinse water properly will significantly reduce this already low possibility.

4.1.2 Barriers to elimination; remedies or policy to remove barriers

Material located far from normal waste collection will be discarded using the lowest-cost and most convenient method. Burning could be reduced by institution of a collection scheme for the material, particularly if many farmers in an area use the same material. Governments can also institute education programmes and laws prohibiting burning, supporting recycling and developing economic instruments to support such initiatives.

4.1.3 Strategies and policy instruments to avoid, reduce or divert waste

Agricultural film is recycled extensively in some countries. This is facilitated when material is collected explicitly. Where there is no opportunity for recycling other forms of disposal are utilized, including landfill. Use of additives such as UV-inhibitors can extend the life of greenhouse films and reduce the need for disposal. In the absence of specific programmes, materials used for wrapping bales or bagging compost is discarded in the same way as any packaging in a particular area. In some areas, film can be recycled explicitly, compounded into wood-plastic composites or processed into refuse-derived fuel for combustion in an incinerator using best available techniques. For bottles, the

World Health Organization recommends triple-rinsing, then puncturing and burying them (Rosendaal 1997, ch. 10).

4.1.4 Alternatives, barriers to use and policy instruments to remove barriers

Strategies for waste reduction and available alternatives to open burning are largely congruent.

4.1.5 Burning techniques and attributes, and means of improvement

Agricultural film, while combustible, because of the way it has been manufactured, will tend to melt and shrink. Proper incineration could depend on shredding to increase surface-to-volume ratio or relatively slow feeding of material. High-temperature, well-ventilated combustion is possible, but may be challenging on a large scale if film is the only material burnt.

Bottles may not burn well due to their surface-to-mass ratio even if dry and combustible. Alternative fuel may be required and should be material consistent with the general guidance.

4.2 Tyres

4.2.1 Material composition

Tyres are a composite of styrene-butadiene copolymer or natural rubber, chloroprene, polyamide, steel wire, carbon black and numerous other organic and inorganic additives. Tyres contain low concentrations of chlorine; they also contain significant sulphur, similar to that of medium sulphur coal, as a result of vulcanization. Sulphur inhibits formation of persistent organic pollutants in combustion; the probability for generation of chlorinated persistent organic pollutants in this waste is probably lower than for mixed waste. However, poor combustion of large volumes of tyres in open burning situations is a source of PCDD/PCDF and will certainly be a prodigious generator of other hazardous pollutants, including SO_2 and polycyclic aromatic hydrocarbons.

4.2.2 Barriers to elimination; remedies or policy to remove barriers

Ignition of tyre fires can be natural (lightning) or anthropogenic. Tyre dumps present a number of hazards, including culture of insect disease vectors. Additionally, they occupy large spaces. Anthropogenic burning of tyres can and has been undertaken to alleviate either of these problems.

4.2.3 Strategies and policy instruments to avoid, reduce or divert waste

Worn tyres can be retreaded and reused in many cases. Modern technology has extended the life of the average tyre by a factor of ten over the past thirty years. Utilizing tyres with the longest life minimizes the need for disposal. Alternatively, they may be recycled to various uses, either whole or as shredded material. Whole, or preferably shredded, tyres can be landfilled. However, whole tyres and similar articles like uncrushed bottles may tend to float to the surface of a dump. Collection of tyres in above-ground dumps constitutes an eyesore and a hazard for insect control and potential for uncontrolled combustion.

4.2.4 Alternatives, barriers to use and policy instruments to remove barriers

Waste tyres may be reused whole, shredded or cryoground into powder. Processed tyres may be used in rubber-modified asphalt for road surfacing materials. Shredded and ground tyres have also been compressed and used in building materials. Shredded tyres are used as a cushioning material for playgrounds. Additionally, tyres may be pressed into service as materials for fabrication of articles including fencing, reef creation, soil erosion control, sandals, doorstops and waste bins, recognizing that as a composite, thermoset material recycled rubber is subject to certain processing constraints. Use of whole tyres above ground must take into consideration and mitigate their tendency to collect water and harbour insect infestation.

If shredded and whole tyres are to be combusted in cement kilns, it must be done under proper combustion conditions and operation corresponding to best available techniques as described in section V.B of the present guidelines. Thus, kiln should meet the performance level associated with best available techniques (0.1 ng I-TEQ/Nm^3) and releases of chemicals listed in Annex C in stack gases should be low.[2] Releases of chemicals listed in Annex C via cement kiln dust and possibly clinker have been reported, however, and are currently under further investigation.

4.2.5 Burning techniques and attributes, and means of improvement

Open burning of tyres results in the formation and release of chemicals listed in Annex C. As a mass or in dumps there is virtually no way in which the open burning of tyres can be improved; in addition, extinguishment of large-scale fires is almost impossible and they may burn for years.

4.3 Oil spills and gas flares

4.3.1 Material composition

Crude oil, natural gas and associated gas consist largely of carbon and hydrogen with smaller constituent amounts of oxygen, sulphur and chlorine. As found in nature, or as a result of recovery techniques, they may also contain salt or salt water. Particularly of concern is combustion of oil spilled on ground that contains salt or other chlorinated materials, or on seawater, or combustion of oil contaminated by intrusion of water into wells drilled near a saline body of water. Spilled oil from pipeline breaks has been burnt to mitigate potential contamination of a frozen river (Kruglov, Amirova and Loshkina 1996).

The open burning of oil from off-shore facilities under certain circumstances may be a significant emission source. For accidental spills of oil, biological remediation methods may be useful in some circumstances.

4.3.2 Barriers to elimination; remedies or policy to remove barriers

Barriers to elimination include considerations related to cost, convenience and safety, and lack of alternative recovery or disposal methods.

4.3.3 Strategies and policy instruments to avoid, reduce or divert waste

Gas flaring is common. To the extent that this is a waste issue and not one of recovery from accident, better procedures for handling materials or recovery for sale may improve normal performance.

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[2] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, paragraph 3 of the present guidelines.

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Part III Source category (b):
Thermal processes in the metallurgical industry not mentioned in Annex C, Part II

VI. B. Thermal processes in the metallurgical industry not mentioned in Annex C, Part II

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(i) Secondary lead production

Summary

Secondary lead smelting involves the production of lead and lead alloys, primarily from scrap automobile batteries, and also from other used lead sources (pipe, solder, drosses, lead sheathing). Production processes include scrap pretreatment, smelting and refining. Incomplete combustion; high levels of oils, plastics and other organic materials in feed; and temperatures between 250° and 500° C may all give rise to chemicals listed in Annex C of the Stockholm Convention.

Best available techniques include the use of plastic-free and oil-free feed material, high furnace temperatures above 850° C, effective gas collection, afterburners and rapid quench, activated carbon adsorption, and dedusting fabric filters.

Performance levels associated with best available techniques for secondary lead smelters: < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations)

1. Process description

The following summary of the process is drawn from EPA 1986. Figure 1 summarizes the process in diagrammatic form.

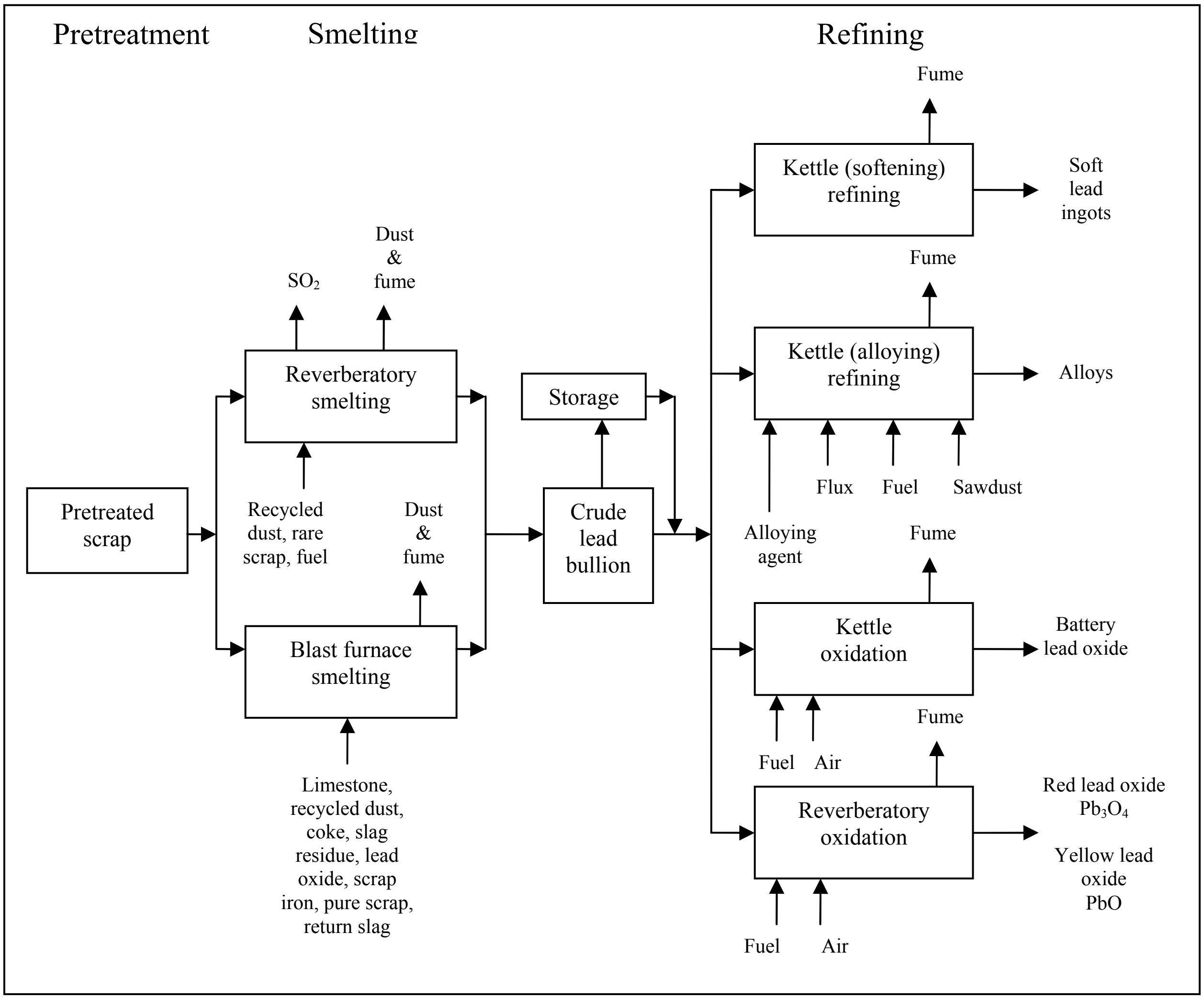
“Secondary lead smelters produce lead and lead alloys from lead-bearing scrap material. More than 60 percent of all secondary lead is derived from scrap automobile batteries. Other raw materials used in secondary lead smelting include wheel balance weights, pipe, solder, drosses, and lead sheathing.

Secondary lead smelting includes 3 major operations: scrap pretreatment, smelting, and refining. Scrap pretreatment is the partial removal of metal and nonmetal contaminants from leadbearing scrap and residue. Processes used for scrap pretreatment include battery breaking, crushing, and sweating. Battery breaking is the draining and crushing of batteries, followed by manual separation of the lead from nonmetallic materials. This separated lead scrap is then sweated in a gas- or oil-fired reverberatory or rotary furnace to separate lead from metals with higher melting points. Rotary furnaces are usually used to process low-lead-content scrap and residue, while reverberatory furnaces are used to process high-lead-content scrap. The partially purified lead is periodically tapped from these furnaces for further processing in smelting furnaces or pot furnaces.

Smelting produces lead by melting and separating the lead from metal and non-metallic contaminants and by reducing oxides to elemental lead. Smelting is carried out in blast, reverberatory, and rotary kiln furnaces. In blast furnaces pretreated scrap metal, rerun slag, scrap iron, coke, recycled dross, flue dust, and limestone are used as charge materials to the furnace. The process heat needed to melt the lead is produced by the reaction of the charged coke with blast air that is blown into the furnace. Some of the coke combusts to melt the charge, while the remainder reduces lead oxides to elemental lead. As the lead charge melts, limestone and iron float to the top of the molten bath and form a flux that retards oxidation of the product lead. The molten lead flows from the furnace into a holding pot at a nearly continuous rate.

Refining and casting the crude lead from the smelting furnaces can consist of softening, alloying, and oxidation depending on the degree of purity or alloy type desired. These operations can be performed in reverberatory furnaces; however, kettle-type furnaces are most commonly used. Alloying furnaces simply melt and mix ingots of lead and alloy materials. Antimony, tin, arsenic, copper, and nickel are the most common alloying materials. Oxidizing furnaces, either kettle or reverberatory units, are used to oxidize lead and to entrain the product lead oxides in the combustion air stream for subsequent recovery in high-efficiency baghouses."

Figure 1. Secondary lead smelting



Source: EPA 1986.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

The formation of chemicals listed in Annex C of the Stockholm Convention can result from the presence of unburnt fuels and organic compounds reacting with chlorine-containing compounds in zones where temperatures are in the range 250°–450° C.

2.1 General information on emissions from secondary lead smelters

Air emissions from secondary lead smelting can escape as stack or fugitive emissions, depending on the facility age or technology. Main contaminants are sulphur dioxide (SO_2), other sulphur compounds and acid mists, nitrogen oxides (NO_x), metals (especially lead) and their compounds, dusts and traces of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). SO_2 is collected and processed into sulphuric acid in acid plants. Fugitive SO_2 emissions can be controlled by good extraction and sealing of furnaces. NO_x can be reduced using low-NO_x or oxy-fuel burners. Particulate matter is collected using high-efficiency dust removal methods such as fabric filters and returned to the process (European Commission 2001, p. 359–368).

2.2 Emissions of PCDD/PCDF to air

PCDD/PCDF are formed during base metals smelting through reaction of products of incomplete combustion, unburnt organic contaminants and chlorine compounds, usually by de novo synthesis in the cooling zone at temperatures between 250° and 450° C.

The process is described in European Commission 2001, p. 133:

“PCDD/PCDF or their precursors may be present in some raw materials and there is a possibility of de novo synthesis in furnaces or abatement systems. PCDD/PCDF are easily adsorbed onto solid matter and may be collected by all environmental media as dust, scrubber solids and filter dust.

The presence of oils and other organic materials on scrap or other sources of carbon (partially burnt fuels and reductants, such as coke), can produce fine carbon particles which react with inorganic chlorides or organically bound chlorine in the temperature range of 250° to 500° C to produce PCDD/PCDF. This process is known as de novo synthesis and is catalysed by the presence of metals such as copper or iron.

Although PCDD/PCDF are destroyed at high temperature (above 850° C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled through the ‘reformation window’. This window can be present in abatement systems and in cooler parts of the furnace e.g. the feed area. Care taken in the design of cooling systems to minimise the residence time in the window is practised to prevent de novo synthesis.”

2.3 Releases to other media

The use of wet scrubbing can result in a liquid effluent and solid residue that is likely to contain chemicals listed in Annex C. Dry particulate capture will contain chemicals listed in Annex C. All should be treated or disposed of appropriately.

3. Recommended processes

Variation in feed material and desired product quality influences process design and configuration. These processes should be applied in combination with good process control, gas collection and abatement systems. Processes considered as best available techniques include the blast furnace (with good process control), the ISA Smelt/Ausmelt furnace, the top-blown rotary furnace, the electric furnace and the rotary furnace (European Commission 2001, p. 379).

The submerged electric arc furnace is a sealed unit for mixed copper and lead materials. It is cleaner than other processes if the gas extraction system is well designed and sized (European Commission 2001, p. 395).

“The injection of fine material via the tuyeres of a blast furnace has been successfully used and reduces the handling of dusty material and the energy involved in returning the fines to a sinter plant” (European Commission 2001, p. 404). This technique minimizes dust emissions during charging and thus reduces the release of PCDD/PCDF through adsorption on particulate matter.

No information is available on alternative processes to smelting for secondary lead processing.

4. Primary and secondary measures

Primary and secondary measures of PCDD/PCDF reduction and elimination are discussed below.

4.1 Primary measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of persistent organic pollutants. Possible measures include:

4.1.1 Presorting of feed material

Scrap should be sorted and pretreated to remove organic compounds and plastics to reduce PCDD/PCDF generation from incomplete combustion or by de novo synthesis. Whole battery feed or incomplete separation should be avoided. Feed storage, handling and pretreatment techniques will be determined by material size, distribution, contaminants and metal content.

Milling and grinding, in conjunction with pneumatic or density separation techniques, can be used to remove plastics. Oil removal can be achieved through thermal decoating and de-oiling processes. Thermal decoating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas (European Commission 2001, p. 232).

4.1.2 Effective process control

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation, such as maintaining furnace temperature above 850° C to destroy PCDD/PCDF. Ideally, PCDD/PCDF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (for example, waste incineration), but research is still developing in this field. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF. As installations may differ considerably, variables to be monitored would need to be established on a site-specific basis.

“Particular attention is needed for the temperature measurement and control for furnaces and kettles used for melting the metals in this group so that fume formation is prevented or minimised” (European Commission 2001, p. 390).

4.2 Secondary measures

Secondary measures are pollution control techniques to contain and prevent emissions. These methods do not prevent the formation of contaminants.

4.2.1 Fume and gas collection

Fume and off-gas collection should be implemented in all stages of the smelting process to control PCDD/PCDF emissions.

“The fume collection systems used can exploit furnace-sealing systems and be designed to maintain a suitable furnace depression that avoids leaks and fugitive emissions. Systems that maintain furnace sealing or hood deployment can be used. Examples are through hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems. An [efficient] fume collection system capable of targeting the fume extraction to the source and duration of any fume will consume less energy. Best available techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter except when carried out as part of the production of sulphuric acid” (European Commission 2001, p. 397).

4.2.2 High-efficiency dust removal

Dusts and metal compounds generated from the smelting process should be removed. This particulate matter possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions. Techniques to be considered are the use of fabric filters, wet and dry scrubbers and ceramic filters. Collected particulate should be recycled in the furnace.

Fabric filters using high-performance materials are the most effective option. Innovations regarding this method include bag burst detection systems, online cleaning methods and catalytic coatings to destroy PCDD/PCDF (European Commission 2001, p. 139–140).

4.2.3 Afterburners and quenching

Afterburners (post-combustion) should be used at a minimum temperature of 950° C to ensure full combustion of organic compounds (Hübner et al. 2000). This stage is to be followed by rapid quenching of hot gases to temperatures below 250° C. Oxygen injection in the upper portion of the furnace will promote complete combustion (European Commission 2001, p. 189).

It has been observed that PCDD/PCDF are formed in the temperature range of 250° to 500° C. These are destroyed above 850° C in the presence of oxygen. Yet, de novo synthesis is still possible as the gases are cooled through the reformation window present in abatement systems and cooler areas of the furnace. Proper operation of cooling systems to minimize reformation time should be implemented (European Commission 2001, p. 133).

4.2.4 Adsorption on activated carbon

Activated carbon treatment should be considered for PCDD/PCDF removal from smelter off-gases. Activated carbon possesses large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or injection of carbon particulate into the gas stream followed by removal as a filter dust using high-efficiency dust removal systems such as fabric filters.

5. Emerging research

Catalytic oxidation is an emerging technology used in waste incinerators to eliminate PCDD/PCDF emissions. This process should be considered by secondary base metals smelters as it has proven effective for PCDD/PCDF destruction in waste incinerators. Catalytic oxidation can, subject to catalyst selection, be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process.

Catalytic oxidation processes organic compounds into water, carbon dioxide (CO_2) and hydrochloric acid using a precious metal catalyst to increase the rate of reaction at 370° to 450° C. In comparison, incineration occurs typically at 980° C. Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency, and should be considered. Off-gases should be treated for particulate removal prior to catalytic oxidation for optimum efficiency. This method is effective for the vapour phase of contaminants. The resulting hydrochloric acid is treated in a scrubber while the water and CO_2 are released to the air after cooling (Parvesse 2001).

6. Summary of measures

Table 1. Measures for new secondary lead smelters

Measure	Description	Considerations	Other comments
Recommended processes	Various recommended smelting processes should be considered for new facilities	Processes to consider include: •1 Blast furnace (with good process control), ISA Smelt/Ausmelt furnace, top-blown rotary furnace, electric furnace and rotary furnace •2 Submerged electric arc furnace (it is a sealed unit for mixed copper and lead materials, cleaner than other processes if the gas extraction system is well designed and sized) •3 Injection of fine material via the tuyeres of a blast furnace reduces handling of dusty material	These processes should be applied in combination with good process control, gas collection and abatement systems

Table 2. Summary of primary and secondary measures for secondary lead smelters

Measure	Description	Considerations	Other comments
Primary measures			
Presorting of feed material	Scrap should be sorted and pretreated to remove organic compounds and plastics to reduce PCDD/PCDF generation from incomplete combustion or by de novo synthesis. Batteries should be broken prior to charging into the furnace and plastics and other non-lead materials removed rather than being added to the furnace	Processes to consider include: •Avoidance of whole battery feed or incomplete separation •Milling and grinding, followed by pneumatic or density separation techniques, to remove plastics • Oil removal conducted through thermal decoating and de-oiling processes	Thermal decoating and de-oiling processes for oil removal should be followed by afterburning to destroy any organic material in the off-gas
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gas components and fume collection damper controls after having established	Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but

	contribute to the minimization of PCDD/PCDF generation	optimum operating conditions for the reduction of PCDD/PCDF	research is still developing in this field. Particular attention is needed for the temperature measurement and control for furnaces and kettles used for melting the metals in this group so that fume formation is prevented or minimized
Secondary measures			
Fume and gas collection	Fume and off-gas collection should be implemented in all stages of the smelting process to capture PCDD/PCDF emissions	Processes to consider include: •Furnace-sealing systems to maintain a suitable furnace vacuum that avoids leaks and fugitive emissions •Use of hooding •Hood additions of material, additions via tuyeres or lances and the use of robust rotary valves on feed systems	Best available techniques for gas and fume treatment systems are those that use cooling and heat recovery if practical before a fabric filter
High-efficiency dust removal	Dusts and metal compounds should be removed as this material possesses high surface area on which PCDD/PCDF easily adsorb. Removal of these dusts would contribute to the reduction of PCDD/PCDF emissions	Processes to consider include: •Use of fabric filters, wet/dry scrubbers and ceramic filters	Fabric filters using high-performance materials are the most effective option. Collected particulate matter should be recycled in the furnace
Afterburners and quenching	Afterburners should be used at temperatures > 950° C to ensure full combustion of organic compounds, followed by rapid quenching of hot gases to temperatures below 250° C	Considerations include: •PCDD/PCDF formation between 250° and 500° C, and destruction > 850° C with O_2 •Requirement for sufficient O_2 in the upper region of the furnace for complete combustion •Need for proper design of cooling systems to minimize reformation time	De novo synthesis is still possible as the gases are cooled through the reformation window
Adsorption on activated carbon	Activated carbon treatment should be considered as this material is an ideal medium for adsorption of PCDD/PCDF due to its large surface area	Processes to consider include: •Treatment with activated carbon using fixed or moving bed reactors •Injection of carbon particulate into the gas stream followed by	Lime/carbon mixtures can also be used

		removal as a filter dust	
Emerging research			
Catalytic oxidation	Catalytic oxidation is an emerging technology that should be considered due to its high efficiency and lower energy consumption. Catalytic oxidation transforms organic compounds into water, CO_2 and hydrochloric acid using a precious metal catalyst	Considerations include: •Process efficiency for the vapour phase of contaminants •Hydrochloric acid treatment using scrubbers while water and CO_2 are released to the air after cooling	Catalytic oxidation has been shown to destroy PCDD/PCDF with shorter residence times, lower energy consumption and 99% efficiency. Off-gases should be treated for particulate removal prior to catalytic oxidation for optimum efficiency

7. Performance level associated with best available techniques

Performance level, associated with best available techniques, for emissions of PCDD/PCDF from secondary lead smelters is < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations)[1]

References

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Parvesse T. 2001. "Controlling Emissions from Halogenated Solvents." *Chemical Processing* 64(4):48–51.

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[1] 1 ng (nanogram) = 1 x 10^{-12} kilogram (1 x 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0^0C and 101.3kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.

(ii) Primary aluminium production

Summary

Primary aluminium is produced directly from the mined ore, bauxite. The bauxite is refined into alumina through the Bayer process. The alumina is reduced into metallic aluminium by electrolysis through the Hall-Héroult process (either using self-baking anodes – Söderberg anodes – or using prebaked anodes).

Primary aluminium production is generally thought not to be a significant source of chemicals listed in Annex C of the Stockholm Convention. However, contamination with PCDD and PCDF is possible through the graphite-based electrodes used in the electrolytic smelting process.

Possible techniques to reduce the production and release of chemicals listed in Annex C from the primary aluminium sector include improved anode production and control, and using advanced smelting processes. The performance level associated with best available techniques for emissions of PCDD/PCDF in the primary aluminium sector is < < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations).

1. Process description

Primary aluminium production refers to aluminium produced directly from the mined ore, bauxite. The bauxite is refined into alumina by the Bayer process, and then the alumina is reduced by electrolysis (the Hall-Héroult process) into metallic aluminium. This section does not cover the secondary aluminium process, which is covered in section V.D (iii) of the present guidelines.

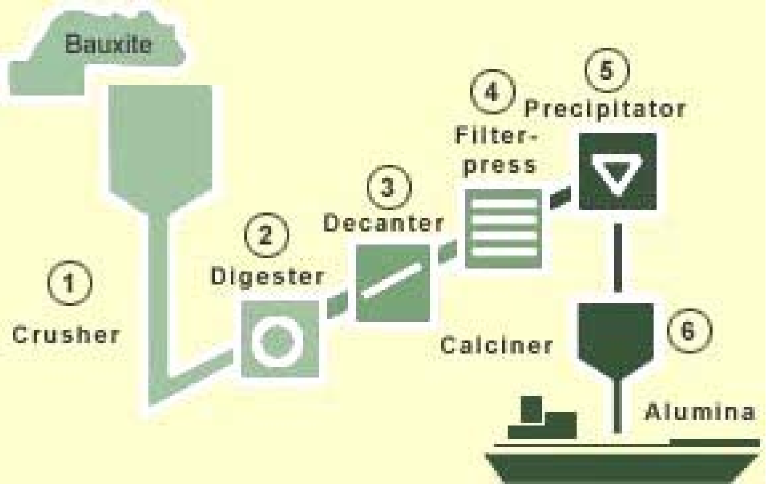
1.1 The Bayer process: Refining bauxite to alumina

Bauxite is converted to alumina using the Bayer process (Figure 1). The bauxite ore is dried, crushed and ground into a powder and mixed with a solution of caustic soda to extract the alumina at elevated temperatures and pressures in digesters. A slurry is produced which contains dissolved sodium aluminate and a mixture of metal oxides, called red mud, which is removed in thickeners. The red mud is washed to recover the chemicals and is disposed of. The aluminate solution is cooled and seeded with alumina to crystallize the hydrated alumina in precipitator tanks. The crystals are washed and then calcined in rotary kilns or fluid bed/fluid flash calciners to produce the aluminium oxide or alumina, which is a white powder resembling table salt.

1.2 The Hall-Héroult process: Reduction by electrolysis of alumina to aluminium

Aluminium is produced from alumina by electrolysis in a process known as the Hall-Héroult process. The alumina is dissolved in an electrolytic bath of molten cryolite (sodium aluminium fluoride). An electric current is passed through the electrolyte and flows between the anode and cathode. Molten aluminium is produced, deposited at the bottom of the electrolytic cell or pot, and periodically siphoned off and transferred to a reverberatory holding furnace. There it is alloyed, fluxed and degassed to remove trace impurities. Finally, the aluminium is cast or transported to the fabricating plants.

Figure 2 . Simplified flow sheet for alumina production



1) Source: Aluminium Association of Canada.

1.3 Production of aluminium

There are two types of technologies used for the production of aluminium (Figure 2): those using self-baking anodes (Söderberg anodes) and those using prebaked anodes.

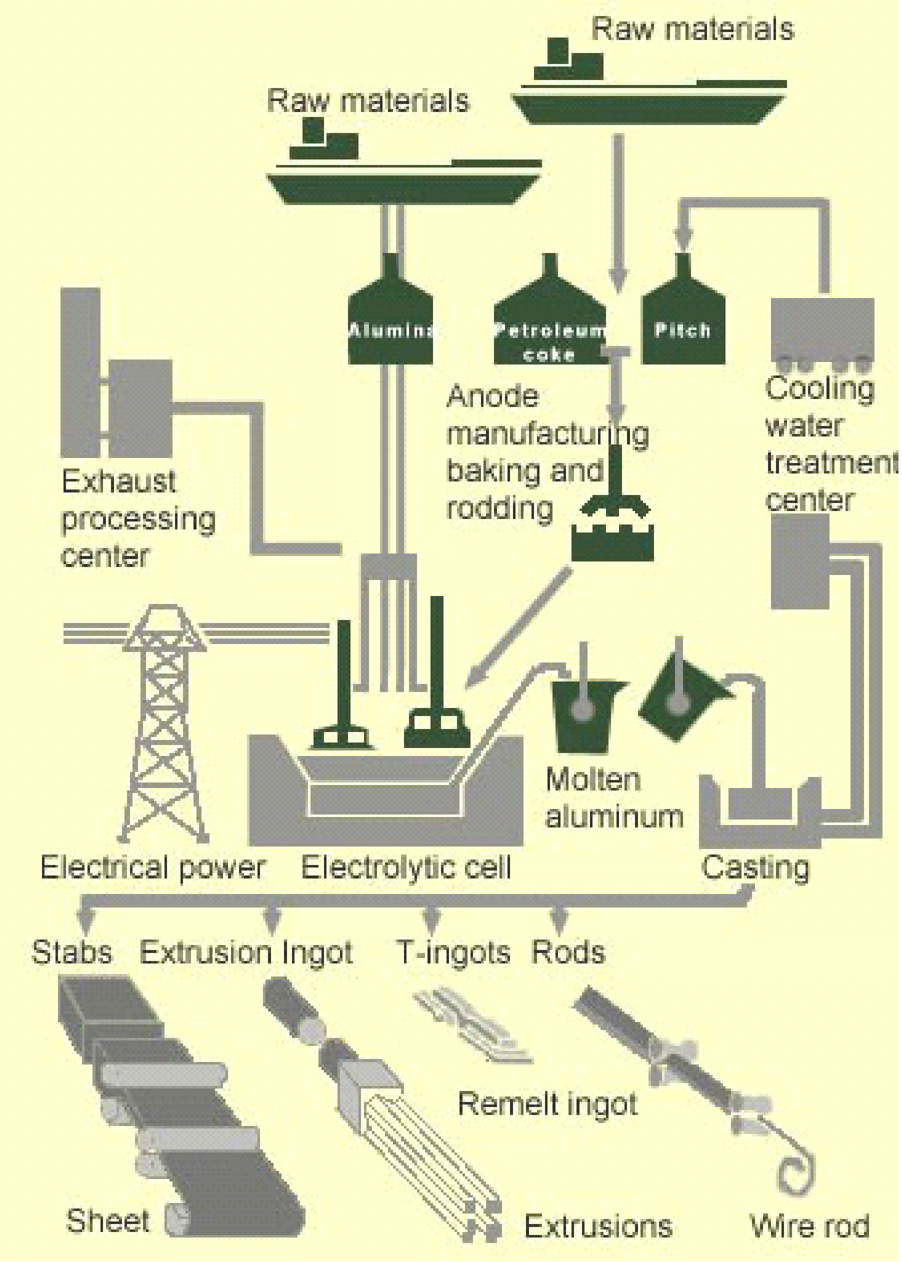
The older Söderberg anodes are made in situ from a paste of calcined petroleum coke and coal tar pitch, and are baked by the heat from the molten electrolytic bath. As the anode is consumed, more paste descends through the anode shell in a process that does not require anode changes. Alumina is added periodically to Söderberg cells through holes made by breaking the crust alumina and frozen electrolyte that covers the molten bath. Depending on the placement of the anode studs, these are known as vertical stud Söderberg or horizontal stud Söderberg cells or pots. Automatic point feeding systems are used in upgraded plants, eliminating the need for regular breaking of the crust.

Prebaked anodes are manufactured in a carbon plant from a mixture of calcined petroleum coke and coal tar pitch, which is formed into a block and baked in an anode furnace. The prebaked anode production plants are often an integrated part of the primary aluminium plant. The prebaked anodes are gradually lowered into the pots as they are consumed, and need to be replaced before the entire block has been consumed. The anode remnants, known as anode butts, are cleaned and returned to the carbon plant for recycling. Depending on the method of feeding the alumina into the electrolytic cells, the cells are called side-worked prebake or centre-worked prebake. For side-worked prebake cells, the alumina is fed to the cells after the crust is broken around the perimeter. For centre-worked prebake cells, the alumina is fed to the cells after the crust is broken along the centre line or at selected points on the centre line of the cell.

The cathode typically has to be replaced every five to eight years because of deterioration, which can allow the molten electrolyte and aluminium to penetrate the cathode conductor bar and steel shell. The spent cathode, known as spent potlining, contains hazardous and toxic substances such as cyanides and fluorides, which must be disposed of properly.

Molten alumina is periodically withdrawn from the cells by vacuum siphon and is transferred to crucibles. The crucibles containing liquid metal are transported to the casting plant, where the aluminium is transferred to the holding furnaces. Alloying elements are added in these furnaces. Dross (“skimmings”) formed by the oxidation of molten aluminium is skimmed off, and sealed containers are used to minimize further oxidation of the dross. Nitrogen and argon blanketing is used. This is followed by removal of sodium, magnesium, calcium and hydrogen. The treatment gas used varies depending on the impurities. Argon or nitrogen is used to remove hydrogen; mixtures of chlorine with nitrogen or argon are used to remove metallic impurities.

Figure 3.General schematic of the electrolytic process for aluminium production



Source: Aluminium Association of Canada.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

Primary aluminium production is unlikely to be a significant source of releases of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), although contamination is possible through the graphite-based electrodes (AEA Technology Environment 1999, p. 63). PCDD/PCDF release levels are generally thought to be low and the main interest is in the thermal processing of scrap materials (UNEP 2003, p. 73). This is discussed further in paragraph 2.3 below.

2.1 Emissions of PCDD/PCDF

There is limited information available on chemicals listed in Annex C of the Stockholm Convention, including PCDD/PCDF formation from primary aluminium processes. Some literature suggests that initial emissions testing indicates that PCDD/PCDF are not considered significant from this sector.

It is reported that it is unlikely that the Söderberg and prebaked processes release significantly different emissions per ton of aluminium produced (AEA Technology Environment 1999, p. 63). Test results on emission sources and abatement units associated with prebaked anode manufacturing indicate that PCDD are not significant from these sources. However, if chlorine compounds or additives are used, emissions will need to be examined (European Commission 2001, p. 669).

Some studies have tested for PCDD in fume from the casting process because the use of chlorine for degassing and the presence of carbon from the combustion gases may lead to the formation of PCDD. Results from primary smelter cast houses have shown that releases are significantly below 1 gram per year (European Commission 2001, p. 289). The potential for PCDD/PCDF formation during the refining processes for both primary and secondary aluminium production has not been fully investigated. It has been recommended that this source be quantified (European Commission 2001, p. 318).

2.2 Releases to land

The production of primary aluminium from ores is not thought to produce significant quantities of PCDD/PCDF (New Zealand Ministry for the Environment 2000). The *Review of Dioxin Releases to Land and Water in the UK* states that there may be the possibility of graphite-based electrodes having some PCDD/PCDF contamination (UK Environment Agency 1997). Swedish data suggest that the spent sludge from the cells may contain 7.8 ng Nordic-TEQ kg^{-1}. However, if the cathode is high-purity carbon material and the reduction process does not involve chlorine or chloride materials, it is unlikely that PCDD/PCDF will be present.

Metal reclaim fines may contain PCDD/PCDF because chlorine or chlorine-based products are used to degas the fraction of the aluminium that is poured into the extrusion billets.

2.3 Research findings of interest

Limited information exists on the unintentional formation of PCDD/PCDF from this sector. It has been suggested that primary aluminium production is not considered to be a significant source of releases. One paper reported non-detect levels for dioxin and furan emissions (ESP Environmental Ltd., 2000). However, a 2001 Russian study of the PCDD/PCDF emissions in the city of Krasnoyarsk concluded that the aluminium factory was responsible for 70% of industrial PCDD/PCDF emissions to air and 22% of industrial releases to land (Kucherenko et al. 2001). More studies in this area would be needed in order to show whether or not primary aluminium production is a significant source of dioxins and furans.

2.4 General information on releases from primary aluminium plants

Greenhouse gases are a major pollutant from aluminium production and result from fossil fuel combustion, carbon anode consumption, and perfluorocarbons from anode effects. In addition to greenhouse gases, aluminium smelters also discharge other atmospheric emissions, as well as some solid wastes (spent potliners) and liquid effluents (SNC-Lavalin Environment 2002, p. 3:14).

"The use of carbon anodes leads to emissions of sulphur dioxide (SO_2), carbonyl sulphide (COS), polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides (NO_x). Most of the sulphur in the carbon anode is released as COS, which is not entirely oxidized to SO_2 before being emitted at the potroom gas scrubber stacks. Sulphur emissions are predominately in the form of SO_2 with a minor component of COS. The emission of sulphur gases from aluminium reduction is expected to rise with the increasing sulphur content of petroleum cokes used for anode manufacture. PAHs are the result of incomplete combustion of hydrocarbons found in certain pitch used to form the anodes. The use of prebake anodes has virtually eliminated the emissions of PAHs, mainly associated with Söderberg anodes. The NO_x emissions mainly come from the combustion of fuel in the anode baking furnace" (SNC-Lavalin Environment 2002, p. 3:14).

"The electrolysis of alumina also leads to the emission of fluorides (particulate fluorides and gaseous HF) and other particulates. The removal of fluorides from the cell gases in modern alumina injection dry scrubber systems is now greater than 99% efficient and the final fluoride emissions from modern prebake smelters are significantly lower. Anode changing and cooling of spent anode butts are the most important sources of fugitive fluoride emissions from an aluminium smelter and these are estimated to be 4 to 5 times greater than stack emissions (after the scrubber)" (SNC-Lavalin Environment 2002, p. 3:16).

> The "anode effect" results in generation of perfluorocarbons in smelting pots when the concentration of alumina falls below a certain level due to the lack of fresh feed. The carbon anode preferentially reacts with the fluorine in the cryolite solution because there is insufficient oxygen available from the alumina. When this event occurs, carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6) are produced, along with a surge in voltage. The amount of perfluorocarbons generated depends on the efficiency of feed control in the pot. For pots not equipped with proper controls, perfluorocarbon emissions from anode effects can be the largest source, accounting for over 50% of the total smelter emissions (on a CO_2-equivalent basis). Practically any point-fed, computer-controlled pot can operate at low anode effect frequency. Older technologies, such as horizontal stud and vertical stud Söderberg cells, have higher perfluorocarbon generation rates. These technologies typically do not have individual pot sensing systems and the feed is usually a non-automated bulk system. The process control techniques in modern prebaked smelters are such that perfluorocarbon emissions can be reduced to less than 5% of the total greenhouse gas emissions from the smelter. CO_2 emissions from anode consumption are the next largest source for pots without modern controls (SNC-Lavalin Environment 2002, p. 3:10–11).

Table 3. Emissions, effluents, by-products and solid wastes from primary aluminium production

Process	**Air emissions**[a]	**Effluents**	**By-products and solid wastes**
Alumina refining	Particulate	Wastewater containing starch, sand and caustic	Red mud, sodium oxalate
Anode production	Particulates, fluorides, polycyclic aromatic hydrocarbons, SO_2, PCDD/PCDF[b]	Wastewater containing suspended solids, fluorides, and organics	Carbon dust, tar, refractory waste
Aluminium smelting	CO, CO_2, SO_2, fluorides (gaseous and particulate), perfluorocarbons (CF_4, C_2F_6), polycyclic aromatic hydrocarbons, PCDD/PCDF[b]	Wet air pollution control effluents (wet electrostatic precipitator)	Spent potliners, wet air pollution control wastes, sludges

a. Excluding combustion-related emissions.

b. Based on the Krasnoyarsk study (Kucherenko et al. 2001).

Source: Energetics Inc. 1997.

3. Alternative processes to primary aluminium smelting (emerging technologies)

The Stockholm Convention states that when consideration is being given to proposals for construction of a new primary aluminium plant, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but avoid the formation and release of the identified substances.

There are a number of research initiatives currently under way to produce primary aluminium while concurrently reducing energy consumption and emissions (European Commission 2001, p. 335; SNC-Lavalin Environment 2002; Welch 1999; USGS 2001; BCS Inc. 2003, p. 41–58). These initiatives include:

Inert anodes: Carbon-free anodes that are inert, dimensionally stable, slowly consumed, and produce oxygen instead of CO_2. The use of inert anodes eliminates the need for an anode carbon plant (and emissions of polycyclic aromatic hydrocarbons from the process);

Wettable cathodes: New cathode materials or coatings for existing cathode materials that allow for better energy efficiency;

Vertical electrodes – low-temperature electrolysis (VELTE): The process uses a non-consumable metal alloy anode, a wetted cathode and an electrolytic bath, which is kept saturated with alumina at the relatively low temperature of 750° C by means of free alumina particles suspended in the bath. This technology could produce primary aluminium metal with lower energy consumption, lower cost and lower environmental degradation than the conventional Hall-Héroult process;

Drained cell technology: Features the coating of aluminium cell cathodes with titanium dibromide and eliminating the metal pad, which reduces the distance between anode and cathode, thereby lowering the required cell voltage and reducing heat loss;

Carbothermic technology: Carbothermic reduction produces aluminium using a chemical reaction that takes place within a reactor and requires much less physical space than the Hall-Héroult reaction. This process would result in significantly reduced electrical consumption, and the elimination of perfluorocarbon emissions resulting from carbon anode effects, hazardous spent potliners, and hydrocarbon emissions associated with the baking of consumable carbon anodes;

Kaolinite reduction technology: The production of aluminium by reduction of aluminium chloride using clays holds appeal because the raw materials are readily available and inexpensive. The thermodynamics also provide high-speed conversion reactions with lower electrical demand and no bauxite residue is produced.

4. Primary and secondary measures

Primary and secondary measures for reducing emissions of PCDD/PCDF from primary aluminium production processes are outlined below.

The extent of emission reduction possible with the implementation of primary measures only is not readily known. It is therefore recommended that consideration be given to implementation of both primary and secondary measures at existing plants.

Note that no secondary measures have been developed specifically for primary aluminium smelters to control the unintentional formation of PCDD/PCDF. The following are general measures that may result in lower pollutant emissions at primary aluminium smelters, including releases of PCDD/PCDF.

4.1 Primary measures

Primary measures are understood to be pollution prevention measures that prevent or minimize the formation and release of the identified substances (particulates, fluorides, polycyclic aromatic hydrocarbons, sulphur dioxide, carbon dioxide, carbon monoxide and perfluorocarbons). These are sometimes referred to as process optimization or integration measures. Pollution prevention is defined as "the use of processes, practices, materials, products or energy that avoid or minimize the creation of pollutants and waste, and reduce overall risk to human health or the environment" (see section III.B of the present guidelines). Note that there are no primary measures identified for PCDD/PCDF.

For new smelters, using the prebake technology rather than the Söderberg technology for aluminium smelting is a significant pollution prevention measure (World Bank 1998). The use of centre-worked prebaked cells with automatic multiple feeding points is considered to be a best available technique for the production of primary aluminium (European Commission 2001, p. 325).

"Point feeders enable more precise, incremental feeding for better cell operation. They are generally located at the centre of the cell and thereby cut down on the diffusion required to move dissolved alumina to the anodic reaction sites. The controlled addition of discrete amounts of alumina enhances the dissolution process, which aids in improving cell stability and control, minimizing anode effects, and decreasing the formation of undissolved sludge on the cathode. In the jargon of modern commerce, point feeders enable 'just-in-time alumina supply' to permit optimum cell operation. Point feeder improvements continue to be made as more accurate cell controllers become available" (BCS Inc. 2003, p. 47).

Advanced process controllers are also being adopted by industry to reduce the frequency of anode effects and control operational variables, particularly bath chemistry and alumina saturation, so that cells remain at their optimal conditions (BCS Inc. 2003).

Primary measures that may assist in reducing the formation and release of the identified substances include (European Commission 2001, p. 326, 675–676):

1 An established system for environmental management, operational control and maintenance;

2 Computer control of the electrolysis process based on active cell databases and monitoring of cell operating parameters to minimize the energy consumption and reduce the number and duration of anode effects;

3 If local, regional or long-range environmental impacts require SO_2 reductions, the use of low-sulphur carbon for the anodes or anode paste if practicable, or an SO_2 scrubbing system.

4.2 Secondary measures

Secondary measures are understood to be pollution control technologies or techniques, sometimes described as end-of-pipe treatments. Note that the following are not considered secondary measures specific to minimization of PCDD/PCDF releases, but for pollutant releases generally.

The following measures have been shown to effectively reduce releases from primary aluminium production and should be considered best available techniques (European Commission 2001, p. 326, 675–676):

1 Feed preparation: Enclosed and extracted grinding and blending of raw materials, fabric filters for abatement;

2 Complete hood coverage of the cells, which is connected to a gas exhaust and filter; use of robust cell covers and adequate extraction rates; sealed anode butt cooling system;

3 Better than 99% fume collection from cells on a long-term basis; minimization of the time taken for opening covers and changing anodes;

4 Gases from the primary smelting process should be treated to remove dust, fluorides and hydrogen fluoride using an alumina scrubber and fabric filter. The scrubbing efficiency for total fluoride should be > 99.8%, and the collected alumina used in the electrolytic cells;

5 Use of low-NO_x burners or oxy-fuel firing; control of firing of furnaces to optimize the energy use and reduce polycyclic aromatic hydrocarbons and NO_x emissions;

6 If there is an integrated anode plant the process gases should be treated in an alumina scrubber and fabric filter system and the collected alumina used in the electrolytic cells. Tars from mixing and forming processes can be treated in a coke filter;

7 Destruction of cyanides, tars and hydrocarbons in an afterburner if they have not been removed by other abatement techniques;

8 Use of wet or semi-dry scrubbing to remove SO_2 if necessary;

9 Use of biofilters to remove odorous components if necessary;

10 Use of sealed or indirect cooling systems.

5. Summary of measures

Tables 4 and 5 present a summary of the measures discussed in previous sections.

Table 4. Measures for new primary aluminium production plants

Measure	Description	Considerations	Other comments
Alternative processes	Priority should be given to alternative processes with less environmental impacts than tradition primary aluminium production plants	Examples include: •Inert anodes •Wettable cathodes •Vertical electrodes – low-temperature electrolysis •Drained cell technology •Carbothermic technology •Kaolinite reduction technology	These processes are still in the development phase
Prebake technology	The use of centre-worked prebaked cells with automatic multiple feeding points is considered a best available technique		
Performance levels	New primary aluminium production plants should be required to achieve stringent performance and reporting requirements associated with best available technologies and techniques	Consideration should be given to the primary and secondary measures listed in Table 3	No performance requirements have been determined for releases of PCDD/PCDF from primary aluminium plants

Table 5. Summary of primary and secondary measures for primary aluminium production plants

Measure	Description	Considerations	Other comments
Primary measures			
Environmental management system, operational control and maintenance			

Computer-controlled process and monitoring	To minimize energy consumption and reduce number and duration of anode effects		
Feed selection: Use of low sulphur carbon for anodes or anode paste	To control sulphur dioxide emissions, if necessary	SO_2 scrubbing system may be used	
Secondary measures			
Feed preparation: Enclosed grinding and blending of raw materials. Use of fabric filters	To prevent the releases of particulates		
Complete hood coverage of cells	The use of hoods that completely cover cells to collect gases to the exhaust and filter		
Fume collection and treatment	Fume collection efficiency should be greater than 99%. Gases should be treated to remove dust, fluorides and HF using an alumina scrubber and fabric filter		The time taken for opening the covers and changing the anodes should be minimized
Low NO_x burners or oxy-fuel firing	The firing of the furnace should be optimized to reduce emissions of polycyclic aromatic hydrocarbons and NO_x		
Alumina scrubber	Process gases from anode plant should be treated in an alumina scrubber and fabric filter system		The alumina should be used in the electrolytic cells. Tars can be treated in a coke filter
Afterburner	To destroy cyanides, tars and polycyclic aromatic hydrocarbons if not removed by other abatement		
Wet or semi-dry scrubbing	To remove SO_2 if necessary		
Biofilters	To remove odorous components if necessary		

6. Performance level associated with best available techniques

Performance level associated with best available techniques for emissions of PCDD/PCDF in the primary aluminium sector is < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations).[2]

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[2] 1 ng (nanogram) = 1 x 10^{-12} kilogram (1 x 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0^0C and 101.3kPa. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.

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(iii) Magnesium production

Summary

Magnesium is produced either from raw magnesium chloride with molten salt electrolysis, or magnesium oxide reduction with ferrosilicon or aluminium at high temperatures, as well as through secondary magnesium recovery (for example, from asbestos tailings).

The addition of chlorine or chlorides, the presence of carbon anodes and high process temperatures in magnesium production can lead to the formation of chemicals listed in Annex C of the Stockholm Convention and their emission to air and discharge to water.

Alternative techniques may include the elimination of the carbon source by using non-graphite anodes, and the application of activated carbon. However, performance levels associated with best available techniques depend on the type of process and controls utilized for air and water releases.

1. Process description

There are two major process routes utilized for production of magnesium metal. The first process recovers magnesium chloride from the raw materials and converts it to metal through molten salt electrolysis. The second type of process involves reducing magnesium oxide with ferrosilicon or aluminium at high temperatures. Examples of the two types of processes are described below.

Magnesium can also be recovered and produced from a variety of magnesium-containing secondary raw materials and from scrap (VAMI 2004).

1.1 Magnesium production process from magnesium oxide resources

The process allows magnesium to be produced from oxide raw materials: magnesite, brusite, serpentine and others. It is also suitable for magnesium production from raw materials containing magnesium sulphate or its mixture with chlorides, including seawater. In all cases chlorine produced by electrolysis is recycled and used for conversion of magnesium oxide or sulphate into magnesium chloride (VAMI 2004).

The process of magnesium production from magnesium oxides consists of the following stages (see Figure 4):

1 Leaching of raw material by hydrochloric acid and purification of the solution produced;

2 Separation of magnesium chloride product in the form of synthetic carnallite or mixture of chlorides from said solution;

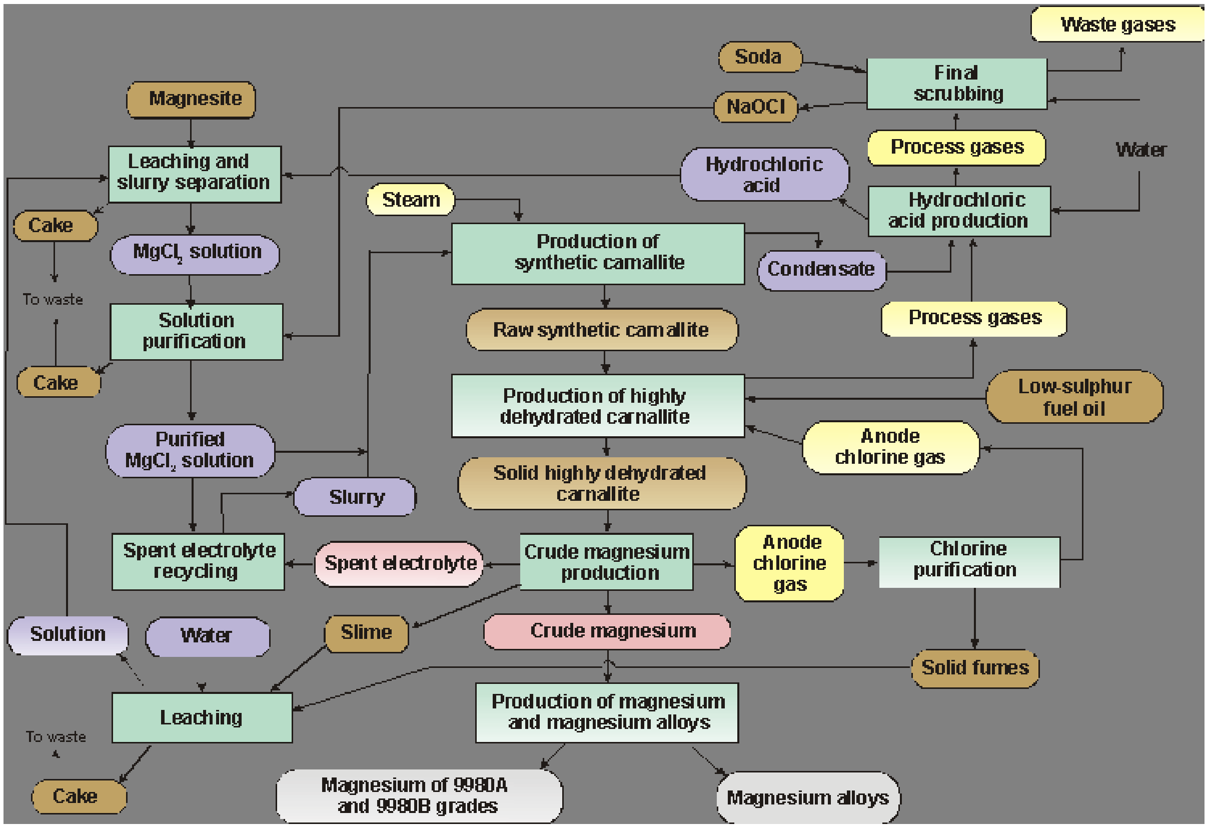
3 Dehydration of said product in a fluidized bed by the stream of hot gases, containing hydrogen chloride, with production of solid dehydrated product, containing not more than 0.3 wt.% of magnesium oxide and water each;

4 Feeding of said product into electrolyzers or head unit of flow line and its electrolysis, with production of magnesium and chlorine.

Chlorine produced by electrolysis is fed into the burners of fluidized bed furnaces, where it is converted into hydrogen chloride (HCl). Waste gases of the fluidized bed furnaces, containing HCl, are either treated by water to produce hydrochloric acid, which is used for raw material leaching, or neutralized by aqueous suspension of magnesium oxide to produce magnesium chloride solution.

Spent electrolyte forming in the course of electrolysis is used for synthetic carnallite production. All the waste products containing chlorine are utilized with the production of neutral oxides. It is a significant advantage of the process from an environmental point of view.

Figure 4. Flow diagram of magnesium production process from magnesium oxide resources



Source: VAMI 2004.

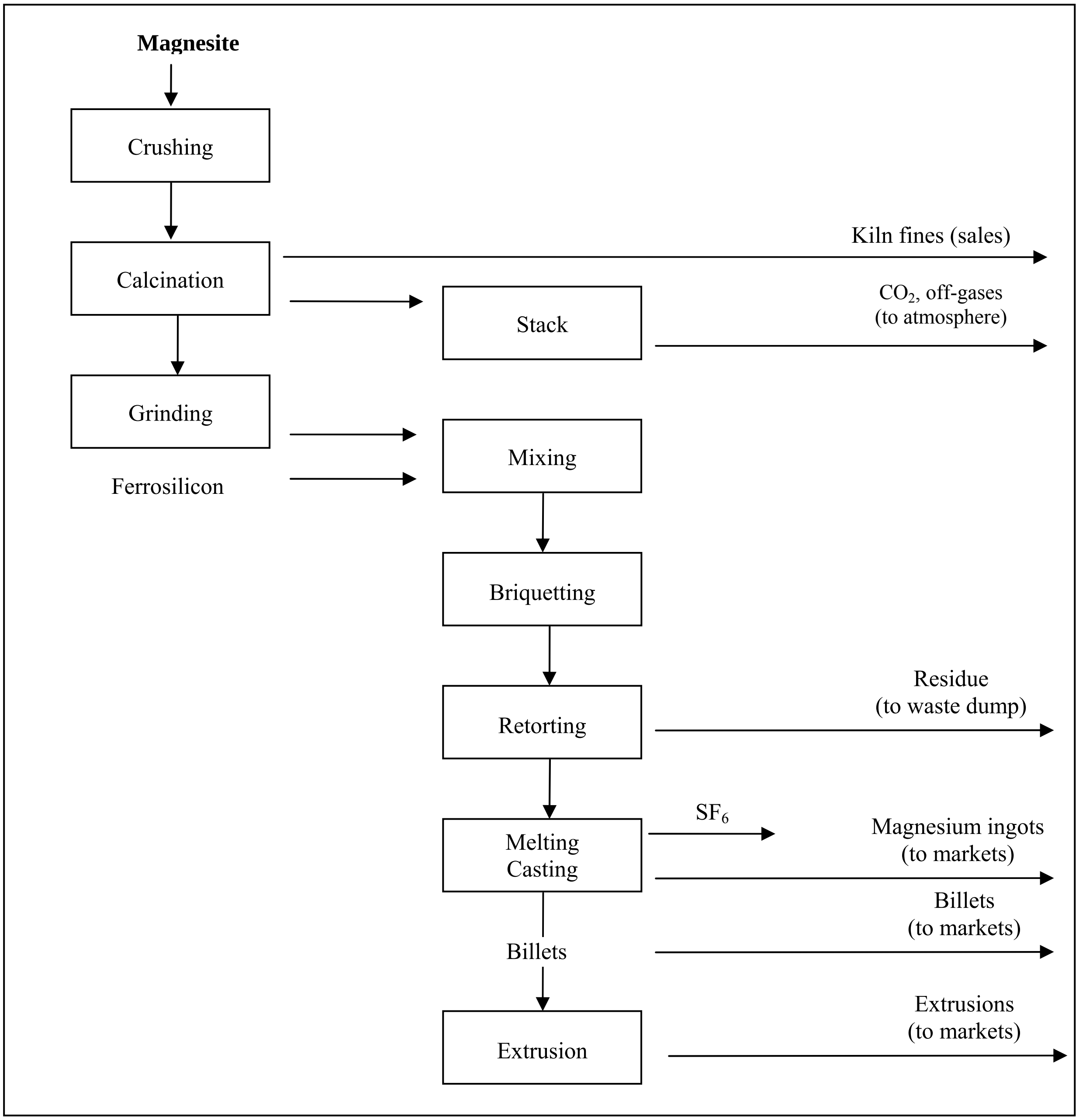
1.2 The Pidgeon process (thermal reduction process)

In the Pidgeon process, magnesium is produced from calcined dolomite under vacuum and at high temperatures using silicon as a reducing agent. In the process, the finely crushed dolomite (magnesium/calcium) carbonate is fed to rotary kilns where it is calcined, and where the carbon dioxide is driven off, leaving a product of calcined dolomite. The calcined dolomite is then pulverized in a roller mill prior to mixing with finely ground ferrosilicon and fluorspar. The fine calcined dolomite, ferrosilicon, and fluorspar are weighed in batch lots and mixed in a rotary blender. This mixture is then briquetted in briquetting presses (Noranda Magnesium website).

Briquettes are then conveyed to the reduction furnaces. The reduction operation is a batch process releasing magnesium in vapour form, which condenses in the water-cooled section of the retort outside the furnace wall. After removal from the furnace, the magnesium crown is pressed from the sleeve in a hydraulic press. The residue from the reduction charge is removed from the retort and sent to a waste dump.

Figure 5 illustrates the process in diagrammatic form.

Figure 5. Process flow chart: Timminco magnesium plant



Source: Hatch and Associates 1995.

1.3 Various processes and considerations

Various thermal processes for magnesium production are used in a number of countries. These are based around the Pidgeon process developed in Canada in the 1940s. Calcined dolomite (CaO:MgO), is fused with ferrosilicon (FeSi) under vacuum. The magnesium is released from the melt as a vapour and condensed away from the reactor to form a metal deposit that can be removed and recast into ingots for industrial use. The retort is in many cases heated with coal. This can lead to significant emissions of persistent organic pollutants. A waste slag containing iron and calcium silicates together with a proportion of unreacted magnesium oxide is produced and the ash from the coal combustion must also be disposed of. While cooling water is used this need not be contaminated with process wastes.

The processes will depend on the nature of the raw materials that are available, the size of the proposed facility, the available infrastructure and local conditions. Improved processes are now available that minimize environmental impacts by reducing energy demand. These processes however are only available under licence and so may not be accessible to all. One process that operates almost near continuously has been developed developed in South Africa, which operates at atmospheric pressure (Mintek process) and is available for licence. Effective control of releases depends on careful specification of the plant and effective operation of the plant to minimize energy use while maximizing conversion of raw materials into product. A range of approaches is available and the choice will be determined by the actual combination of economic and process demands. Suitable air pollution controls would need to be fitted and adequate facilities provided to handle and dispose of solid wastes.

The selection of a process that minimizes energy consumption may minimize the production of persistent organic pollutants. Hence continuous processes tend to be more energy efficient as less heat is required to return the reactor to operating temperature between cycles. One widely used process available for licence is the Magnatherm process, which replaces the coal heating of the retort with electrical induction heating. As a result, no fuel-generated emissions of persistent organic pollutants occur. This also operates semi-continuously and at a lower vacuum than the original Pidgeon process plant. Heating with oil or gas fuels instead of coal can greatly reduce the amount of persistent organic pollutants formed and is recommended where the distribution network for these fuels is reliable.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

2.1 Emissions to air

2.1.1 General information on emission from magnesium production

Magnesium production facilities generate several types of pollutants, including dust, sulphur dioxide (SO_2), nitrogen oxides (NO_x), chlorine (Cl_2), hydrochloric acid (HCl), and in several cases emission of sulphur hexafluoride (SF_6) throughout the manufacturing process.

Dust and sulphur dioxide are mainly emitted from the calcinations of dolomite and magnesium oxide (MgO), from pellet drying as well as from chlorination off-gas treatment.

The source of nitrogen oxides emissions are dolomite and MgO calcinations and pellet drying. Chlorine and hydrochloric acid are released from electrolysis and chlorination processes, and the chlorination off-gas treatment system.

While carbon dioxide is emitted from the whole manufacturing process, the source of sulphur hexafluoride discharges is the cast-house.

2.1.2 Emissions of PCDD and PCDF

According to tests conducted on an electrolytic process in a magnesium production plant in Norway, the main process causing the formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) was a furnace converting pellets of MgO and coke to magnesium chloride ($MgCl_2$) by heating in a Cl_2 atmosphere at 700°–800° C (Oehme, Manø and Bjerke 1989; European Commission 2001).

The purification of MgO using HCl and graphite blades ("chlorination") or electrolysis of $MgCl_2$ using graphite electrodes are also possible other sources of PCDD/PCDF formation (UNEP 2003).

Timminco Ltd, in Ontario, Canada, which utilizes the thermal reduction Pidgeon process technology, reported PCDD/PCDF release to air of 0.416 g I-TEQ/year (CCME 2003).

Dioxin emission data of a former Norwegian magnesium production plant (Norsk Hydro) in the period 1992–2001 provided by Norway show that emission to air was approximately 0.03–0.25 mg I-TEQ/tonne Mg produced. The emission decreased from approximately 0.3 mg I-TEQ/tonne Mg to below 0.1 mg I-TEQ/tonne Mg after installation of an extra gas cleaning system in the plant.

(Personal Communication, Norway Member, June 2006).

Table 6 shows emissions to air from different magnesium production processes; note that values provided as representative of Norsk Hydro performance vary from those noted above.

Table 6. PCDD/PCDF emissions to air from different magnesium production processes

Process type	Source	Emissions[3] (ng/Nm^3)	Concentration (μg TEQ/t)
	From chlorination of off-gas treatment	0.8	12
	From chlorination vent gas	0.8	28
	From electrolysis/chlorination		13
Thermal	Reduction, refining and melting	0.08	3
Norsk Hydro process			< 1.0

Hydro Magnesium Canada reported a total of 0.456 g I-TEQ/year[4] emissions of PCDD/PCDF to air, broken down as shown in Table 7.

Table 7. Emissions of PCDD/PCDF by source: Hydro Magnesium Canada

Source	g TEQ/year
Dissolving	0.001
Dehydration	0.112
Electrolysis	0.277
Foundry	0.025
HCl synthesis	0.0003
Mg remelting	0.050

2.2 Releases to other media

2.2.1 Water

The main water pollutants in the magnesium manufacturing process are metal compounds as suspended solids. However, chlorinated hydrocarbons and PCDD/PCDF are also found in wastewater from the magnesium electrolysis process (Table 8).

Table 8. Releases of PCDD/PCDF to water from different magnesium production processes

Type	ng/m^3	ug TEQ/t of Mg
Electrolytic	100	13
Thermal	0.08	3
Norsk Hydro process		< 0.1

Source: Hydro Magnesium Canada.

Emissions data of Norsk Hydro in the period 1992–2001 provided by Norway are as follows (Personal Communication, Norway Member, June 2006) (note that values provided above as representative of Norsk Hydro performance vary from these):

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[3] 1 ng (nanogram) = 1×10^{-12} kilogram (1×10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0^0C and 101.3kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

[4] Hydro Magnesium Canada presentation at Electrolytic Magnesium Industry Bi-national Informative Meeting, Montreal, 12 December 2000, by Jean Laperriere, Environment Chief.

1 Dioxin discharges to water: Approximately 0.03–0.09 mg I-TEQ/tonne Mg produced

2 Hexachlorobenzene discharges to water: Approximately 0.02–0.2 g I-TEQ/tonne Mg produced.

2.2.2 Land

The wet scrubbing process utilized in treatment of gas streams would be expected to generate residues containing PCDD/PCDF. A water treatment system that includes settling of these residues in a lagoon would then constitute a release to land (UNEP 2003).

Table 9. Emission Factors in the magnesium industry: PCDD/PCDF

	Emission factors: µg TEQ/t of Mg				
	Air	**Water**	**Land**	**Product**	**Residue**
Production using MgO/C thermal treatment in Cl_2 no effluent, limited gas treatment	250	9,000	n.a.	n.a.	0
Production using MgO/C thermal treatment	50	30	n.a.	n.a.	9000
Thermal reduction process	3	n.d.	n.a.	n.a.	n.a.

n.a. Not applicable.

n.d. Not determined.

Source: UNEP 2005.

Table 10. Emission factors in the magnesium industry: Hexachlorobenzene (HCB)

	Emission factors: µg/kg				
	Air	**Water**	**Land**	**Process generated**	**Volatilized from land**
Norsk Hydro, Posrgrunn[a]	700–3,000	n.d.	n.d.	n.d.	n.d.
Norsk Hydro, Bécancour[a]	90–170	2.4	60–120	n.d.	n.d.
Noranda, Asbestos[b]	439	0	8	Not estimated	~6

n.d. Not determined.

a. Source: Bramley 1998.

b. Source: Kemp 2004,; note that facility was operating at only 50% of design capacity and emission factor is believed to be overstated as a result.

3. Alternative processes for magnesium production

Although process efficiency and productivity could be the main driving forces in the advancement and development of alternative new technologies, it is expected that environmental aspects will be given due consideration. This means elimination or minimization of the formation of pollutants at source, and the incorporation of effective pollution abatement systems, should be part of the initial design of the project.

3.1 Norsk Hydro dehydration process

Norsk Hydro has developed and successfully implemented a new technology, an $MgCl_2$ dehydration process, in its plant in Canada (European Commission 2001). Releases of pollutants, especially PCDD/PCDF, generated from this process are significantly lower than from existing processes (Tables 1 and 3).

The plant produces $MgCl_2$ brine by dissolving magnesite rock in hydrochloric acid. Impurities such as aluminium, iron and manganese are removed from the leach liquor by purification. The brine is then subjected to evaporation and prilling and drying using the fluidized bed technique. This will result in an anhydrous $MgCl_2$ product.

Hydro's electrolysis cells are operated at around 400 kA. The $MgCl_2$ prills are fed continuously from the dehydration plant into the electrolysis cells. This operation produces magnesium metal and chlorine gas. The chlorine gas is reacted with hydrogen to produce hydrochloric acid, which is recycled to the magnesite dissolving stage. The molten magnesium is cast under controlled conditions. The final products are pure metal and alloys in the form of ingots and grinding slabs.

3.2 Noranda's magnesium recovery from asbestos tailings

A new technology in use by Noranda[5] involves recovery of magnesium from asbestos tailings (Noranda Inc. website). The process description is as follows:

Transforming serpentine into high-grade magnesium: In Noranda's proprietary magnesium process, serpentine undergoes a series of chemical processes and filtration steps to produce a very pure anhydrous magnesium chloride. This is electrolytically reduced in state-of-the-art high-efficiency cells into magnesium and chlorine. The chlorine is completely captured and recycled. The company's projections for its environmental performance include emission levels of no more than 0.09 g TEQ of PCDD/PCDF to air, using an activated carbon adsorption system.

Feed preparation: Noranda's magnesium process starts with crysotile serpentine ($3MgO•2SiO_2•2H_2O$), a mining residue containing 23% magnesium. The material is already mined and above ground, adjacent to the plant. Serpentine is crushed, screened and magnetically separated. The material is then leached with hydrochloric acid to create magnesium chloride brine, along with a silica and iron residue.

Brine purification: To purify the magnesium chloride solution, the brine goes through further purification steps to remove major impurities such as boron. The impurities are extracted from the brine by precipitation.

Fluid bed drying: High-purity brine is dried to produce granular magnesium chloride. This yields partially dehydrated magnesium chloride ($MgCl_2$). HCl is recycled for use in the leaching phase.

Melt chlorinator: The magnesium chloride granules are melted in an electrolyte and treated by a chlorination process involving the injection of gaseous HCl. The acid and water are recovered in the process for use in the leaching phase.

Electrolytic cell: Metallic magnesium is produced through electrolysis by sending a strong electrical current through the electrolyte. The chlorine gas that is produced during the electrolysis phase is washed and combined with hydrogen and thereby reconverted into acid, which will be reconverted into gas and reused for the chlorination process.

Casting: The metallic magnesium is tapped and then cast in ingots.

Purification of emissions: The production facility is equipped with gas scrubbers throughout the process to purify the process and ventilation emissions. The chlorine is completely captured, recycled and returned to

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[5] In April 2003 this plant was shut down for an indefinite time due to market conditions.

the process. Emissions are washed to extract particles and other contaminants before being released into the atmosphere. The process releases no water effluent to the environment.

3.3 Thermal processing and recovery of magnesium from scrap

Where magnesium is recovered from scrap there will be the potential for formation and release of chemicals listed in Annex C of the Stockholm Convention. A variety of furnace types may be used.

As with other secondary metal processes formation will be enhanced by the presence of incomplete combustion, contaminated feed materials, inadequate process control, inadequate temperature in the furnace and particularly by reactions in the cooling zones (200°–450° C).

Effective process operation and various secondary measures including afterburning as appropriate, rapid gas cooling, effective dust abatement and possibly injection of carbon will reduce releases. Dusts and effluents may contain elevated levels of chemicals listed in Annex C and will need to be properly treated.

4. Primary and secondary measures

4.1 Primary measures

The electrolysis process is of most interest from the point of view of PCDD/PCDF emissions because of the presence of carbon and of chlorine in the process and the high temperature conditions.

Primary measures that may assist in reducing the formation and release of the identified substances include eliminating the carbon source by substituting the graphite by non-graphite anodes, possibly metal anodes. Replacement of graphite anodes by metal anodes took place in the chlorine industry at the start of the 1970s, and very minor amounts of PCDF were formed (Eurochlor 2001).

The new $MgCl_2$ dehydrating process has been found to produce much lower levels of PCDD/PCDF (Tables 1 and 3).

It is expected that in the proposed Cogburn magnesium project in British Columbia the STI/VAMI technology will produce less chlorinated hydrocarbons than produced at Magnola due to the absence of chlorinators. See subsection 5 below for additional information.

4.2 Secondary measures

Measures include:

1. Treatment of effluents using techniques such as nanofiltration and use of specially designed containment for solid residues and effluents;

2. Treatment of off-gases by cleaning of the off-gas from the chlorinators in a series of wet scrubbers and wet electrostatic precipitators before incineration, and using bag filters to clean and remove entrained salts from the magnesium electrolysis process;

3. Use of activated carbon: In the Cogburn magnesium project, there are two chlorinated hydrocarbon removal systems; both are based on activated carbon removal of chlorinated hyrdocarbons in liquid effluents.

5. Emerging research

A Cogburn magnesium project in British Columbia is expected to utilize the STI/VAMI electrolytic cell technology for the decomposition of $MgCl_2$ to magnesium metal and chlorine gas (Figure 6). Presently in the magnesium industry, this is done largely in monopolar diaphragmless electrolytic cells. The STI/VAMI technology is based on a flow-through design in which all the cells in the cell hall are linked together. Each cell is fed individually. The magnesium and electrolyte flow from one cell to the next via a system of enclosed launders. The magnesium is collected at the end of the flow line in a separator cell, and is siphoned out for casting at the cast house. This system is currently utilized at the Dead Sea magnesium plant in Israel (Hatch and Associates 2003).

Figure 6 Simplified flow diagram: Cogburn magnesium plant

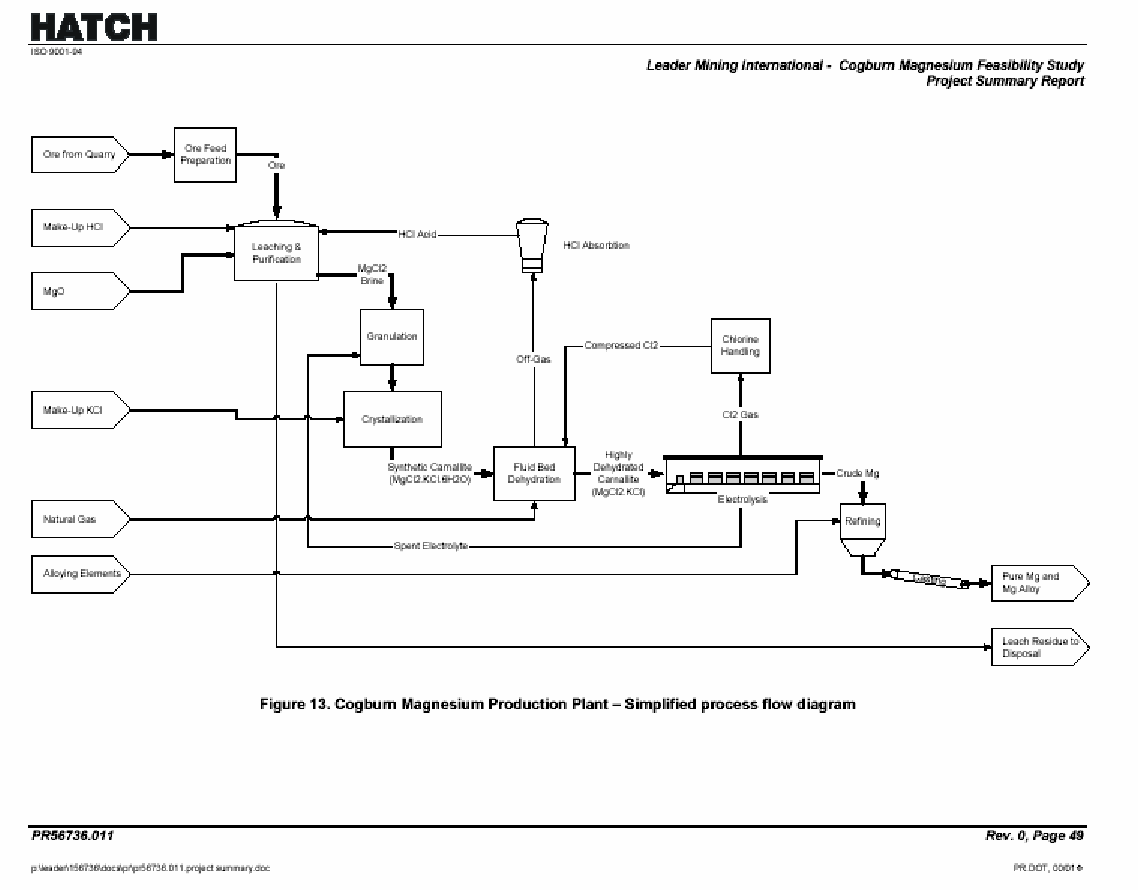

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Figure 13. Cogburn Magnesium Production Plant – Simplified process flow diagram

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Source: Hatch and Associates 2003.

6. Summary of measures

Tables 11 and 12 present a summary of the measures discussed in previous sections.

Table 11. Summary of primary measures for magnesium plants

Measure	Description	Considerations
Alternative processes	Priority consideration should be given to alternative processes with less environmental impacts than traditional magnesium manufacturing processes	Examples include: • Norsk Hydro’s $MgCl_2$ brine dehydration process • Elimination of carbon source: replaces graphite with non-graphite anode
Feed quality	Increasing availability of magnesium scrap and other magnesium-containing	Smelter should ensure that only high-grade scrap, free of contaminants, is used

	raw materials would make it attractive for smelters to use it in their process	
Pretreatment techniques	The calcinations of dolomite creates significant amount of dust	Use of gas suspension calciner could reduce it significantly

Table 12. Summary of secondary measures for magnesium plants

Measure	Description	Considerations
Treatment of off-gases	Off-gases from chlorination furnaces in magnesium plants contain pollutants such as PCDD, PCDF and chlorinated hydrocarbons	Use of wet scrubbers and wet electrostatic precipitators remove aerosols, followed by incineration to destroy PCDD/PCDF and other volatile organic compounds. Activated carbon is also used to absorb pollutants
Treatment of effluent	Wastewater collected from the various parts of the magnesium plant, such as the scrubbing effluent from the chlorination stage, contain PCDD/PCDF and chlorinated hydrocarbons	Removal of solids by flocculation, sedimentation and filtration, followed by activated carbon injection to remove contaminants

7. Performance levels associated with best available techniques for HCB for Magnesium production process

Performance levels as associated with best available techniques for HCB for different Magnesium production processes are not available.

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(iv) Secondary steel production

Summary

Secondary steel is produced through direct smelting of ferrous scrap using electric arc furnaces. The furnace melts and refines a metallic charge of scrap steel to produce carbon, alloy and stainless steels at non-integrated steel mills. Ferrous feed materials may include scrap, such as shredded vehicles and metal turnings, or direct reduced iron. In addition scrap may be added to other melting furnaces in the foundry and primary iron and steel sectors.

Chemicals listed in Annex C of the Stockholm Convention, such as PCDD and PCDF, appear to be most probably formed in the electric arc furnace steel-making process via de novo synthesis by the combustion of non-chlorinated organic matter such as plastics, coal and particulate carbon in the presence of chlorine donors. Many of these substances are contained in trace concentrations in the steel scrap or are process raw materials such as injected carbon.

Primary measures include adequate off-gas handling and appropriate off-gas conditioning to prevent conditions leading to de novo synthesis formation of PCDD/PCDF. This may include post-combustion afterburners, followed by rapid quench of off-gases. Secondary measures include adsorbent injection (for example, activated carbon) and high-level dedusting with fabric filters.

Performance levels associated with best available techniques for secondary steel production is < 0.1 ng/Nm^3 (at operating oxygen concentrations).

1. Process description

1.1 General process description

The direct smelting of iron-containing materials, such as scrap, is usually performed in electric arc furnaces, which play an important and increasing role in modern steelworks. The furnace melts and refines a metallic charge of scrap steel to produce carbon, alloy and stainless steels at non-integrated (secondary steel) mills.

An electric arc furnace is a cylindrical vessel with a dish-shaped refractory hearth and electrodes that lower from the dome-shaped, removable roof. Refractory bricks form the lining of the furnace. The walls typically contain water-cooled panels, which are covered to minimize heat loss. The electrodes may also be equipped with water-cooling systems.

Electric arc furnace steel making consists of scrap charging, melting, refining, deslagging and tapping. In addition to scrap steel, the charge may include pig iron and alloying elements. As the steel scrap is melted, additional scrap may be added to the furnace. The electric arc furnace generates heat by passing an electric current between electrodes through the charge in the furnace. This energy is supplemented by natural gas, oxygen and other fuels.

Other technologies used to smelt iron-containing materials are cupola furnaces (hot and cold), induction furnaces and blast furnaces.

Cupola furnaces are used for the production of cast iron and cast steel. Cupola furnaces are coke-heated vertical furnaces that are charged batch-wise with raw materials, or sometimes charged continuously using vibrating chutes. The necessary heat for smelting of the charged materials is produced by means of coke combustion and air (hot or cold) blown in through tuyeres at the sides of the furnace. The actual smelting zone is found in the lower third of the vertical furnace. With regard to heat utilization the operation is similar to residential coal-fired stoves. The smelting capacity depends mainly on the air volume blown in for combustion, the amount of fuel and the diameter of the furnace (Quass, Fermann and Bröker 2000).

Induction furnaces are simple crucibles or channels that are heated by an external electrical coil. Channel induction furnaces are mainly used for melting items with large dimensions. Current is induced in the metal that has been charged into the furnace and heat is generated. The furnaces may be equipped with fume extraction hoods and dust abatement that can be used during drossing and pouring operations. Access to an induction furnace for charging and tapping means that a movable hooding system is often used. The hoods are robust so that they can withstand some mechanical impact. Alternatively, efficient fixed or lip extraction is used. The efficiency of this furnace can be low for some materials but can be increased, particularly if the feed material is small. Large items can be cut to improve efficiency and also to allow the fume collection hoods to be deployed properly. Some continuous processes also retain a heel of molten metal in the bottom of the furnace between charges if the operation allows it. They may also be operated under vacuum, for example when melting super alloys, high-alloyed steel or pure metals, and in some cases for metal distillation. The temperature of the furnace can be automatically controlled to minimize the production of fume when melting volatile or oxidizable metals such as zinc or alloys containing zinc. These furnaces are also used to hold molten metal for alloying and casting. The current induced in these furnaces causes the metal to be stirred electromagnetically, which promotes mixing of the charge and any alloying materials that are added (European Commission 2001).

A blast furnace is a vertical furnace using tuyeres to blast heated or cold air into the furnace burden to smelt the contents. Sinter is charged into the top of the blast furnace in alternating layers with coke.

1.2 Furnace feedstock

The major feedstock for the furnace is ferrous scrap, which may include ferrous scrap from inside the steelworks (e.g. offcuts), cut-offs from steel product manufacturers (e.g. vehicle builders) and capital or post-consumer scrap (e.g. end-of-life vehicles and appliances) (European Commission 2000). Additional inputs are fluxes and additions like deoxidants or alloying elements. Direct reduced iron is also increasingly being used as a feedstock, due to both its low gangue content and variable scrap prices (European Commission 2000).

Fluxing materials are added to combine with unwanted materials and form a slag. Slag removes the steel impurities (e.g. silicon, sulphur and phosphorus) from the molten steel. Oxygen may be added to the furnace to speed up the steel-making process. At the end of a heat, the furnace tips forward and the molten steel is poured off.

1.3 The electric arc furnace

Many steel plants increase productivity by using the electric arc furnace for the melting phase and a ladle metallurgy facility for the final refining and alloying phase. In some cases the steel ladle is taken to a vacuum degassing station where the gas content of the molten steel is reduced for quality requirements.

The molten steel from the electric arc furnace or the ladle metallurgical facility is cast in a continuous casting machine to produce cast shapes including slabs, billets or beam blanks. In some processes, the cast shape is torch cut to length and transported hot to the hot rolling mill for further processing. Other steel mills have reheat furnaces. Steel billets are allowed to cool, and are then reheated in a furnace prior to rolling the billets into bars or other shapes.

Production of steel from scrap consumes considerably less energy than production of steel from iron ores (EPRI 1997). Electric arc furnace steel manufacturing is an important recycling activity that contributes to the recovery of steel resources and waste minimization.

The use of electric arc furnaces in the production of steel provides three major benefits: lower capital cost for a steel-making shop; significantly less energy required to produce steel compared to the coke oven, blast furnace and basic oxygen furnace methods of the integrated steel makers; and avoidance of coke ovens.

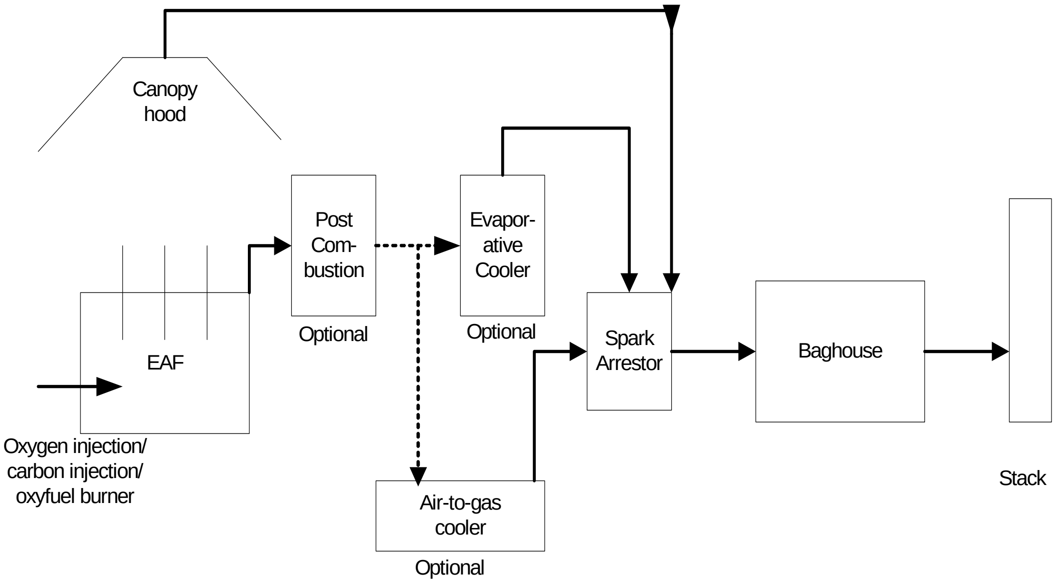
Electric arc furnace steel making is a dynamic batch process with steel tap-to-tap times of one hour or less for a heat, except for stainless and specialty steel producers. The process is constantly changing, from the removal of the furnace roof for charging the steel scrap and the meltdown of the steel scrap (with the resultant emissions from scrap contaminants such as oils and plastics), to the refining period, and finally tapping of the steel. The conditions within the electric arc furnace and the combustion processes vary throughout the heat production cycle.

In recent years, more new and existing electric arc furnaces have been equipped with a system for preheating the scrap in the off-gas in order to recover energy. The so-called shaft technology and the Consteel process are the two proven systems that have been introduced. The shaft system can be designed to reheat 100% of the scrap (European Commission 2000).

Some electric arc furnaces also use a water spray or evaporative cooling system to cool the hot off-gases, and some use heat exchangers ahead of the emission control device. The furnaces may be equipped with dry, semi-wet or wet air pollution controls. Semi-wet and wet gas cleaning systems may be sources of wastewater.

Figure 7 shows the electric arc furnace and a generic fabric filter emission control system.

Figure 7.Generic electric arc furnace emission control system



Source: William Lemmon and Associates Ltd 2004.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

2.1 Emissions

2.1.1 PCDD/PCDF formation

Electric arc furnace steel making is a batch process that can result in fluctuating emissions during heating of the charge and from heat to heat. Gas handling systems vary from facility to facility, both in configuration and design. These factors contribute to a varying concentration in process off-gases.

As a high-temperature metallurgical process, particulate matter that contains a fine fume of metal and metal oxides is generated. High-efficiency pollution control systems are required to remove the fine particulate matter in the off-gases.

Aromatic organohalogen compounds, including polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), chlorobenzenes and polychlorinated biphenyls (PCB), may be formed as a consequence of the thermal process and have been detected in electric arc furnace off-gas. The most important members of this group of compounds are PCDD/PCDF. Scrap preheating may result in higher emissions of aromatic organohalogen compounds.

A report entitled *Research on Technical Pollution Prevention Options for Steel Manufacturing Electric Arc Furnaces* (William Lemmon and Associates Ltd 2004), prepared for the Canadian Council of Ministers of the Environment, takes into account the United Nations Environment Programme (UNEP) document *Formation of PCDD/PCDF: An Overview* (UNEP 2003a), and provides an understanding of the basic formation mechanism of PCDD/PCDF. Information from this report is summarized below.

> The processes by which PCDD/PCDF are formed are not completely understood. Most information about these substances in combustion processes has been obtained from laboratory experiments, pilot-scale systems and municipal waste incinerators.
>
> PCDD/PCDF appear to be most probably formed in the electric arc furnace steel-making process via de novo synthesis by the combustion of non-chlorinated organic matter such as plastics, coal and particulate carbon in the presence of chlorine donors. Many of these substances are contained in trace concentrations in the steel scrap or are process raw materials such as injected carbon. The Ohio Valley Aluminium Company (Ovaco) has commented that it is well known that the emission of PCDD/PCDF is very low when using stainless steel scrap as raw material, a fraction only of that of other electric arc furnaces, and speculates that this is possibly due to catalytic effects of metals present in the dusts (Ovaco 2006 communication).
>
> There is an inherent dualism of formation and dechlorination of PCDD/PCDF which occurs in the same temperature range and especially under the conditions present in the electric arc furnace. In general, dechlorination of PCDD/PCDF appears to take place at temperatures above 750° C in the presence of oxygen. As the temperature increases above 750° C, the rate of dechlorination increases and the required residence time decreases.
>
> Increasing the oxygen concentrations results in increasing formation of PCDD/PCDF. It is not known whether this continues at elevated oxygen concentrations (for example, above 10% O_2). Under pyrolytic conditions (oxygen deficiency) dechlorination of PCDD/PCDF occurs at temperatures above 300° C.
>
> Some metals act as catalysts in the formation of PCDD/PCDF. Copper is a strong catalyst and iron is a weaker one.
>
> Condensation starts in the 125°–60° C range with the higher-chlorinated PCDD and increases very rapidly as the temperature drops. The lower-chlorinated PCDF are the last to condense, which explains

why the tetra and penta PCDF constitute the majority of the PCDF in electric arc furnace emission tests.

Emission test results had higher PCDD/PCDF emission concentrations when the gas temperature exiting the gas conditioning system/gas cooling device was consistently above 225° C, indicating that de novo synthesis had taken place in the gas conditioning system.

PCDF consistently accounted for 60–90% of the PCDD/PCDF concentration in electric arc furnace emission tests.

Two furan congeners, 2,3,7,8-TCDF (tetrachlorodibenzofuran) and 2,3,4,7,8-TCDF, consistently accounted for 60–75% of the PCDD/PCDF I-TEQ concentration in electric arc furnace emission tests. These results are comparable to the theoretical condensation calculations for PCDD/PCDF, as these two congeners would be the last to condense as the gas temperature decreases.

These latter findings indicate that there is a predominant PCDD/PCDF formation mechanism, de novo synthesis, for the electric arc furnace steel-making process. It appears likely that variations in the PCDD/PCDF fingerprint for the process are due to variations in the constituents of the scrap charge, varying conditions in the furnace resulting from changes in operating practices from heat to heat and plant to plant, varying conditions in the gas conditioning and cleaning system, and differences in baghouse collection efficiencies.

Electric induction furnaces require cleaner scrap charges than electric arc furnaces can tolerate, and melt their charge using magnetic fields. While there are some similarities to electric arc furnaces, dioxin and furan generation in such units is expected to be significantly lower than from electric arc furnaces.

With regard to emissions from cupola furnaces employed in cast iron and steel foundries, a German submission to *The European Dioxin Emission Inventory Stage II* (Quass, Fermann and Bröker 2000) summarized the results of a study collecting data on 25 cold blast cupolas located in Germany. Cold blast cupola furnaces (also termed cold air or cold wind cupolas) were identified in UNEP 2003b as having a higher potential than other designs for significant emissions:

“For foundries, there are hardly any data available: testing in Germany (SCEP 1994) showed that hot air cupolas and induction furnaces fitted with fabric filters had low emissions to air, an emission factor of 0.03 μg TEQ/t of product should be used. Cold air cupolas showed higher emissions and a factor of 1 μg TEQ/t is used for plants with fabric filters.

Limited testing on rotary drum furnaces showed higher levels again and a factor of 4.3 μg TEQ/t is applied to plants with fabric filters for gas cleaning. Where cold air cupolas or rotary drum furnaces are used which do not have fabric filters or equivalent for gas cleaning a higher emission factor of 10 μg TEQ/t should be used. If poor quality scrap (high contamination) or poorly controlled furnaces with gas cleaning other than effective fabric filters is found this should be noted.”

The more recent work reported for Quass, Fermann and Bröker 2000 focused on well-controlled cold blast cupolas producing iron for castings, equipped with fabric filters for particulate emission control. This study indicates that the range of the 18 individual emission samples obtained was 0.003 to 0.184 ng I-TEQ/Nm^3, and that the three-run averages for four of the six furnaces tested were below 0.1 ng I-TEQ/Nm^3 (the emission limit value for municipal waste incinerators). It also concluded that “For all furnaces studied the average emission factor was found to amount to 0.35 μg I-TEQ/t of smelted iron in the furnaces with a maximum value reaching 1.45 μg I-TEQ/t.” The conclusions of this chapter of Quass, Fermann and Bröker 2000 were:

“Looking at the concentrations found in the waste gases cold-blast cupola furnaces operated in iron and steel foundries cannot be considered as important sources of dioxins and furans due to their emitted total amounts of PCDD and PCDF. Thus, the results of the measurements agree with a few known data that existed before the investigations were started.

Note however, that the emissions for North Rhine-Westphalia were extrapolated from only 6 furnaces. It cannot be said with certainty that these furnaces are representative for all cold-blast cupola furnaces operated in Germany. Within this project one furnace was found having PCDD and PCDF concentrations in the filter-collected dust of up to approximately 12 µg I-TEQ/kg. This is considerably higher than from those plants where emissions were measured (highest concentration in the filter-collected dust from these plants was 0.4 µg I-TEQ). In addition, a high temporal fluctuation of PCDD and PCDF concentrations in the filter-collected dusts became apparent. Therefore, despite an indication of a positive correlation between the concentrations in the filter-collected dust and the concentrations in the waste gas – obtained from measurement results – it is not allowed to assume that this correlation may be extrapolated on furnaces with higher concentrations in the filter-collected dusts. For clarification, a further study programme would be necessary which, for example, would allow measurements of PCDD and PCDF concentrations in the filter-collected dust of a furnace over a longer period of time.

From the observed interdependence of PCDD and PCDF emissions and the amounts of cast scrap and recycled material applied it can be concluded that the contaminants adhering to the cast scrap (remnants of paint, oils etc.) have an influence on the emissions. In order to reduce dioxin concentrations a decrease of the amount of cast scrap would make sense; however, this would considerably reduce the cost efficiency of foundries. The question arises, whether certain contaminants on the cast scrap play a major role in the development and emission of PCDD and PCDF. If this is so, it would require a selective elimination from the charged input material."

2.1.2 PCDD/PCDF research on electric arc furnaces

Most of the research on PCDD/PCDF formation and control has been carried out for electric arc furnaces in Europe. The earliest reported work was by Badische Stahlwerke GmbH (BSW) in Kehl/Rheim, Germany, in the early 1990s (Weiss and Karcher 1996). Other European steel companies followed BSW's lead under regulatory pressure from national environmental agencies.

A summary of the electric arc furnace operational findings follows:

The BSW research project confirmed that a high concentration of hydrocarbon material in the steel scrap significantly increased the emissions of volatile organic compounds and PCDD/PCDF.

Emission test results from BSW, ProfilARBED, Differdange and Gerdau Ameristeel Cambridge emission-testing programmes had higher PCDD/PCDF emission concentrations when the gas temperature exiting the gas conditioning system or gas cooling device was consistently above 225° C, indicating that de novo synthesis had taken place in the gas conditioning system.

PCDF consistently accounted for 60–90% of the PCDD/PCDF I-TEQ concentration in the Canadian electric arc furnace emission tests. Similar results have been reported in European emission tests of electric arc furnaces.

Two PCDF congeners, 2,3,7,8-TCDF and 2,3,4,7,8-TCDF, consistently accounted for 60–75% of the PCDD/PCDF I-TEQ concentration in the Canadian electric arc furnace emission tests. Similar results have been reported in European emission tests of electric arc furnaces. These results are comparable to the theoretical condensation calculations for PCDD/PCDF, as these two congeners would be the last to condense as the gas temperature decreases.

The congener I-TEQ concentration distributions in the Canadian electric arc furnace emission tests were similar regardless of the total PCDD/PCDF I-TEQ concentrations.

The findings indicate that de novo synthesis is the predominant PCDD/PCDF formation mechanism for the electric arc furnace steel-making process.

It appears likely that variations in the PCDD/PCDF emission fingerprint for the electric arc furnace steel-making process are due to variations in the constituents of the scrap charge, varying conditions in the furnace resulting from changes in operating practices from heat to heat and plant to plant, varying conditions in the gas conditioning and cleaning system, and differences in baghouse collection efficiencies. There is insufficient publicly available information to determine the relative importance of these factors.

A report prepared by the Government of Japan studied the implementation of measures specified in the present guidelines to reduce emissions of PCDD/PCDF and coplanar polychlorinated biphenyls from steel-manufacturing electric are furnaces, targeting 19 factories out of 38 non-integrated steel producers in Japan. The emissions concentration was reduced by between 80% and 87.2% in the factories that implemented a single measure, while reductions of 96% or more were achieved for those implementing two or more measures. The emissions concentration was reduced by 84% on average compared to those not implementing any of the measures. The average concentration was 0.42 ng I-TEQ/Nm^3. Two factories (10% of all targeted factories) attained the achievable performance level value, which is below 0.1 ng I-TEQ/Nm^3 (Government of Japan 2006).

2.1.3 Review of electric arc combustion chemistry and PCDD/PCDF formation

A review of the relationship of electric arc furnace combustion chemistry with PCDD/PCDF formation in the furnace may be summarized as follows:

PCDD/PCDF can be formed from related chlorinated precursors such as polychlorinated biphenyls, chlorinated phenols and chlorinated benzenes.

The environment inside a steel-making electric arc furnace is very complex and is constantly varying. The combustion chemistry produces conditions that are amenable to PCDD/PCDF formation. The hydrocarbons entering the furnace in the scrap may be vaporized, cracked, partially combusted or completely combusted, depending on the conditions in the furnace or parts of the furnace during or after charging. Other sources of carbon include injected carbon and the graphite electrodes. The dual processes of PCDD/PCDF formation and dechlorination may be proceeding at the same time if the oxygen concentration and temperature are such that some PCDD or PCDF congeners are being formed while other congeners are being dechlorinated.

The research on optimization of internal post-combustion indicates that under normal steel-making operations, conditions favourable to PCDD/PCDF formation – oxygen-rich atmosphere, reactive carbon particles and temperatures under 800° C – are present in parts of the furnace during the meltdown phase and possibly for some time afterwards. Given that metals that act as catalysts are present and that trace amounts of chlorine may be present in some of the charge materials and fluxes, the conditions appear to be present for de novo synthesis to occur. Since ideal mixing conditions are not present, it appears that a portion of the PCDD/PCDF that are formed will leave the electric arc furnace in the off-gas without encountering sufficiently high temperatures for dechlorination to take place.

Most of the research on combustion chemistry and internal post-combustion in electric arc furnace steel making has aimed to increase productivity by taking advantage of fuels within the furnace – such as hydrocarbons, carbon monoxide and hydrogen – to replace electric energy with chemical energy, thus reducing the total energy input, which results in lower production costs per ton of product.

Scrap preheating may result in elevated emissions of chlorinated aromatic compounds such as PCDD/PCDF, chlorobenzenes, polychlorinated biphenyls, as well as polycyclic aromatic hydrocarbons, and other products of incomplete combustion from scrap contaminated with paints, plastics, lubricants or other organic compounds. The formation of these pollutants may be minimized by post-combustion within the furnace (as opposed to external post-combustion of the off-gas) by additional oxygen burners developed for burning the carbon monoxide and hydrocarbons, which recovers chemical energy. It has been suggested that scrap preheating increases the organic matter in the flue gas and maybe also the formation of chlorinated compounds. What happens to the emissions depends on total heat energy balance of the flue gas system. In Ovaco's case, scrap preheating decreases the emission of PCDD/PCDF (and most probably increases emission of light organic compounds), due to the fact that scrap preheating acts as an efficient gas cooler; low gas temperature at the filter means that heavy organic compounds are separated with dust.

Indications are that internal post-combustion may be a more attractive option than external post-combustion for PCDD/PCDF formation prevention.

2.2 PCDD/PCDF releases in solid waste and wastewater sources

Most mills worldwide operate electric arc furnaces with dry off-gas cleaning systems (i.e., fabric filter dust collectors), which produce no process wastewater that would require treatment.

Some existing electric arc furnaces may be equipped with semi-wet air pollution control systems (European Commission 2000). Semi-wet systems apply water to the furnace off-gases in order to partially cool and condition the off-gases prior to particulate removal in an electrostatic precipitator. Sites are able to achieve zero wastewater discharge from semi-wet systems by balancing the applied water with water that evaporates in the conditioning process. Non-contact cooling water is the predominant water source; however, some facilities may use treated process water and plant service water (EPA 2002).

Standards of some jurisdictions identify zero discharge as the best available technique for semi-dry gas cleaning systems.

In some European Union countries wet scrubbers are used to clean the off-gases from electric arc furnaces at some mills. However, no information from these facilities is available on wastewater quantities and methods of treatment (European Commission 2000). Consequently, no findings were concluded as to best available techniques for treating and minimizing PCDD/PCDF releases from wastewater from wet air pollution control systems.

Residues in the form of dust collected by the dry air pollution control system for electric arc furnaces have been found to contain significant levels of PCDD/PCDF.

3. Electric arc furnace process improvements and alternative processes for electric steel making

3.1 Process improvements

The electric arc furnace steel-making process has been undergoing change over the past decades. Research and development for electric arc furnace steel making, especially in Europe, is focused on furnace design improvements to increase productivity and energy efficiency, and to reduce steel-making costs.

There are two major driving forces – reduction of steel-making costs as exemplified by increased productivity, and increased product quality as exemplified by quality demands from the automotive industry. Added to these is a third driving force – environmental pressures. Productivity improvements have resulted in shorter tap-to-tap times, increased energy efficiency and increased use of chemical energy.

Quality demands have been met through selection of scrap, furnace operating practices and increased use of ancillary processes such as ladle metallurgy and vacuum degassing. Environmental pressures include the requirements for PCDD/PCDF emission reduction and smog precursor reduction of substances such as fine particulate. One option for these producers is to use higher-quality scrap with lower contaminant levels (William Lemmon and Associates Ltd 2004).

A second option is to replace part of the scrap charge by direct reduced iron or similar products that are produced from iron ore and have contaminant concentrations lower than the lower-quality scrap steel grades. Merchant direct reduced iron production is increasing and the international market is growing, so greater availability may mean that some electric arc furnace steel makers have the option of buying direct reduced iron rather than on-site production. There is very limited available information on PCDD/PCDF emissions from the direct reduced iron process but, given the characteristics of the process, PCDD/PCDF emissions are likely to be very small. Information on the formation and emissions of PCDD/PCDF from the use of direct reduced iron in electric arc furnace steel making is not available.

A third option is the use of hot metal in electric arc furnace steel making. This is forecast to increase as steel makers strive for shorter heat cycles and higher productivity (Fruehan 1998). Information on the impact of this option on PCDD/PCDF emissions is not available. With preheating of part of the scrap about 60 kWh/t can be saved; in the case of preheating the total scrap amount up to 100 kWh/t liquid steel can be saved. The applicability of scrap preheating depends on the local circumstances and has to be proved on a plant-by-plant basis.

Advances in the electric arc furnace steel-making process often have collateral benefits, including the reduction of particulate matter and PCDD/PCDF emissions, except for scrap preheating as noted above. Usually the objective of advanced operating practices is improved operational and energy efficiency to increase productivity and thus increase production and reduce operating costs.

3.2 Alternative processes

No alternative steel-making technology would replace the electric arc furnace for the high production operations of steel plants. While other electrode materials have been used for a few furnaces in the past, there are no alternatives to the graphite electrode at the present time.

4. Primary and secondary measures

Primary and secondary measures for reducing emissions of PCDD/PCDF from electric arc furnaces are outlined in the ensuing section. Much of this material has been drawn from William Lemmon and Associates Ltd 2004. Some of these measures also apply to cupola and electric induction furnaces.

The extent of emission reductions possible with implementation of primary measures only is not readily known. Implementation of both primary and secondary measures at existing and new plants is probably necessary to achieve the desired emission levels. A case study of a steelmaking electric arc furnace facility upgrade of pollution prevention and control systems is provided by Finlay and Peng, 2006.

It should be feasible for plants to implement some or all of the pollution prevention practices identified below.

4.1 Primary measures for emissions

Primary measures, often called pollution prevention techniques, are able to avoid, suppress or minimize the formation of PCDD/PCDF or dechlorinate PCDD/PCDF in the secondary steel-making process.

As a general measure, an integral part of a facility’s pollution prevention programme should include best environmental, operating and maintenance practices for all operations and aspects of the electric arc furnace steel-making process.

The following list presents a range of options as primary measures; some may not be applicable to all furnace designs or plants, and some may require further investigation. This list of techniques has been developed based on work done with electric arc furnaces, and while many of the same principles are expected to hold for electric induction and cupola furnaces, they have not been documented for those applications. However, the fact that most of the existing test results for the other furnace types are below 0.1 ng I-TEQ/Nm^3 indicates that a combination of these measures and the secondary measures listed below should be effective to limit emissions.

4.1.1 Raw material quality

The major raw material used in the secondary steel-making process is iron or steel scrap. Contaminants, including oil, plastics and other hydrocarbons, are often present in the scrap. Pollution prevention practices to prevent or minimize the entry of contaminants into furnaces for iron and steel making include changes in material specifications, improved quality control programmes, changes in the types of raw materials (such as controlling the use of oily scrap or cleaning oily scrap) and programmes to prevent the entry of contaminants.

4.1.2 Furnace operation

Recent changes in electric arc furnace operational practices that have been adopted to improve operational and energy efficiency appear to have collateral benefits to reduce PCDD/PCDF or, in certain conditions, to dechlorinate PCDD/PCDF. Pollution prevention practices that appear to reduce PCDD/PCDF emissions include minimizing the duration of the roof being open for charging, reduction of air infiltration into the furnace and avoiding or minimizing operational delays. Condensation of PCDD/PCDF increases rapidly at temperatures below 125° C, starting with the higher-chlorinated dioxins.

4.1.3 Off-gas conditioning system design

Off-gas conditioning includes the collection, cooling and ducting of furnace off-gases prior to cleaning in a baghouse. Off-gas conditioning system conditions may be conducive to de novo synthesis formation of PCDD/PCDF unless care is taken to avoid conditions leading to de novo synthesis. Pollution prevention techniques include an adequately sized system, maximization of off-gas mixing, rapid cooling of off-gas to below 200° C and development and implementation of good operating and maintenance practices.

4.1.4 Continuous parameter monitoring system

A continuous parameter monitoring system based on optimizing the appropriate parameters for the operation of the gas conditioning system and documented operating and maintenance procedures should minimize the formation of PCDD/PCDF by de novo synthesis in the gas conditioning system.

4.2 Secondary measures for emissions

Secondary measures, often called pollution control techniques, may be summarized as follows:

4.2.1 Off-gas dust collection

Capturing all of the off-gas, including fugitive emissions, from the electric arc furnace area is an important part of the control system. Dust collection efficiency of primary and secondary emissions from the furnace should be maximized by a combination off-gas and hood system, or doghouse and hood system, or building air evacuation.

4.2.2 Fabric filter dust collectors (or baghouses)

Some of the PCDD/PCDF in the electric arc furnace off-gases adsorb onto fine particulate matter. As the gas temperature decreases through the PCDD/PCDF condensation temperature of the various congeners, more of the PCDD/PCDF either adsorb onto the fine particulate matter or condense and form fine particulate matter. Well designed and operated fabric filters achieve less than 5 mg dust/Nm^3. Minimizing dust levels also minimizes PCDD/PCDF emissions.

4.2.3 External post-combustion system coupled with a rapid water quench

This technique was the early PCDD/PCDF emission control technique applied to electric arc furnace steel making. External post-combustion systems were originally developed to combust carbon monoxide (CO) and hydrogen (H_2) in the furnace off-gas in a refractory lined combustion chamber, usually with supplementary fuel. Subsequently a number of European electric arc furnace steel-making plants adopted the external post-combustion technology to dechlorinate PCDD/PCDF emissions by maintaining the post-combustion temperature above 800° C. This emission control technique is not able to consistently meet the Canada-wide standard of 100 pg I-TEQ/Nm^3 (0.1 ng I-TEQ/Nm^3). It may not be feasible for some plants to install external post-combustion and improvements to gas conditioning systems due to site-specific space considerations. For some furnaces, internal post combustion within the furnace may be effective in helping prevent PCDD/PCDF emissions.

4.2.4 Adsorbent injection

This control technique was originally developed to control PCDD/PCDF emissions from waste incinerators. Sized lignite coke (activated carbon is a similar adsorbent) injection technology is used in a number of European electric arc furnace steel-making plants to supplement the fabric filter baghouse technology to achieve low PCDD/PCDF emission concentrations consistently. This technique also reduces emissions of mercury. Reported emission test results from electric arc furnace steel-making plants in Europe indicate that this technique, in combination with a high-efficiency fabric filter baghouse, consistently achieves PCDD/PCDF emission concentrations of less than 0.1 ng I-TEQ/Nm^3 [6]. However other techniques may also be effective in reducing emissions to these levels.

The sized lignite coke is injected into the off-gas upstream of the baghouse. The coke (or activated carbon) adsorbs the PCDD/PCDF in the off-gas. Good mixing of the coke with the off-gas, and appropriate sizing of the coke (to a size similar to particles in the gas stream), are essential for optimum PCDD/PCDF removal.

Sized lignite coke production and activated carbon do not release captured PCDD/PCDF at normal product storage and landfill temperatures, and are resistant to leaching. Use of sized lignite coke as an adsorbent increases baghouse dust volume by 2%.

Activated carbon or sized coke injection systems should be considered for use at steel plants to reduce emissions of PCDD/PCDF. Site-specific considerations, such as lack of available space, configuration of existing emission control systems and cost impacts may influence the feasibility of using this technique.

4.3 Primary and secondary measures for solid wastes and wastewater

The measures in this section generally apply for electric arc, electric induction and cupola furnaces. With respect to solid wastes, electric furnace slag and filter dusts from any furnace should be recycled to the maximum extent possible. Filter dust from high-alloy steel production, where possible, may be treated to recover valuable metals. Excess solid waste should be disposed of in an environmentally sound manner.

Ovaco has commented that the landfilling of electric arc furnace dust is no longer allowed in most industrial countries. The standard method is recovery of valuable metals in a separate treatment process or processes outside the steelworks. If stainless steel scrap is used as raw material, chromium, nickel, zinc and lead are recovered, otherwise (for the main part of dust) zinc and lead are separated only. The measured dioxin content of Ovaco's dust is around 1,300 pg I-TEQ/g and it represents 96% of the total amount synthesized in their process. Consequently electric arc furnace dust may be a significant reservoir of PCDD/PCDF and should be managed appropriately as a waste with respect to containments and disposal.

With respect to wastewater, closed-loop water-cooling systems for electric furnace components avoid

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[6] 1 ng (nanogram) = 1 x 10^{-12} kilogram (1 x 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0^0C and 101.3kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.

wastewater being generated, or ensure it is recycled to the maximum extent possible to minimize waste volume for treatment.

Semi-dry emission control systems may be used at some plants. While replacement with dry dust collectors would be the desirable option, semi-dry systems can be designed to avoid the generation of wastewater.

Wastewater may originate at facilities that use wet scrubbing systems. The desired approach is the replacement of existing systems with dry dust collectors. If replacement of existing emission control systems is not feasible, the wastewater would need treatment. However, standards for treated wastewater quality concerning PCDD/PCDF discharge levels or other parameters were not found.

5. Summary of measures

Tables 13 and 14 present a summary of the measures discussed in previous sections.

Table 13. Measures for new electric arc furnaces

Measure	**Description**	**Considerations**	**Other comments**
Process design	Priority consideration should be given to the latest proven process designs based on process and emissions performance	An example is internal post-combustion design for a new electric arc furnace	
Performance requirements	Arc furnaces should be required by the applicable jurisdiction to achieve stringent performance and reporting levels	Consideration should be given to the primary and secondary measures listed in Table 2, in particular appropriate sizing of ventilation systems and use and appropriate maintenance of high efficiency fabric filters.	Achievable emission limits expected are: < 0.1 ng I-TEQ/Nm^3 for PCDD/PCDF

Table 14. Measures for new and existing electric arc furnaces

Measure	**Description**	**Considerations**	**Other comments**
Primary measures			
General operating practices	An integral part of a facility's pollution prevention programme should include best environmental, operating and maintenance practices for all operations and aspects of the electric arc furnace steel-making process	Generally applicable; part of an integrated concept for pollution prevention	
Raw material quality	A review of feed materials and identification of alternative inputs and/or procedures to minimize unwanted inputs should be conducted. Documented procedures should be developed and implemented to carry out the appropriate changes	Generally applicable. Measures include changes in material specifications, improved quality control programmes, changes in the types of raw materials (such as	

		controlling the use of oily scrap) and programmes to prevent the entry of contaminants	
Electric arc furnace operation	Minimizing the duration of the roof being open for charging, reduction of air infiltration into the furnace, and avoiding or minimizing operational delays	Collateral benefit is reduced PCDD/PCDF	Other pollutants are reduced, including aromatic organohalogen compounds, carbon monoxide, hydrocarbons and greenhouse gases
Off-gas conditioning	Design and installation of an adequately sized gas conditioning system based on optimum system parameters should prevent or minimize formation of PCDD/PCDF in the gas conditioning system. Development and implementation of documented operating and maintenance procedures should be developed to assist in optimizing the operation of the gas conditioning system	A reduction in de novo synthesis in the gas conditioning system has been linked to the rapid cooling of the furnace off-gases to below a range of 225° to 200° C	
Continuous parameter monitoring	A continuous parameter monitoring system such as Conitnuous Opacity Monitors (COMs) or Bag Leak Detection (BLD) systems should be employed to ensure optimum operation. Operators should prepare a site-specific monitoring plan for the continuous parameter monitoring system and keep records that document conformance with the plan	Correlations between parameter values and stack emissions (stable operation) should be established. Parameters are then continuously monitored in comparison to optimum values	System can be alarmed and corrective action taken when significant deviations occur
Secondary measures The following secondary measures can effectively reduce releases of PCDD/PCDF and serve as examples of best available techniques			
Off-gas collection	Dust collection efficiency of primary and secondary emissions from the electric arc furnace should be maximized by a combination off-gas and hood system, or doghouse and hood system, or building air evacuation	Ventilation systems in the EAF melt shop should be appropriately sized to ensure capture of process emissions within the building and conveyance to the air pollution control system.	98% efficiency or more of dust collection is achievable
Fabric filters	Well-designed fabric filters achieve low dust emissions. Procedures should be developed for the operation and maintenance of the fabric filter dust collector to optimize and improve collection performance,	There is are correlations between PCDD/PCDF emissions and dust emissions. At various flue gas temperatures, PCDD/PCDF will be	Maintaining the off-gases in the baghouse to below 60° C will reduce PCDD/PCDF evaporation and

	including optimization of fabric bag cleaning cycles, improved fabric bag material and preventive maintenance practices. A continuous temperature monitoring and alarm system should be provided to monitor the off-gas inlet temperature to the emission control device. A bag leak detection system should be provided with documented operating and maintenance procedures for responding to monitoring system alarms	absorbed and adsorbed on the dust captured in the fabric filter. Modern baghouses that are appropriately sized, operated, maintained and monitored are capable of dust emissions < 5 mg/Nm3.	increase capture of PCDD/PCDF associated with the dust. The collected dust should be appropriately managed, considering the pollutants contained in the dust. Enclosing the filter dust collection areas and transfer points minimizes fugitive dust The use of appropriately sized and operated ventilation systems will reduce facility workers to occupational exposure of pollutants.
Post-combustion of off-gas	PCDD/PCDF formation may be minimized by post-combustion within the off-gas duct system or in a separate post-combustion chamber. Indications are that internal post-combustion may be a more attractive option than external post-combustion for PCDD/PCDF formation prevention		PCDD/PCDF that have been formed in the process undergo dechlorination reactions as the off-gas is burnt by the additional oxygen burners. This technique with a rapid water quench has been an early PCDD/PCDF emission control technique applied to electric arc furnace steel making
Adsorbent injection	Injection of activated carbon or similar adsorptive material into the off-gas upstream of high-efficiency fabric filters in electric arc furnaces at European steel-making plants has consistently achieved low levels of PCDD/PCDF emissions, according to data from demonstration projects		
Minimize solid waste generation	Electric arc furnace slag and filter dust should be recycled to the extent possible. Filter dust from high-alloy steel production, where possible, may be		

	treated to recover valuable metals. Best management practices should be developed and implemented for hauling and handling dust-generating solid wastes. Excess solid waste should be disposed of in an environmentally sound manner		
Minimize wastewater	Closed-loop water-cooling systems for electric arc furnace components avoid wastewater being generated. Recycle wastewater to the maximum extent possible. Residual wastewater should be treated. Semi-dry air pollution control systems can be designed to have zero discharge of excess wastewater. Wastewater from wet gas cleaning systems should be treated before discharging to the environment	These measures would be primarily associated with general pollution prevention and control practices rather than being applied specifically, or only, for the purpose of PCDD/PCDF	No standards were found on PCDD/PCDF limits for treated wastewater discharged as final effluent from wet off-gas cleaning systems

6. Performance level associated with best available techniques

A performance level associated with best available techniques for emissions of PCDD/PCDF from secondary steel-making plants and iron and steel foundries is < 0.1 ng I-TEQ/Nm^3. (at operating oxygen concentrations)

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(v) Primary base metals smelting

Summary

Primary base metals smelting involves the extraction and refining of nickel, lead, copper, zinc and cobalt. Generally, primary base metals smelting facilities process ore concentrates. Most primary smelters have the technical capability to supplement primary concentrate feed with secondary materials (e.g. recyclables).

Production techniques may include pyrometallurgical or hydrometallurgical processes. Chemicals listed in Annex C of the Stockholm Convention are thought to originate through high-temperature thermal metallurgical processes; hydrometallurgical processes are therefore not considered in this section on best available techniques for primary base metals smelting.

Available information on emissions of PCDD and PCDF from a variety of source sectors (e.g. incinerators, steel electric arc furnaces, iron sintering plants) suggests that process technologies and techniques, and associated off-gas conditioning, can influence the formation and subsequent release of PCDD/PCDF. Consideration should be given to hydrometallurgical processes, where technically and economically feasible, as alternatives to pyrometallurgical processes when considering proposals for the construction and commissioning of new base metals smelting facilities or processes.

Primary measures include the use of hydrometallurgical processes, quality control of feed materials and scrap to minimize contaminants leading to PCDD/PCDF formation, effective process control to avoid conditions leading to PCDD/PCDF formation, and use of flash smelting technology. Identified secondary measures include high-efficiency gas cleaning and conversion of sulphur dioxide to sulphuric acid, effective fume and gas collection and high-efficiency dust removal.

A performance level associated with best available techniques for base metals smelters is < 0.1 ng I-TEQ/Nm^3 (at operating oxygen concentrations)

1. Process description

The technical processes involved in the extraction and refining of base metals (nickel, lead, copper, zinc and cobalt) generally proceed as shown in Figure 7. Key metal recovery technologies that are used to produce refined metals can be categorized as follows:

1. Pyrometallurgical technologies use heat to separate desired metals from unwanted materials. These processes exploit the differences between constituent oxidation potential, melting point, vapour pressure, density and miscibility when melted;

2. Hydrometallurgical technologies use differences between constituent's solubility and electrochemical properties while in aqueous acid solutions to separate desired metals from unwanted materials;

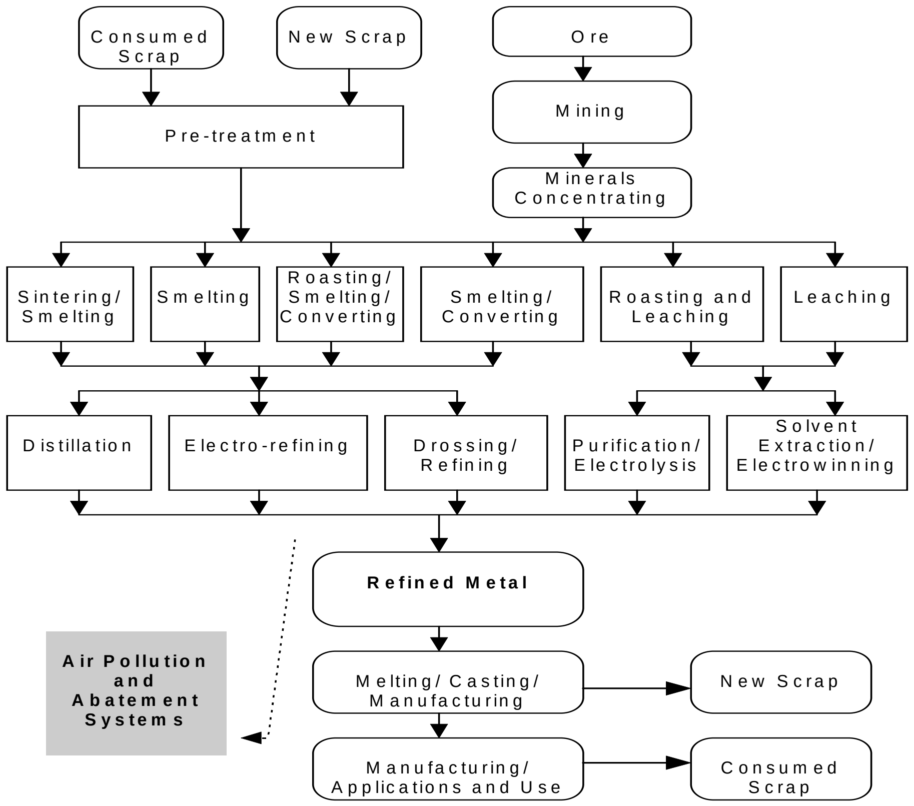
3. Vapometallurgical technologies apply to the Inco carbonyl process whereby nickel alloys are treated with carbon monoxide gas to form nickel carbonyl.

Generally, primary base metals smelting facilities process ore concentrates. Most primary smelters have the technical capability to supplement primary concentrate feed with secondary materials (e.g. recyclables).

Figure 8 provides a generic flow sheet showing the main production processes associated with primary smelting and refining.

Chemicals listed in Annex C of the Stockholm Convention are thought to originate through high-temperature thermal metallurgical processes; hydrometallurgical processes are therefore not considered in this section on best available techniques for primary base metals smelting.

Figure 8. Generic flow sheet for primary base metals smelting



Artisanal and small enterprise metal recovery activities are sometimes used in developing countries and countries with economies in transition. These artisanal processes may be significant sources of pollution and of adverse human health impacts. Metals that are known to be produced by artisanal and small enterprise metal recovery activities include aluminium, antimony, copper, gold, iron, lead, manganese, mercury, tin, tungsten, silver and zinc. These activities usually do not have any pollution controls and may be sources of chemicals listed in Annex C.

While artisanal metal recovery activities are not considered best available techniques or best environmental practices, it is recommended that, as a minimum, appropriate ventilation and material handling should be carried out to minimize human exposure to pollutants from these activities.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

Primary base metals smelters can be sources of chemicals listed in Annex C. The formation and release of such chemicals from primary smelters are not well understood, and it has been shown that emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) can range significantly between operations using similar processes.

2.1 Releases to air

2.1.1 General information on emissions from base metals smelting

"The main environmental issues for the production of most non-ferrous metals from primary raw materials are the potential emission to air of dust and metals/metal compounds and of sulphur dioxide if roasting and smelting sulphide concentrates or using sulphur containing fuels or other materials. The capture of sulphur and its conversion or removal is therefore an important factor in the production of non-ferrous metals. The pyrometallurgical processes are potential sources of dust, fugitive fumes and metals from furnaces, reactors and from the launders and ladles during the transfer of molten metal" (European Commission 2001).

2.1.2 Emissions of PCDD and PCDF

"There is limited published information on dioxin/furan mechanisms of formation for the base metals smelting sector, most of which is based on European experience for secondary base metal smelters. There are a few general statements that dioxins and furans might be present in some of the raw materials for secondary base metals smelting and that oils and organic materials are present in many of these raw materials. The presence of oils and other organic materials in scrap or other sources of carbon (partially burnt fuels and reductants such as coke) can produce fine carbon particles or gaseous precursors which react with inorganic chlorides or organically bound chlorine in the temperature range of 250° to 500° C to produce dioxins and furans. This process is known as de novo synthesis which is dependent on catalysts such as copper and iron. Although dioxins and furans are destroyed at high temperature (above 850° C) in the presence of oxygen, the process of de novo synthesis is still possible as the gases are cooled" (Charles E. Napier Co. Ltd 2002).

Available information on emissions of PCDD and PCDF from a variety of source sectors (e.g. incinerators, steel electric arc furnaces, iron sintering plants) suggests that process technologies and techniques, and associated off-gas conditioning, can influence the formation and subsequent release of PCDD/PCDF.

Canadian base metals smelting and refining facilities undertook emissions testing for PCDD and PCDF, and results from their work showed that concentration levels varied with the type of off-gas conditioning system.

Smelting facilities in Canada generally process sulphide concentrates and, at some facilities, also process some secondary materials. Off-gas conditioning varies from extensive cleaning (e.g. high-efficiency dedusting) and conversion to sulphuric acid, to dedusting by fabric filters, to dedusting by electrostatic precipitator. These facilities produce nickel, copper, lead, zinc and co-product metals. There were 11 participating facilities in the Canadian test programme, conducting approximately 20 emission tests on 16 different sources. No two facilities had the same combination and configuration of production processes and off-gas conditioning systems, further complicating any possible analysis. As such, the observations noted below are general in nature.

Where off-gases were cleaned (i.e., dedusted, scrubbed) and processed through an acid plant for conversion of off-gases rich in sulphur dioxide (SO_2) to sulphuric acid, emission test results showed concentrations below 5 pg (0.005 ng) I-TEQ/m^3.[7]

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[7] 1 pg (picogram) = 1 x 10^{-15} kilogram (1 x 10^{-12} gram); 1ng (nanogram) = 1 x 10^{-12} (1 x 10^{-9} gram), for information on toxicity measurement see section I.C, subsection 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources.

Where off-gases were dedusted by baghouse, concentration levels typically ranged from a few pg I-TEQ/m^3 to < 30 pg I-TEQ/m^3.

Where off-gases were dedusted by electrostatic precipitator, concentration levels ranged from approximately 30 pg I-TEQ/m^3 to approximately 500 pg I-TEQ/m^3.

2.2 Releases to other media

No information was found on releases of chemicals listed in Annex C from primary base metals smelters to media other than air. However, they are likely to be present in some liquid effluents from wet scrubbers and in some dusts and scrubber residues collected in air pollution abatement systems.

3. Alternative processes for base metals smelting

In accordance with the Stockholm Convention, when consideration is being given to proposals for construction of a new base metals smelting facility, priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of the identified substances.

As indicated in Figure 7, there is a wide range of processes used in the primary production of base metals smelting. The processes used to produce crude or refined base metals from primary sources will depend to a large extent on the available ore or concentrate (e.g. laterite ore or sulphide ore), and other considerations (e.g. properties of the desired metal(s), properties of the feed materials, available fuel and energy sources, capacity and economic considerations).

The formation and release of chemicals listed in Annex C is considered to be a result of high-temperature thermal metallurgical operations. Consideration should be given to hydrometallurgical processes (e.g. leaching, electrowinning), where technically feasible, as alternatives to pyrometallurgical processes (e.g. roasting, smelting, converting, fire refining) when considering proposals for the construction and commissioning of new base metals smelting facilities or processes.

4. Primary and secondary measures

There is a paucity of information on the release of chemicals listed in Annex C from primary base metals smelting operations. No techniques were identified specifically for the primary base metals smelting sector to prevent or control the unintentional formation and release of PCDD/PCDF and other chemicals listed in Annex C. The following measures constitute general measures that may result in lower pollutant emissions at primary base metals smelters, including releases of PCDD/PCDF.

The extent of emission reduction possible with implementation of primary measures only is not readily known. It is therefore recommended that consideration be given to implementation of both primary and secondary measures.

4.1 Primary measures

Primary measures are regarded as pollution prevention measures that will prevent or minimize the formation and release of the identified substances, namely PCDD, PCDF, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB). These are sometimes referred to as process optimization or integration measures. Pollution prevention is defined as “the use of processes, practices, materials, products or energy that avoid or minimize the creation of pollutants and waste, and reduce overall risk to human health or the environment” (See section III.B of the present guidelines).

Primary measures that may assist in reducing the formation and release of pollutant emissions include:

4.1.1 Use of hydrometallurgical processes

Use of hydrometallurgical processes rather than pyrometallurgical processes where possible is a significant means of preventing emissions. Closed-loop electrolysis plants will contribute to prevention of pollution.

4.1.2 Quality control of (scrap) feed material

The presence of oils, plastics and chlorine compounds in scrap feed materials should be avoided to reduce the generation of PCDD/PCDF during incomplete combustion or by de novo synthesis. Feed material should be classified according to composition and possible contaminants. Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for PCDD/PCDF formation. Storage, handling and pretreatment techniques will be determined by feed size distribution and contamination.

Methods to be considered are (European Commission 2001, p. 232):

1 Sufficient blending of material to provide a homogeneous feed in order to promote steady-state conditions

2 Oil removal from feed (e.g. thermal decoating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas);

3 Use of milling and grinding techniques with good dust extraction and abatement. The resulting particles can be treated to recover valuable metals using density or pneumatic separation;

4 Elimination of plastic by stripping cable insulation (e.g. possible cryogenic techniques to make plastics friable and easily separable).

4.1.3 Effective process control

Process control systems should be utilized to maintain process stability and ensure operation at parameter levels that will contribute to the minimization of PCDD/PCDF generation, such as maintaining furnace temperature above 850° C to destroy PCDD/PCDF. Ideally, PCDD/PCDF emissions would be monitored continuously to ensure reduced releases. Continuous emissions sampling of PCDD/PCDF has been demonstrated for some sectors (e.g. waste incineration), but research is still developing in this field. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF.

4.1.4 Use of flash smelting technology

The most effective pollution prevention option is to choose a process that entails lower energy usage and lower emissions. Where pyrometallurgical techniques are used, use of flash smelting technology rather than older technologies (e.g. roasters, blast furnace) is a significant means of reducing energy use and reducing emissions. Flash smelting will also result in high concentration of sulphur dioxide in the off-gas stream, which would permit the efficient fixation or recovery of sulphur dioxide prior to off-gas venting.

4.1.5 Maximization of SO_2 content for sulphur fixation

A general measure involves operation of processes in a manner that maximizes the concentration of the SO_2 in the off-gas (when processing sulphide ores or concentrates). It is important, therefore, that a process be selected that uses oxygen-enriched air (or pure oxygen) to raise the SO_2 content of the process gas stream and reduce the total volume of the stream, thus permitting efficient fixation of SO_2.

4.2 Secondary measures

Secondary measures are understood to be pollution control technologies or techniques, sometimes described as end-of-pipe treatments.

Secondary measures that may assist in reducing the formation and release of pollutant emissions include:

4.2.1 High-efficiency gas cleaning and conversion of SO_2 to sulphuric acid

For SO_2-rich off-gases (typically 5% or greater) generated by pyrometallurgical processing of sulphide ores or concentrates, high-efficiency precleaning of off-gases followed by conversion of SO_2 to sulphuric acid are together considered best available techniques for this type of source. Emission concentrations of PCDD/PCDF with use of this combination of techniques are < 0.005 ng I-TEQ/m^3.

For conversion to sulphuric acid, a double-contact, double-absorption process is considered a best available technique. A double-contact, double-absorption plant should emit no more than 0.2 kg of SO_2 per ton of sulphuric acid produced (based on a conversion efficiency of 99.7%) (World Bank 1998).

SO_2-rich off-gases from smelting facilities pass through a gas-cleaning train, which typically includes high-efficiency dedusting, prior to the sulphuric acid plant.

This combination of techniques has the co-benefit of controlling dust and SO_2 emissions, in addition to PCDD/PCDF.

Other techniques for sulphur fixation, which may require precleaning of off-gases prior to conversion or recovery, may potentially contribute to the minimization of PCDD/PCDF emissions (World Bank 1998). These techniques include:

1 Recovery as liquid sulphur dioxide (absorption of clean, dry off-gas in water or chemical absorption by ammonium bisulphite or dimethyl aniline);

2 Recovery as elemental sulphur, using reductants such as hydrocarbons, carbon or hydrogen sulphide. Normally the sulphur content in the gas is still higher than acceptable when using this technique. The reduction conditions are also favourable for dioxins formation. Thus, after the recovery, the gas should be post-combusted and cleaned using techniques such as scrubbing.

4.2.2 Fume and gas collection

Air emissions should be controlled at all stages of the process, including material handling, smelting and material transfer points, to control the emission of PCDD/PCDF. Sealed furnaces are essential to contain fugitive emissions while permitting heat recovery and collecting off-gases for process recycling. Proper design of hooding and ductwork is essential to trap fumes. Furnace or reactor enclosures may be necessary. If primary extraction and enclosure of fumes is not possible, the furnace should be enclosed so that ventilation air can be extracted, treated and discharged. Roofline collection of fume should be avoided due to high energy requirements. The use of intelligent damper controls can improve fume capture and reduce fan sizes and hence costs. Sealed charging cars or skips used with a reverberatory furnace can significantly reduce fugitive emissions to air by containing emissions during charging (European Commission 2001, p. 187–188).

The use of reverberatory furnaces is steadily decreasing because of the difficulty of controlling emissions and the high costs involved. It is difficult to imagine that further reverberatory furnaces will be built.

(Personal Communication, February 2006)

4.2.3 High-efficiency dust removal

The smelting process generates high volumes of particulate matter with large surface area on which PCDD/PCDF can adsorb. These dusts and metal compounds should be removed to reduce PCDD/PCDF emissions. Very high-efficiency dust removal techniques should be employed, for example ceramic filters, high-efficiency fabric filters or the gas cleaning train prior to a sulphuric acid plant.

Preference should be given to fabric filters over wet scrubbers, wet electrostatic precipitators or hot electrostatic precipitators for dust control. Dust from dust control equipment should be returned to the process. Returned or collected dust should be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals, preferably by recycling the dust back into the smelting process. Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner.

Fabric filter operations should be constantly monitored by devices to detect bag failure.

5. Emerging research

Selective catalytic reduction has been used for controlling emissions of nitrogen oxides (NO_x) from a number of industrial processes. Modified selective catalytic reduction technology (i.e., increased reactive area) and select catalytic processes have been shown to decompose PCDD and PCDF contained in off-gases, probably through catalytic oxidation reactions. This may be considered as an evolving technique with potential for effectively reducing emissions of persistent organic pollutants from base metals smelting operations and other applications. However, catalytic oxidation can, subject to catalyst selection, be subject to poisoning from trace metals and other exhaust gas contaminants. Validation work would be necessary before use of this process.

6. Summary of measures

Tables 15 and 16 present a summary of the measures discussed in previous sections.

Table 15. Measures for new primary base metals smelting operations

Measure	**Description**	**Considerations**	**Other comments**
Alternative processes	Priority consideration should be given to alternative processes with potentially less environmental impacts than pyrometallurgical base metals smelting	Hydrometallurgical processes are a significant means of preventing emissions. It has been commented that direct atmospheric leaching of sulphide concentrations (Fex to Zn concentrates) should be considered. (Finnish representative, 2006) Closed-loop electrolysis plants will contribute to prevention of pollution	
Performance requirements	New primary base metals smelting operations should be permitted to achieve stringent performance and reporting levels associated with best available	Consideration should be given to the primary and secondary measures listed in Table 2	Performance requirements for achievement should take into consideration achievable emission levels of PCDD/PCDF identified in subsection 7 below

	techniques		

Table 16. Summary of primary and secondary measures for primary base metals smelting operations

Measure	**Description**	**Considerations**	**Other comments**
Primary measures			
Use of hydrometallurgical processes	Use of hydrometallurgical processes rather than pyrometallurgical processes where possible, as a significant means of preventing emissions. Closed-loop electrolysis plants will contribute to prevention of pollution	Use of hydrometallurgical processes will depend in large part on the ore and concentrate to be processed (e.g. laterite or sulphide). The combination of hydrometallurgy and pyrometallurgy, emerging for metals such at nickel and copper, may offer potential for zinc smelting (Finnish representative, 2006)	
Quality control of (scrap) feed material	Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential for PCDD/PCDF formation	Methods to be considered are: Oil removal from feed (e.g. thermal decoating and de-oiling processes followed by afterburning to destroy any organic material in the off-gas) Use of milling and grinding techniques with good dust extraction and abatement. The resulting particles can be treated to recover valuable metals using density or pneumatic separation Elimination of plastic by stripping cable insulation (e.g. possible cryogenic techniques to make plastics friable and easily separable) Sufficient blending of material to provide a homogeneous feed in order to promote steady-state conditions is possibly the first priority (Finnish representative, 2006)	
Effective process control	Process control systems should be utilized to maintain process	For example, furnace temperatures should be	

	stability and operate at parameter levels that will contribute to the minimization of PCDD/PCDF generation. In the absence of continuous PCDD/PCDF monitoring, other variables such as temperature, residence time, gas components and fume collection damper controls should be continuously monitored and maintained to establish optimum operating conditions for the reduction of PCDD/PCDF	maintained above 850° C to destroy PCDD/PCDF	
Use flash smelting technology	Where pyrometallurgical techniques are used, use of flash smelting technology rather than older technologies (e.g. roasters, blast furnace) is a significant means of reducing energy use and reducing emissions	Flash smelting will also result in high concentration of SO_2 in the off-gas stream, which would permit the efficient fixation or recovery of SO_2 prior to off-gas venting	
Maximize SO_2 content for sulphur fixation	This general measure involves operation of processes in a manner that maximizes the concentration of the SO_2 in the off-gas (where processing sulphide ores or concentrates), to enable recovery or fixation of the sulphur. Preference should be given to processes that use oxygen-enriched air (or pure oxygen) to raise the SO_2 content of the process gas stream and reduce the total volume of the stream		
Secondary measures The following secondary measures can effectively reduce emissions of PCDD/PCDF and should be considered as examples of best available techniques			
High-efficiency gas cleaning and conversion of SO_2 to sulphuric acid	SO_2-rich off-gases, high-efficiency precleaning of off-gases followed by conversion of SO_2 to sulphuric acid should be employed, and are together considered best available techniques	This combination of techniques has the co-benefit of controlling dust and SO_2 emissions, in addition to PCDD/PCDF	Emission concentrations of PCDD/PCDF with use of high-efficiency gas cleaning and conversion of SO_2 to sulphuric acid are < 0.005 ng I-TEQ/m^3
Fume and gas collection	Air emissions should be controlled at all stages of the process, including material handling, smelting and material transfer points, to control the emission of PCDD/PCDF		

High-efficiency dust removal	Dusts and metal compounds should be removed to reduce PCDD/PCDF emissions. Very high-efficiency dust removal techniques should be employed, e.g. ceramic filters, high-efficiency fabric filters or the gas-cleaning train prior to a sulphuric acid plant. Dust from dust control equipment should be returned to the process. Returned/collected dust should be treated in high-temperature furnaces to destroy PCDD/PCDF and recover metals. Fabric filter operations should be constantly monitored by devices to detect bag failure	Preference should be given to fabric filters over wet scrubbers, wet electrostatic precipitators, or hot electrostatic precipitators for dust control. Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner	

7. Performance level associated with best available techniques

A performance level associated with best available techniques for base metals smelters is <0.1 ng I-TEQ/m3 (at operating oxygen concentrations).[8]

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[8] 1 ng (nanogram) = 1 x 10^{-12} kilogram (1 x 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0^0C and 101.3kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines. The operating oxygen concentration conditions of exhaust gases are used for metallurgical sources

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Part III Source category (c): Residential combustion sources

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VI.C Residential combustion sources

Summary

This section considers the combustion of wood, coal, gas, as well as other organic matter mainly for residential heating and cooking. Combustion takes place in hand-fired stoves or fireplaces or, in the case of larger central heating systems, in automatically fired installations. Studies have shown that significant levels of chemicals listed in Annex C of the Stockholm Convention are released from residential combustion sources. The amount of chemicals released depends primarily on the fuel used (household waste, sea-salt laden driftwood and treated wood are significant sources of PCDD/F) as well as combustion efficiency. The efficiency of combustion depends upon the combustion temperature, how well the gases are mixed, residence time, sufficient oxygen and the fuel properties. Given their large numbers, residential combustion appliances contribute noticeably to overall releases of chemicals listed in Annex C.

The use of efficient combustion of clean, untreated fuels for cooking and heating is of primary importance for reducing the formation and release of chemicals listed in Annex C. Strategies to minimize releases of chemicals listed in Annex C from residential combustion sources include public education, awareness and training programmes on the proper use of the appliances, use of appropriate fuels and the health impacts from uncontrolled residential combustion. The abatement technologies commonly used in industrial settings are not generally available for smaller residential heating and cooking appliances. However, the use of well-designed stoves with good operation can be effective in reducing chemicals listed in Annex C, with the important added benefit of improving indoor air quality.

Best available techniques include enclosed low emission burners with ducted flues and the use of dry, well-seasoned wood. For countries or regions where these fuels and appliances are not available, best available techniques and best environmental practices for residential combustion include ensuring separation of household waste from fuel to avoid burning of such waste in cooking and heating appliances. In all countries the use of treated wood or sea-salt laden driftwood and the use of plastics as a firelighter or fuel should be avoided.

Cooking and heating with wood is a common and significant practice in all countries of the world. Any action for reducing the emissions of chemicals listed in Annex C from residential combustion will also have to take into consideration local social, cultural and economic factors. Case studies from Australia and New Zealand are provided to highlight this.

Introduction

Because it is cheap and readily available, biomass is used extensively as an energy source by low-income groups. In the developing world 75–80% of the population relies on wood and waste biomass as fuel for cooking and room heating. Furthermore, this dependence of the global rural population on biomass energy is not expected to decrease significantly for at least a century, and some studies indicate it may increase. In most cases waste biomass from agriculture and forests is used as fuel, but in certain regions of the world the demands of the domestic energy sector have put severe pressure on forest resources (Karve 2000).

Cooking stoves using biomass are generally crude in nature. In most cases they are simple structures consisting of three stones (i.e. open fires). There is no chimney or ventilation for smoke and soot, which means that any emission is inhaled directly by the people in the vicinity of the stove. Indoor air pollution (soot and smoke) produced by inefficient combustion of biomass fuels inside homes is an important public health issue. Studies conducted during the last two decades have revealed that poor indoor air quality is one of the major factors contributing to death, respiratory disease and the poor health of rural women and children in developing countries and among low income groups. In India, for example, 1.5% of total deaths among women are attributable to chronic diseases of the respiratory system.

The incidence of blindness and tuberculosis is greater among women using traditional stoves than for any other population group. Several recent studies have indicated a direct correlation between death and disease in infants and children and use of wood and biomass as fuel in the house. (Concern about the relationship between cooking and heating in developing countries, indoor air quality and public health led, in 2003, to the establishment of the Global Partnership for Clean Indoor Air (http://www.pciaonline.org/ at Nov. 2006), which supports the development of clean and low-cost technologies for residential cooking and heating appliances.) In addition, household waste is being used as a source of fuel for cooking and heating, which can contribute to the formation and release of chemicals listed in Annex C from residential combustion.

1. Releases of chemicals listed in Annex C of the Stockholm Convention from residential combustion

1.1 Emissions from the combustion of fossil fuel and biomass

Residential heating and cooking takes place in a wide array of devices ranging from small, open pit stoves and fireplaces to large highly sophisticated wood-burning stoves and ovens. Because different countries use different terminology (e.g. stove, heater) the term burner is used as a generic description where appropriate.

Fossil fuel is used extensively for domestic heating, especially in developed countries and in countries with economies in transition. Coal, (light fuel) oil and (natural) gas are the main types of fossil fuel used for domestic heating.

Fossil fuel is burnt in devices from small stoker-fired furnaces to large, highly sophisticated boilers for central heat generation in large multi-unit residential buildings. Heat output is maximized when these appliances are well operated and maintained. Two general types of heating system are used and these are distinguished by the way the heat is transported and released. The so-called central heating systems, which usually use oil or gas as a fuel, use one large unit to heat water or air, which is then circulated through the building to release its heat in numerous decentralized radiators or ducts. These modern systems are typically highly efficient and fairly clean burning, leaving little or no residue for disposal.

The second type of heating system is mostly based on solid fuels (coal) and consists of individual stoves, which are located in each room of the building or inside the wall to provide direct access to several rooms at the same time. These stoves consist of fairly small furnaces but provide a system for air to circulate inside the stove and around the furnace. These systems are typically older, less efficient and less clean burning, and can generate bottom ash as a result of the nonorganic content of the fuel, which must be disposed of. Some of these systems are also capable of burning oil.

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) may be formed as a result of incomplete combustion and are released primarily to air. In the case of coal combustion, residues may also be a potential release vector. Emission factors derived from studies in Europe are given in Table 1.

Table 1. PCDD/PCDF emission factors for fossil fuel combustion

Appliance type	**Emission factors: µg TEQ/TJ of fossil fuel burnt to air[a]**	**Concentration ng TEQ/ kg ash residue**
High chlorine coal fired stoves	15,000	30,000
Coal-fired stoves	100	5,000
Oil-fired stoves	10	NA
Natural gas-fired stoves	1.5	NA

NA Not available.

a. TJ = terajoule = 1 x 10^{12} joule.

Source: UNEP 2005.

Biomass is a term used to describe natural organic matter such as wood, straw, coconut shell, husks, animal dung, etc. used as fuel in residential heating and cooking. In general, there is substantial variation and uncertainty associated with emission factors derived for residential combustion. The following is a summary of available data at time of publication grouped by fuel type and technology.

PCDD/F emissions testing from home heating was undertaken in Austria (Thanner and Moche 2002). The assessment involved emission measurements from three different types of solid fuel stoves. The appliances included in the experiments were a new low-budget stove suited for all types of solid fuel, a cast-iron stove for coke approximately 20 years old, and a cast-iron stove approximately 10 years old. Measurements were conducted using coal and coke as well as wood, and all fuel was of regularly retailed quality. The samples were taken over a complete heating cycle, starting with the kindling of the fire and concluding when the fire had burnt out. The fumes were analysed for PCCD/PCDF and polychlorinated biphenyls (PCB); the ashes and the chimney soot were sampled after completion of each heating cycle and analysed for PCDD/PCDF and PCB. Emission factors are presented in Tables 2 and 3.

Only small amounts of the PCDD/PCDF and PCB formed during combustion of wood and fossil fuels were found in the ashes and chimney soot; over 90% of these pollutants were present in the gaseous and aerosol by-products. The remainder was mainly accumulated in the soot, while the ashes contained only insignificant amounts.

Measurements in the field with real-life appliances running under normal (i.e., realistic) conditions can yield substantially higher variations using the same type of stove and identical type of fuel. PCDD/PCDF concentrations ranging from 0.09 to 9.0 ng I-TEQ/MJ were recorded in a project surveying seven individual wood-fuelled heating devices conducted by a private institute.

Table 2. PCDD/PCDF and PCB emission factors for residential combustion

Fuel	**PCDD/PCDF TEQ (I-TEF)** ng/Nm^3 (0% O_2)[a]	**PCDD/PCDF TEQ (WHO)** ng/Nm^3 (0% O_2)	**PCB TEQ (WHO)** ng/Nm^3 (0% O_2)
Wood	0.1–2.0	0.1–2.0	0.01–0.08
Coal	7.5–38.7	8.0–41.8	1.7–2.4
Coke	0.9–4.4	0.9–4.6	0.03–0.2

Source: Thanner and Moche 2002.

a. 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa.

Table 3. PCDD/PCDF and PCB emission factors for different fuels

		PCDD/PCDF	**PCB**	
Fuel		**I-TEQ** ng/MJ	**WHO-TEQ** ng/MJ	**Σ Ballschmiter*** ng/MJ
Wood		n=8	n=3	n=3
	Median	0.27	0.01	65.2
	Average	0.32	0.01	50.3
Coal		n=8	n=2	n=2
	Median	8.80	0.51	64.0
	Average	7.74	0.51	64.0
Coke		n=4	n=4	n=4
	Median	1.53	0.06	82.0
	Average	1.47	0.06	81.1

* Source: Thanner and Moche 2002.

1.2. Emissions from the combustion of mixed and contaminated fuels

The European Emission Inventory reveals residential wood combustion to be one of the largest contributors to air emissions of PCDD/F (Berdowski et al. 1997). Whilst special attention has been paid to the combustion of wood, it should be noted that material burnt often includes not only natural wood but also wood wastes coated and treated with different chemical compounds including organochlorines. Wood residues (waste and industrial) often contain various types of contaminants (chromated copper arsenate, pentachlorophenol, creosote, adhesives, resins, paint and other surface coatings). It is also common practice that any combustible material, including waste, be used as fuel (e.g. textiles, rubber, plastics, printed matter, packaging material, waste oil etc.).

Comparative emission factors were derived from studies carried out in different European countries for the combustion of treated versus untreated wood and is given in Table 4. Emission factors for releases with residues are given on the basis of measured concentrations in the ash and are not related to the heating value of the fuel.

Table 4. Comparative PCDD/F emission factors from the combustion of clean and contaminated wood

Appliance type	**Emission factors: µg TEQ/TJ of biomass burnt to air**[a]	**Concentration: ng TEQ/ kg ash residue**
Contaminated wood/biomass-fired stoves	1,500	1,000
Virgin wood/biomass-fired stoves	100	10

a. TJ = terajoule = 1 x 10^{12} joule.

Source: UNEP 2005.

Studies were conducted in the United States on residential wood combustion to find out whether PCDD/F formation took place (Lavric, Konnov and De Ruyck 2004). Evaluations were made of soot scrapings from the chimneys of wood stoves from the central, eastern and western regions of the country. The average total PCDD/F levels in chimney deposits were 8.3 ng/kg in the eastern region, 42.1 ng/kg in the central region and 10 ng/kg in the west. The wide variability was attributed to the differences in the design of different units and contamination of the fuel wood.

Measurable levels of tetrachlorodibenzo-p-dioxins (TCDD) have been found in chimney soot and in bottom ash from wood-burning stoves and fireplaces. Chimney deposits from residential wood burning have been found to have PCDD/F congener profiles similar to those in flue gases from municipal waste incinerators. This indicates that wood used in residential combustion appliances may be highly contaminated, and inappropriate materials such as plastics may also be used as fuel sources.

Soot from two wood stoves in British Columbia, Canada, was analysed for PCDD. The soot from the wood stove burning salt-laden wood in a coastal area was found to have 20 to 90 times greater levels of PCDD than the stoves from non-coastal areas. The concentration of PCDD in fly ash increased when the concentration of chlorine (from sea salt) increased.

According to the data from chemical analysis performed in Poland, residential sources may emit stack gases containing about 3 times higher concentration of PCB than industrial sources (excluding manufacturing industries), about 2 times higher concentration of hexachlorobenzene (HCB) and 25 times higher concentration of PCDD/F. The main reason for these high concentrations of PCDD/F, PCB and HCB is the co-combustion of domestic wastes with hard coal or wood, generally in simple kitchen stoves or heating boilers (Lassen et al. 2002, 2003).

Co-combustion of wood or coal with domestic wastes takes place in rural and suburban areas located close to forests, in recreation houses and also in residential areas. Public statistics data give a value of

95,000 TJ for combined combustion of wood and peat. The contribution of the latter was considered to be small. According to expert estimates, about 15% of the total amount of burnt wood or coal is substituted by domestic wastes. The total amount of contaminated fuel is estimated at 9,500–19,000 TJ. PCDD/F concentrations in stack gases from chimneys of stoves in Poland, where domestic wastes are co-incinerated, ranged widely from 0.32 to 77 ng I-TEQ/Nm^3. Emission factors for hard coal ranged from 17 to 570 µg TEQ/Mg. Total annual emission of PCDD/F in Poland from residential sources was estimated at 30 to 85 g I-TEQ. The PCDD/F congener mass distribution profile in stack gas was similar to that recorded for flue gas from waste incinerators.

There is little control over emissions from residential sources. Most stoves and fireplaces are poorly operated with inadequate oxygen levels and low turbulence of burning gases (due to overloading or use of over-large wood feed items). In such circumstances combustion releases not only gaseous pollutants but solid pollutants containing PCDD/F, which constitute releases to land.

2. Best available techniques

High-quality, efficient combustion in cooking and heating appliances is very important for reducing formation and release of chemicals listed in Annex C. For enclosed burners, this primarily depends on the combustion chamber temperature, the turbulence of the burning gases, residence time, excess oxygen and the type of fuel used. These parameters are governed by factors such as:

- Combustion technology (e.g. combustion chamber design, process control technology);
- Operating conditions (e.g. primary and secondary air ratio, distribution of the air nozzles);
- Load condition (full or part load);
- Fuel characteristics (shape, size distribution, moisture content).

Any recommendations made regarding best available techniques and best environmental practices for biomass or wood-burning appliances should take into consideration that dependence on biomass fuel for cooking and heating will remain common practice for many years to come in the low-income and rural communities. The implementation of the guidelines related to such appliances will depend on a range of circumstances, including socio-economic factors. As part of their national implementation plans, countries should undertake assessments to determine the possible socio-economic consequences of applying any new standards or regulations.

Replacing poorly designed stoves with improved stoves that burn fuel more efficiently will be an effective strategy for reducing releases of chemicals listed in Annex C, and has the added benefit of improving indoor air quality. In addition, some studies have indicated that improved designs save 50–80% fuel compared to traditional ones. Optimal designs for improved stoves can save fuel, reduce air pollution, be easy to manufacture, install and operate, and be affordable to rural users. Such designs would also improve safety by reducing direct exposure to flames and heat, and job opportunities through the production, sale and maintenance of improved stoves.

Designs for improved stoves should take into consideration the needs and concerns of the users. For instance, studies have shown that the users of improved stoves are concerned about fuel and fuel economy, pollution emissions, cost, cooking time, convenience of operation and maintenance, adaptability to existing kitchen utensils, fuel and cooking practices, ease of firing and control of heat level, and safety of operation. Efforts to design improved stoves need to take social, cultural, scientific, economic, ergonomic and health aspects into consideration.

2.1 Fuels and appliances: General principles

Best available techniques include enclosed, low-emission burners with ducted flues and the use of dry, well-seasoned wood. For countries with no greenhouse gas reduction requirements the use of cleaner-burning fuels such as liquid petroleum gas, natural gas, oil and kerosene may also be appropriate, although this requires appliances that can use these fuels.

For countries or regions where these fuels and appliances are not available, best available techniques and best environmental practices for residential combustion sources includes ensuring separation of household waste from the fuel used in the appliances to avoid burning of household waste in cooking and heating appliances. In all countries, the use of treated wood or sea-salt laden driftwood and the use of plastics as a firelighter or fuel should be avoided.

Measures to control emissions from waste gases are desirable but not recognized as common for domestic fire and combustion appliances. Large systems comparable to those used for industrial processes should be equipped with cyclones or fabric filters. It is noted that catalytic converters are available in some countries but are not routinely employed.

2.2 Cooking and heating appliances

For individual stoves and furnaces, emissions can be reduced by using optimized heating elements. Different installation types are available, varying by country according to general technical standards, social, cultural and economic background, and climatic conditions.

Optimized combustion technology should have the following characteristics:

- Good mixing quality of gas and air (high turbulence or mixing);
- Sufficient residence time in the hot zone;
- Minimal disturbance of the glow bed and homogeneous distribution of the primary air;
- Minimal residence time in the temperature range between 180° C and 500° C and minimal dust deposition ability;
- The emission stack should be kept clean and free of soot by ensuring complete combustion and regular cleaning (at least annually).

3 Best environmental practices

3.1 Combustion appliances and potential problems

Table 5 identifies some typical appliance problems that may cause the release of pollutants. Many of these problems are difficult for a homeowner to identify. This information should be provided by the manufacturer or retailer at the point of sale of these appliances. Public awareness through mass media can also be a good means of disseminating this information.

Table 5. Combustion appliances and potential problems

Appliances	**Fuel**	**Typical potential problems**
Central furnaces Room heaters Fireplaces	Natural or liquefied petroleum gas	Cracked heat exchanger Not enough air to burn fuel properly Defective/blocked flue Maladjusted burner
Central furnaces	Oil	Cracked heat exchanger Not enough air to burn fuel properly Defective/blocked flue Maladjusted burner
Central heaters Room heaters	Wood	Cracked heat exchanger Not enough air to burn fuel properly Defective/blocked flue

Appliances	**Fuel**	**Typical potential problems**
		Green or treated wood
Central furnaces Stoves	Coal	Cracked heat exchanger Not enough air to burn fuel properly Defective grate Defective or blocked flue Low-quality coal High moisture content of fuel
Ranges Ovens	Natural or liquefied petroleum gas	Not enough air to burn fuel properly Maladjusted burner Misuse as a room heater
Room heaters Central heaters	Kerosene	Improper adjustment Wrong fuel (not K-1) Wrong wick or wick height Not enough air to burn fuel properly
Stoves Fireplaces	Wood Coal	Not enough air to burn fuel properly Defective/blocked flue Green or treated wood Cracked heat exchanger or firebox Inappropriate fuel such as residential refuge
Water heaters	Natural or liquefied petroleum gas	Not enough air to burn fuel properly Defective/blocked flue Maladjusted burner

Source: CPSC 2004.

3.2 Ventilation

To reduce indoor air pollution, movement of air into and out of a residence is very important, helping to reduce the level of harmful pollutants indoors by carrying them up the chimney, stovepipe or flue to the outside. This also ensures adequate air for proper combustion, thereby reducing levels of pollutants.

Ventilation can be improved by:

- Using a hood fan over stoves to assist ventilation;
- Ensuring sufficient airflow into the house when an exhaust fan is used (e.g. by slightly opening a door or window, especially if other appliances are in use);
- For proper operation of most combustion appliances and their venting systems, the air pressure in the house should be greater than that outside. If not, the vented appliances could release combustion pollutants into the house rather than outdoors;
- Ensuring the vented appliance has the vent connected and that nothing is blocking it, and there are no holes or cracks in the vent;
- Opening the stove or heater's damper when adding wood allows more air into the appliance. More air helps the wood burn properly and prevents pollutants from being drawn back into the house instead of going up the chimney. Visible smoke or a constant smoky odour inside the home when using a wood-burning stove are signs that the stove is not working properly, as is deposition of

soot on furniture in the room where the stove is being used. Smoke and soot are signs that the stove is releasing pollutants into the indoor air.

Unvented combustion heaters or stoves should never be used in rooms where people are sleeping as this can result in exposure to dangerous or deadly levels of carbon monoxide.

3.3 Inspection and maintenance

Combustion appliances should be regularly inspected and maintained (Table 6) to reduce exposure to pollutants. It is important to clean chimneys and vents, especially when changing heating systems.

Table 6. Inspection and maintenance schedules

Appliance	Inspection		Maintenance	
	Tasks	Frequency	Tasks	Frequency
Gas hot air heating system	Air filters: clean/change filter Look at flues for rust and soot	Monthly as needed Yearly	Qualified person check/clean chimney, clean/adjust burners, check heat exchanger and operation	Yearly (at start of heating season)
Gas/oil water/steam heating systems and water heaters	Look at flues for rust and soot	Yearly	Qualified person check/clean chimney, clean combustion chamber, adjust burners, check operation	Yearly (at start of heating season)
Kerosene space heaters	Look to see that mantle is properly seated Look to see that fuel tank is free of water and other contaminants	Daily when in use Daily or before refuelling	Check and replace wick Clean combustion chamber Drain fuel tank	Yearly (at start of heating season) Yearly (at start of heating season) Yearly (at end of heating season)
Wood/coal stoves and residential boilers & furnaces	Look at flues for rust and soot	Monthly	Qualified person check/clean chimney, check seams and gaskets, check operation	Yearly (at start of heating season)

Source: CPSC 2004.

3.4 Correct use of appliances and fuel

It is important to understand and follow the operating instructions for all appliances and to use the recommended type of fuel.

Where available, seasoned hardwoods (instead of softwoods) should be used in wood-burning stoves and fireplaces. Hardwoods burn hotter and form less creosote (an oily, black tar that sticks to chimneys and stovepipes, posing a fire hazard).

Green, wet woods or salt-laden (sea) driftwood should be totally avoided. This is because green and/or wet wood burns less efficiently and may result in increased emissions of PCDD/F. Comparative studies of wood from coastal versus non-coastal areas have further shown that sea-salt laden wood has higher chlorine content with increased PCDD/F emissions (see also section 1.2) when burned.

Painted scrap wood or wood treated with preservatives are never to be burnt, because they could release highly toxic pollutants, including chemicals listed in Annex C.

It is important to avoid waste loads containing high chlorine content and/or bromine content, whether inorganic such as salts, or halogenated organics such as PVC (Lemieux et al. 2003). The co-incineration of waste is, however, common practice in solid fuel-fired appliances. It should be strongly discouraged through policies and awareness campaigns (see subparagraph 3.5 below). Many studies show that combustion of chlorine containing waste such as PVC, leads to increased formation of unintentional persistent organic pollutants as shown in Table 7 (Gullett *et al* 1999). A regulation specifying standard fuels could be implemented. This is also valid for such fuels as treated wood, waste oil, transformer oil, plastics and other combustible waste.

Table 7. Relation of PCDD/F emission factors on PVC content in burned material

PVC content [%]	**0**	**0.2**	**1**	**7.5**
Average Emission factor in I-TEQ/kg [ng]	14	80	200	4,900
Range I-TEQ/kg [ng]	2 - 28	9 - 150	180 - 240	3,500 – 6,700

3.5 Education, awareness and training programmes

Typically emissions of other pollutants (such as fine particles or carbon monoxide) drive regulatory efforts to improve emissions from residential combustion. Education, awareness and training programmes to improve understanding of best practices related to chemicals listed in Annex C should be a major component of such efforts (see case studies in Box I appended to this section).

Any education and awareness programmes are best developed in conjunction with local communities to ensure they are specific and useful. Key components of effective programmes include:

- Education and awareness on the appropriate use of fuel. Critical factors to include are:
    - Use of dry, well-seasoned wood, which will reduce PCCD/PCDF releases and can also give up to 40% more heat;
    - Use of cleaner-burning fuels such as natural gas for reducing releases of chemicals listed in Annex C;
    - The undesirability of burning of residential wastes in these appliances;
    - Effective operation of appliances to ensure complete combustion of fuel;
- Simple, easy-to-understand information on the effects of chemicals listed in Annex C on human health and the environment, and the significance of releases from residential sources;
- Programmes for those who sell and those who purchase and operate residential combustion appliances, highlighting the issues raised in subparagraphs 3.1 to 3.4.

3.6 Residential combustion management

Complete combustion of fuel is important for ensuring low emissions and efficient operation of the appliance. This can be achieved by ensuring the following:

- Sufficient firing temperature;
- Sufficient airflow to provide enough oxygen for combustion;
- Avoidance of fuel overloading (more than the fire can burn efficiently);
- Sufficient mixing of air and the hot gases given off by the fire.

Specific measures to achieve these desired outcomes are:

- Good-quality, dry fuel;

- Collecting and seasoning wood to ensure it is dry when burnt;
- Ensuring adequate airflow (for example, preventing incoming air from being blocked by pieces of wood;
- Enough space in the firebox for optimal airflow.

3.7 Management of releases to other media

The primary emission of chemicals listed in Annex C from residential combustion is to air. Ash and soot are also released and, when arising from clean wood or biomass combustion, typically contain only small quantities of chemicals listed in Annex C. Minor amounts of ash may be safely used for fertilizer as long as it is not spread in the same place on a regular basis. Larger quantities should be disposed of in a sanitary landfill.

4 Effective implementation of best available techniques and best environmental practices

In most cases end-users of improved combustion appliances will have minimal or no understanding of the adverse health and environment effects of chemicals listed in Annex C. Increased awareness of these concerns can help in encouraging effective operation of these appliances, as well as avoiding such practices as using household waste as fuel. Governments should include in their training and awareness programmes information on the impacts of releases of chemicals listed in Annex C from residential combustion appliances such as stoves, ovens and other devices.

Possible barriers and options for effective implementation of best available techniques and best environmental practices are discussed by Atikullah S.M. and Eusuf M. (2003). These are summarized in Table 8 below.

Table 8. Possible barriers and options for effective implementation of best available techniques and best environmental practices for residential combustion appliances

Barriers	Options for effective implementation of best available techniques and best environmental practices
Mismatch between the appliance design and the types of fuel used and available	Appliance design should be specific to community needs. A detailed assessment of community needs should be undertaken before implementing any particular design
Lack of public awareness about improved technology	Governments and communities should use appropriate means (for example, mass media, awareness campaigns) to publicize and popularize improved appliances. Training programmes at the community level are important to ensure that the appliances are used appropriately and to eliminate the possible use of inappropriate fuel such as household waste
Lack of local capacity to maintain and repair improved appliances	Implementing training programmes to establish capacity for appliance maintenance and repair is important
Lack of resources to purchase, operate and maintain appliances	Those with limited income will only be attracted to improved appliances if they are convinced that such appliances will not be an extra financial burden and will be cost effective to maintain and use
Lack of understanding of the health impacts of chemicals listed in Annex C and other	Raise awareness on possible health impacts of indoor air pollution (including Annex C chemicals) due to the use

pollutants	of inappropriate household heating/cooking devices and fuels

Additional sources of information for clean burning and improved wood stove design are provided in the references.

Box 1 Awareness raising and education: Case studies

Whilst the regulatory approaches below focus on particles, they have important co-benefits for the reduction of PCDD/F, which may be formed through incomplete combustion. Reduction of particle emissions will at the same time reduce also PCDD/F emissions since PCDD/F are adsorbed on particles.

Case study 1: New Zealand

Urban pollution due to emissions from residential wood combustion is a widespread problem. In New Zealand, many towns and cities suffer from poor air quality in wintertime due to emissions from domestic combustion for heating. Exceedances of the national environmental standard for fine particles of 50 $\mu g/m^3$ (as a 24-hour average) are not uncommon and in some areas occur on more than 30 days a year. This has the potential to contribute to national PCDD/F emission releases. The problem is largely historical, with a prevalence of uninsulated houses resulting from the plentiful (and in many cases free) wood or coal supply. This has important socio-economic considerations for local authorities charged with reducing air pollution.

An awareness raising campaign on emissions from residential combustion was carried out in four small towns in New Zealand in 2005/06. The key finding from the campaign was the importance of tailoring solutions to each local community (no “one size fits all”). This required engagement with key stakeholders such as community health professionals and trust organizations but was highly successful in creating positive synergies for community action and awareness.

Case study 2: Tasmania, Australia

In many parts of southern Australia, woodheaters are commonly used to heat houses. Launceston, Tasmania (population approximately 10,000) averaged up to 14 exceedances of the Australian fine particle standard per month in winter, primarily due to emissions from woodheaters.

In 2001, a woodheater replacement programme was introduced to improve air quality and since that time approximately 25% of woodheaters have been removed through financial incentives to replace older, polluting woodheaters with cleaner appliances. At the same time a targeted community education campaign was introduced (Launceston Air Quality website) as well as a regulation limiting particle emissions from new woodheaters to 4 g/kg (emission/kilogram of wood burnt).

A 2005 study found that the programme accelerated the existing trend away from older woodheaters and contributed to improved air quality. Although there are no data available there is likely to have been a reduction in dioxin emissions. In the year 2006, for the first time, Launceston did not breach the Australian fine particle standard.

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Part III Source category (d):
Fossil fuel-fired utility and industrial boilers

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VI.D Fossil fuel-fired utility and industrial boilers

Summary

Utility and industrial boilers are facilities designed to burn fuel to heat water or to produce steam for use in electricity generation or in industrial processes. The volumetric concentrations of chemicals listed in Annex C of the Stockholm Convention in the emissions from fossil fuel-fired boilers are generally very low. However, the total mass emissions from the boiler sector may be significant because of the scale of fossil fuel combustion, in terms of both tonnage and distribution, for electricity generation and heat or steam production.

Measures that can be taken to decrease the formation and release of chemicals listed in Annex C include: maintenance of efficient combustion conditions within the boiler and ensuring sufficient time is available to allow complete combustion to occur; undertaking measures to ensure fuel is not contaminated with PCB, HCB or chlorine, and is low in other components known to act as catalysts in the formation of PCDD and PCDF; use of appropriate gas-cleaning methods to lower emissions that may contain entrained pollutants; and appropriate strategies for disposal, storage or ongoing use of collected ash.

Emission levels associated with best available techniques can be significantly lower than 0.1ng I-TEQ/Nm^3 (oxygen content: 6% for solid fuels; 3% for liquid fuels).

1. Introduction

1.1 Overview of boilers

Boilers are facilities designed to burn fuel to heat water or to produce steam. The majority of boilers use fossil fuels to provide the energy source, although boilers can also be designed to burn biomass and wastes. The steam produced from the boiler can be used for electricity production or used in industrial processes; likewise hot water can be used in industrial processing, or for domestic and industrial heating. There are significant differences between utility and industrial boilers, with the major differences occurring in three principal areas:

- Size of the boilers;
- Applications for the steam and hot water produced by the boilers;
- Design of the boilers.

1.1.1 Size of boilers

Utility boilers are very large in comparison to modern industrial boilers (sometimes known as industrial/commercial/institutional boilers). A typical large utility boiler produces in the order of 1,600 tons of steam per hour compared to about 45 tons of steam for the average industrial boiler, although industrial boilers may range from one-tenth to ten times this size (CIBO 2002).[1]

1.1.2 Applications for output steam

Utility boilers are designed to generate steam at a constant rate to power turbines for electricity production. Because of this constant demand for steam they generally operate continuously at a steady state, though changes in energy market structures may see some utilities varying operating conditions to address fluctuations in daily national energy demands.

By contrast, industrial boilers have markedly different purposes in different industrial applications and the demands can vary depending on the industrial activities and processes operating at any given time and their demand for steam; compare, for example, the production and use of both hot water and

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[1] For a rough estimation a conversion factor of 0.8–0.9 (MWh per ton of high pressure steam) can be used.

steam for food processing with the demand cycle in a large hospital boiler. These widely fluctuating steam demands mean that the industrial boiler does not generally operate steadily at maximum capacity, although the design will be optimized to the plant and its operation. In general, industrial boilers will have much lower annual operating loads or capacity factors than typical utility boilers.

1.1.3 Boiler design

Utility boilers are usually large units combusting primarily pulverized coal, fuel oil or natural gas at high pressure and temperature. Individual utility boiler types tend to have relatively similar design and fuel combustion technologies. Industrial boilers, however, can incorporate a wide range of combustion systems, although they are usually designed to specific fuel types. Utility plant facilities are designed around the boilers and turbine(s) and their size allows for significant economies of scale in the control of emissions. However, the design of industrial boilers can be constrained by the necessity for flexibility of steam output and plant space limitations. This may lead to more difficulty in applying effective emission controls to these industrial boiler applications.

1.2 Boiler types

1.2.1 Utility boilers

Utility boilers are usually designated by the combustion furnace configuration:

- Tangentially fired: Commonly used for pulverized coal combustion but may be used for oil or gas; single flame zone with air-fuel mixture projected from the four corners of the furnace tangential to furnace centre line;
- Wall fired: Multiple burners located on a single wall or on opposing furnace walls can burn pulverized coal, oil or natural gas;
- Cyclone fired: Typically crushed coal combustion, where the air-fuel mixture is burnt in horizontal cylinders;
- Stoker fired: Older plants burning all solid fuel types; spreader stokers feed solid fuel onto a combustion grate and remove ash residue;
- Fluidized bed combustion: Lower furnace combustion temperature, efficient combustion promoted by turbulent mixing in the combustion zone, crushed coal feed with the potential for sorbent additions to remove pollutants, particularly sulphur dioxide;
- Pressurized fluid bed combustion: Similar to fluidized bed combustion, but at pressures greater than atmospheric, and with higher efficiency.

1.2.2 Industrial/commercial/institutional boilers

Industrial/commercial/institutional boilers are normally identified by the methods of heat transfer and combustion system utilized. A detailed discussion of the various boiler types can be found in Oland 2002. In summary, the heat transfer systems are:

- Water tube boilers: Heat transfer tubes containing water are directly contacted by hot combustion gases. Commonly used in coal-fired installations but can accommodate almost any combustible fuel including oil, gas, biomass, municipal solid waste and tyre-derived fuel;
- Fire tube boilers: Water surrounds tubes through which hot combustion gases are circulated. The application is more common for pulverized coal, gas and oil-fired boilers, but various types can also burn biomass and other fuels. Generally used for lower-pressure applications;
- Cast-iron boilers: Cast sections of the boiler contain passages for both water and combustion gas. Used for low-pressure steam and hot water production, generally oil or gas fired with a smaller number of coal-fired units.

And the combustion systems are mainly:

- Stokers: There are a variety of different stoker types and functions. Underfeed stokers supply both fuel and combustion air from below the grate, discharging ash to the side or rear. Overfeed stokers, which may be mass feed or the more popular spreader stoker, supply the combustion air from below the grate, with the fuel for combustion being distributed above the grate. Spreader stokers with a stationary grate are used extensively in the sugar industry to combust bagasse;
- Burners: This diverse group of devices manages the delivery of air-fuel mixtures into the furnace under conditions of velocity, turbulence and concentration appropriate to maintain both ignition and combustion.

2. Generation of PCDD/PCDF, PCB and HCB from combustion

In a properly operated combustion system, volatiles should be subjected to sufficient time at high temperature, with adequate oxygen and mixing, to enable uniform and complete combustion. When those conditions are not present the potentially toxic airborne emissions polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) can be produced in or survive the combustion process (Van Remmen 1998; UNEP 2005).

In large, well-controlled fossil fuel-fired power plants, the formation of PCDD/PCDF (and other persistent organic pollutants) is low since the combustion efficiency is usually high, the process is stable and the fuels used are generally homogeneous. However, significant mass emissions are still possible as large volumes of flue gases are emitted with small concentrations of PCDD/PCDF (UNEP 2005). In smaller less well controlled systems there exists the potential for emissions of persistent organic pollutants at greater concentrations but at lower overall throughputs, therefore resulting in lower mass emission of such pollutants.

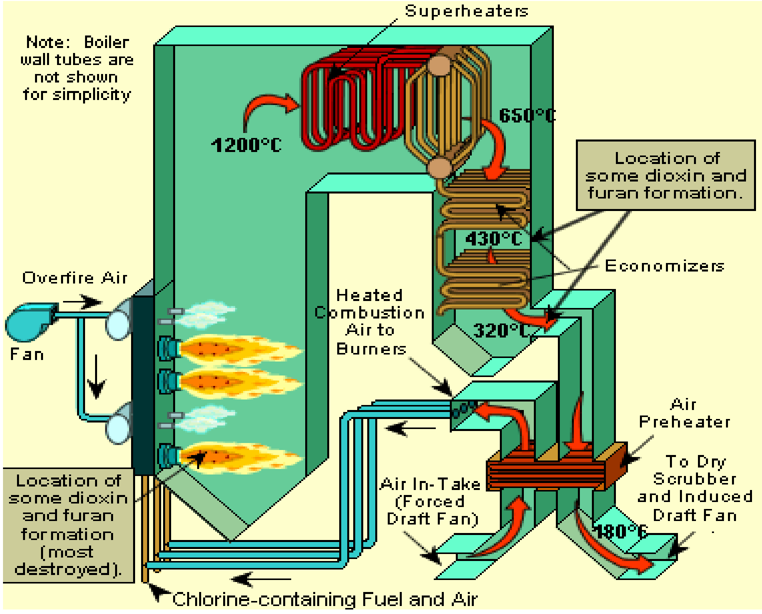
2.1 PCDD and PCDF

2.1.1 Generation of PCDD/PCDF

Fossil fuel combustion in utility or industrial boilers is known to generate much less PCDD/PCDF than combustion of waste-derived fuels (Sloss and Smith 1993; Sloss 2001; Dyke 2004). Griffin, in 1986, established a hypothesis to explain the formation of PCDD/PCDF as a result of the sulphur-to-chlorine ratio in the fuel feedstock (Griffin 1986). The hypothesis states that in coal there is a sulphur-to-chlorine ratio of 5:1, which is much greater than that found in municipal solid waste. This surplus of sulphur over chlorine in fossil fuels, such as coal, crude oil and gas, enables the capture of the molecular chlorine, thus preventing the formation of chlorinated aromatics that arise in the combustion waste-derived fuels, where chlorine dominates over sulphur.

PCDD/PCDF arise by a variety of mechanisms. Figure 1 shows a schematic representation of possible locations for PCDD/PCDF formation in a boiler. Further details on formation of PCDD/PCDF appear in section III.C (i) of the present guidelines.

Figure 1. Location of possible PCDD and PCDF formation in a boiler



Source: Modified from Richards 2004.

2.1.2 PCDD/PCDF control mechanisms

Combustion conditions, fuel quality and plant design and operating conditions can have a major influence on PCDD/PCDF formation. It has been shown (Williams 1994; Eduljee and Cains 1996) that combustion conditions can be improved to reduce PCDD emissions. Lemieux (1998) summarizes work at the United States Environmental Protection Agency that shows, in decreasing order of importance, the parameters that can be controlled to reduce PCDD/PCDF emissions:

1. Combustion quality as indicated by:
    - Carbon monoxide (CO), total hydrocarbons, soot formation;
    - Particle entrainment and burnout;
2. Air pollution control temperatures;
3. Fuel/waste parameters:
    - Sulphur;
    - Metals;
    - Chlorine.

These can be achieved by the following conditions (Lemieux 1998):

- Uniform high combustor temperature;
- Good mixing with sufficient air;
- Minimize entrained, unburnt particulate matter;
- Feed rate uniformity;
- Active monitoring and control of CO and total hydrocarbons.

Finally, a number of operating parameters for air pollution control devices have been identified to result in lower PCDD/PCDF emissions. These are:

- Low temperature at the particulate control device inlet;
- Minimization of gas or particle residence time in the 200°–400° C temperature window.

As mentioned previously, the presence of sulphur has also been shown to inhibit PCDD formation, based on the generally low emissions from coal-fired power plants, and results obtained from the co-firing of high-sulphur coal with refuse-derived fuel (Tsai et al. 2002). Thus there may be benefits in maintaining a high sulphur-low chlorine ratio (Luthe, Karidio and Uloth 1997), although it should be recognized that the use of high-sulphur fuels may result in the development of a different set of air pollution problems.

2.2 PCB and HCB

PCB emissions may arise from the use of recovered oils and other waste-derived fuels. Coal combustion is the third-largest global source of HCB emissions (Bailey 2001). Further details on the formation of these compounds appear in section III.C (i) of the present guidelines. Similar emission control strategies to those used for minimizing PCDD/PCDF emissions can be used for the control of PCB and HCB emissions.

3. Effect of fuel types on generation of emissions

The fossil fuels – coal, oil and gas – are used, either individually or in combination with energy-containing fuels from other processes, for steam generation in boilers. The type of fuel used depends on fuel availability and process economics.

3.1 Light fuel oil and natural gas

Light fuel oil and natural gas are always fired in specially designed burners and are generally unlikely to generate large amounts of PCDD/PCDF, as both are very high-calorific, clean-burning fuels leaving little ash. Increased gas use for power generation (as a replacement fuel for coal and oil) will result in reductions of PCDD/PCDF from the generation sector (UNECE 1998).

3.2 Heavy fuel oil

Heavy fuel oil is combusted for both steam generation and power generation purposes and is usually burnt in specially designed burners incorporated in the boiler walls. Heavy fuel oil that is free from contaminants will generally result in low levels of organic emissions.

3.3 Coal

Efficient coal combustion in large coal-fired power plants results in very low levels of emissions (Rentz, Gütling and Karl 2002). Coal use in less-efficient sectors could be a significant source of local emissions (Sloss 2001). UNECE 1998 recommends the improvement of energy efficiency and energy conservation for utility and industrial boilers over 50 MW as an emissions reduction strategy due to lowered fuel requirements. However, it is acknowledged that while techniques for the reduction of particles, sulphur oxides (SO_x) and nitrogen oxides (NO_x) may result in the reduction or removal of PCDD/PCDF (and presumably PCB and HCB), the removal efficiencies will be variable (see also section III.C (iii) on co-benefits). Chlorine removal from fossil fuel feeds is not seen as a cost-effective measure for PCDD/PCDF reduction (UNECE 1998).

3.4 Lignite

Lignite-fired power plants are typically operated close to the mining region. Due to the significantly lower calorific value of lignite compared to coal it is mainly transported via belt conveyors from the storage area of the mine to the power station. Pulverized lignite-fired combustion and fluidized bed combustion are appropriate techniques for power generation from lignite. Due to lower combustion temperatures, pulverized lignite-fired boilers can achieve current NO_x emission standards by primary measures. Therefore, they typically do not use selective catalytic reduction.

PCDD/PCDF emissions from lignite-fired power plants have been reported in a range of 0.0002 to 0.04 ng I-TEQ/Nm^3 (Detzel et al. 1998).[2]

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[2] 1 ng (nanogram) = 1×10^{-12} kilogram (1×10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

3.5 Co-firing with other fuel types

Most electricity-generating plants use a single fuel, but it is possible to modify the boiler and the fuel processing equipment to blend other materials, such as waste, into the fuel mix. This process of co-firing means that more than one fuel type can be used simultaneously.

Boilers, however, are often limited in their capability to use waste or waste-derived fuels due to a lack of hydrogen chloride emission control, and sometimes by combustion condition limitations and possible boiler corrosion problems. The potential for emission of persistent organic pollutants may be increased by co-firing if boiler efficiency is not maintained by appropriate system redesign or control.

Wastes (also known as waste-derived fuels) are materials that are rich in energy, such as used oil, tyres, waste wood and spent solvents, which can be used to replace fossil fuels as a source of thermal energy. However, in many cases waste fractions with a low calorific value (such as dewatered sewage sludge) are also co-incinerated for disposal. Potential contamination of waste by undesirable materials or pollutants is an issue associated with this fuel source. In particular, the presence of PCB, HCB and chlorine in the waste should either be specifically precluded or limited. For further guidance on the issues and implications of using waste types refer to the guidance presented in the sections on waste incinerators, cement kilns firing hazardous waste, firing installations for wood and other biomass fuels, and waste oil refineries (sections V.A, V.B, VI.E and VI.M of the present guidelines).

Fuel quality management and good combustion conditions, in combination with an effective collection device, appear to offer the most successful control strategies for minimization of persistent organic pollutants when waste material is included amongst the fuel loading. For the most effective operation, waste materials should be specifically excluded from the process during start-up, shutdown or in stationary operating conditions, when combustion conditions are less likely to be both stable and controlled.

Co-incineration of waste should be done in such a way that disposal options of solid residues (e.g. fly ash, coarse ash, flue gas treatment residues) are not negatively affected (see section V.A (waste incinerators) of the present guidelines).

If an emission value of 0.1 ng/Nm^3 is not met, secondary measures are available and should be installed.

4. Estimation of emissions of persistent organic pollutants from boilers

Measurement of the low levels of PCDD, PCDF, PCB and HCB from the combustion of fossil fuels in boilers is technically challenging and costly compared with the measurement of criteria pollutants such as sulphur dioxide, oxides of nitrogen and particulates. Although the direct measurement of persistent organic pollutants from individual facilities is encouraged to improve the knowledge base of emissions of these toxic components, it is acknowledged that in some circumstances this may not be possible except for those operating large and technically advanced facilities.

In an efficient combustion process the levels of pollutants may be up to several orders of magnitude below prevailing standards (Brain et al., cited in Sloss 2001). As a result, although PCDD, PCDF, PCB and HCB may possibly be present, they may be below the detection limits of currently available analytical methods.

An alternative to direct measurement is the calculation of an imputed emission output given some knowledge of fuel type, throughput and process conditions. PCDD/PCDF emission factors (I-TEQ) for a number of boiler processes are given in Table 1, with additional information on emission of particular congeners included as annex I to the present chapter (UNEP 2005).

Table 1. Emission factors for heat and power generation plants in industry fuelled with fossil fuels

Classification	Emission Factors - µg TEQ/TJ of Fossil Fuel Burned		
	Air	Water	Residue
1. Fossil fuel/waste co-fired power boilers	35	ND	ND
2. Coal fired power boilers	10	ND	14
3. Heavy fuel fired power boilers	2.5	ND	ND
4. Shale oil fired power plants	1.5	ND	*
5. Light fuel oil/natural gas fired power boilers	0.5	ND	ND

* Releases with residues can be calculated on a mass basis
Source: UNEP 2005

ND Not determined.

a. These default emission factors are based on the assumption that the fuels burnt lead to PCDD/PCDF releases associated with the disposal of fly ash. Emissions through bottom ash are negligible. The removal efficiency of particulate matter also increases with the quality of the air pollution control system employed at the plant (UNEP 2003).

b. Energy throughput basis: µg TEQ/TJ of fuel consumed.

Information on emissions is more readily available for PCDD/PCDF than for PCB and HCB. Where waste-derived fuels comprise a significant proportion of the fuel feed it may be appropriate to source emission factors from the waste incineration sector (UNEP 2003). For PCB and HCB emissions few or no reliable data are available for the boiler combustion sector.

5. Best environmental practices

The best environmental practices described in this section constitute general guidance applicable to any kind of boiler, regardless of its size or type:

- Identify key process parameters, either from site-specific investigations or research undertaken on similar facilities elsewhere;
- Introduce measures that enable control of key process parameters;
- Introduce monitoring and reporting protocols for key process parameters;
- Introduce and follow planning cycles, implement appropriate inspection and maintenance cycles;
- Introduce an environmental management system that clearly defines responsibilities at all levels;
- Ensure adequate resources are available to implement and continue best environmental practices;
- Introduce process improvements to reduce technical bottlenecks and delays;
- Ensure all staff are appropriately trained in the application of the best environmental practices relevant to their duties;
- Define a fuel specification for key fuel parameters and introduce a monitoring and reporting protocol;
- Ensure the environmentally sound management of fly ash, coarse ash and flue gas treatment residues;
- Ensure that, when co-firing biomass or waste, they should not be added until the boiler furnace combustion conditions are stable and it has reached its operating temperature.

6. Best available techniques

In order to reduce the emission of persistent organic pollutants from fossil fuel-fired utility and industrial boilers, the pathways for generation and release of such pollutants must be minimized in the design and operation of the process. This will be effectively achieved by addressing:

- Fuel quality;
- Combustion conditions;
- Installation of the most appropriate air pollution control devices.

6.1 Primary measures

6.1.1 Fuel specification and monitoring

While the low levels of precursors necessary to promote the formation of chemicals listed in Annex C of the Stockholm Convention via gas formation above 500º C occur in most fuels, measures must be taken to reduce, to the extent possible, the unintentional introduction of contaminated fuels, which may promote the formation of persistent organic pollutants. This is especially valid when co-firing fossil fuels with other fuel types. Controls should be introduced (e.g. measurement of the chlorine content of fuel oil to prevent the introduction of PCB-contaminated waste oils) to ensure that the fuels used are within the required specifications.

6.1.2 Combustion conditions

To achieve the complete combustion of persistent organic pollutants contained in the fuel, special attention must be paid to the four cornerstones of high destruction efficiency: temperature, time, turbulence and excess oxygen (McKay 2002). This will also ensure the destruction of precursors and reduce soot formation and therefore provide fewer possible sites for solid catalysis in the cooling gas effluent. Table 2 illustrates the influence of combustion conditions on emission of pollutants from waste-derived fuel. While the values in Table 2 are higher than might be expected from combustion using fossil fuels, the values illustrate the significant influence of combustion conditions (Environment Canada, cited in Dyke 2004).

Table 2. Trace organic concentrations (ng/Sm³ at 12% O_2)[a] for waste derived fuel combustion

Species	Good combustion	Poor combustion
PCDD (total)	70–230	200–600
PCDF (total)	220–600	700–1,300
Cl_{3-6} benzenes[b]	4,000–6,000	7,000–16,000

a. Sm^3 = standard cubic metre, dry gas volume measured at 15º C and 101.3 kPa (compare Nm^3, normal cubic metre, dry gas volume measured at 0º C and 101.3 kPa).

b. Includes all of the congeners of tri, tetra and penta as well as the fully substituted hexa.

It is generally accepted that a temperature in excess of 900º C (McKay 2002) and a gas residence time of 2 seconds are sufficient to achieve complete oxidation of PCDD, as long as the gas flow is sufficiently turbulent and excess O_2 is present. McKay (2002) suggests that a furnace temperature higher than 1,000º C should be maintained to ensure that all persistent organic pollutants are oxidized.

Other important factors are the excess air and turbulent conditions in the furnace. High degrees of turbulence will avoid the formation of cold pockets where oxidation temperatures will not be reached. High turbulence will also lead to uniform distribution of oxygen to ensure total combustion, avoiding substoichiometric zones, providing that air is in excess. To assess the efficiency of combustion, real-time monitoring of CO can be useful. Good combustion is accompanied by low CO emissions (i.e., 30–50 mg/Nm³, 6% oxygen for pulverized coal; < 100 mg/Nm³ for fluidized bed combustion) (European Commission 2003). High CO levels indicate incomplete combustion and conditions under which persistent organic pollutants may survive or be created.

When solid fuel is used, in order to maximize mixing and combustion conditions, low-moisture pulverized fuels are to be preferred to crushed or lumpy fuels. Evaporation is an endothermic reaction and when moisture is introduced into the furnace combustion temperature decreases. Introducing pulverized fuel will allow, under good turbulent conditions, isothermal conditions throughout the entire furnace and optimum mixing with oxygen.

6.2 Secondary measures: Air pollution control devices

Air pollution control devices can be installed to further control and limit emissions, although in the case of fossil fuel-fired utilities and industrial boilers, these devices are additional or secondary measures. More details on air pollution control devices are provided in section III.C (iv) of the present guidelines.

6.3 Other considerations

It should be noted that the formation of PCDD, PCDF, PCB and HCB is complex and the removal of particles in the flue gases does not mean persistent organic pollutants will not be emitted. These cleaning techniques, while still of great importance to our environment, should not be considered as the only solution. As mentioned earlier, fuel quality and combustion control are most important steps in minimizing emissions of persistent organic pollutants.

The capture of particles from the flue gases may produce an amount of contaminated dust waste, which should be handled with care as a possible product containing persistent organic pollutants (UNECE 1998). Generally, combustion products such as fly ash and bottom ash from pulverized coal combustion contain very low residual levels of persistent organic pollutants, with PCDD less than 1 pg I-TEQ/g (Meij and te Winkel 2001). Disposal methods are therefore likely to be dictated by prevention of release of other possible contaminants in the material rather than by any persistent organic pollutants that may be present. For residues containing higher levels of contamination, several techniques are recommended for reduction of persistent organic pollutants before disposal. These include catalytic treatment at low temperatures and with reduced oxygen concentrations, extraction of the heavy metals and combustion to destroy organic matter, vitrification and plasma technology (UNECE 1998).

A summary of measures constituting best environmental practices and best available techniques is presented in Table 3.

Table 3. Summary of recommended measures for fossil fuel-fired utilities and industrial boilers

Issue	Best environmental practices	Best available techniques	Environmental benefit
Fuel	Fuel sourcing Fuel monitoring Fuel specifications	Control fuel input to meet specifications by rejection, substitution, purification or blending	Minimization of persistent organic pollutants introduced into the combustion system
Combustion conditions	Design appropriate reactor for the specified fuel usage Monitor combustion conditions, particularly: • Temperature (> 900º C) • Time (> 1 second) • Turbulence (high) • Oxygen (in excess) Operate and maintain to achieve designed conditions Develop specific conditions and operating procedures for co-firing, particularly during	Automated or computerized combustion control system to maintain ideal combustion conditions Maximized oxidation by maintaining ideal fuel/oxygen mix	Destruction of compounds of persistent organic pollutants present in the fuel Minimization of formation of persistent organic pollutants during combustion

Issue	Best environmental practices	Best available techniques	Environmental benefit
	furnace start-up and shutdown		
Collection	Operation and maintenance of existing air pollution control devices	Assess potential for environmental improvement by installation of air pollution control device Install air pollution control device when environmental benefits can be demonstrated	Minimize persistent organic pollutant content of gases
Waste disposal	Collect solid and liquid wastes from the combustion process and air pollution control device Handle and store appropriately to minimize environmental release	Assess potential for waste volume reduction and recycling Safe disposal	Minimize and control the release to the environment

7. Performance levels associated with best available techniques

The available data suggest that for an effective boiler system using only coal, oil or gas as the fuel, achievable performance level for volumetric emissions of PCDD/PCDF from fossil fuel-fired utility and industrial boilers will usually be well below 0.1 ng I-TEQ/Nm^3. (Oxygen content 6% for solid fuels; 3% for liquid fuels).

Annex I. Emission factors[a] for PCDD/PCDF from controlled bituminous and sub-bituminous coal combustion (TEQ ng/kg[b])

Congener	**Flue gas desulphurization spray dryer absorber and fabric filter**[c]	**Electrostatic precipitator or fabric filter**[d]
2,3,7,8-TCDD	n.d.	0.0072
Total TCDD	0.197	0.046
Total PeCDD	0.353	0.022
Total HxCDD	1.50	0.014
Total HpCDD	5.00	0.042
Total OCDD	14.4	0.208
Total PCDD[e]	**21.4**	**0.333**
2,3,7,8-TCDF	n.d.	0.026
Total TCDF	1.25	0.202
Total PeCDF	2.42	0.177
Total HxCDF	6.35	0.096
Total HpCDF	22.0	0.038
Total OCDF	68.5	0.033
Total PCDF[e]	**101**	**0.545**
TOTAL PCDD/PCDF	**122**	**0.880**

n.d. Not determined.

a. EPA (1998) data converted from lb/ton coal combusted to ng/kg.

b. Emission factor should be applied to coal feed, as fired. Emissions are ng of pollutant per kg of coal combusted.

c. Factors apply to boilers equipped with both flue gas desulphurization spray dryer absorber and fabric filter. SCCs = pulverized coal-fired, dry bottom boilers, 1-01-002-02/22, 1-02-002-02/22, and 1-03-002-06/22.

d. Factors apply to boilers equipped with electrostatic precipitator or fabric filter. SCCs = pulverized coal-fired, dry bottom boilers, 1-01-002-02/22, 1-02-002-02/22, and 1-03-002-06/22; and cyclone boilers, 1-01-002-03/23, 1-02-002-03/23, and 1-03-002-03/23.

e. Total PCDD is the sum of total TCDD through total OCDD. Total PCDF is the sum of total TCDF through total OCDF.

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Part III Source category (e):
Firing installations for wood and other biomass fuels

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VI.E Firing installations for wood and other biomass fuels

Summary

The main purpose of firing installations for wood and other biomass fuels is energy conversion. Large-scale installations for firing wood and other biomass fuels mainly use fluidized bed combustion and grate furnaces. Technologies for small-scale plants include underfeed furnaces and cyclone suspension furnaces. Recovery boilers in the pulp and paper industry apply specific combustion conditions. Technology selection is related to fuel properties and required thermal capacity.

Chemicals listed in Annex C of the Stockholm Convention can result from the firing of wood and other biomass fuels, particularly in the case of fuel contamination. For biomass-fired plants, particularly wood-fired installations, emission levels associated with best available techniques are generally below 0.1 ng I-TEQ/Nm^3. Among the primary measures, control of fuel quality is a key issue (including exclusion of treated wood). Control measures for non-contaminated biomass include optimized combustion techniques and dust removal. Straw combustion increases fouling of surfaces and requires combustion techniques that are not sensitive to the slagging of ashes.

Combustion of contaminated biomass, such as wood waste, should be avoided in these installations. Fly ash (especially the finest fraction) from biomass combustion has to be landfilled due to its high heavy metal content. In many countries (including in the European Union), wood treated with chlorinated compounds or heavy metals is regarded as waste and falls within the scope of waste incineration directives or regulations.

Other environmental benefits that accrue from applying best available techniques and best environmental practices include resource conservation and avoidance of carbon dioxide emissions originating from fossil fuels (in the case of substitution).

1. Introduction

At present around 12% of the global energy requirement is generated by combustion of biomass fuels, which vary from wood and wood waste, materials from agricultural crops and black liquor in pulp mills. Table 1 shows some of the types of materials used. A wide variety of appliances are used to convert this biomass into useful energy. In developing countries, around 35% of the energy used originates from biomass, but most of this is for non-commercial use in traditional applications such as cooking (see section VI.C of these guidelines). In a country such as Nepal, over 90% of the primary energy is produced from traditional biomass fuels, mainly forest timbers.

This section addresses the best available techniques and best environmental practices for large-scale applications in, for example, industry, power generation and district heating which combust biomass fuels as a source of energy.

Contaminated wood and other contaminated biomass can result from many anthropogenic activities, particularly wood processing industries (e.g. building materials, furniture, packing materials, toys, shipbuilding and general construction). The wood/biomass waste may contain paints, coatings, pesticides, preservatives, antifouling agents and many other contaminants. These materials can enhance the formation of PCDD/PCDF during combustion. As such, their use in firing installations for energy conversion should be avoided and they should only be burnt in dedicated hazardous waste incinerators. For further information refer to section V.A of these guidelines.

Table 1. Types of biomass fuels used

Wood: sawdust, bark, chips, wood shavings pellets
Timber and logs
Straw
Citrus pellets
Coconut husks
Nut husks (e.g. almonds, peanuts)
Coffee seed husks
Rice husks
Peat
Sugar cane bagasse
Animal dung
Black liquor in pulp mills

In industrialized countries, the total contribution of biomass to the primary energy mix is only 3%, but this amount is expected to increase as more countries use biomass fuels to reduce greenhouse gas emissions instead of burning fossil fuels. This mainly involves the combustion of commercial biomass fuels in modern devices (e.g. woodchip-fired co-generation plants for heat and power). Other applications are domestic space heating and cooking, industrial heat supply, and large-scale power generation in coal-fired plants (IEA Bioenergy 2004).

2. Biomass combustion technologies

2.1 Technology selection and furnace types

For technology selection the total heat input and the wood fuel quantity are of major importance. For large-scale plants, fluidized bed combustion and grate furnaces are most suitable. Technologies for small-scale plants include underfeed furnaces and cyclone suspension furnaces. Table 2 shows typical thermal capacities and required fuel properties for different types of wood combustion techniques.

Table 2. Types of biomass furnaces with typical applications and fuels

Application	Type	Typical size range[a]	Fuels	Ash	Water content
Manual	Log wood boilers	5 kW–50 kW	Log wood, sticky wood residues	< 2	5–30
Automatic	Understoker furnaces	20 kW–2.5 MW	Woodchips, wood residues	< 2	5–50
	Moving grate furnaces	150 kW–15 MW	All wood fuels and most biomass	< 50	5–60
	Pre-oven with grate	20 kW–1.5 MW	Dry wood (residues)	< 5	5–35
	Understoker with rotating grate	2 MW–5 MW	Woodchips, high water content	< 50	40–65
	Cigar burner	3 MW–5 MW	Straw bales	< 5	20
	Whole bale furnaces	3 MW–5 MW	Whole bales	< 5	20
	Straw furnaces	100 kW–5 MW	Straw bales with bale cutter	< 5	20
	Stationary fluidized bed	5 MW–15 MW	Various biomass d < 10 mm	< 50	5–60
	Circulating fluidized bed	15 MW–100 MW	Various biomass d < 10 mm	< 50	5–60
	Dust combustor, entrained flow	5 MW–10 MW	Various biomass d < 5 mm	< 5	< 20
Co-firing[b]	Stationary fluidized bed	Total 50 MW–150 MW	Various biomass d < 10 mm	< 50	5–60
	Circulating fluidized bed	Total 100 MW–300 MW	Various biomass d < 10 mm	< 50	5–60
	Cigar burner	Straw 5 MW–20 MW	Straw bales	< 5	20
	Dust combustor in coal boilers	Total 100 MW–1 GW	Various biomass d < 2–5 mm	< 5	< 20

a. kW = kilowatt; MW = megawatt; GW = gigawatt.

b. Biomass covers typically less than 10% of the total fuel input.

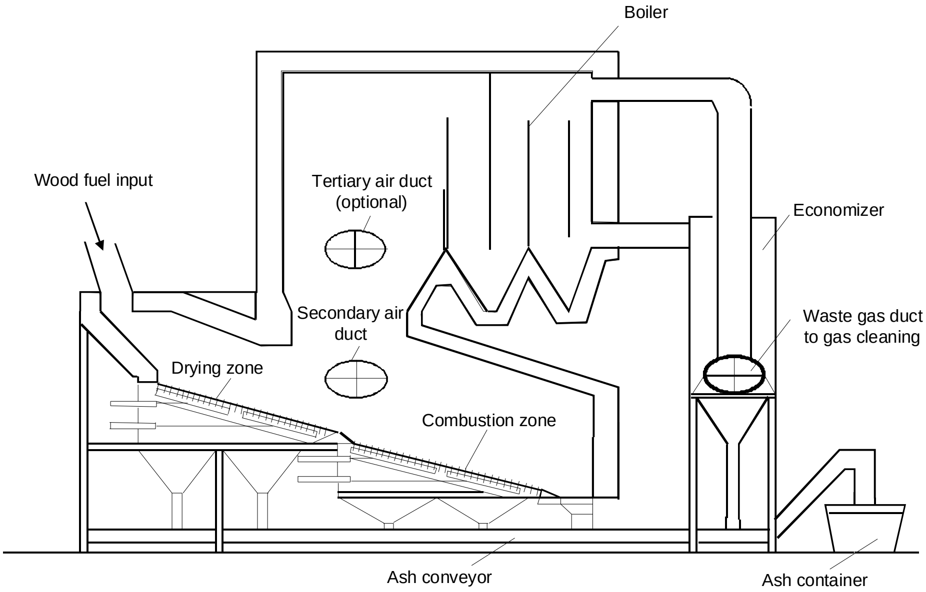
Source: Nussbaumer 2003.

Typical biomass based on wood, has an ash content below 5%; higher ash contents can be attributed to other biomass such as sewage sludge. The disposal of the ash content is an important issue, as it may contain unintentionally produced persistent organic pollutants and other toxic substances depending on the source material burnt (for further information, refer to section III.C, iv, subsection 2.1 of these guidelines).

2.2 Grate furnaces

Grate furnace systems are today the most common combustion technology used for wood wastes and wood residues. According to the technique, the wood fuel is moved through the combustion chamber using stationary sloping grates, travelling grates, vibrating grates (Figure 1) or moving grates. Grate firing systems are suitable for all types of wood residues and wood waste with particle sizes between 20 and 300 mm. However, fine particles, as pulverized wood, may be injected through additional burner lances. A major influence on the combustion efficiency, both for travelling grates and vibrating grates, is the fuel and air guidance. As regards steam generation, the furnace design of grate firing systems offers various options for primary emission reduction, including staged combustion and flue gas recirculation. The investment for grate firing systems depends considerably on the grate technology and flue gas cleaning technology used. Compared to fluidized bed combustion plants, especially for lower capacities, the specific investment relative to the total heat input is considerably lower (CSTB 2000).

Figure 1. General scheme of a vibrating grate furnace



2.3 Fluidized bed combustion

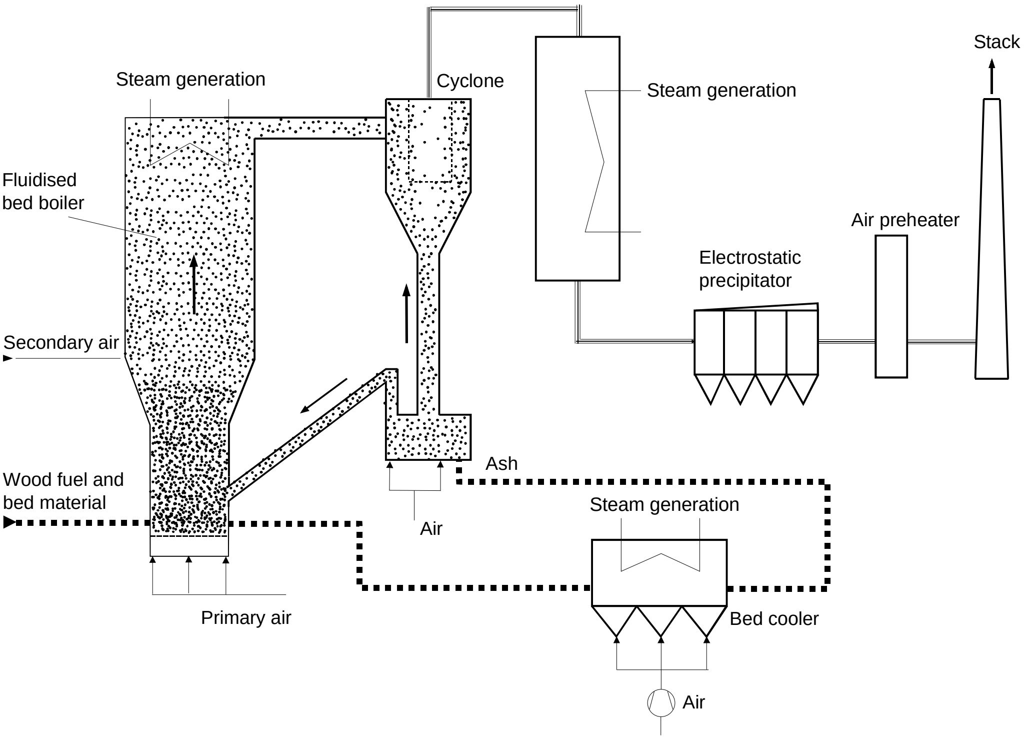
Fluidized bed combustion is utilized for various types of solid fuels. In a typical fluidized bed combustion unit, the solid fuel is kept fluidized by injected air together with an inert bed material mainly consisting of limestone or sand and the fuel ash. Two basic fluidized bed combustion technologies are primarily used for wood combustion. These are atmospheric bubbling fluidized bed combustion and atmospheric circulating fluidized bed combustion (Figure 2). Fluidized bed combustion is suitable for even lowest fuel qualities and for a great variety of fuels. For wood combustion, nearly all types of wood residues and wood waste can be used. Water contents up to 60% are possible. Fluidized bed systems are adaptable even to low operation loads. A cycle between low and high loads is generally possible without support fuel and at a higher speed than other combustion technologies.

Chlorine-induced high-temperature corrosion can be suppressed by installing the last superheater unit in the bed. The low combustion temperature in fluidized bed systems, compared to many other combustion technologies, offers several operational advantages for emission control. The investment for fluidized bed combustion plants is mainly influenced by the technology used and the type of flue gas cleaning installed. Circulating fluidized bed combustion entails a considerably higher specific investment than bubbling fluidized bed combustion for plant sizes below 30 MWth (CSTB 2000).

2.4 Further combustion technologies for wood

Further combustion technologies for wood include underfeed stoker furnaces, cyclone suspension furnaces (muffle suspension furnaces), rotary furnaces, turbulent bottom furnaces, fan blower furnaces and dust burners. Underfeed furnaces or underfeed stoker furnaces are particularly suitable for the combustion of dry and not too coarse wood particles with a low ash content. This technique is used for total heat inputs up to 5 MW. Compared to normal grate furnaces the specific investment is generally lower. As cyclone suspension furnaces require a dust content of at least 50% their application is limited mainly to the wood processing industry. Dust burners are used for wood dust with a particle size of up to 1 mm. Applications of this burner type include woodchip dryers and the injection of wood dust in cement furnaces (CSTB 2000).

Figure 2. General scheme of furnace using circulating fluidized bed combustion



2.5 Energy conversion techniques

For energy conversion downstream of wood combustion furnaces, heat exchanger systems (boilers) and subsequent systems for combined heat and power production (e.g. steam turbines, steam engines) have to be distinguished. The type of boiler used depends on the heat transfer medium, the plant size and the energy quality required. Firetube boilers are used for hot water or steam production downstream of small-scale and medium-scale wood furnaces. Heat transfer only takes place by convection. Watertube boilers are used for large-scale and medium-scale wood waste combustion plants. The water to be evaporated flows through tubes surrounded by the hot flue gases. Heat transfer takes place predominantly by radiation. Compared to firetube boilers, considerably higher operating pressures are possible – up to 100 bar. Downstream of wood furnaces only heat or combined heat and power are generally produced. For this reason condensing power generation can be neglected. Nevertheless, combined heat and power plants may also need condensing capacities in case the heat generated is not used (CSTB 2000).

2.6 Co-combustion of (untreated) wood and wood-related biomass

Co-combustion means the burning of wood wastes and wood residues together with other waste materials or together with fossil fuels. The objective is to realize synergy effects between two combustion processes. Benefits include savings in operating costs through the use of cheaper secondary fuels, and the greater combustion efficiency of the combined process compared to the two processes operated separately. For wood waste and wood residues, relevant practices include co-combustion in cement furnaces, co-combustion in coal-fired power plants, co-gasification with fossil fuels and waste and co-incineration in waste incineration plants (CSTB 2000). For further information see sections V.A, V.B, and VI.D of these guidelines.

2.7 Wood gasification

Gasification of wood and wood waste is the conversion of solid and liquid residues derived from the thermochemical decomposition of the organic matter in the wood at high temperatures in a gaseous fuel by adding oxidizing reactants. The main objective of wood gasification is to transfer as much as possible of the chemical energy of the wood feedstock into a gaseous fraction (producer gas) consisting mainly of combustible gaseous products with a low molecular weight.

The gasification technique is in general related to the reactor type. The two basic gasification techniques available are fixed bed gasification and fluidized bed gasification. For wood gasification the utilization of fixed bed gasifiers is in general preferred for smaller total heat inputs below 5 MW. For larger capacities fluidized bed gasifiers are mainly used.

The energy content of the producer gas from gasification can be used either thermally for the firing of a boiler or for another thermal process (either separately or using co-combustion, for example in an existing utility boiler or in a cement furnace) or mechanically for power generation in gas engines or gas turbines. Further possibilities are the utilization of the producer gas for methanol synthesis or in fuel cells.

The system needed for producer gas cleaning is determined by the concentration of impurities and by the requirements of the gas utilization technique used. Depending on the gas utilization technique, gas cleaning is required to avoid erosion, corrosion and unwanted deposits, and to ensure fulfilment of emission limits. Two different gas cleaning concepts, cold (or wet) gas cleaning and hot gas cleaning, can be distinguished. Hot gas cleaning is considered advantageous for advanced highly efficient systems due to the higher achievable electrical and overall efficiencies and due to the non-generation of contaminated wastewater or condensate. Even though gasification can be seen as a proven and reliable technique, for all plants with electricity generation, either in gas turbines or gas motors, gas cleaning is still a crucial restriction. Problems associated with the gas cleaning process include process control, the cost of gasification residue disposal, and the high investment and operating costs of the gas cleaning unit itself (CSTB 2000).

2.8 Combustion of other biomass

Other biomass fuels include other solid biofuels, such as straw and crops, and liquid fuels, such as canola oil. Straw combustion increases fouling of surfaces and requires combustion techniques that are not sensitive to the slagging of ashes. Due to the greater input of mineral matter and chlorine compared to wood combustion, there is also an increase in emissions of dust, hydrogen chloride (HCl), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (LfU 2002). Exemplary results from emission tests are given in subsection 4 below.

2.9 Recovery boilers in the pulp and paper industry

The manufacture of pulp utilizes mechanical, thermomechanical, chemimechanical and chemical methods (see section V.C of these guidelines). In chemical pulping, the fibres are broken down chemically. Chemicals are used in a cooking process to enter the fibre lumen and dissolve lignin in the cell walls to gain access to the compound middle lamella. Lignin has to be removed from the lamella to free the fibres. The lignin and many other organic substances are thus put into solution. The chemicals used in sulphate (kraft) and sulphite pulping are recovered from this solution through combustion in boilers, which also allows for energy recovery.

Recovery boilers in sulphate (kraft) pulping operate in a first step under reducing conditions, leading to the formation of sodium sulphide. A molten residue consists of sodium sulphide and sodium carbonate. In the second and third steps of the combustion process, a staged supply of combustion air occurs in order to assure complete burnout. Here, collected odorous gases can be supplied.

Recovery boilers in sulphite pulping do not operate with staged combustion. The lye is burnt in oxidizing conditions with a low air excess.

2.10 Combustion of peat

Within the European Union, peat is a significant fuel (regarded as a fossil fuel) in Ireland and Finland. Combustion technologies for peat are similar to coal combustion (section VI.D of the present guidelines). Today, peat is mainly burnt in fluidized bed boilers (bubbling and circulating fluidized bed combustion). These boilers typically have a fuel input of less than 200 MW, and they produce either electricity, or electricity and heat to local industry or the district heating system. Peat-fired boilers are usually also designed to combust other low-calorific fuels and sometimes coal. Heavy oil is commonly used as an auxiliary start-up fuel.

Due to its characteristics, peat is applicable for co-firing with wood. Technically it would be more difficult to use only wood fuel in existing plants because of corrosion and fouling problems. The ability to burn peat also assures continuous fuel supply in areas where the availability of wood is insufficient for the fuel demand (European Commission 2006).

3. Emission control measures

3.1 Relevant primary and secondary measures

Reduction of PCDD/PCDF emissions includes the primary and secondary measures summarized in Table 3 (Baumbach and Zuberbühler 2002; CSTB 2000; LfU 2002).

Relevant primary measures are similar to those used in the waste incineration sector. In the case of untreated biomass, secondary measures are restricted to dust abatement. Smaller furnaces may use multicyclones to achieve dust concentrations in the cleaned flue gas of 100–150 mg/Nm^3. Fabric filters or electrostatic precipitators achieve dust concentrations in the range of < 5 to 25 mg/Nm^3 (see section III.C (iv) of the present guidelines for general guidance on flue gas cleaning).

Downstream of wood waste combustion, additional flue gas cleaning can be carried out with absorption or adsorption processes. Generally only adsorption processes are used, due to their lower costs. Dry sorbent injection (entrained flow reactor) has gained major importance downstream of wood combustion due to its technical simplicity and its low costs. A mixture of calciferous substance and activated carbon or lignite activated carbon (activated carbon produced from lignite) is generally used as an adsorption agent. Possible calciferous agents are limestone ($CaCO_3$), lime (CaO) and hydrated lime ($Ca(OH)_2$). While the calciferous agents remove sulphur dioxide (SO_2), hydrogen chloride (HCl) and hydrogen fluoride (HF), the various types of activated carbon minimize heavy metal emissions (mercury, cadmium and arsenic), PCDD/PCDF emissions and emissions of polycyclic aromatic hydrocarbons. A typical mixture used in an entrained flow reactor consists of 85–95% calciferous agent and 5–15% activated carbon. As a secondary measure for reduction of emissions of nitrogen oxides (NO_x), particularly downstream of large-scale wood waste combustion installations, selective non-catalytic reduction can be used, but selective catalytic reduction may also apply. The selective catalytic reduction has been applied to biomass fired fluidized bed combustors. One problem with this technique is the deactivation of the catalyst which is faster when firing biomass, compared with coal, especially in the case of grate furnaces and the case of straw.

Table 3. PCDD/PCDF emission control measures for biomass firing installations

Management options	Emission level (%)	Estimated costs	Management risks
Primary measures			
Control of fuel quality (e.g. calorific value, water content, contaminants)	Resulting emission level not quantified	Higher fuel price	High water content increases PCDD/PCDF formation
Optimized burnout (e.g. reduction of excess air)		No additional cost for new installations	
Sufficient residence time of flue gases in the hot zone of the furnace			

Management options	Emission level (%)	Estimated costs	Management risks
Secondary measures			
Efficient dust abatement	Medium efficiency		Filter temperature < 200° C
Dry sorbent injection Selective catalytic reduction	High efficiency	Additional investment:[a] selective catalytic reduction 110–180%	Disposal of used sorbents necessary, not common in combustion plants firing virgin biomass

a. Percentage related to investment for furnace, boiler and dust collector of wood combustion plants with 1^{-10} MW thermal capacity.

3.2 Fuel characteristics

Fuel quality plays a major role in PCDD/PCDF formation during biomass combustion. PCDD/PCDF are always formed during wood combustion via precursors such as phenols and lignin, or via de novo reactions in the presence of particulate carbon and chlorine. High emission levels can be expected from burning treated wood (wood waste). Wood residues (waste and industrial) often contain various types of contaminants (chromated copper arsenate, pentachlorophenol, creosote, adhesives, resins, paint and other surface coatings). Another major source of PCDD can be salt-laden wood waste burnt in power boilers at pulp and paper mills (Lavric, Konnov and De Ruyck 2004).

Combustion of contaminated wood, such as urban wood waste and demolition wood, should be strictly limited to installations with efficient emission control systems such as waste incineration plants (see section V.A of these guidelines) (Nussbaumer 2003).

The moisture content of biomass can be high. Therefore, dryers may be used prior to combustion. Steam dryers are considered to be safe, with low environmental impact. Another method is based on drying with flue gas, which is subsequently fed to the stack. In this case emissions of organic compounds such as waxes or aromatic compounds are possible (European Commission 2006).

4. Process outputs

4.1 Formation of PCDD and PCDF in combustion processes

The dominant reaction resulting in the formation of PCDD/PCDF in combustion processes is de novo synthesis. Section III.C (i) of these guidelines provides general information on PCDD/PCDF formation mechanisms. Specific considerations for biomass combustion are given below.

PCDD can be formed in the absence of organic chlorinated compounds. The presence of particulate carbon and a chlorine source is sufficient. Investigations at a stationary grate combustor have shown that the total amount of PCDD/PCDF and coplanar polychlorinated biphenyls (PCB) formed was proportional to the chlorine content of the combustion samples when the temperature of the combustion chamber was lower than 700° C. On the other hand, when the grate temperature of the combustion chamber was higher than 800° C, there was only slight formation of PCDD/PCDF and coplanar PCB, regardless of the chlorine content of the fuel (Yasuhara, Katami and Shibamoto 2003).

The better combustion conditions in larger facilities tend to have an influence on PCDD/PCDF concentration. Tests have shown that even when processing materials containing high halogen quantities, the concentrations remained below those obtained from small facilities using natural wood. When halogenated input materials were added, a very clear relationship between carbon monoxide (CO) and PCDD/PCDF concentrations was observed. The dominant influence of combustion quality on PCDD/PCDF emission concentrations could be seen from the increasing CO concentrations and simultaneously decreasing flue gas temperature (Lavric, Konnov and De Ruyck 2004).

4.2 Emissions of PCDD/PCDF

4.2.1 Combustion of wood or wood waste

The influence of fuel quality and combustion conditions on PCDD/PCDF emissions is illustrated in Table 4.

Table 4. PCDD/PCDF concentrations for different types of wood fuels

Type of wood	PCDD/PCDF min. ng I-TEQ/m³ (at 11% O_2)[a]	PCDD/PCDF max. ng I-TEQ/m³ (at 11% O_2)
Lump wood (natural)	0.02	0.13
Woodchips (natural)	0.004	0.88
Wood waste	0.03	18.0
Chlorine/heavy metal-free particle board	0.03	0.10
Particle board with PVC or ammonium chloride (NH_4Cl)	0.05	12.28
Particle board with pentachlorophenol	0.21	5.14

a. 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram). For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

Source: Nussbaumer 2004.

A comprehensive review of PCDD/PCDF test results from wood-fired installations can be found in Lavric, Konnov and De Ruyck 2004.

4.2.2 Combustion of other biomass

Launhardt and Thoma tested various herbaceous biofuels (straw, whole plant cereals and set-aside hay) and spruce wood for their potential to form PCDD/PCDF, polychlorinated phenols, polychlorinated benzenes and polycyclic aromatic hydrocarbons during combustion. The trials were conducted in an automatically charged multifuel furnace for domestic applications of 50 kW. Relatively uniform combustion conditions were indicated by the CO emission results. Flue gas and different ash fractions were analysed. The concentration of PCDD was in the range of 0.052–0.891 ng I-TEQ/Nm^3 at 13% O_2 (Table 5). All the emissions from wood were at a relatively low level. Increased emissions, between 10 and 25 times higher, of PCDD/PCDF, polychlorinated phenols and polychlorinated benzenes were detected when herbaceous fuels were used (Lavric, Konnov and De Ruyck 2004).

Table 5. PCDD/PCDF emissions from different types of biomass

Fuel type	PCDD/PCDF ng I-TEQ/m³
Wood (spruce)	0.052
Straw (wheat)	0.656
Hay	0.891
Triticale	0.052
Canola pellets	0.245

Source: LfU 2002.

PCDD/PCDF emission data for liquid biomass combustion are scarce. Tests at a canola oil motor for combined heat and power production (90 kW) showed PCDD/PCDF concentrations of 4–7 pg I-TEQ/m^3. PCB concentrations amounted to 40–81 ng/m^3 (LfU 2002).

4.2.3 Combustion of black liquor

Table 6 shows selected emission factors from kraft black liquor recovery boilers.

Table 6. PCDD/PCDF emissions from kraft black liquor recovery boilers

Fuel	Emission factor (I-TEQ)	Emission factor (WHO-TEQ)	Reference
Black liquor solids[a]	0.10–0.15 ng/kg	0.10–0.16 ng/kg	EPA 2000
	0.029–0.065 ng/kg	0.028–0.072 ng/kg	EPA 2000
	0.07 ng/kg		UNEP 2005

a. In general 1 kg black liquor (water content 70 %) corresponds to a flue gas volume of 5–8 m^3 (oxygen content between 5 and 8%).

4.2.4 Combustion of peat

In European Commission 2006, PCDD emissions are reported from an atmospheric fluidized bed boiler equipped with a fabric filter firing 50% peat and 50% bark. PCDD/PCDF emissions amounted to 0.008 ng I-TEQ/Nm^3 (dust emission level: 10 mg/Nm^3).

4.2.5 Other releases of PCDD/PCDF from biomass combustion

PCDD/PCDF are discharged with solid combustion residues such as bottom ashes and fly ash. In general, PCDD/PCDF concentrations increase with decreasing particle size (LfU 2002). Therefore, pollutant concentrations in fly ash tend to be higher than in bottom ash.

Pohlandt and Marutzky analysed furnace, boiler and fly ash. The samples were collected at different plants in the wood working industry, from a smoke house and from combustion of wood impregnated with inorganic wood preservative consisting of boron, chromium and copper in a two-stage laboratory furnace. They found that the fly ashes exhibited the highest levels of PCDD/PCDF. The concentrations of PCDD/PCDF in the ashes originating from the impregnated wood were higher than those of the ashes from the combustion of the diluted impregnated wood, but below those determined for the fly ash of industrial wood firing plants. The concentration of PCDD in the fly ash was higher than in the bottom ash. This observation was confirmed by Wunderli et al. and Yamamura et al. (Lavric, Konnov and De Ruyck 2004).

Particularly in the case of wood waste combustion, captured fly ash has to be disposed of in an environmentally sound manner (see section III.C (iv), paragraph 2.1 of the present guidelines).

The fly ash from straw combustion units should be disposed of to sanitary landfill, primarily due to its high content of cadmium. The bottom ash is normally brought back to the fields or used as a road construction material when certain requirements with regard to physical and chemical properties are met (European Commission 2006).

The finest fraction of fly ash has to be sent to landfills due to its high content of heavy metals and persistent organic pollutants. Used adsorbent also has to be landfilled.

5. Best available techniques and best environmental practices

5.1 Primary measures and process optimization to reduce PCDD/PCDF emissions

Best available techniques to reduce PCDD/PCDF emissions may include the following measures (Nussbaumer and Hasler 1998).

1. Prevention of illegal incineration of waste;
2. Combustion of contaminated wood, such as urban wood waste and demolition wood, should be strictly limited to installations with efficient emission control – it is preferable that this material is not used in boilers and is instead treated as waste;
3. Control of fuel quality (e.g. calorific value, water content, contaminants);
4. Optimized combustion technology: Improved burnout of gases and fly ash and reduction of dust content:

  - Optimize excess air ratio to < 1.5–2, though care must be taken as any changes made to the air ratio can also affect the amount of other emissions;
  - Good mixing quality of gas and air (high turbulence);
  - Sufficient residence time in the hot zone;
  - Minimal disturbance of the glow bed and homogeneous distribution of the primary air;
  - Optional integration of selective non-catalytic reduction for NO_x reduction;
5. Measures in the boiler:
   - Minimal residence time in the temperature range 180° and 500° C and minimal dust deposition ability;
6. Optimized plant operation:
   - Application of advanced combustion control technologies to ensure optimal burnout in practice;
   - Stationary operation, no on/off operation and prevention of rapid changes of heat and demand;
   - Cleaning of the hot zone of flue gases at regular intervals.

5.2 Secondary measures

Secondary control measures are pollution control techniques and include the following measures:

1. Optimized gas cleaning:
   - Rapid quench of combustion gases (< 200° C) before passing through filters in order to avoid the de novo reformation (or synthesis) window;
   - PCDD/PCDF separation in dust separators (electrostatic precipitators, fabric filters) in combination with sorbent injection (if necessary);
2. Optional destruction of PCDD/PCDF by catalytic oxidation, i.e., in combination with selective catalytic reduction for NO_x reduction.

6. Performance levels associated with best available techniques

For biomass-fired plants, particularly wood-fired installations, emission levels associated with best available techniques are generally below 0.1 ng I-TEQ/m^3.

7. Performance monitoring and reporting

PCDD/PCDF emissions should be monitored in accordance with international standard methods.

In order to ensure complete combustion, furnaces should be equipped with measuring instruments that continuously determine carbon monoxide emission mass concentrations.

In order to ensure the performance of emission control equipment, furnaces should be equipped with measuring instruments that continuously determine dust emission mass concentrations qualitatively and quantitatively (according to the requirements of different plant sizes). For further information on monitoring see Section III (vi) of these guidelines.

In addition, quality control procedures should be implemented with regard to fuel composition.

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Part III Source category (f): Specific chemical production processes releasing chemicals listed in Annex C

Section VI. F Specific chemical production processes releasing chemicals listed in Annex C

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VI.F Specific chemical production processes releasing chemicals listed in Annex C

Summary

This section focuses on processes for the manufacture of industrial chemicals that could theoretically give rise to persistent organic pollutants (particularly those chemicals listed in Annex C of the Stockholm Convention). Most of the processes described share common steps, including chlorination of organic or inorganic raw materials, purification of the products, separation of product streams (usually by distillation), destruction of high-molecular-weight side products and recycle or sale of hydrogen chloride. Efficient separation and destruction of chlorinated organic side products, which may include persistent organic pollutants, is key to best available techniques applicable to these processes, as is the associated guidance for any incorporated incineration processes. For certain products, modernized manufacturing processes that reduce formation of persistent organic pollutants are also presented. A range of performance standards associated with best available techniques are provided relevant to the individual processes

1. Process description

1.1 Introduction to organic chemical processes

This section focuses on processes for the manufacture of industrial chemicals that could theoretically give rise to chemicals listed in Annex C of the Stockholm Convention. Chlorination processes are used in the synthesis of hundreds of industrial and specialty chemicals (Wiley Interscience 2000; World Chlorine Council 2002). Chlorine chemistry may also be used in processes where the final product contains no chlorine atoms. Under modern conditions of operation, however, these processes are typically not a major source of emission of chemicals listed in Annex C (UNEP 2003; EPA 2001).

Many of the general principles developed here – including more efficient use of raw materials and minimization of by-products and waste – are principles that support both better economic and environmental performance, consistent with modern principles of what is called green chemistry and engineering. They can also be applied to the much larger number of manufacturing processes used to produce a wide range of fine (low-volume speciality) chemicals, including pesticides and pharmaceuticals. Production of such chemicals can depend on the unique properties of chlorine that make it a valuable synthetic tool.

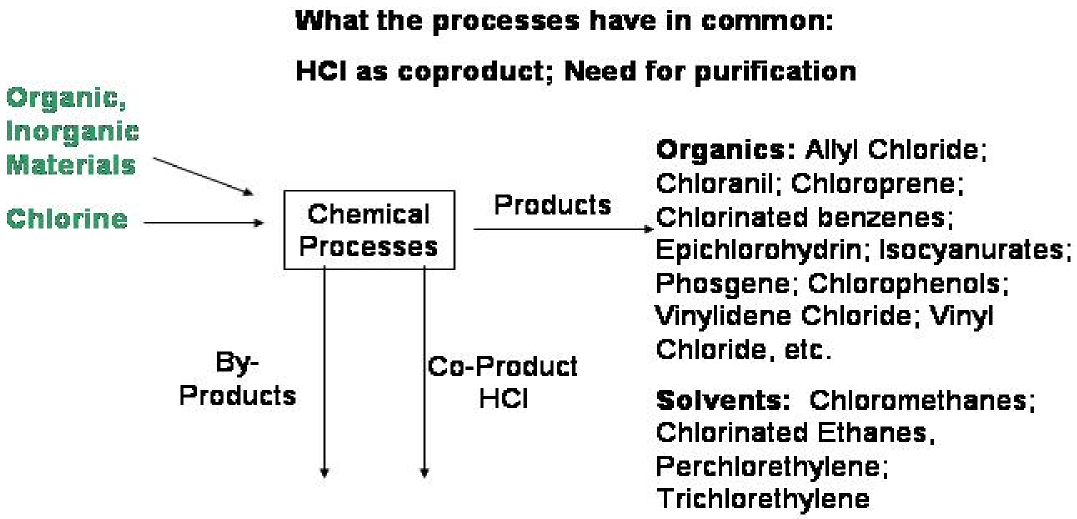
A list of some of the processes leading to industrial chemicals is included in annex I to this section (Wiley Interscience 2000). It is beyond the scope of this section to attempt to define best available techniques and best environmental practices for each of these processes individually; rather, the processes will be examined for what they have in common and how those common practices can be addressed to reduce the formation, and particularly the release, of chemicals listed in Annex C of the Stockholm Convention.

Most of the processes involve a hydrocarbon, saturated or unsaturated, treated with elemental chlorine and in most processes also a catalyst. Reactions can be electrophilic additions to olefins, chlorination of aromatics or homolytic cleavage of carbon-hydrogen bonds with subsequent formation of the aliphatic chloride. In many cases chlorine atoms are present in the final product; on the other hand, in some processes (addition of an alcohol or amine to phosgene to produce, for example, polycarbonate and polyurethane plastics) no chlorine atoms are present in the final product. In addition, most of the processes involve generation of hydrogen chloride (HCl) as a co-product, via dehydrohalogenation or free radical reaction of chlorine with aliphatic hydrogen (Figures 1 and 2).

Crude products of these reactions vary in overall yield and purity, and as with virtually all industrial chemical processes, purification of the final product is required prior to sale or further internal use. Purification can involve separation of a mixture of saleable products – in many cases a spectrum of useful products results from a single reaction treatment – or separation of saleable products from the inevitable formation of high-molecular-weight by-products. For most organics and some inorganics that purification step involves distillation.

Generally, high-molecular-weight by-products are not saleable as themselves. In some cases they are thermally oxidized, with HCl, carbon monoxide (CO) and carbon dioxide (CO_2) as products of this oxidation. HCl is recovered and reused as an integral part of the process. In some cases they are viewed as wastes to be destroyed, usually by hazardous waste combustion, though HCl recycling is common.

Figure 1. General process overview



1.2 Co-product hydrogen chloride

Hydrogen chloride (HCl) is handled in one or more of the following ways. It can simply be neutralized and discharged as salt (sodium chloride). However, in some processes HCl can constitute a large amount of the effective use of input chlorine, so neutralization and discharge carries with it a large opportunity cost in the loss of potential raw material.

HCl can be recovered, hydrated and then sold as the commercial product muriatic (hydrochloric) acid or used for pH adjustment in chloralkali cells. Thus, there is some recycling of HCl electrolytically to chlorine. In the United States of America, muriatic acid, arising as a by-product of vinyl chloride production, has been analysed for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) and found to contain about 20 pg I-TEQ/L range (0.004 g I-TEQ/yr for United States commercial production) (Carroll et al. 1997).[1]

HCl can also be dried, oxidized catalytically and, in the presence of organic raw material, reacted as elemental chlorine to generate more of the desired product. The process by which this is accomplished is called oxychlorination and constitutes a means of in-process recovery of a valuable chlorine feedstock.

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[1] For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

1.3 Direct chlorination

Free radical addition of chlorine to aliphatic hydrocarbons, typically methane, and direct electrophilic addition of a halogen to an alkene are well known from basic organic chemistry. As utilized in industry, the former is catalysed by light and the latter is typically a low-temperature operation catalysed by ferric chloride ($FeCl_3$) (OxyVinyls website). In the former, a free radical mechanism is desired. On the other hand, in the latter, unproductive side reactions result from free radicals, which can be inhibited with low concentrations of oxygen.

There is little if any potential for formation of by-product persistent organic pollutants in direct chlorination processes of pure aliphatic hydrocarbons. Aromatic feedstocks can also be chlorinated directly under mediation of a Lewis acid catalyst. The presence of aromatic chlorides as products of the process leaves open the possibility for generation of persistent organic pollutants under some conditions.

1.4 Oxychlorination

In oxychlorination, an organic such as ethylene reacts with dry HCl and either air or pure oxygen in a heterogeneous catalytic reaction (Figure 3). An example is the reaction involving HCl, oxygen and ethylene to form ethylene dichloride and water.

$$C_2H_4 + 2HCl + \frac{1}{2}O_2 \longrightarrow C_2H_4Cl_2 + H_2O$$

While there are many different commercial oxychlorination processes, in each case the reaction is carried out in the vapour phase over a modified Deacon catalyst. Unlike the Deacon process (which uses air or oxygen to oxidize HCl to chlorine (Cl_2) and H_2O under heat and catalysis) oxychlorination of ethylene occurs readily at temperatures well below those required for HCl oxidation per se. The catalyst typically contains cupric chloride ($CuCl_2$) as the primary active ingredient, impregnated on a porous support such as alumina, and may also contain numerous other additives.

The oxychlorination reaction generates heat and thus requires cooling for temperature control, which is essential for efficient production of ethylene dichloride. While there is an effective minimum temperature for the reactions, excessively high reactor temperatures lead to more by-products, mainly through increased ethylene oxidation to carbon oxides and increased ethylene dichloride cracking. Cracking of ethylene dichloride yields vinyl chloride monomer and subsequent oxychlorination and cracking steps can lead progressively to higher-molecular-weight by-products with higher levels of chlorine substitution. Excessive temperatures (> 300° C) can also deactivate the catalyst through increased sublimation of $CuCl_2$. There is a strong commercial incentive to avoid those reaction conditions (overheating) that have the potential to lead to the production of polychlorinated by-products.

There are two types of catalyst systems used in oxychlorination: fixed bed and fluid bed. Both can be considered best available techniques (European Commission 2003).

Use of certain feedstocks in an oxychlorination process may lead to higher formation of persistent organic pollutants. For example, oxychlorination of heavy ends on a vinyl chloride plant can give considerable yields of PCDD/PCDF (UK Environment Agency 1997).

Figure 2. C_1 and C_2 processes

(Wiley Interscience 2000)

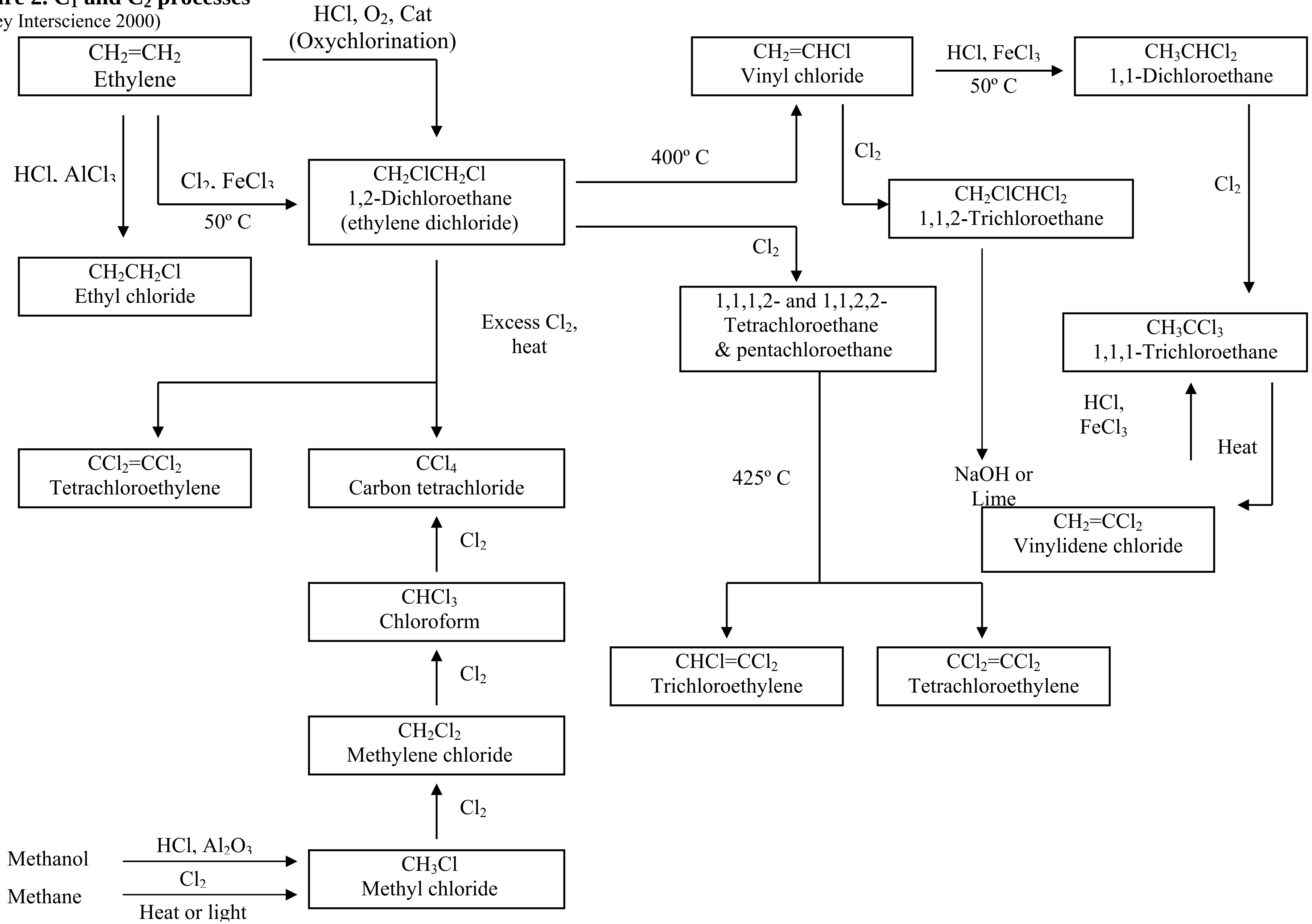
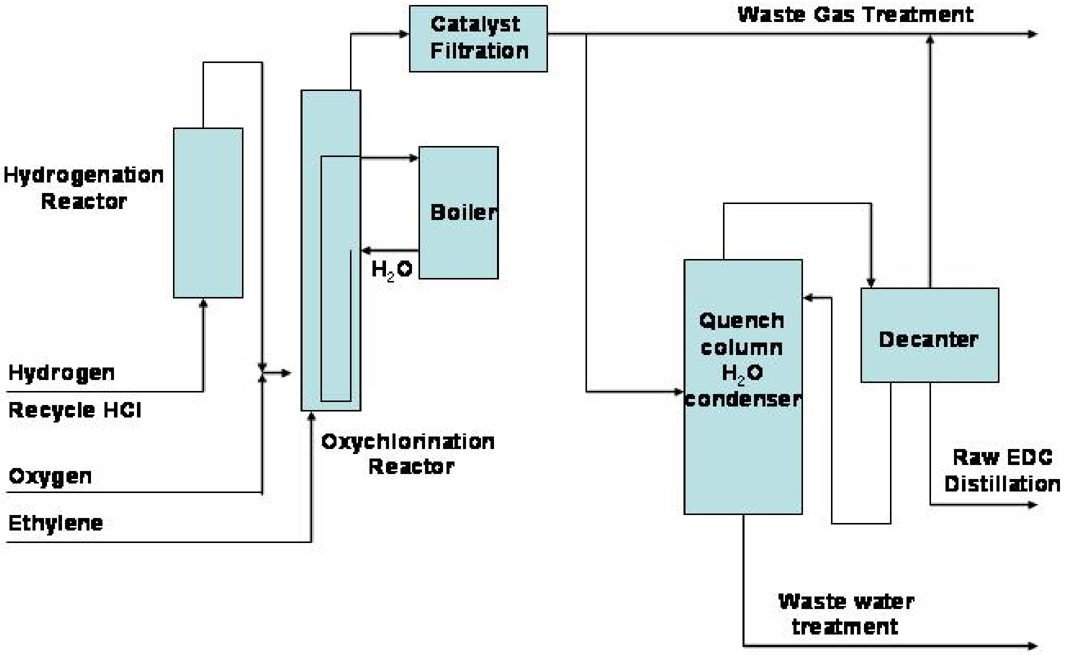


Figure 3. Oxychlorination flow diagram



Source: Vinnolit website.

1.4.1 Fixed bed oxychlorination

Fixed bed reactors resemble multitube heat exchangers, with the catalyst packed in vertical tubes held in a tubesheet at top and bottom. Uniform packing of the catalyst within the tubes is important to ensure uniform pressure drop, flow and residence time through each tube. Reaction heat is removed by generating steam on the shell side of the reactor, or by flowing some other heat transfer fluid through it.

Temperature control in these reactions is important. The tendency to develop hot spots in a fixed bed can be minimized by packing the reactor tubes with active catalyst and inert diluent mixtures in proportions that vary along the length of the tubes, so that there is low catalyst activity at the inlet, but the activity steadily increases to a maximum at the outlet.

Alternatively, tubes can be packed with catalyst formulated to have an activity gradient along the length of the tubes. Multiple reactors in series can also be used in fixed bed oxychlorination, providing a similar activity gradient. Using pure oxygen as feed instead of air permits lower temperature and therefore lowers the formation of chlorinated by-products; however, this must be balanced against the cost of energy expended in producing pure oxygen. Staging the air or oxygen feed and grading the catalyst activity flatten the temperature profile and allow improved temperature control (OxyVinyls website).

1.4.2 Fluid bed oxychlorination

Fluid bed oxychlorination reactors are typically vertical cylindrical vessels equipped with a support grid and feed sparger system designed to provide good fluidization and feed distribution. They contain internal cooling coils for heat removal, and use either internal or external cyclones to minimize catalyst carry-over. Fluidization of the catalyst assures intimate contact between feed and product vapours, catalyst and heat transfer surfaces, and results in a uniform temperature within the reactor.

Reaction heat is removed by generating steam within the cooling coils or by passing some other heat transfer medium through them.

Operating temperature of 220°–245° C and gauge pressure of 150–500 kPa (22–73 psig) are typical for oxychlorination with a fluid bed reactor. Fixed bed oxychlorination generally operates at higher temperatures (230°–300° C) and gauge pressures of 150–1,400 kPa (22–203 psig). Chlorinated by-products of ethylene oxychlorination typically include 1,1,2-trichloroethane, chloroform, carbon tetrachloride, ethyl chloride, chloral, 2-chloroethanol, all of the chloroethylene congeners, and higher-boiling compounds (OxyVinyls website).

1.5 Main product isolation

Another common facet of these processes is the need to purify products that will either be sold or used in subsequent process steps. In virtually all cases, organic reaction products will be distilled. Fractional distillation separates streams of desired products and also separates desired products from unwanted high-molecular-weight materials called heavy ends or tars.

In the European Union the Integrated Pollution Prevention and Control (IPPC) Directive requires the use of best available techniques in generating a plant permit. To facilitate this, best available techniques reference documents (BREFs) are produced under the Directive by the European IPPC Bureau. Several of these are relevant to the application of best available techniques to processes using chlorination: for example, the BREF relating to large volume organic chemical processes, produced under the IPPC Directive, contains discussion of distillation (European Commission 2003).

Distillation is a standard engineering unit operation. It is based on sequential vaporization and condensation of liquid in a column, which typically includes packing or trays in order to maximize its internal surface area. Vapour that reaches the top of the column is enriched in the lowest-boiling material present in the distillation mixture.

Design and operation of distillation units are well understood, both in separations theory and in practice. For non-azeotroping materials with widely separated boiling points – for example, vinyl chloride and PCDD/PCDF – virtually complete separations can be accomplished in a well-designed and operated column (ChEResources website).

Desired materials are isolated and transported as liquids. For materials with boiling points above ambient temperature (e.g. ethylene dichloride) closed but not pressurized containers are used. For materials with boiling point below ambient temperature (e.g. vinyl chloride, chlorine) pressurized containers are used.

Some product isolations will not lend themselves to distillation. In principle, similarly useful and rigorous techniques (e.g. recrystallization) may be devised for specific materials. To the extent that those practices can demonstrate a similar result, such as isolation of by-products into a separate stream, these may, in some circumstances, also qualify as best available techniques.

1.6 By-product destruction

Undesired materials, including heavy ends, are usually destroyed in thermal processes, with or without oxygen. Figure 4 shows a prototypical heavy ends destruction train with HCl recovery.

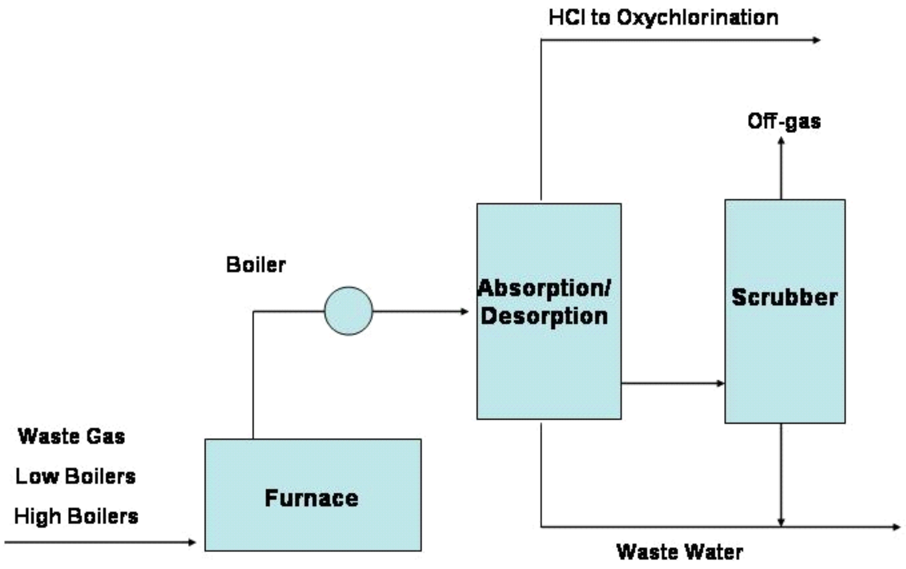
Environmentally sound management of by-product and waste streams from chemical operations is critical to preventing the release of chemicals listed in Annex C into the environment. This management includes both effective and high-performance destruction of waste within a process and effective end-of-pipe methods to prevent release. Such destruction and end-of-pipe systems for the chemical and other industries are usually well defined by regulation, and should be monitored closely by operators and authorities.

Air, water and solid emissions from these processes can be analysed for chemicals listed in Annex C and treated appropriately. Further information is available in the European Union BREFs on large-volume organic chemical processes and on treatment of water and gas outputs from the chemical sector. A basic review of the technology of air, water and solids treatment is found in the cross-cutting considerations section (III.C) of the present guidelines.

In general, best available techniques for airstreams can involve recovery and recycling of HCl, combustion of trace volatiles, scrubbing of incinerator output streams with water, alkaline solutions or dry alkali, and addition of activated carbon and baghouses for removal of particulate. These may be used alone or in combination. Treatment of water streams can involve stripping and recovery (condensation or absorption) of volatile materials from water.

Subsequent biological purification of water streams with removal of solids is done in a dedicated water treatment system. Best available techniques for both streams will be considered in the granting of permits for facilities combusting heavy ends.

Figure 4. By-product destruction



1.7 Summary: What organic processes have in common

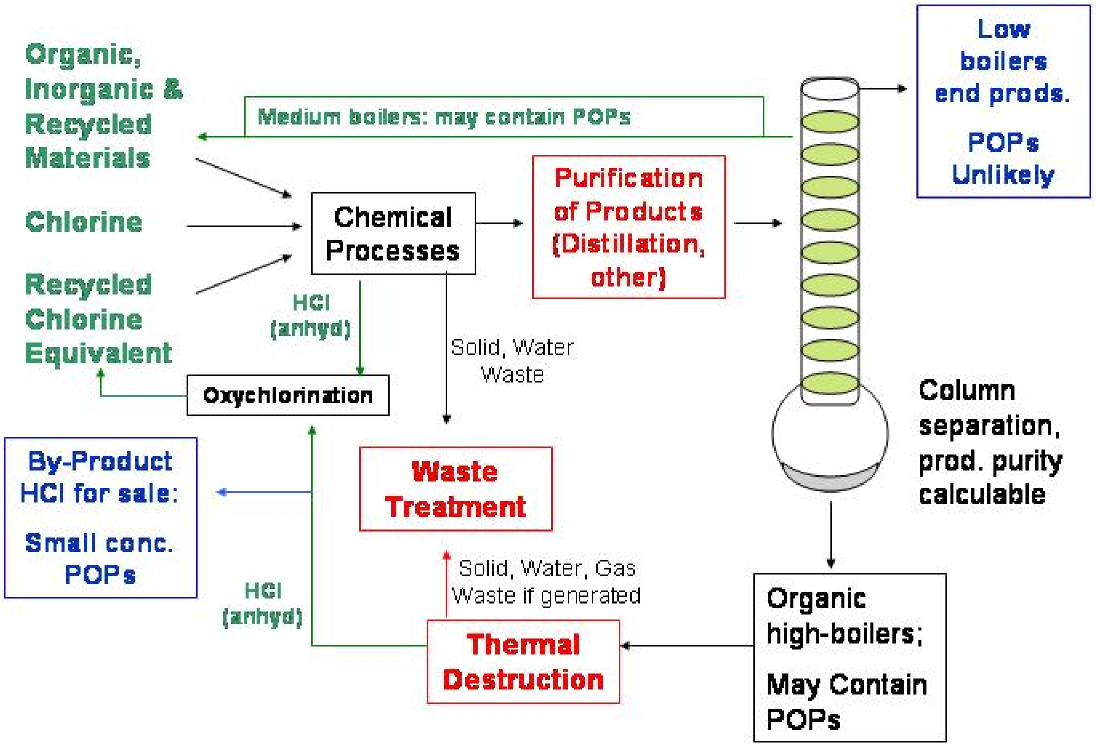
Figure 5 summarizes generically many of the processes described, including chlorination of organic or inorganic raw materials, purification of the products, separation of streams for recycle (HCl, medium boilers), destruction of by-products (organic high boilers) and sale of products (low boilers, HCl, end products).

The United States Environmental Protection Agency notes: “Four major mechanisms have been postulated for the formation of halogenated dioxins and furans in the manufacture of halogenated organic chemicals: (1) direct halogenation of dioxins or furans…; (2) reaction of an ortho halogen with a phenate; (3) loss of the halogen (e.g., chlorine or bromine) from a halogenated phenate to form halogenated furans…; and (4) reactions between ortho- and meta-substituted halogens” (EPA 1997).

Mechanism (1) assumes a preformed PCDD or PCDF ring structure, possibly unhalogenated. Mechanisms 2–4 describe reactions of aromatic halides or halogenated phenols. A number of factors influence the amount of PCDD and PCDF that may be formed in a given manufacturing process, including temperature, pH, catalyst, and reaction kinetics (EPA 1997). The influence of these factors may be modulated by the specific chemistry: for example, the presence of aromatic or aliphatic organic materials.

Similarly, Fiedler et al. (2000) note that the likelihood of PCDD/PCDF generation in chemical processes to manufacture chlorine-containing materials generally decreases in the order chlorophenols > chlorobenzenes > aliphatic chlorides > inorganic chlorides. This may also be modulated by other reaction conditions. Total production will be affected both by propensity (ease) of formation and volume throughput so a large-volume process such as chlorine production may give a larger mass flow than a high-concentration/higher-yielding but smaller-volume process.

Figure 5. Block diagram of generic organic process



1.8 Inorganic chemical processes

Chlorine is used in generating inorganics whether it remains in the final product (NaOCl, ClO_2, $FeCl_3$, $AlCl_3$, $ZnCl_2$, etc.) or is simply used in the process (TiO_2, Si). These inorganic compounds may be used either stoichiometrically (NaOCl, ClO_2) or as catalysts ($FeCl_3$, $AlCl_3$, $ZnCl_2$, etc.). There are two inorganic chemical manufacturing processes identified with some production of chemicals listed in Annex C: chloride process manufacture of titanium dioxide (TiO_2) by certain manufacturers and production of anhydrous magnesium chloride ($MgCl_2$), an intermediate in the manufacture of magnesium metal. Other metal carbochlorination processes for purification of ore may involve similar conditions.

1.8.1 Chlorine and sodium/potassium hydroxide

Chlorine and either sodium or potassium hydroxide are produced by electrolysis of aqueous solutions of sodium or potassium chloride respectively. There are numerous technologies associated with this process, and while a full treatment of the process is beyond the scope of this guidance, an overview is provided in many general references (European Commission 2001, Appendix 1; Wiley Interscience 2000).

It is known anecdotally, and confirmed by reports of releases of persistent organic pollutants from modern chloralkali facilities, that there is the possibility of dioxin and furan generation at some point in the chloralkali process.

The use of graphite electrodes in this process is known to be a source of chemicals listed in Annex C. This process is generally considered obsolete in modern facilities (see subparagraph 4.2.2 below). With respect to other sources in the process, full mechanistic understanding of formation is lacking; however, it is believed that contact of elemental chlorine with preformed furan-like structures in organic gaskets and seals could be a source (see paragraph 2.2). Even with modern processes PCDD/PCDF have been measured in releases and are formed in the process.

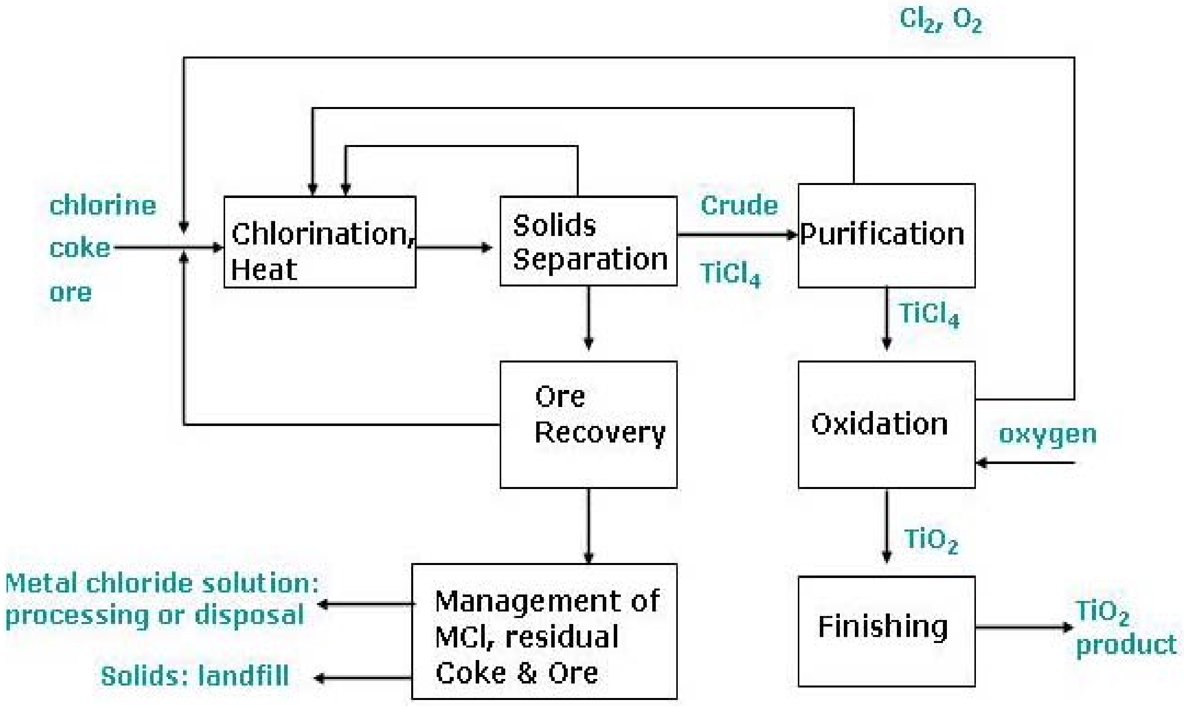
1.8.2 Titanium dioxide

There are two processes for manufacture of titanium dioxide (TiO_2): the chloride process and the sulphate process. They present an interesting case study: the chloride process produces much less waste but can be a source of persistent organic pollutants. The sulphate process involves much more waste in other categories, which is a problem as titanium dioxide is a high-volume chemical.

The production of titanium dioxide on the basis of the sulphate process gives rise to high amounts of contaminated spent acids of different concentrations. In the past those spent acids could not recycled and used in other production processes. Methods for reuse and recycling of spent acids have been developed during the last decades and are currently standard operation for titanium dioxide production in industrialized countries.

The chloride process has grown in use over the past thirty years as an alternative for the sulphate route with its high amounts of spent acids. The chlorine route is a relatively compact process, giving the opportunity to recycle process materials directly without side products and with better product properties and considerably lower generation of waste. TiO_2 ore, such as rutile or ilmenite – containing other metal oxides – is chlorinated under high temperature to produce titanium tetrachloride ($TiCl_4$), a stable, distillable liquid. Other metal halides are removed after cooling. $TiCl_4$ is then purified and oxidized with O_2, liberating chlorine, which is recycled in the process. This oxidation process is thermodynamically favoured at temperatures above 600° C. A generalized overview of the chloride process is shown in Figure 6 and a more complete description of the competing sulphate process is found in paragraph 3.1 below.

Figure 6. Chloride process for manufacturing titanium dioxide



1.8.3 Anhydrous magnesium chloride

Magnesium chloride ($MgCl_2$) can be produced by the reaction of magnesium oxide (MgO) and coke with elemental chlorine at 700–800° C. Details of this process and releases from it are presented in section VI.B (iii) of the present guidelines (magnesium production).

2. Potential sources of chemicals listed in Annex C

Central to formation of the basic structure of PCDD, PCDF, polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) is the presence or generation of aromatic materials. Those materials must, at some point, be chlorinated. UNEP 2003 notes that for chemical processes, generation of PCDD/PCDF may be favoured in processes that utilize, alone or together, elemental chlorine, elevated temperature, alkaline conditions and a source of free radicals.

For formation of PCDD/PCDF a source of oxygen or non-chlorinated dioxin/furan or related structures must be present. While it is difficult to imagine situations where PCDD/PCDF are generated without any possibility of generating PCB or HCB, PCDD/PCDF are favoured as by-products in processes where chlorinated phenols are a substrate or phenols are reacted with chlorine, especially if treated with alkali (see subparagraphs 4.2.3, 4.2.4 and 4.2.5 below). Combustion is a likely source of all of these materials; formation of by-products is dependent upon the exact technology employed in combustion processes, especially those involving uncontrolled combustion. Carbochlorination reactions (e.g. MgO to $MgCl_2$) may also be a source (see paragraph 1.8 above).

HCB may be formed preferentially in similar kinds of reactions to those named above if oxygen or oxygenated materials are excluded. Electrolysis reactions with graphite electrodes fall into this category. A similar result may be obtained where chlorinated aliphatic rings are present and dehydrohalogenation can occur, as in reactions with hexachlorocyclohexane as a starting material.

In some cases, the source of aromatic carbon may be adventitious. Benzene as an impurity in raw materials of almost any chlorination reaction could result in HCB as a by-product even where it would not be expected from the chemistry of the desired reaction. Some patent work refers to reduction of aromatics in feed streams to other chemical synthesis as a means of reducing inadvertent manufacture of by-product persistent organic pollutants (see subparagraph 4.2.8). Finally, if HCB is a raw material for a process, carry-over of this material into final product will cause contamination (see subparagraph 4.2.5).

Many national inventories of emission estimates exist for PCDD/PCDF and PCB. For PCDD/PCDF, inventories typically involve unintentional generation. This is covered in the UNEP Toolkit (UNEP 2003). For PCB, inventories, if they exist, are mainly of legacy product still in use, waste in storage or recent production. Very few data on inadvertent generation of PCB exist.

It is important to note that there are sources of all of these by-products that are not related to chemical processes, but their release can only be prevented by installing high-performance technologies, closing the cycles and installing internal and external control of by-product and waste streams and the emissions connected with their destruction.

For HCB, both a product and a by-product, the situation is similar to that for PCB; however, some inventories of HCB as a by-product exist. The worldwide peak production and releases of HCB occurred in the late 1970s and early 1980s. Production was about 10,000 tons per year from 1978 to 1981 (Rippen and Frank 1986) of which 80% is believed to have been in Europe. A major input into the environment was its use as a pesticide, mainly as a fungicide for seeds of onions and sorghum and for crops such as wheat, barley, oats and rye, and as a fungicide to control bunt in wheat.

Since then, due to several regulations and bans, the production and releases have declined significantly. Bailey (2001) published a review of HCB sources and emissions worldwide in the mid-1990s. The total worldwide emission for that period was estimated at 10–90 tons per year. In the 1990s the contribution of different sources to the total emissions worldwide was as follows: fuel combustion 3.7%; iron and steel industry 0.3%; non-ferrous metal industry 36%; organic chemical industry 5.8%; other solvent use 0.004%; waste incineration 26%; and pesticide use 28%. The distribution in Europe, the United States and Canada showed considerable differences.

An extensive recent review of publications on HCB emissions was compiled as a Euro Chlor Science Dossier (Barber, Sweetman and Jones 2005). The dossier provides quite an exhaustive overview of all relevant published information up to 2004. It gives details on the production and releases in different periods, in different geographies and for different uses, and also deals with secondary and historical sources. A shorter version of this dossier was published in the peer-reviewed literature (Barber et al. 2005).

2.1 Oxychlorination process

The presence of heat, elemental chlorine, copper chloride catalyst and organic material makes the oxychlorination process a potential source of chemicals listed in Annex C, especially PCDD/PCDF and HCB. Aromatics may be generated in high-temperature processes and may also be present in feed materials, including HCl or air. Conditions in an oxychlorination reactor are in some ways similar to conditions in the areas of an incinerator downstream of the combustion zone, but may or may not contain similar amounts of soot-like elemental carbon or polycyclic aromatic hydrocarbons, which may contribute to de novo formation of PCDF (Lenoir et al. 2001; OxyVinyls website). Chemicals listed in Annex C created in this process, however, can be virtually completely removed from product and isolated in high-boiling materials (heavy ends) as a result of the distillation process.

Some chemicals listed in Annex C will adhere to particles of catalyst. In the case of fixed bed systems, they can be a part of the spent catalyst that is removed from service. This material can be treated thermally to destroy adsorbed organics or placed in a secure landfill. In reactors, fluidized bed catalyst particles undergo size attrition and can become entrained in the vapour stream. These particles eventually show up in solid waste or in the biological solids removed at the end of water treatment.

2.1.1 Acetylene process for vinyl chloride

Use of the balanced process for production of ethylene dichloride, and subsequent cracking to vinyl chloride, has, over the past fifty years, largely – but not entirely – superseded production of vinyl chloride via the acetylene route. In the acetylene process, calcium oxide and coke or coal are heated together at about 2,000° C to produce calcium carbide (CaC_2). When CaC_2 is reacted with water, acetylene is produced. Vinyl chloride results from a mercury catalyst-mediated addition of HCl to acetylene. Limited testing of effluents in the vinyl chloride process shows few if any chemicals listed in Annex C. The process to produce calcium carbide is uncharacterized; however, recent increases in capacity for this process may warrant further study.

2.1.2 Chlorinated solvents

Because the process to generate trichloroethylene, perchloroethylene and carbon tetrachloride involves chlorination, oxychlorination and pyrolysis, by-product will include chemicals listed in Annex C. These materials can be separated from final product by distillation and isolated in a fraction known as heavy ends. Many years ago, heavy ends material was commonly landfilled; however, since the 1970s, hazardous waste incineration, or thermal destruction with recovery and reuse of HCl, is by far the more common treatment.

There are a few examples of large extant stocks of HCB-containing material resulting from early solvent manufacture or more recent poor manufacturing practice. Annex II of this section is a case study of a Czech factory (IPEN 2006a). Included in the Euro Chlor dossier is a description of a long-standing situation in Australia (Barber, Sweetman and Jones 2005). It should be noted that neither of these case studies represents either best available techniques or best environmental practices; in fact, they are examples of the opposite.

2.2 Other process contact with elemental chlorine

There is anecdotal evidence that contact of elemental chlorine with organic process equipment (seals, gaskets, fibreglass equipment) that may contain aromatics, polycyclic aromatic hydrocarbons or elemental carbon can give rise to chemicals listed in Annex C, usually PCDF. In certain processes where high-boiling material or condensate is separated from manufactured elemental chlorine and not recycled in the process, chemicals listed in Annex C can be found in solid or liquid effluent.

2.3 Titanium dioxide, chlorine process

The presence of coke, chlorine, metals and elevated temperature may give rise to PCDD and PCDF analogous to those generated in oxychlorination. PCDD/PCDF, if formed, are expected to partition into stream(s) containing residual coke. If the residual coke is used for energy production, the potential content of PCDD/PCDF must be considered.

The emission from the chlorination process into atmosphere contains traces of $TiCl_4$, Cl_2, HCl, CO and COS, even after the $TiCl_4$ condensation. $TiCl_4$, Cl_2 and HCl are eliminated by an acid off-gas washing in several steps. The wash liquors are recycled in the process or recovered and partly sold as pure hydrochloric acid (28%).

2.4 By-product destruction

There are three types of treatment commonly in use for wastes, especially heavy ends: hazardous waste combustion, thermal oxidation and catalytic oxidation. Some detail on each is presented in the chapter on ethylene dichloride and vinyl chloride in European Commission 2003. When heavy ends are burnt some chemicals listed in Annex C are generated, as in any hazardous waste combustion. The European IPPC Bureau is in the process of generating a BREF on waste combustion processes; however, there are legal requirements and best available technologies are already in use in the United States, the European Union and Japan, among others. Alternatives to the incineration of municipal solid waste, hazardous waste and sewage sludge that are presented in section V.A of the present guidelines (for example gas phase chemical reduction, base catalysed dechlorination and mechanochemical dehalogenation) may also be of use for certain types of by-product destruction. The Catoxid® process is a fluidized bed catalytic process for oxidation of organics. It generates a stream of HCl and CO_2, which is sent in totality to the oxychlorination reactor for internal recycle (Randall 1994).

Alternatives to incineration described in this guidance document may also be of use for certain types of by-product destruction.

2.5 Products

Many products of these processes have been analysed for chemicals listed in Annex C, especially PCDD/PCDF. In general, products of the chloralkali-through-vinyl chloride chain are very low in such contamination; however, for these and other products the concentration of persistent organic pollutants may be a function of the efficiency of distillation or other purification.

IPEN (2006b) and references included therein contains reports of residual PCDD and PCDF in various products. PCDD/PCDF were also detected in five chlorinated chemicals, including triclosan, by Ni et al. (2005). HCB content of pesticides is described in Barber, Sweetman and Jones 2005 and references included therein. Chlorinated solvents prepared using modern techniques of purification have been tested for HCB and found to be in the low µg/kg (parts per billion) range (< 20 for trichloroethylene and < 10 for perchloroethylene). Some similar information is also contained in UNEP 2003. Clearly, effective operation of the purification steps helps to ensure low levels of residual contaminants in products.

3. Alternative processes that avoid formation of chemicals listed in Annex C

3.1 General considerations

In many cases there are alternative processes by which desired chemicals can be manufactured. For processes where chemicals listed in Annex C are generated, there may be alternative processes that do not involve generation of such chemicals. Consistent with the Convention, the guidance on alternatives in this document, and good business practice, a thorough review of alternative processes and technologies should be conducted before building new or substantially modifying production facilities.

3.2 Titanium dioxide, sulphate process

For TiO_2, there is an alternative commercial process utilizing sulphuric acid instead of chlorine.

In the sulphate process for TiO_2 ore is dried, ground and classified to ensure efficient sulphation by agitation with concentrated sulphuric acid in a batch or continuous exothermic digestion reaction. Controlled conditions maximize conversion of TiO_2 to water-soluble titanyl sulphate using the minimum acid. The resultant dry, green-brown cake of metal sulphates is dissolved in water or weak acid, and the solution is treated to ensure that only ferrous-state iron is present. The solution temperature is reduced to avoid premature hydrolysis and clarified by settling and chemical flocculation. The clear solution is then further cooled to crystallize coarse ferrous sulphate heptahydrate (known as copperas, $FeSO_4.7H_2O$), which is separated from the process and sold as a by-product.

The insoluble “mud” is washed to recover titanyl sulphate liquor. That liquid is filtered to remove final insoluble impurities, then evaporated to a precise composition. Hydrolysis to produce a suspension (“pulp”) consisting predominantly of clusters of colloidal hydrous titanium oxide follows.

Precipitation is carefully controlled to achieve the necessary particle size, usually employing a seeding or nucleating technique. The pulp is then separated from the mother liquor and extensively washed to remove residual traces of metallic impurities, using chelating agents if necessary. The washed pulp is treated with chemicals, which adjust the physical texture and act as catalysts in the calcination step. This process can produce either anatase or rutile crystal forms, depending on the additives used prior to calcination (Millennium Chemical Corporation website).

The sulphate process requires 2.4–3.5 tons of concentrated H_2SO_4 per ton of TiO_2, depending on the used raw material. Sulphuric acid is discharged from the process as sulphate, especially as iron(II) sulphate, or as free sulphuric acid in the spent acid. The total volume of spent acid caused by this process amounts to approximately 6–9 tons per ton of pigment. The recovery of the sulphuric acid from the used acid is divided into two processes:

- Recovery of the free acid by evaporation;
- Thermal decomposition of the sulphates and H_2SO_4 production on the basis of sulphur dioxide.

The spent acid is concentrated by evaporation to approximately 70%, where iron sulphate has a minimum solubility. Then the acid is cooled. After crystallization of the salts they are separated from the acid by filtration. The almost salt-free acid can be recycled directly or after a further concentration. Alternatively it can be used for other chemical processes or be decomposed to SO_2.

The separated sulphates, strongly loaded with sulphuric acid, are thermally decomposed in flowing bed reactors at temperatures of 800°–1,000° C (under the addition of sulphur, coal or oil as fuel) to sulphur dioxide and iron oxide. After cleaning, the obtained sulphur dioxide is processed to virgin sulphuric acid. The residual iron oxide can be reused in the cement industry.

The chloride process does not generate spent acids, and this means far less waste generation. There is, however, the possibility of some generation of chemicals listed in Annex C, specifically highly chlorinated furans (EPA 2006). Waste generation in the sulphate process, including of sulphuric acid and other mineral waste, is much higher but is not known to involve chemicals listed in Annex C. Trading elimination of small amounts of such chemicals for generation of large quantities of other waste materials may not be the optimal environmental approach. Best available techniques can be plant specific and viewed on a case-by-case basis.

4. Primary and secondary measures

4.1 Production approaches reducing emission of chemicals listed in Annex C

It is beyond the scope of this basic guidance to provide detailed comment on chemical plant and process design. However, responsible operation requires the recognition that chemical processes, while necessary for modern life, carry risks. To mitigate those risks to the greatest extent, processes must be designed to state-of-the-art safety and environmental standards as outlined, for example, in the European Union BREFs and comparable regulations in the United States and Japan. Experienced engineers must be engaged in the design of specific chemical processes.

Acceptable design must take into account the potential for side products and wastes, and make provisions for their safe handling or destruction. It must recognize that if the process carries the potential for generation of chemicals listed in Annex C, the four streams being emitted from a facility – air, water, solids and product – also carry that potential. Modern process design takes into account that potential, measures its reality, controls for it and includes operations to reduce or eliminate emission of those materials, commensurate with the requirements of the Convention. Modern safety management includes extensive training for operators and sufficient analytical and control instrumentation so that the facility as a whole operates to responsible standards.

The main demands for modern and safe chemical production can be stated as:

- Application of best available techniques, including high-performance technologies, in the design and construction of installations;
- Efficient closed cycles for the control of side products and destruction of wastes and emissions;
- Effective management of side products and handling of wastes;
- Dedicated facilities for destruction of wastes and emissions under the responsibility of the enterprise itself and with external control;
- Commitment to a standard of 0.1 ng I-TEQ/m^3 for air emissions in destruction of any side products, wastes and emissions;[1]
- Development of a clearly defined regime for internal and external monitoring of key operating parameters.

4.2 Primary measures

4.2.1 Distillation and internal recycling of by-products

Distillation is used primarily to produce product of purity appropriate to downstream processing. As an example, vinyl chloride is manufactured via oxychlorination and purified by distillation. Rigorous distillation is used due to the potential for disruption of subsequent polymerization process by impurities. Unsaturated materials that might act as co-monomers competing in the polymerization and saturated or aromatic materials susceptible to free radical reactions other than polymerization can negatively impact polymerization reaction kinetics.

Distillation and high purity are important for good production. Distillation systems can be designed to effect separation of materials of closely or widely separated boiling points. The boiling points of chemical products of direct chlorination and the boiling points of competing impurities allow for their practical separation. Their boiling points are also sufficiently different from those of the chemicals listed in Annex C, however, that virtually complete separation can be accomplished. European Commission 2003 notes that purified ethylene dichloride does not contain significant amounts of PCDD/PCDF.

Destruction of chlorinated by-product materials allows for HCl to be harvested and reused (Vinnolit website). This is deemed to have greater impact because small changes in generation of persistent organic pollutants upstream of distillation are not reflected in the quality of desired products after distillation.

Distillation is a means of separating desired product from inadvertent by-products used across the chemical production industry from commodities to pesticides. Adapting the design and operation of the distillation apparatus is, in principle, relatively straightforward. Residual by-product contained in

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[1] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

commercial product can be minimized by appropriate design and operation of the distillation apparatus. Effecting more complete separation for materials with boiling points that are not so widely separated as, for example, those of vinyl chloride and the various lower-molecular-weight by-products is for the most part a matter of correct design and construction and operation cost. Differences in concentration of residual chemicals listed in Annex C in commercial product may be due to differences in local regulation of products.

4.2.2 Elimination of carbon electrodes for chloralkali production

Older technology in the manufacture of chlorine and caustic soda utilized graphite anodes. Residues found from cells so constructed contained significant amounts of PCDD and especially PCDF (UNEP 2003). This problem was eliminated in much of the world following the invention of the coated titanium anode by H.B. Beer in 1965 and subsequent substitution for graphite in these processes (European Commission 2001). To the extent that the technology is still employed, the use of graphite electrodes is not a best available technique.

4.2.3 Elimination of alkali treatment of 1,2,4,5-tetrachlorophenol and 2,4,5-trichlorophenol

Manufacture of 2,4,5-trichlorophenol was accomplished by alkali treatment of 1,2,4,5-tetrachlorobenzene. This chlorinated phenol, in the presence of excess alkali, could generate significant amounts of by-product tetrachlorodibenzo-p-dioxins (TCDD). This process is not a best available technique.

4.2.4 Elimination of phenol route to chloranil

This process is described in UNEP 2003. Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione) is the precursor for production of dioxazine dyes. When prepared by chlorination of phenol or aniline via elemental chlorine, significant amounts of PCDD/PCDF are generated as by-products. This process is not a best available technique. Chlorination of hydroquinone by HCl generates much cleaner product.

4.2.5 Modified production of pentachlorophenol and sodium pentachlorophenate

The following processes are also described in UNEP 2003. Three routes to pentachlorophenol are known commercially: chlorination of phenol by Cl_2 over a catalyst, hydrolysis of HCB with sodium hydroxide and thermolysis of HCB. The most common route today is the first. Sodium pentachlorophenate can be produced via hydrolysis of HCB or, more commonly, by treatment of pentachlorophenol by sodium hydroxide.

For both products, careful control of reaction conditions (e.g. temperature, chlorine feed rate and purity of catalyst) leads to significant reductions of PCDD microcontaminants. In the United States, emission of these materials was reduced from about 3–4 mg I-TEQ/kg in the mid- to late 1980s to about 1 mg I-TEQ/kg in the years since 1988 (EPA 2001).

Facilities utilizing products manufactured in the processes named above should also examine the need for secondary measures of their own, especially waste disposal practices using best available techniques.

4.2.6 Use of hydrogen in oxychlorination

Oxychlorination process feed purity can be a factor in by-product formation, although the problem usually is only with the low levels of acetylene, which are normally present in HCl from the ethylene dichloride cracking process. Acetylene fed to the oxychlorination reactor could in principle be converted to highly chlorinated C_2 products, and chlorinated C_2 products could give rise to chlorinated aromatics via cyclotrimerization (OxyVinyls website, Oxychlorination Technology and Hydrogenation Technology pages). Selective hydrogenation of this acetylene to ethylene and ethane in a reactor prior to the oxychlorination reaction is widely used as a measure to avoid by-product synthesis, especially of polychlorinated aliphatics (see Figure 2).

4.2.7 Catalyst maintenance and temperature uniformity control

Fluidized bed reactors tend to have better temperature control and more uniform performance, although the previously mentioned attrition of catalyst particles can allow for carry-over into other streams within the facility. For fixed bed oxychlorination catalysts, appropriate packing and maintenance can reduce hot spots and can reduce fouling of the catalyst bed, loss of productivity and the potential for generation of high-molecular-weight products. Catalyst beds are changed on a regular basis to maintain efficiency.

4.2.8 Reduction in aromatic hydrocarbons in feeds to oxychlorination processes

Two patents specify pretreatment of air or HCl reagents used in oxychlorination to remove aromatics, presumably precursors to various persistent organic pollutants (Cowfer, Johnston and Popiel 1998, 2001). This patented technology is proprietary and as such may not be appropriate for any required implementation of best available techniques, but indicates another primary approach.

Feeds to oxychlorinators should be controlled to minimize or eliminate feed of higher organics and aromatics that could lead to high formation of Annex C compounds. Because raw heavy ends from ethylene dichloride or solvent streams may contain these compounds, heavy ends should be suitably treated prior to use in solvent production.

4.3 Secondary measures: Best available techniques for waste treatment practices

The purpose of distillation or other purification steps is to separate desired product from by-products, and to concentrate chemicals listed in Annex C in the by-product stream. There are a number of processes that are capable of treating by-product streams, many of which are described in section V.A of the present guidelines. Alternatives to incineration described in this section may also be appropriate to the task of destruction of chemicals listed in Annex C in this context.

5. Summary of measures

Measures for the reduction of chemicals listed in Annex C arising from certain chemical production processes might be summarized as follows:

- Modify processes to reduce generation of chemicals listed in Annex C;
- Incorporate steps that treat impurities in raw materials, and use rigorous operational maintenance;
- Purify products by distillation where physical properties allow;
- Internally recycle inadvertently generated high-molecular-weight by-products as an integral part of the process;
- Manage wastes appropriately taking full account of the potential release of chemicals listed in Annex C to air, water and land and avoid any inadvertent formation.

6. Performance standards and measures

6.1 Performance standards

Performance standards can be set locally in individual plant permits, and will vary. By-product PCDD/PCDF emission is mentioned in the Charter of the European Council of Vinyl Manufacturers, and reflected in the OSPAR (Oslo and Paris Convention for the Protection of the Marine Environment of the North-East Atlantic) process via Decision 98/4 and adoption of best available techniques via PARCOM (Paris Commission) Recommendation 96/2. That standard is 1 µg I-TEQ/ton annual oxychlorination capacity release to water. Air emission limits in the Charter of the European Council of Vinyl Manufacturers are 0.1 ng I-TEQ/Nm^3 (ECVM website). This limit corresponds to the European Union regulatory limit for emissions of PCDD/PCDF to air from incinerators.

In the European Union, requirements for the chemical industry are based on the Council Directive 69/61/EC on integrated pollution prevention and control. Four BREFs on best available techniques in the large-volume and speciality organic and inorganic chemical industries describe comprehensive requirements for environmentally sound operation of all chemical industry installations, including standards for emissions of PCDD/PCDF (European Commission 2001, 2003, 2006a, 2006b). For any combustion installation or part of it in the chemical industry within the European Union a limit value requirement of 0.1 ng I-TEQ/Nm^3 is the basis for its operation.

Air emissions from combustors in Japan are regulated according to size and whether they are new or retrofitted. Large new incinerators must achieve emission limits below 0.1 ng I-TEQ/Nm^3. Water emissions from these processes are limited to 10 pg I-TEQ/L effluent. Limits in other regions or countries will typically be congruent with hazardous waste combustor regulations in local areas.

In the United States as well as in other regions, regulations based on maximum achievable control technology (MACT) have been proposed to control HCB and other hazardous air pollutant emissions from incinerators, medical waste incinerators, cement kilns, and lightweight aggregate kilns that burn hazardous wastes.

The United States Environmental Protection Agency (EPA) regulates the maximum allowable concentrations of HCB as a contaminant in certain pesticides. The established microcontaminant level for HCB in certain pesticides is in the order of 40–50 parts per million. As noted in Bailey 2001, because of process improvements, actual HCB concentrations in pesticide products may be significantly lower.

In Canada, as in many countries, HCB is a prohibited substance. Canadian law prohibits the manufacture, use, sale or import of HCB. However, these restrictions do not apply to HCB that is:

- An incidental by-product of the manufacturing process of a product and that is present in the product in a concentration not exceeding 20 parts per billion; or
- Contained in a control product (pesticides, herbicides, etc.) within the meaning of Section 2 of the Canadian Pest Control Products Act.

6.2 Performance measures

These may include analytical chemistry on emission streams and, in some areas, reporting of persistent organic pollutants to a pollutant release and transfer registry, such as the Toxics Release Inventory in the United States (EPA 2006; CCC website).

Annex I. Synthesis of commodity chemicals

Chemical	**Process**	**Process use**	**Co-products**
Chlorine, caustic soda	$NaCl + H_2O \rightarrow Cl_2 + NaOH + H_2$ See European Commission 2001, 2003	More common	
Organics			
Allyl chloride	Direct chlorination of propylene > 300° C	More common	HCl
	Pyrolysis of 1,2-dichloropropane	Less common	Chlorinated olefins, HCl
Chloranil dye	See UNEP 2003		
Chloroprene (2-chloro-1,3-butadiene)	$C_2H_2 + CuCl/NH_4Cl \rightarrow$ vinyl acetylene + HCl → chloroprene	Less common	
	Vapour phase: butadiene + $Cl_2 \rightarrow$ 1,4- & 3,4-dichloro; isomerized (Cu catalyst) to 3,4-dichloro; HCl via NaOH; distilled to separate low-boiling mono-Cls; 3,4-di; 1,4-di; heavies	More common	NaCl; overchlorinated products
Chlorinated benzenes	Vapour phase: benzene + chlorine + HCl	Less common	Mixed product
	Liquid phase: $Cl_2/FeCl_3$ to yield mix; controlled by amount of chlorinating agent (monos); some other specialized processes for certain isomers; high-Cl materials can precipitate. Purified by distillation and crystallization; separations difficult	More common	HCl
Epichlorohydrin	Allyl chloride + HOCl (chlorine water) → glycerol chlorohydrins + $NaOH/(CaOH)_2 \rightarrow$ epichlorohydrin Steam stripped then distilled Also: propylene + O_2 (Pd catalyst) → allyl acetate → allyl alcohol + $Cl_2 \rightarrow$ allyl chloride	More common	Hydrolysed product; polymers
Isocyanurate disinfectants	Isocyanuric acid + NaOH + Cl_2		
Phosgene	CO + Cl_2 used virtually immediately to produce polycarbonate and polyurethane		
Chlorinated phenols	Lesser chlorinated phenols; phenol + Cl_2; various Lewis acid catalysts; $FeCl_3$, $ZnCl_2$	More common	
Pentachlorophenol (PCP)	Phenol + Cl_2; $AlCl_3$ as main industrial catalyst; 100°–180° C	More common	HCl
	hexachlorobenzene (HCB) + NaOH	Less common	NaCl
Sodium pentachlorophenate	PCP + NaOH	More common	NaCl
	HCB + NaOH	Less common	NaCl

Chemical	**Process**	**Process use**	**Co-products**
Vinylidene chloride ($ViCl_2$)	1,1,2-trichloroethane + NaOH or $Ca(OH)_2$; can also be a co-product of high-temperature chlorination of C_2 materials	More common	NaCl or $CaCl_2$
Vinyl chloride (VCM)	Acetylene + HCl → vinyl chloride; Hg catalyst	Less common	
	Ethylene + Cl_2 → EDC (direct; Fe catalyst); HCl + O_2 + ethylene → EDC (oxychlor; Cu catalyst)	More common	
	See European Commission 2001, 2003		
C_1 products			
Methyl chloride	$CH_4 + Cl_2$ via heat or light	More common	
	$CH_3OH + HCl \rightarrow CH_3Cl$	More common	
Other chlorinated methanes	$CH_3Cl + Cl_2$ heat or light → CH_2Cl_2, $CHCl_3$, CCl_4	More common	
	$CS_2 + Cl_2 \rightarrow S_2Cl_2 + CCl_4$	Less common	
	$CS_2 + S_2Cl_2 \rightarrow S + CCl_4$		
C_2 products			
Chlorinated ethanes			
1,1-di	VC + $HCl/FeCl_3$	More common	
1,2-di (EDC)	Ethylene + Cl_2 → EDC (Fe cat) (direct chlorination)	More common	
	Ethylene + HCl + O_2 (Cu cat) → EDC (oxychlorination)		
1,1,1-tri	1,1-di + Cl_2 (photochemical)	More common	HCl
	1,1,2-tri → 1,1,1-tri	More common	
	Ethane + Cl_2	Less common	
1,1,2-tri	VC + Cl_2	More common	
	EDC + Cl_2	More common	HCl
1,1,1,2-tetra, 1,1,2,2-tetra	EDC + Cl_2 (can include oxychlor)	More common	HCl
	$C_2H_2 + Cl_2$		
	$C_2H_4 + Cl_2$	More common	HCl
1,1,1,2,2-penta	TCE + Cl_2 → penta		
Chlorinated ethylenes			
Trichloroethylene (TCE) and perchloroethylene (PCE)	EDC + Cl_2 → TCE + PCE	More common	HCl
	EDC + Cl_2 → PCE + CCl_4	More common	HCl
	2 CCl_4 → PCE	More common	
	EDC + Cl_2 + O_2 → PCE/TCE	More common	
	Tetrachloroethanes + heat → TCE	More common	HCl
	Pentachloroethane + heat → PCE	Less common	HCl

Chemical	Process	Process use	Co-products
Inorganics			
HCl	By-product; salt + sulphuric acid; hydrogen + chlorine; recovery from combustion of chlorinated organics	More common	
TiO_2	C, Cl_2, TiO_2 ore → $TiCl_4$ + O_2 → TiO_2 TiO_2 ore + H_2SO_4 → $Ti(SO_4)_2$ → TiO_2	More common Less common	Cl_2, recycle sulphates
$FeCl_3$	Iron or iron oxide + HCl → $FeCl_3$		
Hypochlorites	Na: 2NaOH + Cl_2 → NaOCl Ca: $Ca(OH)_2$ + $2Cl_2$ → $Ca(OCl)_2$ also via NaOCl used as aid in chloride removal; recovered, then dried		NaCl $CaCl_2$
$ZnCl_2$	Zn + HCl → $ZnCl_2$		
ClO_2	Generated from $HClO_2$ or $NaClO_3$		

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Part III Source category (g): Crematoria

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VI.G Crematoria

Summary

From early history to the present day cremation has been a religiously and culturally important and accepted practice used by many cultures and countries as a way of dealing with the death of human beings. In many cases, cremation is integral to the religious and funeral practices of a particular country or culture; in others, it is a voluntary alternative to burial. These guidelines are not an attempt to redefine these practices or to demean their significance for the people involved. For those countries where cremation is practised and in keeping with the provisions of the Stockholm Convention, these guidelines seek to provide approaches that minimize or eliminate the formation and release of chemicals listed in Annex C of the Convention during the process of cremation.

The formation and release of PCDD and PCDF, HCB and PCB from crematoria is possible due to the presence of these chlorinated materials, precursors and chlorine in the cadavers and in some co-combusted plastics. Measures to minimize formation and release of chemicals listed in Annex C would include the avoidance of chlorinated material, the design of crematoria to deliver a minimum furnace temperature of 850° C, a 2-second residence time for the combustion gases and sufficient air to ensure combustion. Larger new crematoria should also be fitted with air pollution control equipment to minimize emission of sulphur dioxide, hydrogen chloride, carbon monoxide, volatile organic compounds, particulate matter and persistent organic pollutants. A performance level of < 0.1 ng I-TEQ/Nm^3 for PCDD/PCDF is associated with best available techniques.

1. Process description

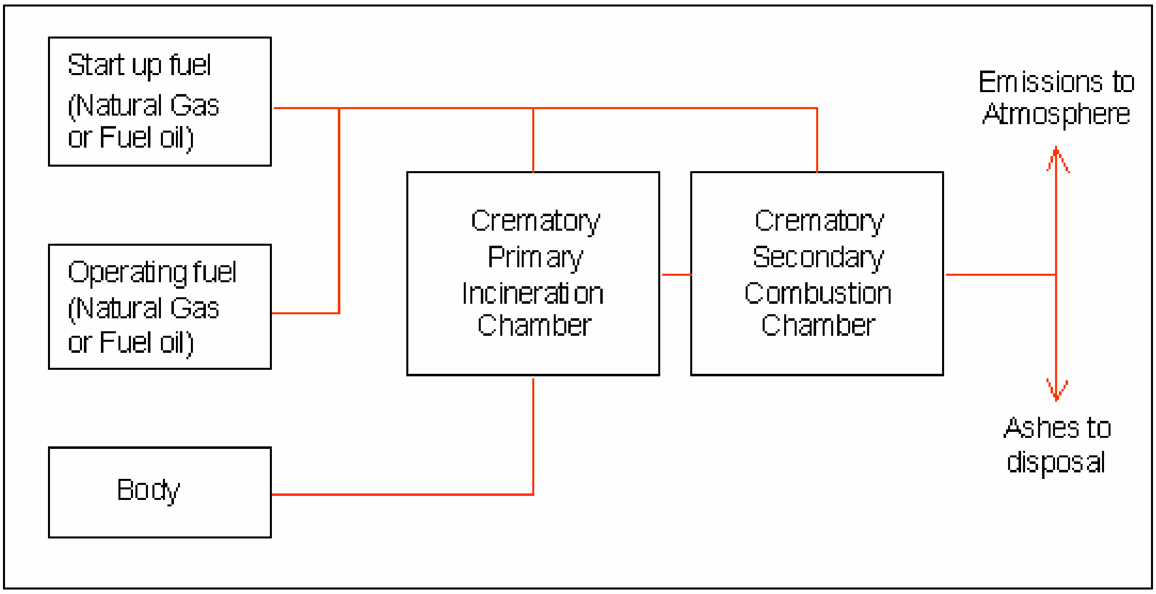
Cremation is the disposal of a cadaver by the process of burning. This can be undertaken in either an uncontrolled, open burning fashion on funeral pyres, or in a controlled fashion within a cremator, installed within a crematorium or crematory. For the purposes of this document, only the cremator installations are discussed with respect to preventing releases of persistent organic pollutants, and not open burning or non-combustion alternatives. It is noted, however, that in certain countries, cultural and societal practices can dictate the types of processes that are available for cadaver disposal. Proper consideration of such issues is therefore important.

Cremators typically consist of two main combustion chambers (Figure 1). The first, or primary, contains the hearth on which the coffin is received. This is supplied with forced draught air and one or two main support burners (typically in the order of 200–300 kW). These are usually gas fired, although in some locations they are oil fired. There are also a few designs of electrically heated cremators in operation. Primary chambers are typically between 1.5 and 2.5 m^3. Burning of the coffin and cadaver takes place on the fixed hearth and combustion gases, products of incomplete combustion and entrained particulate material produced by this process are then passed into the secondary combustion chamber.

Within the secondary chamber, further combustion air may be added, and an afterburner system supports completion of combustion. The secondary chamber is sometimes also used to preheat combustion air for the primary chamber.

Combustion gases are ejected from the cremator by either an induced draught fan or venture ejector system. Few countries require air pollution control equipment to be installed following the cremator, but where it is installed, the system typically adopted is the dry injection/filtration system. Here a suitable adsorbent, such as a mix of powdered lime and activated carbon, is injected into the cooled gas stream, and then a high-efficiency bag filter arrangement removes the injected powder together with entrained particulate matter. In the United Kingdom, for example, new crematoria and some existing crematoria are to be fitted with such adsorption systems for control of mercury emissions, which will have the co-benefit of controlling dioxin emissions.

Figure 1. Schematic of a typical cremation process



Many installations worldwide are equipped with cremators of an older design incorporating smaller secondary chambers, with short gas residence times and occasionally with no afterburner arrangement installed. Older cremators often rely on manual control, with an operator deciding burner duration and air distribution.

Cremation is a religiously and culturally important and accepted practice for many cultures and countries as a way of dealing with the death of human beings. In many cases, cremation is integral to the religious and funeral practices of a particular country or culture; in others, it is a voluntary alternative to burial. It is absolutely essential to remember that any discussion regarding the design and operation of crematoria must bear in mind that the process concerns the disposal of human remains. For this reason, such discussions must be duly dignified, with consideration of the sometimes conflicting relationship between social and cultural requirements and environmental desires.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

The formation and emission of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) from cremators is possible due to the presence of these materials, precursors and chlorine in the cadavers and in some co-combusted plastics (e.g. coffin furnishings, which have been phased out in some countries). However, although measurements of PCDD/PCDF have been undertaken from crematoria, there are few or no consistent data for PCB and HCB emissions. Consequently levels of PCB and HCB emissions are much more uncertain than PCDD/PCDF emissions from such sources.

2.1 General information on emissions from crematoria

Airborne emissions consist of nitrogen oxides (NO_x), carbon monoxide (CO), sulphur dioxide (SO_2), particulate matter, metal compounds, including mercury, organic compounds and PCDD/PCDF.

As discussed above, some cremator plant may have air pollution control equipment installed, for example lime and activated carbon injection and fabric filtration. However, most have pollution control ranging from minimal (i.e., a combustion chamber and stack) to reasonably improved systems with secondary combustion chambers and afterburners.

2.2 Emissions of PCDD/PCDF to air

PCDD/PCDF are formed through incomplete combustion or by de novo synthesis when organic and chlorine compounds are present in the feed material or flue gas matrix.

Although it is considered that PCDD/PCDF, PCB and HCB will be destroyed at high temperature (minimum 850° C) in the presence of oxygen, the de novo process of PCDD/PCDF synthesis is still possible if the combustion gases are cooled over an extended period through the reformation temperature window (between 200° and 400° C). This window can be present in abatement systems, energy recovery equipment and in cooler parts of the furnace, for example the feed area. Care taken in the design of cooling systems to minimize the residence time in the reformation window is practised to prevent de novo synthesis.

In many countries, cremator equipment is often installed in old buildings that are not purpose built. Thus there are often long runs of horizontal ductwork, operating at temperatures within this reformation window. Such systems are also subject to deposition of particulate matter, often containing adsorbed precursors, which enhance the reformation reactions.

In the United Kingdom, for example, cremators are generally required to achieve PCDD/PCDF emission concentrations of less than 0.1 ng I-TEQ/m^3 standardized at 11% oxygen, dry and standard temperature and pressure (0° C, 101.3 kPa).[1] However, this is not required to be demonstrated other than by achieving technical combustion requirements of minimum residence time, temperature and oxygen in the secondary chamber.

An emissions survey of typical cremators was undertaken during discussion of revised regulatory guidance. These tests indicated PCDD/PCDF concentrations ranging between 0.01 and 0.12 ng I-TEQ/m^3, and PCB concentrations were low, although limits of detection played a significant role in the estimation of releases.

2.3 Releases to other media

Due to the nature of the process, ashes are an ethical product and are often not subject to any control; spreading of ashes on water, for example, is a potential release route. However, there are often depositions left within the cremator chambers and flueways that are removed during routine maintenance. In the United Kingdom such material is buried at depth within the crematorium grounds (in the same way as metals recovered from the hearth and recovered ashes). A brief study was undertaken for the Federation of British Cremation Authorities and the Cremation Society of Great Britain, which investigated levels of PCDD/PCDF in ashes (Edwards 2001). Levels in the ashes were low enough to be considered insignificant in terms of potential exposure risk.

3. Recommended processes

3.1 Overview

Cremators should be designed to address the requirement for a minimum furnace temperature of 850º C, a 2-second residence time for the combustion gases and sufficient excess air to ensure combustion. The use of designs that cannot achieve these criteria should be discouraged unless demonstrated to be capable of operating without significant emissions of persistent organic pollutants.

Larger facilities, such as may be regulated under the Integrated Pollution Prevention and Control Directive in the European Union, may also have substantial air pollution control requirements to meet emission requirements for other species. These may include, for example, selective non-catalytic reduction for NO_x control, lime injection for acid gas control (SO_2 and HCl), carbon injection for mercury and PCDD/PCDF control and fabric filtration for particulate matter control.

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[1] 1 ng (nanogram) = 1 × 10^{-12} kilogram (1 × 10^{-9} gram). For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

3.2 Best available techniques

Best available techniques are those that consider both technology and management. Control of persistent organic pollutants would comprise the following items and considerations:

- A cremator meeting the minimum temperature, residence time and oxygen requirements and demonstrated to meet those requirements;
- Suitable air pollution control equipment (for control of persistent organic pollutants this would need to include temperature management to control residence time in reformation window, carbon injection and fabric filtration or equivalent) along with culturally and environmentally appropriate burying of any collected material;
- Combustion chambers and casings should be made as airtight as possible and operate under reduced pressure to minimize release of furnace gases;
- Gas temperatures should be monitored to allow control systems to maintain minimum temperature criteria (through use of support fuel burners) and provide interlocking to stop charge when temperature falls below minimum;
- Flue gas oxygen and carbon monoxide levels should be monitored and linked to the control system to ensure adequate control of air supplies and address any combustion problems;
- Mechanized loading and handling of coffins to minimize exposure to operators;
- Coffin storage facilities to be refrigerated, lockable and rodent and bird proof and have odour control;
- Coffin and coffin fittings should be made of combustible material. Avoid use, or inclusion, of articles containing PVC, metals and other chlorinated compounds;
- Effective operation control, inspection and preventive maintenance of components whose failure could impact on the environment by releasing persistent organic pollutants;
- Operator competencies to be identified and met by suitable training;
- Application of emission limit values and monitoring of emissions to demonstrate emission compliance for persistent organic pollutants.

Best available techniques for other pollutants have not been considered and it should be recognized that other factors will also impact on the definition of best available techniques for a facility (e.g. water and energy use considerations).

3.3 Best environmental practices

For best environmental practices, countries should aim in the first instance to develop facilities that are capable of meeting the minimum furnace temperature, residence time and oxygen criteria. It should be noted that air pollution equipment may be required to meet local emissions and air quality regulations for pollutants other than persistent organic pollutants.

Where heat recovery or air pollution control equipment is installed then the design of such equipment must address the risk of de novo PCDD/PCDF formation by minimizing the residence time of material in the reformation temperature window. Emissions from such plant should be demonstrated to be free of persistent organic pollutants by measurement on commissioning.

4. Primary and secondary measures

4.1 Primary measures

Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation and release of persistent organic pollutants. Possible measures include:

4.1.1 Cremator design

The cremator should provide conditions whereby a minimum temperature of 850° C can be maintained throughout charging, burning and ash recovery of the coffin and cadaver with a gas residence time of 2 seconds and sufficient oxygen to ensure destruction of any residual pollutants.

A secondary combustion chamber will be required with afterburners or air injection to meet these criteria. Particular care should be taken to ensure adequate sizing of the secondary chamber and the qualifying volume (the volume downstream of the last injection of fuel or combustion air and with a minimum gas temperature of 850° C throughout the volume). The importance of avoiding cooling of flue gases to temperatures within the reformation window is emphasized.

It is recognized that ash recovery at 850^0C will be difficult in small and unmechanized crematoria.

4.1.2 Pre-preparation of cremation

The presence of PVC, metals and other contaminants (particularly chlorine compounds) in the coffin material and furnishings should be avoided to reduce the generation of persistent organic pollutants during incomplete combustion or by de novo synthesis. The correct choice of materials can effectively control emissions of pollutants.

Similarly, placing personal items in the coffin should be avoided or allowed within guidelines to discourage placing of materials in the coffin that would increase the potential for generation of persistent organic pollutants. Crematoria can provide guidelines on (for example) medical implants and items of sentimental value (Australasian Cemeteries and Crematoria Association 2004).

4.1.3 Fuels

Use of waste-derived or other fuels potentially contaminated with persistent organic pollutants should be minimized and must not be used during start-up or process upset when temperatures are below 850° C and unstable conditions may be present. Larger facilities should aim for self-sustaining combustion in the furnace to minimize fuel use.

4.1.4 Effective combustion control

There are three principles at the heart of good combustion control for cremators:

- Maintaining the temperature at the entry and the exit of the secondary chamber at a minimum temperature of 850° C;
- Maintaining the oxygen concentration (and therefore the excess air) within the secondary chamber greater than 6% by volume;
- Holding the combustion gases within the secondary chamber for at least 2 seconds.

4.1.5 Effective process control

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to minimizing generation of persistent organic pollutants, such as maintaining a minimum furnace temperature of 850° C. Variables such as temperature, residence time, and levels of CO, volatile organic compounds and other gas components should be continuously monitored and maintained to establish optimum operating conditions.

4.1.6 Operator competency

The management of the facility is the key to ensuring safe and environmentally benign operation. All personnel operating the facility should be fully conversant with their duties, in particular with regard to routine operation, maintenance, process upset conditions and local environmental legislation. The competency of operators should be addressed by suitable training at an appropriate level for the facility.

4.2 Secondary measures

Secondary measures are pollution control techniques. These methods do not eliminate the generation of contaminants, but serve as means to contain and prevent emissions.

4.2.1 Fume and gas collection

Air emissions should be controlled at all stages of the process, including material handling, combustion and material transfer points, to control the emission of persistent organic pollutants. Sealed furnaces are essential to contain fugitive emissions while permitting heat recovery and collecting off-gases for abatement or discharge. Proper design of hooding and ductwork is essential to minimize fugitive discharge.

4.2.2 Air pollution control equipment

Large facilities should employ a range of air pollution control equipment to provide control for all significant emissions to atmosphere. Care in selection, design and use of air pollution control equipment for other pollutants will also, in general, reduce emissions of persistent organic pollutants. The design has to recognize the potential for de novo formation of selected persistent organic pollutants and minimize the potential for such formation. Particulate matter should be removed to reduce PCDD/PCDF emissions to atmosphere (although they will be discharged to landfill). Fabric filters are an effective technique but are essentially low-temperature devices (up to 200° C).

Air pollution control operations should be constantly monitored by devices to detect failure. Other developments include online cleaning methods and use of catalytic coatings to destroy PCDD/PCDF.

Activated carbon treatment should be considered for removal of persistent organic pollutants from off-gases. Activated carbon possesses large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or by injection of powdered activated carbon into the gas stream followed by removal as a filter dust using high-efficiency dust removal systems such as fabric filters.

5. Summary of measures

Table 1. Measures for recommended processes for crematoria

Measure	Description	Considerations	Other comments
Recommended processes	Large, new installations in developed countries	Minimum 850° C, 2-second residence time in qualifying volume with sufficient air to ensure destruction of persistent organic pollutants. Fit with air pollution control equipment to minimize emissions of SO_2, HCl, CO, volatile organic compounds, particulate matter and persistent organic pollutants	These are considered to be best available techniques. Should also have management systems in place, demonstration that facility meets emission limit values and regular monitoring to ensure compliance
	Small installations	Minimum 850° C, 2-second residence time in qualifying volume with sufficient air to ensure destruction of persistent organic pollutants	For smaller plant these conditions should be minimum to address issue of persistent organic pollutants. Could be adopted using a type approval mechanism and inspection of management of facility (rather than expensive emission tests)

Table 2. Summary of primary and secondary measures for crematoria

Measure	**Description**	**Considerations**	**Other comments**
Primary measures			
Furnace design			Best place to maximize destruction of persistent organic pollutants and minimize their formation
Pre-preparation of cremation	The presence of plastics, metals and chlorine compounds in the coffin material and furnishings should be avoided to reduce the generation of persistent organic pollutants during incomplete combustion or by de novo synthesis	Elimination of chlorinated plastics	Fairly low-tech, but has been successfully implemented in the United Kingdom
Fuel	Clean fuels for support		
Effective combustion control	Technical combustion conditions to meet minimum requirements for temperature, oxygen and residence time	Good combustion results from minimum 850° C, 6% O_2 and 2 seconds residence time	Requires good design principles and straightforward control techniques to meet requirements
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of emission of persistent organic pollutants	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gaseous components	Use of temperature is a fairly basic control parameter. Monitoring of oxygen, CO and volatile organic compounds is more complex but straightforward. However, main issue is maintenance of a control system able to use data in real time to address combustion air supply dampers, support burners and other control features
Operator training	In-depth operator training can be provided by cremator manufacturers or trade organizations		e.g. Crematorium Technicians Training Scheme in operation in United Kingdom
Secondary measures			
Fume and gas collection	Effective containment of furnace gases in all conditions of the cremation process to avoid fugitive releases	Processes to be considered include sealed furnaces to contain fugitive emissions while permitting heat recovery and collecting off-gases	

Measure	**Description**	**Considerations**	**Other comments**
Air pollution control equipment	Particulate matter abatement will help reduce potential emission of persistent organic pollutants. Activated carbon treatment should be considered as this material possesses large surface area on which PCDD/PCDF can be adsorbed from off-gases	Fabric filtration is the most effective particulate matter abatement and is consistent with use of dry/semi-dry sorbents for acid gas and metals control. However, it will require a temperature reduction. Injection of powdered activated carbon into the gas stream followed by removal as a filter dust	Use of air pollution control devices gives rise to additional waste streams and requires consumables. Likely need to reduce flue gas temperature (to avoid use of more exotic filtration media), consequently care needed to minimize residence in reformation window. Better to avoid formation of persistent organic pollutants in the furnace. However, this approach allows some back-up for process upset conditions and is considered a best available technique in Europe for incineration processes

6. Performance levels associated with best available techniques and best environmental practices

The performance level for emissions of PCDD/PCDF from crematoria is <0.1 ng I-TEQ/Nm^3. For combustion plant, these emission levels are expressed as mass concentrations at 11% oxygen, dry and standard temperature and pressure (0^0 C, 101.3 kPa). As there is little consistent information available on PCB and HCB emissions from crematoria, it is unclear what emission levels can be achieved for these species.

Data from U.K. crematoria (Edwards 2001) for PCDD/PCDF range between 0.01 and 0.12 ng I-TEQ/Nm^3. Data for existing plant in France for PCDD/PCDF range between 0.1 and 4.2 ng I-TEQ/Nm^3 (Livolsi et al 2006). The average UNEP result at the Bangkok crematoria (having a long brick flue duct) for PCDD/PCDF was 17.6 ng I_TEQ/Nm^3 (Fiedler 2001). A survey of Korean crematoria has reported PCDD/PCDF concentrations of 0.46 to 2.1 ng I-TEQ/Nm^3 (Kim et al 2003).

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Part III Source category (h): Motor vehicles, particularly those burning leaded gasoline

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VI.H Motor vehicles, particularly those burning leaded gasoline

Summary

The major fuels used in motor vehicle transportation are gasoline and diesel. Liquefied petroleum gas, vegetable oil-based and other biofuels, and alcohol-oil mixtures are gaining importance.

PCDD and PCDF have been found in the emissions from motor vehicles fuelled with gasoline or diesel. The higher concentrations identified in emissions from vehicles run on leaded gasoline are due to the presence of chlorinated and brominated scavengers in the fuel.

As alternatives to leaded gasoline, the following fuels may be considered: unleaded gasoline (best when equipped with catalyst); diesel (best when equipped with diesel oxidation catalyst and particulate filter); liquefied petroleum gas; compressed natural gas; propane/butane gas; biofuels; and alcohol-oil mixtures.

Best available techniques include banning of halogenated scavengers, and fitting motor vehicles with an oxidation catalyst or particulate filter.

There are no measured data available for biofuels, alcohol-oil mixtures or liquefied petroleum gas, and no data for 2-stroke engines.

1. Introduction

1.1 Process description

For motor vehicles, the process description is relatively straightforward. The gasoline engine derives its power from the explosion of a mixture of air and gasoline, whereas in the diesel engine the fuel burns rather than explodes. The air-fuel mixture, when ignited, expands rapidly in a cylinder, forcing a piston from the top of the cylinder to the bottom. After its release from a vehicle, the exhaust gas is diluted approximately a thousandfold in the first few seconds and cooled down very rapidly (DEH 2004).

1.2 Fuels, engine types and emissions

The major fuels used in transportation are gasoline, diesel and liquefied petroleum gas. Most gasoline-powered internal combustion engines used today in cars, light trucks, motorcycles and other vehicles are 4-stroke engines. Like many combustion processes, internal combustion engines generate polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) as unwanted byproducts (UNEP 2005).

Most small gasoline-powered internal combustion engines used today in boats, jet skis, mopeds, small motorcycles, tuk-tuks, lawnmowers, chainsaws and other vehicles and appliances are 2-stroke engines. These engines follow the same thermodynamic combustion cycle as the 4-stroke engine; however, it consists of only two strokes, namely the combined exhaust and intake stroke, and the compression, ignition and combustion stroke. The most striking difference from the 4-stroke engine is the fact that all strokes occur during only one full revolution of the crankshaft. Lubrication is usually by oil added to the fuel. Therefore, higher amounts of pollutants may be released and efficiency may be lower compared to 4-stroke engines. However, the simplicity and low production cost of the 2-stroke engine make it an ideal motor for small-scale applications.

Diesel engines are used in heavy trucks, light trucks, passenger cars, heavy construction equipment, boats, generators, pumps and farm equipment, including tractors and other large equipment. They usually use diesel (light oil) and a 4-stroke cycle. Compression is used for ignition rather than a spark. Air is taken into the cylinder and compressed. Diesel fuel is added at high pressure and burnt. This results in a more efficient use of fuel and lower specific emissions. However, particle emissions in the form of soot are associated with the operation of diesel engines due to incomplete combustion, especially during start-up, warming and load changes. Particulate emissions from diesel engines are well known to contain high concentrations of polycyclic aromatic hydrocarbons.

Since PCDD/PCDF were detected for the first time in used motor oil (Ballschmiter et al. 1986), evidence has mounted that PCDD/PCDF are formed and emitted by the combustion processes in gasoline- and diesel-fuelled engines. Incomplete combustion and the presence of chlorine in the fuel , lubricant and air lead to the formation of PCDD/PCDF, chemicals listed in Annex C of the Stockholm Convention (Marklund et al. 1987, 1990; Schwind et al. 1991; Hutzinger et al. 1992; Gullett and Ryan 1997). Whereas for gasoline-powered engines the only relevant release vector for PCDD/PCDF is to air, diesel engines generate considerable amounts of deposits (soot). However, no measured data are available for PCDD/PCDF concentrations in diesel soot (UNEP 2005).

2. PCDD/PCDF formation and release

2.1 Studies of PCDD/PCDF emissions

Several European studies and one study in the United States of America evaluated PCDD/PCDF emissions from vehicles by measuring the presence of PCDD/PCDF in tunnel air. This approach has the advantage that it allows random sampling of large numbers of cars, including a range of ages and maintenance levels. The disadvantage of this approach is that it relies on indirect measurements, which may introduce unknown uncertainties and make interpretation of the findings difficult. Concerns have been raised that in tunnel studies resuspended particulates and absorbed PCDD/PCDF that have accumulated over time may lead to overestimates of emissions. This approach was therefore not deemed appropriate and the results of these studies were not considered in detail in the compilation of these guidelines. For further reading refer to the publications at the end of this section (“Tunnel and ambient air studies”).

The first tailpipe emission study was performed by Marklund et al. (1987) on Swedish cars. Since then several studies either on running engines (passenger cars or trucks) or on motor stands or chassis dynamometers have been performed. Different fuels have been tested under varying conditions (simulating different traffic situations or varying loads). The results of the studies that report emissions based on fuel consumption are summarized in Table 1.

Table 1. PCDD/PCDF emissions from motor vehicles

Fuel	Vehicle type	Emission (pg TEQ/L)	Reference
Leaded gasoline, 4-stroke	Passenger car, old: before muffler/in tailpipe	60/10	Marklund et al. 1990
	Passenger car, new: before muffler/in tailpipe	21/23	Marklund et al. 1990
	Passenger car	0.55–1.66	Schwind et al. 1991
Diesel	Truck	291	Geueke et al. 1999
	Heavy duty vehicles	29.3–47.7	Gullett and Ryan 1997
	Passenger car	2–141	Schwind et al. 1991
	Truck	4–88	Schwind et al. 1991
	No information	0.5, 0.6, 2.0	Kim et al. 2003
	Truck	1.20–103	Government of Japan 2003
	Passenger car	1.47–121	Government of Japan

Fuel	Vehicle type	Emission (pg TEQ/L)	Reference
			2003
	Passenger car (chlorine: 12, 131, 259 ppm)	3–49	Dyke 2005
Unleaded gasoline, 4-stroke	Passenger car, old and new: before muffler or in tailpipe	3.5	Marklund et al. 1990
	Passenger car	5–22	Schwind et al. 1991
	Truck	0.42, 0.99	Government of Japan 2003
	Passenger car	0.34–16.42	Government of Japan 2003
Unleaded gasoline with catalyst, 4-stroke	Passenger car	2–3	Schwind et al. 1991

In 1994, Hagenmaier and co-workers analysed the emissions of a diesel-fuelled bus (Hagenmaier 1994; Hagenmaier et al. 1995). PCDD/PCDF concentrations were around 1 pg/L for individual 2,3,7,8-substituted congeners, resulting in an I-TEQ of 0.01 ng I-TEQ/L. Thus, the 1994 results were much lower than the results obtained in 1990 (Hagenmaier et al. 1990). Whereas in 1990, mixed-halogenated dibenzo-p-dioxins (PXDD) and dibenzofurans (PXDF) (X = Br, Cl) could be quantified, the 1994 emissions did not contain detectable PXDD/PXDF. Similarly, PCDD/PCDF concentrations were below the limit of quantification in an extract from a gasoline-powered motor vehicle (Hagenmaier et al. 1995). These results indicate that with the ban on the use of halogenated scavengers (in Germany: see BImSchV 1992), the main source of PCDD/PCDF (and PXDD/PXDF) was eliminated. The results also showed that cross-contamination did occur since the same containers were used for the transport of diesel, leaded and unleaded gasolines. In a test programme to determine the emission of PCDD/PCDF and polychlorinated biphenyls (PCB) from internal combustion diesel engines, in some runs PCB were detected at levels of 3.6 to 8.0 pg WHO-TEQ/L, which was low compared to the dioxin levels (Dyke 2005). There may have been some uncontrolled effect from insufficient engine conditioning that influenced the early test runs.

2.2 Summary of findings

The literature documenting results of European, Japanese (see also Miyabara et al. 1999), Korean, and United States studies gives evidence that:

- PCDD/PCDF emissions from vehicles burning unleaded fuels are lower than the emissions from vehicles burning leaded gasoline;
- The higher emissions from vehicles run on leaded fuels are due to the presence of brominated scavengers added to the fuels;
- Catalyst-equipped cars – running on unleaded gasoline – have lowest emissions;
- Limited testing shows that diesel oxidation catalysts are effective in reducing emissions of PCDD/PCDF;
- Diesel particulate filters are efficient in reducing PCDD/PCDF emissions from diesel-fuelled vehicles;
- Diesel-fuelled vehicles have lower emissions than leaded-gasoline-fuelled vehicles and slightly higher emissions than vehicles running on unleaded gasoline and equipped with catalytic converters;

- Use of motor oils with low chlorine content (in the diesel experiments) did not result in lower PCDD/PCDF emissions.

The situation is not clear as to the influence of the age of the vehicles. Whereas Marklund et al. (1990) found higher emissions in older vehicles, the German study (Schwind et al. 1991; Hutzinger et al. 1992) did not find such dependence.

There are no measured data available for the following vehicle engine types:

- 2-stroke engines;
- Utilizing liquefied petroleum gas;
- Utilizing alcohol-oil mixtures;
- Utilizing biofuels (canola, etc.)

3. Best available techniques and best environmental practices

Best available techniques to reduce PCDD/PCDF emissions from motor vehicles may include the following:

- Prohibition of halogenated scavengers;
- Prohibition of the use of leaded gasoline;
- Installation of diesel oxidation catalysts, particulate filters and catalytic converters;
- Alternatives to gasoline engine (electricity, solar light and fuel cell).

Best environmental practices may include:

- Avoidance policies such as greater fuel efficiency should be encouraged. Alternative modes of transport, including cycling, rail and other public transportation, should be promoted;
- Separation of transport containers according to the fuel (for example, do not transport leaded gasoline containing halogenated scavengers in containers that are also being used for the transport of diesel or unleaded gasoline);
- Prohibition of the use of leaded gasoline;
- Promotion of vehicles with low fuel consumption;
- Education to identify driving conditions that have low pollutant formation and release;
- Good maintenance of the vehicle.

4. Regulations addressed to reduction of PCDD/PCDF emissions

In Japan, the Special Measures Law on Dioxins (enforced in 1999) regulates concentrations of PCDD/PCDF emissions from specific sources, in which emission gases from motor vehicles are not included. With regard to motor vehicle fuel, 100% lead-free gasoline was achieved in the 1980s and sales of leaded gasoline were prohibited by the law on lead, benzene and sulphur. In Tokyo metropolitan area, diesel vehicles have to be equipped with diesel particulate filters.

In Germany, the 19th BImSchV prohibits the use of halogenated scavengers in motor vehicles as a measure to reduce PCDD/PCDF emissions from motor vehicles fuelled with leaded gasoline (BImSchV 1992).

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Part III Source category (i): Destruction of animal carcasses

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VI.I Destruction of animal carcasses

Summary

The formation and emission of PCDD, PCDF, PCB and HCB from animal carcass incinerators is due to the presence of these chlorinated materials, precursors and chlorine in the carcasses or in some plastics that can be co-incinerated with animal carcasses and by-products. Measures that can be taken to decrease the formation and release of persistent organic pollutants include the avoidance of co-incineration with other wastes, the requirement for a minimum furnace temperature of 850° C, a 2-second residence time for the combustion gases and sufficient excess air to ensure combustion. Larger facilities (> 50 kg/h) should be fitted with air pollution control equipment to minimize emissions of sulphur dioxide, hydrogen chloride, carbon monoxide, volatile organic compounds, particulate matter and persistent organic pollutants. A performance level associated with best available techniques of < 0.1 ng I-TEQ/Nm^3 can be achieved for PCDD/PCDF.

Other methods of disposal, such as burial, landfill or composting, are not considered to contribute significantly to emissions of chemicals listed in Annex C, although environmental, public health, nuisance and animal health issues should be considered. Alkaline hydrolysis digestion is a further technique for the destruction of animal carcasses.

I. Process description

Destruction of animal carcasses is generally achieved by incineration, rendering or a combination of these two activities.

Incineration techniques may include pyrolysis, gasification or other forms of heat treatment, and may involve burning of complete carcasses or parts of carcasses. Rendering covers a range of activities for processing of carcasses to recover materials.

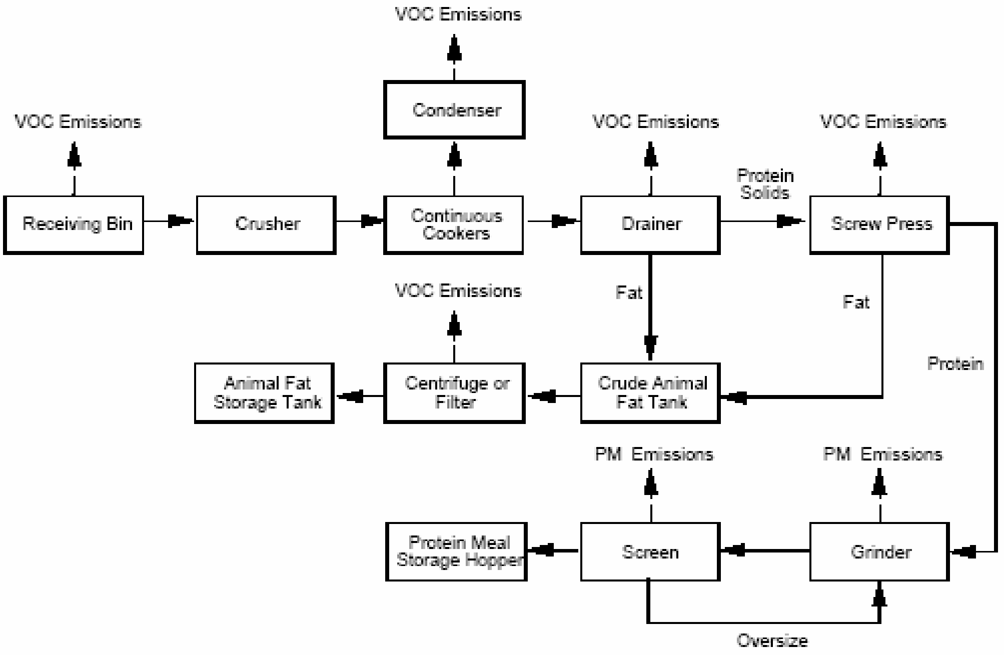
Recent legislation in Europe (EC Directive 1774/2002/EC on Animal By-products) limits the use of materials derived from rendering as human or animal foodstuffs to address public and animal health concerns. In recent years the production of animal by-products has increased, as the market definition of what is considered to be desirable meat products has altered (that is, the proportion of an animal that is considered to be by-product is increasing).

Rendering processes include treatment of hides, skins, feathers, organs, bones, trimmings, fluids and fat. In general the rendering process includes the crushing and grinding of by-products followed by heat treatment (Figure 1). Such processes include high-pressure, high-temperature hydrolysis; high-pressure hydrolysis biogas process; and biodiesel production and gasification. Separation of melted fat (tallow) from solid material is achieved by centrifuge or press. The solid fraction is commonly ground to meat and bone meal.

Meat and bone meal has traditionally been used as a feed supplement for animals but has been banned for such use in the European Union, and is now burnt in appropriate waste incineration facilities or buried. One of the current options is the use of meat and bone meal as alternative fuel in cement kilns (see section V.B of the present guidelines).

Tallow is used in a wide range of industries (including the food industry), particularly the oleochemical industry, which refines tallow into a wide range of products. In the European Union, tallow derived from older animals and other specified risk material is treated separately and is not used for food production but rather is treated as a waste. It can, however, be used as a fuel (within the European Union combustion is governed by further specific legislation – the Waste Incineration Directive, EC Directive 2000/76/EC).

Figure 1. Schematic of traditional continuous rendering process for carcass destruction



Source: EPA 1995.

Animal carcass incineration is undertaken using a variety of furnace types. Small carcass incinerators may have a simple combustion chamber without any active agitation of the carcass. Larger facilities may employ a rotary kiln to aid agitation and breakdown of the carcass. Similarly, a moving hearth furnace may provide similar agitation. In general, combustion of a complete carcass is difficult. Combustion in furnaces is more controllable if a more even feed process can be employed, using maceration, grinding or other techniques.

2. Sources of chemicals listed in Annex C of the Stockholm Convention

2.1 Emissions of persistent organic pollutants from destruction of animal carcasses

The formation and emission of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) from animal carcass incinerators is due to the presence of these materials,[1] precursors or chlorine in the carcasses or in some plastics, which can be co-incinerated with carcass material. However, although measurements of PCDD and PCDF emissions from incineration plant have been undertaken, there are few or no consistent data for PCB and HCB emissions. Consequently PCB and HCB emission levels are much more uncertain than those of PCDD and PCDF from such plant.

In general, rendering processes are considered to be unlikely sources of persistent organic pollutants. However, there is potential for concentration of material in the carcass residues and release from downstream activities (e.g. combustion of material).

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[1] Persistent organic pollutants deposited on grazing areas and those present in prepared animal feeds can be ingested and may be accumulated by animals during their lifetime.

2.2 General information on emissions from destruction of carcasses

2.2.1 Incineration

Airborne emissions consist of nitrogen oxides (NO_x), carbon monoxide (CO), sulphur dioxide (SO_2), particulate matter, metal compounds, organic compounds and PCDD/PCDF.

Larger incineration plant may have sophisticated air pollution control equipment (e.g. fabric filtration, lime injection and activated carbon injection). Smaller units include incinerators for slaughterhouse by-products and for veterinary devices, incinerators on farms for disposal of fallen stock and pet crematoria. These can have pollution control measures ranging from minimal (i.e., a combustion chamber and stack) to reasonably sophisticated systems with secondary combustion chambers, afterburners and filtration.

Other emission routes include ash and air pollution control residues, primarily to land. Significant releases to water are considered unlikely.

2.2.2 Open burning

Open burning of animal carcasses is not uncommon. However, burning of more than a handful of carcasses at any one time is uncommon. The Government of the United Kingdom employed mass burning in 2001 as part of the measures to control an outbreak of foot-and-mouth disease but is unlikely to consider such measures appropriate in the future (Table 1).

Table 1. UK 2001 foot-and-mouth disease outbreak: Carcass disposal

Disposal method	**Provisional statistics**
Burning (on farm)	> 950 sites
Burial (on farm)	900 sites
Mass burial	61,000 tons at 4 sites
Commercial landfill	95,000 tons at 29 sites
Rendering	131,000 tons at 7 plant

Source: Anderson 2002.

The emission to atmosphere of PCDD/PCDF from the foot-and-mouth disposal pyres in 2001 was estimated to be about 0.7 g, compared to a total United Kingdom emission of 314 g (NAEI website). Care was taken to construct the pyres using railway sleepers which had not been treated with wood preservatives containing pentachlorophenol or lindane which minimized the releases of PCDD/PCDF. Air curtain incinerators offer a level of technology intermediate between pyres and incinerators but tend not to be permanent facilities. Larger units are essentially engineered pits with the air blower to aid combustion and direction equipment to control the flow of the air attached alongside. Such units offer improved combustion over open burning and have applications in small-scale animal disposal for disease control. Ash disposal to land and potential releases to water need to be considered for open or pit burning.

2.2.3 Emissions from rendering

Rendering processes include treatment of hides, skins, feathers, organs, bones, trimmings, fluids and fat. Rendering includes the crushing and grinding of by-products followed by heat treatment. Separation of melted fat (tallow) from solid material is achieved by centrifuge and press. The solid fraction is commonly ground to a meat and bone meal.

Generally, the emissions that arise from combustion processes associated with rendering (e.g. furnaces for generating steam for heat treatment) do not contain persistent organic pollutants, but odorous and volatile organic compound emissions can arise from various rendering activities.

Meat and bone meal that is burnt can give rise to emissions of persistent organic pollutants. In the European Union, meat and bone meal is now burnt in appropriate incineration or co-incineration facilities or buried.

2.2.4 Emissions of PCDD and PCDF to air

For general information about PCDD and PCDF formation mechanisms see section III.C (i) of the present guidelines.

As an example, new animal carcass incinerators in the United Kingdom are generally required to achieve PCDD/PCDF emission concentrations of less than 0.1 ng I-TEQ/m^3 standardized at 11% oxygen, dry and standard pressure and temperature (0° C, 101.3 kPa).[2] New low-capacity incinerators (average throughput < 50 kg/h) do not have emission limits but are required to operate under a type approval scheme. To achieve type approval the regulatory guidance requires the incinerator manufacturer to show that the machines operate at a minimum temperature of 850° C for a residence time of 2 seconds. It is also noted that the requirements are likely to be met by designs that include a secondary combustion chamber with afterburners.

An emissions survey of existing low-capacity incinerators in the United Kingdom was undertaken for the Department for Environment, Food and Rural Affairs (DEFRA) prior to introduction of the new rules and indicated average PCDD/PCDF concentrations of 0.05–0.40 ng I-TEQ/Nm^3 (AEA Technology 2002). Monitoring of releases to air from two commercially available on-farm animal cremation units in Ontario, Canada, indicated average concentrations of PCDD/PCDF ranging approximately from 0.0006 to 0.0044 ng I-TEQ/Sm^3 (Environment Canada 2004).

It should be noted that low-capacity, on-farm incineration is banned in several countries.

2.2.5 Releases to other media

Process, surface and cooling water can be contaminated by body fluids, suspended solids, fats and oils. Carcasses, ash and other by-products are disposed of to land. Waste products disposed of properly to landfill are not anticipated to give rise to large risk of population exposure; the main route for such exposure is considered to be emissions to air.

3. Recommended processes

3.1 Overview of disposal options

Some countries have adopted a policy of no burial of animals and by-products. In some countries high-capacity centralized facilities have been adopted for disposal of carcasses; some countries have banned on-farm incineration of animal carcasses. Other countries have a mix of large facilities, small facilities (for example on-farm incinerators) and landfill. Alkaline hydrolysis digestion is used in several countries and provides a non-incineration method for carcass disposal, as does disposal in limepits. Anaerobic digestion is a further possible non-incineration method for some animal remains. However, the disposal of the residues would need to be carefully managed for disease control purposes. Further information on anaerobic digestion can be found in a recent review carried out by Kansas State University (Erickson et al 2004).

Disposal to landfill will not eliminate persistent organic pollutants that may be present within the carcasses but should remove them from potential human exposure.

The approach adopted by a country has to reflect the specific nature and circumstances of food production, slaughterhouses and rendering activities in the country (including infrastructure, and cultural constraints and practices). For example, large-scale central incineration facilities require a sophisticated transport infrastructure to minimize risk of infection from moving potentially infected material and a pricing structure capable of supporting the facility.

In the destruction of animal carcasses, the main source of emissions of chemicals listed in Annex C is the incineration of animal carcasses and by-products (including by-product arising from rendering processes). Combustion facilities for carcasses and rendering residues should therefore be designed to address the requirement for a minimum furnace temperature of 850º C, a 2-second residence time for

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[2] 1 ng (nanogram) = 1×10^{-12} kilogram (1×10^{-9} gram). For information on toxicity measurement see section I.C, subparagraph 3 of the present guidelines.

the combustion gases and sufficient excess air to ensure combustion. Designs that cannot achieve these criteria should not be used unless demonstrated to be capable of operating without significant emission of persistent organic pollutants.

Larger facilities, such as may be regulated under the Integrated Pollution Prevention and Control Directive in the European Union, or equivalent pollution prevention legislation in other countries, may also have substantial air pollution control requirements to meet emission requirements for other species. These may include (for example) selective non-catalytic reduction for NO_x control, lime injection for acid gas control (SO_2 and HCl), carbon injection for mercury and PCDD/PCDF control, and fabric filtration for particulate matter control.

Smaller incineration units are unlikely to have a significant national or local impact on air quality. In such instances it will be adequate to adopt the furnace temperature and residence time requirements for control of emissions of persistent organic pollutants.

3.2 Best available techniques

Best available techniques are considered to include technology, management and operation parameters, and control of emissions of persistent organic pollutants would comprise the following measures:

- Combustion furnace meeting the minimum temperature, residence time and oxygen requirements and demonstrated to meet those requirements;
- Suitable air pollution control equipment, including temperature management to control residence time in reformation window, carbon injection and fabric filtration or equivalent;
- Design of waste feed system to minimize effect of new charges of waste (feed should be macerated and passed to furnace using a sealed system);
- Combustion chambers and casings should be made as airtight as possible and operate under reduced pressure to minimize release of furnace gases;
- Gas temperatures should be monitored to allow control systems to maintain minimum temperature criteria (through use of support fuel burners) and provide interlocking to stop feed when temperature falls below minimum;
- Flue gas oxygen and carbon monoxide levels should be monitored and linked to the control system to ensure adequate control of air supplies and address any combustion problems;
- Support fuels should not be waste-derived fuels unless demonstrated to emit no more persistent organic pollutants than gas, oil or other clean fuel;
- Designated hard standing areas with appropriate drainage for loading, unloading, container washing to facilitate cleaning and disinfection. Consider need to incinerate wash-down residues for control of pathogens;
- Mechanized loading and handling of waste materials to minimize exposure to operators;
- Small incinerator facilities (where operation of these is permitted) should be located on a concrete slab and be located at least 100 metres from any well, spring or surface watercourse. Similarly, such facilities should be located at least 6 metres from any building or potentially flammable structure;
- Waste storage facilities to be refrigerated, lockable and rodent and bird proof and have odour control;
- Minimize use of plastic bags to contain waste; consider use of skips, which avoid need for contact with animal remains;
- Ash recovery to be in sealed conveyors, covered skips and sealed containers to avoid fugitive dust releases (particularly of air pollution control residues). Ash to be disposed of to suitable landfill;

- Management of incoming waste and record keeping;
- Effective operation control, inspection and preventive maintenance of components whose failure could impact on environment by releasing persistent organic pollutants;
- Operator competencies to be identified and met by suitable training;
- Application of emission limit values and monitoring of emissions to demonstrate compliance;
- Disposal of ash and residues by landfill.

Best available techniques for other pollutants have not been considered and it should be recognized that other factors will also impact on the definition of what constitutes best available techniques for a facility (for example water use, energy use considerations).

3.3 Best environmental practices

If incineration is to be pursued, countries should in the first instance aim to develop facilities for burning carcasses and animal by-products that can meet the minimum furnace temperature, residence time and oxygen criteria. It should be noted that air pollution control equipment may be needed to meet local emissions and air quality regulations for pollutants other than persistent organic pollutants.

Where heat recovery or air pollution control equipment is installed, the design of such equipment must address the risk of de novo PCDD/PCDF formation by minimizing the residence time of material in the reformation temperature window. Emissions from such plant should be demonstrated to be free of persistent organic pollutants by measurement on commissioning.

Facilities for co-incineration of waste materials (for example tallow or meat and bone meal in cement kilns) should be assessed to ensure that the minimum furnace temperature, residence time and oxygen criteria can be achieved, and emission monitoring should be used to determine compliance with emission limits. The emissions arising from co-incineration of animal waste should not be more polluting than those arising from operation of the process without waste burning.

For very small incineration facilities (< 50 kg/h) emissions of persistent organic pollutants may be controlled by using furnaces demonstrated (perhaps, for example, by a type approval scheme) to be capable of operating according to minimum furnace temperature and residence time criteria. In addition, operation should be smokeless and loading and operation procedures may be interlocked to ensure that material cannot be burnt until the secondary chamber reaches the minimum temperature. In such instances it is unlikely that the expense of emission measurements can be justified.

Use of pyres should not be considered a best environmental practice. If pyres are used, care is needed to avoid fuels such as treated wood or other fuels containing materials that may lead to release of persistent organic pollutants. Limited measurement data (Sinclair Knight Merz 2005) indicate that air curtain incinerators may give rise to emissions per carcass similar to small incinerators, but the total quantities of fuel and carcasses (and hence potential emissions) are far higher than for small incinerators. Their use should not be considered a best environmental practice, except perhaps as part of a targeted disease control strategy.

Use of digestion techniques and appropriately designed and managed landfill is an alternative to incineration.

4. Primary and secondary measures

4.1 Primary measures

Primary measures are regarded as pollution prevention techniques that reduce or eliminate the generation and release of persistent organic pollutants. Possible measures include:

4.1.1 Furnace design

The furnace should provide conditions whereby a minimum temperature of 850º C can be maintained throughout loading, burning and discharge of the carcasses with a gas residence time of 2 seconds and sufficient oxygen to ensure destruction of any residual persistent organic pollutants.

It is likely that a secondary combustion chamber will be required with afterburners or air injection to meet these criteria. Particular care should be taken to ensure adequate sizing of the secondary chamber and the qualifying volume (the volume downstream of the last injection of fuel or combustion air and with a minimum gas temperature of 850º C throughout the volume).

Ideally the furnace should be designed to allow continuous operation (that is, with automatic continuous feed to the furnace and automatic ash removal) as this will minimize process upsets, which can give rise to emission of persistent organic pollutants. Continuous operation requires maceration of solid materials to ensure consistent feed. It is recognized that, for smaller units and units handling whole carcasses, continuous operation may not be appropriate. The design of the furnace needs to facilitate good burnout of the material (low carbon in ash content).

Where co-incineration is proposed, the same furnace temperature and residence time criteria should be adopted.

4.1.2 Feed material

The presence of plastics and other contaminants (particularly chlorine compounds) in the feed material should be avoided to reduce the generation of persistent organic pollutants during incomplete combustion or by de novo synthesis. It is recognized that use of plastic bags and similar material is necessary for operator and animal hygiene. However, their use should be minimized by use of mechanized and automatic feed devices.

It should be recognized that carcasses and by-products may need to be classified according to source (for example, specified risk material).

Methods to be considered include:

- Use of mechanized loaders to avoid contact with carcasses;
- Use of macerating and grinding techniques to allow automatic, continuous loading and operation;
- Minimizing contamination from packaging, including use of non-halogenated plastics.

4.1.3 Fuels

The use of clean fuels is recommended for start-up, support burners and afterburners. Larger facilities should aim for self-sustaining combustion in the furnace to minimize fuel use. Use of waste-derived or other fuels potentially contaminated with persistent organic pollutants should be minimized and must not be used during start-up or process upset when temperatures are below 850º C and unstable conditions may be present.

4.1.4 Effective process control

Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of generation of persistent organic pollutants, such as maintaining a minimum furnace temperature of 850° C to destroy such pollutants. Ideally, emissions of persistent organic pollutants should be monitored continuously to ensure reduced releases. Variables such as temperature, residence time, and levels of CO, volatile organic compounds and other gas components should be continuously monitored and maintained to establish optimum operating conditions.

4.1.5 Operator competency

The management of the facility is the key to ensuring safe and environmentally benign operation. All personnel operating the facility should be fully conversant with their duties, in particular with regard to routine operation, maintenance, disease control, process upset conditions and local environmental legislation. The competency of operators should be addressed by suitable training at an appropriate level for the facility.

4.2 Secondary measures

Secondary measures are pollution control techniques. These methods do not eliminate the generation of contaminants, but serve as means to contain and prevent emissions.

4.2.1 Fume and gas collection

Air emissions should be controlled at all stages of the process, including material handling, combustion and material transfer points, to control the emission of persistent organic pollutants. Sealed furnaces are essential to contain fugitive emissions while permitting heat recovery and collecting off-gases for abatement or discharge. Proper design of hooding and ductwork is essential to minimize fugitive discharge. Sealed skips or enclosed feed systems may be used and can significantly reduce fugitive emissions to air by containing emissions during charging.

4.2.2 Air pollution control equipment

Large facilities should employ a range of air pollution control equipment to provide control for all significant emissions to atmosphere. Care in selection, design and use of air pollution control equipment for other pollutants will also, in general, reduce emissions of persistent organic pollutants. The design has to recognize the potential for de novo formation of selected persistent organic pollutants and minimize the potential for such formation. Particulate matter should be removed to reduce PCDD/PCDF emissions to atmosphere (although they will be discharged to landfill). Fabric filters are an effective technique but are essentially low-temperature devices (up to 200º C).

For small facility processes the use of afterburners is probably sufficient abatement to control emission of persistent organic pollutants, and particulate abatement is considered unnecessary.

Air pollution control operations should be constantly monitored by devices to detect failure. Other more recent developments include online cleaning methods and use of catalytic coatings to destroy PCDD/PCDF.

Activated carbon treatment should be considered for removal of persistent organic pollutants from off-gases. Activated carbon possesses a large surface area on which PCDD/PCDF can be adsorbed. Off-gases can be treated with activated carbon using fixed or moving bed reactors, or by injection of carbon particulate into the gas stream followed by removal as a filter dust using high-efficiency dust removal systems such as fabric filters.

5. Summary of measures

Table 2. Measures for recommended processes for new animal carcass incinerators

Measure	Description	Considerations	Other comments
Recommended processes	Large (> 50 kg/h) incinerators and co-incinerators	Minimum 850º C, 2-second residence time in qualifying volume with sufficient air to ensure destruction of persistent organic pollutants. Fit with air pollution control equipment to minimize emissions of SO_2, HCl, CO, volatile organic compounds, particulate matter and persistent organic pollutants	These are considered to be best available techniques. Should also have management systems in place, demonstration that facility meets emission limit values and regular monitoring to ensure compliance

Measure	Description	Considerations	Other comments
	Small (< 50 kg/h) incinerators	Minimum 850º C, 2-second residence time in qualifying volume with sufficient air to ensure destruction of persistent organic pollutants	For smaller plant these conditions should be minimum to address issue of persistent organic pollutants. Could be adopted using a type approval mechanism and inspection of management of facility (rather than expensive emission tests)

Table 3. Summary of primary and secondary measures for destruction of animal carcasses

Measure	Description	Considerations	Other comments
Primary measures			
Furnace design			Best place to maximize destruction of persistent organic pollutants and minimize their formation
Control of feed material	The presence of plastics and chlorine compounds in the feed material should be minimized to a level consistent with good hygiene to reduce the generation of persistent organic pollutants during incomplete combustion or by de novo synthesis	Elimination of plastic, maximize use of mechanical handling	Fairly low-tech
Fuel	Clean fuels for support		
Effective process control	Process control systems should be utilized to maintain process stability and operate at parameter levels that will contribute to the minimization of emission of persistent organic pollutants	PCDD/PCDF emissions may be minimized by controlling other variables such as temperature, residence time, gaseous components	Use of temperature is a fairly basic control parameter. Monitoring of oxygen, CO and volatile organic compounds is more complex but straightforward. However, main issue is maintenance of a control system able to use data in real time to address combustion air supply dampers, support burners and other control features
Secondary measures			
Fume and gas collection	Effective containment of furnace gases in all conditions of the incineration process to	Processes to be considered include sealed furnaces to contain fugitive emissions while	

Measure	Description	Considerations	Other comments
	avoid fugitive releases	permitting heat recovery and collecting off-gases	
Air pollution control equipment	Particulate matter abatement will help reduce potential emission of persistent organic pollutants. Activated carbon treatment should be considered as this material possesses large surface area on which PCDD/PCDF can be adsorbed from off-gases	Fabric filtration is the most effective particulate matter abatement and is consistent with use of dry/semi-dry sorbents for acid gas and metals control. However, it will require a temperature reduction. Injection of powdered activated carbon into the gas stream followed by removal as a filter dust	Use of air pollution control devices gives rise to additional waste streams and requires consumables. Likely need to reduce flue gas temperature (to avoid use of more exotic filtration media), consequently care needed to minimize residence in reformation window. Better to avoid formation of persistent organic pollutants in the furnace. However, this approach allows some back-up for process upset conditions and is considered a best available technique in Europe for incineration processes. Most air pollution control equipment is expensive to buy and run, and spares are expensive

6. Performance level associated with best available techniques and best environmental practices

The performance level for emissions of PCDD/PCDF from the destruction of animal carcasses is <0.1 ng I-TEQ/Nm^3 at 11 % oxygen, dry and standard temperature and pressure (0^0 C 101.3 kPa). For further information see European Commission 2003.

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Part III Source category (j):
Textile and leather dyeing and finishing

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VI.J Textile and leather dyeing and finishing

Summary

Contamination with PCDD and PCDF has been found in both textile and leather products. The occurrence of PCDD/PCDF in the textile and leather industries is due to use of chlorinated chemicals, especially pentachlorophenol and chloronitrofen, to protect the raw material (e.g. cotton, wool or other fibres, leather); and use of dioxin-contaminated dyestuffs (e.g. dioxazines or phthalocyanines). Smaller quantities of PCDD/PCDF may be formed during finishing, and during incineration of process-generated sludges.

Alternatives to the above-listed dye pigments exist and those listed should not be applied.

Possible alternatives to pentachlorophenol and chloronitrofen include 2-(thiocyanomethylthio) benzothiazole (TCMTB); *o*-phenylphenol (oPP); 4-chloro-3-methylphenol (CMK); and 2-*n*-octyl-4-isothiazolin-3-one (OIT).

As regards best available techniques, the most efficient primary measure to prevent contamination of textiles and leather goods with PCDD/PCDF would be not to use dioxin-contaminated biocides and dyestuffs in the production chains. Also, if any of the above-mentioned chemicals are being used, preference should be given to batches containing low concentration (e.g. distilled or otherwise purified chemicals). To the extent possible, burning of textile, upholstery, leather products and carpet should be avoided to prevent PCDD/PCDF formation.

In order to prevent or minimize formation and release of PCDD/PCDF when burning sludge from wastewater treatment and flotation, best available techniques should be applied as described in section VI.D of the present guidelines (industrial boilers). However, other environmentally sound techniques should also be explored.

1. Textile industry

1.1 Introduction

The textile industry exhibits one of the most complicated manufacturing chains. It is a fragmented and heterogeneous sector dominated by small and medium-sized enterprises; for example, in 2000 in the European Union, 114,000 companies employed about 2.2 million people (European Commission 2003b). Demand is largely driven by three main end uses: clothing, home furnishing and industrial use.

The textile and clothing chain is composed of a wide number of subsectors covering the entire production cycle from the production of raw materials (artificial fibres) to semi-processed products (yarns, woven and knitted fabrics with their finishing processes) and final or consumer products (carpets, home textiles, clothing and industrial use textiles).

1.2 Process description

Woven and knit fabrics cannot be processed into finished goods until the fabrics have passed through several water-intensive wet processing stages (also known as finishing) such as fabric preparation, dyeing, printing and finishing. Natural fibres typically require more processing steps than artificial fibres. Relatively large volumes of wastewater are generated, containing a wide range of contaminants, which must be treated prior to disposal. Significant quantities of energy are used in heating and cooling chemical baths and drying fabrics and yarns.

Fabric preparation requires desizing, scouring and bleaching as well as singeing and mercerizing. Dyeing operations are used at various stages of production to add colour and intricacy to textiles and increase product value. Dyes used by the textile industry are largely synthetic. Finishing encompasses chemical or mechanical treatments (EPA 1997).

The main environmental concerns in the textile industry are the amounts of water discharged and the chemical load it carries. Other important issues are energy consumption, air emissions, solid wastes and odours.

Although there is a multitude of steps in the production chain and environmental concerns do occur, generation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) could not be associated to individual production steps.

Instead, more attention has to be given to the facts that PCDD/PCDF enter the textile production process through application of pesticides and dyestuffs contaminated with PCDD/PCDF and that the PCDD/PCDF contamination is being carried through the various steps of the production chain. Depending on the individual steps, solvents applied and the physical environment, PCDD/PCDF either stay in the textile product or are discharged as wastes.

1.3 Sources of chemicals listed in Annex C of the Stockholm Convention

In the textile production chain, the finishing processes are typically not sources of PCDD/PCDF formation (Horstmann et al. 1993). Rather, the use of PCDD/PCDF-containing dyes and pigments and the use in some countries of PCDD/PCDF-contaminated fungicides to treat unfinished raw materials such as cotton appear to be the sources of the detected PCDD/PCDF.

New formation of PCDD/PCDF may occur in the textile production chain where effluents are treated and sludge is being removed and incinerated. Such plants typically are considered to be modern.

Thus, measures that constitute best available techniques and best environmental practices will focus on:

- PCDD/PCDF contamination through introduction of dioxin-contaminated chemicals into the textile production chain;
- New formation of PCDD/PCDF in thermal disposal operations of production-specific wastes.

1.3.1 PCDD/PCDF contamination through dioxin-contaminated materials

Chemicals known to be contaminated with PCDD/PCDF are used for the two purposes and include the chemicals listed below (European Commission 2003b):

- Defoliant or fungicide: Pentachlorophenol and 2,4,6-trichlorophenyl-4'-nitrophenyl ether[1] (chloronitrofen);
- Dyes: Chloranil-based dioxazine and phthalocyanine-based dyes.

Results from the analysis of textiles of various origin and fibres gave strong indications that pentachlorophenol has been and perhaps still is being used as a biocide on raw materials, especially on cotton. The PCDD/PCDF pattern clearly revealed that pentachlorophenol was the major source of the PCDD/PCDF in the textiles.

Although no published information was found that chloronitrofen is applied in the textile industry such use cannot be excluded, as it has replaced pentachlorophenol in many applications (Masunaga, Takasuga and Nakanishi 2001; UNEP 2003).

1.3.2 Formation of PCDD/PCDF in thermal disposal operations

There are several steps in the textile production chain where wastewaters or effluents generate sludges that are incinerated: for example, from effluents evaporated in the wool scouring process, or from wastewater containing pigment printing paste or latex from carpet backing. As with any incineration process, PCDD/PCDF can be formed since these sludges contain relatively high contents of chloride as well as organically bound chlorine from ectoparasiticides such as γ-hexachlorocyclohexane (γ-HCH, lindane), dieldrin or DDT that have been applied to the raw materials (especially wood) (European Commission 2003b; UNEP 2003).

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[1] Not in European Commission 2003b.

Concerning the probability of the use of lindane, dieldrin and DDT, all major grower countries have banned the use of organochlorine pesticides for sheep treatment but there is evidence that wool from some former Soviet Union countries and South America contains lindane at detectable concentrations (European Commission 2003b).

Finally, polybrominated flame retardants, such as polybrominated diphenyl ethers and chlorinated paraffins (C_{10-13} chloroparaffins) are used in the textile industry. All halogenated flame retardants are involved in the formation of PCDD/PCDF when incinerated (European Commission 2003b).

If the dirt removal and grease recovery loop is combined with evaporation of the effluent and incineration of the sludge, with full recycling of the water and energy, additional environmental benefits are achieved in terms of water savings and reduced amount of solid waste to be disposed of. The temperature of the incinerator would be around 1,200° C in order to destroy PCDD/PCDF. Fly ashes would be removed in a bag filter. In the gaseous emissions of such an integrated dirt removal and grease recovery loop plant 0.02 ng I-TEQ/Nm^3 were detected (European Commission 2003b, p. 278).[2] However, this technology is complex and is reported to involve very high capital costs and high running costs.

An incinerator may also be present when sludge from flotation is dewatered and then thermally regenerated in a rotary kiln. The flue gas is burnt in an afterburner (about 850° C) and released to ambient air at a temperature of 120° C. In the off-gases from the regeneration plant for lignite coke in the sludge plant, PCDD/PCDF concentration of 0.004 ng I-TEQ/Nm^3 (at 11% O_2) were found (European Commission 2003b, p. 415–417).

Experiences in some countries for sludge from wastewater treatment of wool scouring effluent include:

- Use sludge in brick making (mixed with clay) or adopt any other appropriate recycling routes;
- Incinerate the sludge with heat recovery, provided that measures are taken to control or avoid emissions of PCDD/PCDF arising from organically bound chlorine from pesticides potentially contained in the sludge.

For further information, the guidance related to best available techniques and best environmental practices for industrial facility recovery boilers should be consulted (section VI.D of the present guidelines).

2. Leather refining

2.1 Introduction

The tannery industry, specifically leather refining, consists of converting the raw hide or skin into leather, which can be used in the manufacture of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Among these, tanning is the fundamental stage that gives leather its stability and essential character. Tanneries very often are small enterprises (European Commission 2003a), including artisanal activities in developing countries.

2.2 Process description

The tanning industry is a potentially pollution-intensive industry with relevant water discharges and uses of certain chemicals such as biocides, surfactants and organic solvents.

The production process in a tannery can be divided into four stages:

- Hide and skin storage and beamhouse operations;
- Tanyard operations;

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[2] 1 ng (nanogram) = 1×10^{-12} kilogram (1×10^{-9} gram); Nm^3 = normal cubic metre, dry gas volume measured at 0° C and 101.3 kPa. For information on toxicity measurement see section I.C, subsection 3 of the present guidelines.

- Post-tanning operations;
- Finishing operations.

2.3 Sources of chemicals listed in Annex C of the Stockholm Convention

So far, there are no reports on PCDD/PCDF contamination at or around leather plants. However, contamination of commercial leather products has been reported and, based on the PCDD/PCDF pattern, it can be assumed that principally the processes identified in the textile industry are also responsible for the occurrence of PCDD/PCDF in leather products and in emissions (UNEP 2003).

The primary source of contamination seems to be pentachlorophenol. This assumption is underlined by the fact that since its ban in Germany in 1989[3] the PCDD/PCDF concentrations in leather goods have declined (European Commission 1996).

3. Concentrations of PCDD/PCDF in chemicals used in the textile and leather production chains

Table 1 summarizes the range of PCDD/PCDF concentrations reported in the literature for biocides and chemicals used in the production of dyestuffs. It should be noted that some of the information is quite old and may no longer apply to the present situation. Nevertheless, for historic evaluation and since the presence of some earlier produced batches may still be used or consumer goods treated with these chemicals may still be found in some parts of the world, the information included here may be valuable.

Table 1. Concentrations of PCDD/PCDF in biocides and dye pigments/dyestuffs

Chemical	Country or use	Concentration (ng I-TEQ/kg)	Remark
Biocides			
PCP Pentachlorophenol	China, Europe, USA	800,000–4,445,000	Different production processes
PCP-Na Sodium salt of pentachlorophenol	China, Europe, USA	500–3,374,000	Different production processes
CNP Chloronitrofen	Japan	400/300,000	Old/new technology
Dye pigments/starting materials/dye			
Chloranil	Starting material for production of dioxazine dyes	100–3,065,000	Different production processes
Carbazole violet	Dye pigment	211,000	
Blue 106	Dioxazine dye	19,502–56,428	

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[3] Which sets a maximum concentration of 5 mg pentachlorophenol per kg in the final product.

4. Best available techniques and best environmental practices

General good management practices include staff education and training, maintenance of equipment (and its documentation), chemical storage, handling, dosing and dispensing, and improved knowledge of inputs and outputs of the processes.

Knowledge about the textile raw materials is essential in managing pollution transfers. Raw wool fibres may be contaminated with pesticides, sometimes organochlorine pesticides, including pentachlorophenol and chloronitrofen. Effective washing and wool scouring, for example with perchloroethylene, will effectively remove all grease and pesticides that are typically found in the solvent phase.

For artisanal activities, responsible authorities should advocate improvement in basic housekeeping and occupational safety. Information and awareness programmes should be undertaken.

The primary sources of PCDD/PCDF contamination in textiles and leather goods are the chemicals applied in the respective production or finishing chains, such as fungicides and dyestuffs known to be contaminated with PCDD/PCDF.

The most efficient primary measure to prevent contamination of textiles and leather goods with PCDD/PCDF would be not to use these chemicals in the production chains. If any of the above-mentioned chemicals are being used, preference should be given to batches containing low concentration (e.g. distilled or otherwise purified chemicals).

In order to prevent or minimize formation and release of PCDD/PCDF when burning sludge from wastewater treatment and flotation, the best available techniques should be applied. However, other environmentally sound techniques should also be explored.

5. Alternatives

Since the occurrence of PCDD/PCDF in the textile and leather industries is primarily linked to the use of dioxin-contaminated chemicals such as pentachlorophenol and certain dye pigments, substitution of these chemicals by dioxin-free chemicals would be the alternative. For example, in Germany after the phase-out of pentachlorophenol as a preservative, the following chemicals have been used:

- 2-(thiocyanomethylthio) benzothiazole (TCMTB; CAS Registry No. 21564-17-0);
- *o*-phenylphenol (oPP; CAS Registry No. 90-43-7);
- 4-chloro-3-methylphenol (CMK; CAS Registry No. 59-50-7);
- 2-*n*-octyl-4-isothiazolin-3-one (OIT; CAS Registry No. 26530-26-1).

The above-mentioned chemicals are assessed as less hazardous for the environment than pentachlorophenol but they are not inherently safe at all. Safer alternative chemicals should be explored. As much as possible, it is imperative to avoid burning textile, upholstery, leather products and carpet to prevent PCDD/PCDF formation.

6. Monitoring

There is no simple indicator to identify dioxin-contaminated fibres, wools or textiles. Several analyses confirmed that there is no correlation between pentachlorophenol and PCDD/PCDF concentrations in textiles although the dioxin patterns gave strong indications that pentachlorophenol should be the source. These findings make sense as pentachlorophenol is water soluble and will be removed in the finishing process and final washing processes, whereas the PCDD/PCDF adsorb to the fibre and will stay in the textile. For leather products, in most cases, there was a qualitative correlation between pentachlorophenol and PCDD/PCDF.

National capacity should be built/strengthened for monitoring possible sources of PCDD/PCDF from the textile and leather industry, including imported supply. More guidance is needed on monitoring of pentachlorophenol in wastewater .

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Part III Source category (k): Shredder plants for the treatment of end-of-life vehicles

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VI.K Shredder plants for the treatment of end-of-life vehicles

Summary

Shredder plants for treatment of end-of-life vehicles are lbisted in Annex C of the Stockholm Convention as a source that has the potential to form and release chemicals listed in Annex C. Shredders are large-scale machines equipped inside with one or more anvils or breaker bars and lined with alloy steel wear plates. An electric motor drives the rotor with the free-swinging alloy steel hammers. Beneath the shredder is a vibratory pan, which receives the shredded material discharged through the grates. Typically a ferrous metal stream is produced, which is relatively clean and consists of small (50 mm) pieces of steel and a “fluff” stream, which contains the fragments of non-ferrous metals and other materials that entered the shredder (also known as fragmentizer).

Very few data of stack emission measurements at shredder plants are available. However, the results of some studies have shown levels of dioxin compounds greater than 0.1 ng I-TEQ/m^3. At present there is not sufficient evidence that in the (mechanical) shredding of vehicles, household electrical equipment or other electrical appliances new formation occurs of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) or polychlorinated biphenyls (PCB). The data available indicate that the PCDD/PCDF and PCB released from shredder plants are from industrial, intentional production and have been introduced with oils, dielectric fluids, and other materials contained in these vehicles or consumer goods and which are simply set free through this mechanical process.

In any case, measures to prevent accidental fires (which could result in the formation of chemicals listed in Annex C) should be in place at shredder plants. Shredder light fluff consists of flammable plastic films and fibrous dust, which forces a careful plant operation for the prevention of accidental fire. Systems for dust suppression (e.g. wet shredding) or dust collection (e.g. cyclones, venture scrubbers or baghouse) are normally installed on shredder plants for the treatment of end-of-life vehicles. Dust suppression or collection systems would help to reduce potential emission of persistent organic pollutants. To improve emission control of the dust, fine dry residues should be stored in such a way that dispersion is minimized. Other sources of dioxin precursors that may result in the formation of PCDD/PCDF when burnt include PCB-containing condensers, PCB- or chlorobenzene-contaminated waste oils or textiles, and polymers containing brominated flame retardants (formation of polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans (PBDF) as contaminants).

Preamble

Shredder plants for the treatment of end-of-life vehicles are listed in Annex C of the Convention as a source that has the potential to form and release unintentional persistent organic pollutants. At present, however, there is insufficient evidence that, in this mechanical process, dibenzo-p-dioxins and dibenzofurans or polychlorinated biphenyls are newly formed. The data available indicate that the dibenzo-p-dioxins and dibenzofurans and polychlorinated biphenyls released from shredder plants are from industrial/intentional polychlorinated biphenyl production and have been introduced with the oils and dielectric fluids, etc., contained in the vehicles or more probably in consumer goods. The shredders simply free these contaminants.

1. Process description

End-of-life-vehicles are processed through shredders. The practice is to shred them along with other end-of-life metal products (such as bicycles, office furniture, vending machines and so-called white goods, such as household devices). In the plant, a high-performance-hammer mill produces sized pieces of ferrous scrap of a high physical and chemical purity. The ferrous scrap is sought after by steel makers and other secondary metal producers. An overview of the process is shown in figure 1.

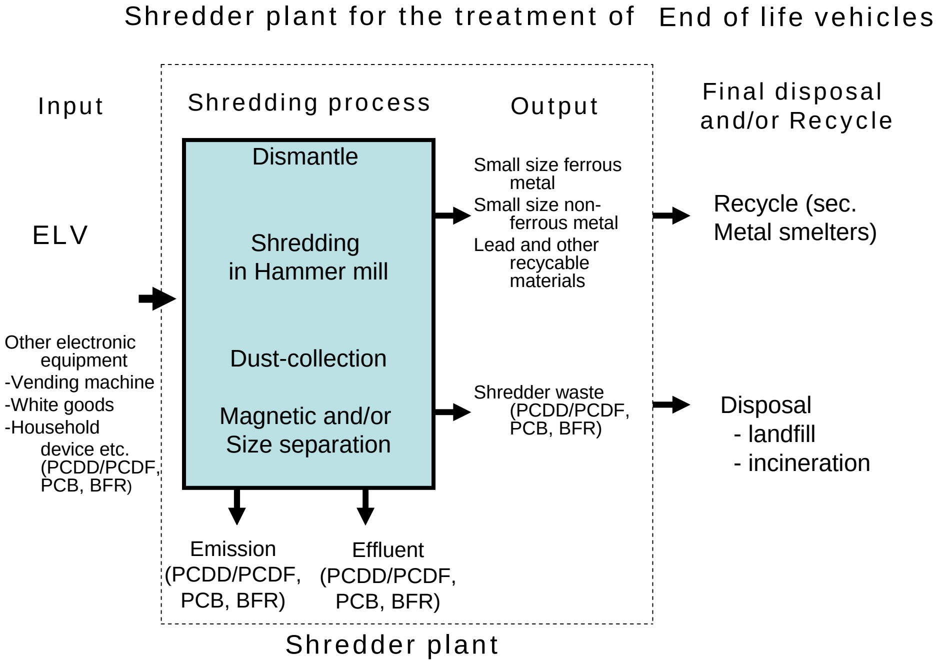
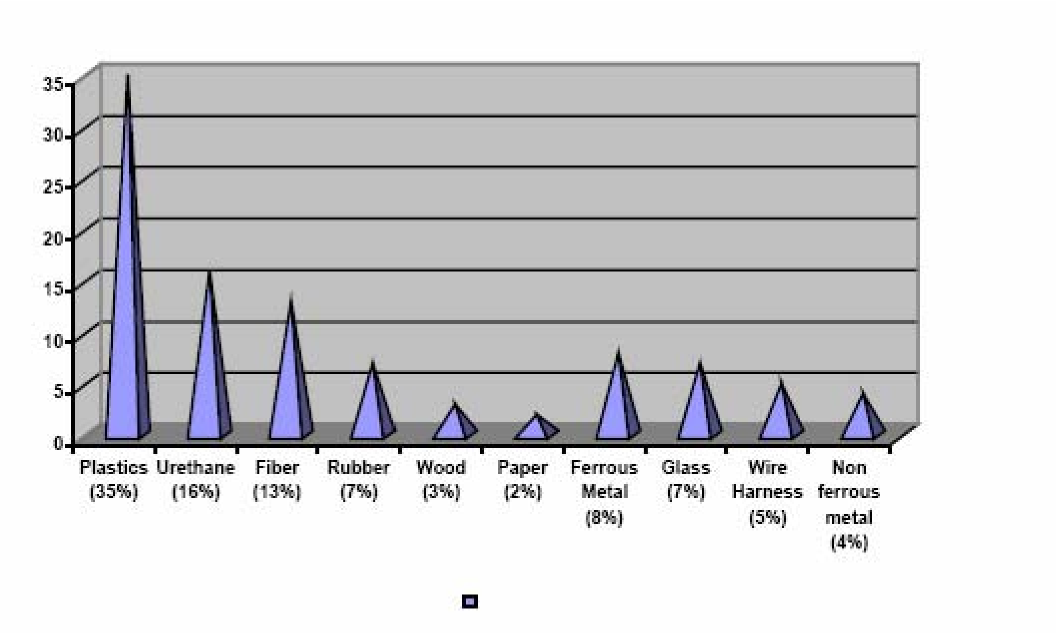


Figure 1 Overview of the shredder process

Many components of vehicles and other electrical devices are made of non-ferrous materials, such as copper, aluminum and zinc. In the shredding process, magnetic separation is used to remove the magnetic ferrous fraction from other materials. The non-ferrous metals, such as copper and aluminum, are normally sorted out at a later stage. The remainder is the so-called shredder waste and is estimated at between 25% and 35% of the weight of end-of-life vehicles (Environment Australia, Department of the Environment and Heritage, 2002). Shredder waste consists of glass, fibre, rubber, automobile liquids, plastics and dirt. Figure 2 illustrates the composition of shredder waste.



(Source: Environment Australia, Department of the Environment and Heritage (2002))

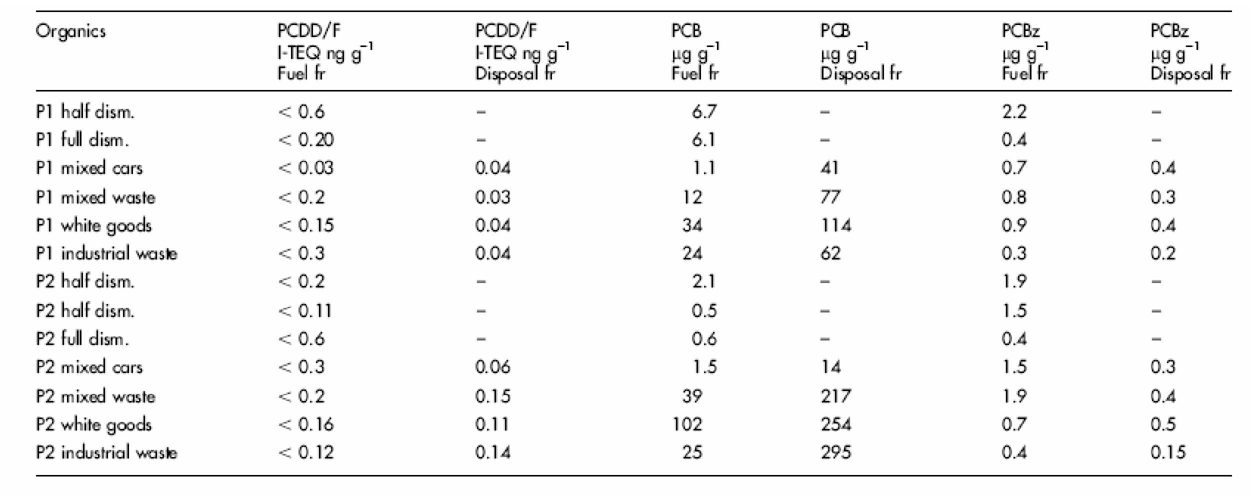
Figure 2 Composition of shredder waste

3. Composition of shredder waste

The composition of shredder fluff will vary considerably from batch to batch and shredder to shredder – due to the different mixes of raw materials being processed and the differing levels of pre-processing and inspection by shredder operators. It should be noted that shredder fluff is likely to vary significantly between shredders due to varying requirements under state and territory licensing conditions and the changes in those conditions over time.

An investigation from Sweden (Börjeson, L.; Löfvenius, G.; Hjelt, M.; Johansson, S.; Marklund, S., 2000) shows that levels of PCDD/PCDF per gram in dry samples of shredder fluff are low in all the fractions (table 1). This conforms to expectations that levels of dioxins and furans should generally be very low, because dibenzo-p-dioxins and dibenzofurans is neither used nor deliberately produced for any technical product or substance.

Unlike the dibenzo-p-dioxins and dibenzofurans levels, however, the levels of polychlorinated biphenyls were high, especially in fractions originating from industrial waste or waste white goods. The presence of polychlorinated biphenyls in white goods contributes most heavily to polychlorinated biphenyls in the shredder process, but is not a result of unintentional formation during the shredder process. Therefore, it is desirable to know and identify before the shredder process which components of an electrical device may include these compounds and to try to dismantle them before shredding.



Organics	PCDD/F I-TEQ ng g^{-1} Fuel fr	PCDD/F I-TEQ ng g^{-1} Disposal fr	PCB µg g^{-1} Fuel fr	PCB µg g^{-1} Disposal fr	PCBz µg g^{-1} Fuel fr	PCBz µg g^{-1} Disposal fr
P1 half dism.	< 0.6	–	6.7	–	2.2	–
P1 full dism.	< 0.20	–	6.1	–	0.4	–
P1 mixed cars	< 0.03	0.04	1.1	41	0.7	0.4
P1 mixed waste	< 0.2	0.03	12	77	0.8	0.3
P1 white goods	< 0.15	0.04	34	114	0.9	0.4
P1 industrial waste	< 0.3	0.04	24	62	0.3	0.2
P2 half dism.	< 0.2	–	2.1	–	1.9	–
P2 half dism.	< 0.11	–	0.5	–	1.5	–
P2 full dism.	< 0.6	–	0.6	–	0.4	–
P2 mixed cars	< 0.3	0.06	1.5	14	1.5	0.3
P2 mixed waste	< 0.2	0.15	39	217	1.9	0.4
P2 white goods	< 0.16	0.11	102	254	0.7	0.5
P2 industrial waste	< 0.12	0.14	25	295	0.4	0.15

(Source. Börjeson, L; Löfvenius, G; Hjelt, M.; Johansson, S.; Marklund, S. 2000)

Table 1 Organics in shredder residues defined in the original reference as "fuel fractions" and "disposal fractions

Studies have confirmed that automotive shredder residues derived from end-of-life vehicles contain PCB in the ppm-range (=mg/kg) (Urano *et al.* 1999, Sakai *et al.* 1998, 2000). dibenzo-p-dioxins and dibenzofurans contamination in engine oil from end-of-life vehicles could not be detected. Taking congener profiles into account, it can be considered that the major reason for this is that polychlorinated biphenyls -containing materials manufactured in the past were mixed in the recycling and waste processes. While emissions of persistent organic pollutants from shredding plants were not examined in these studies, given the levels of PCB in the ppm-range (=mg/kg) in automotive shredder residues, potential emissions of persistent organic pollutants through flue gas should be considered. This polychlorinated biphenyl release originates from the commercial polychlorinated biphenyl mixture that is used in automobiles. These PCBs are not unintentionally generated persistent organic pollutants and thus, in a strict sense, not subject to the polychlorinated biphenyl release inventory under the provisions of Article 5 of the Stockholm Convention. Since there is no way, however, to differentiate between intentional and unintentional polychlorinated biphenyls in shredder wastes and emissions, best available techniques and best environmental practices should be applied to minimize or eliminate release of any polychlorinated biphenyls from the shredder process.

Copper and chlorine in significant amounts are constituents of shredder waste and promote in case of burning the formation of dibenzo-p-dioxins and dibenzofurans and other unintentionally released persistent organic pollutants.

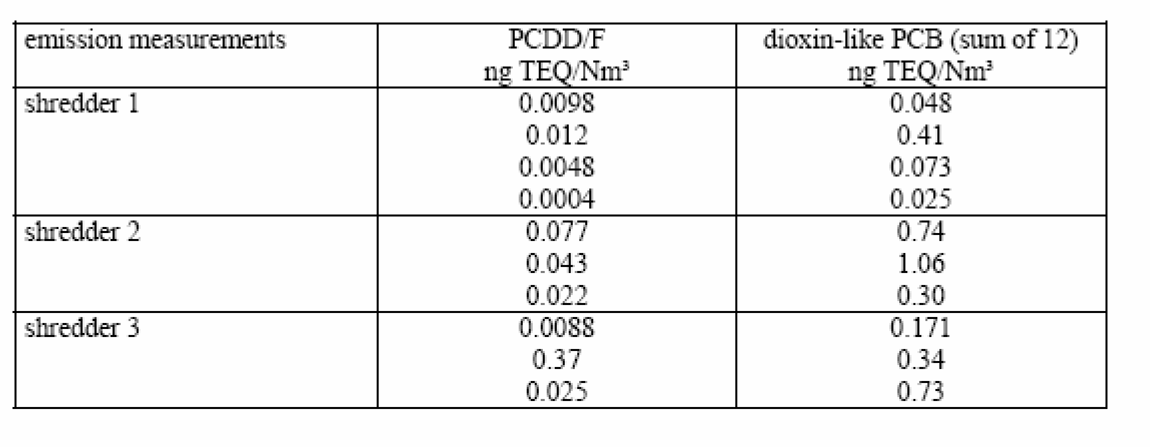
4. Emission concentrations from shredder plants

A report on a European dioxin inventory stated that measured dibenzo-p-dioxins and dibenzofurans data exist for a few shredder installations. Generally, very low concentrations (< 0.01 ng I-TEQ/m³) were found in a plant investigated in Sachsen-Anhalt (Germany). The available data are summarized in table 2 below, showing emissions and emission factors to air.

Table 2 Dibenzo-p-dioxins and dibenzofurans emissions in German shredder plants (LUA 1997)

	Minimum	Maximum	Geometric mean	Arithmetic mean
Emission concentration (ng I-TEQ/m³)	0.002	0.430	0.056	0.140
Emission factor (µg I-TEQ/t)	0.059	0.667	0.236	0.303

A further investigation from Belgium (François, F., Blondeel, M., Bernaert, P., Baert, R., 2004) considered potential specific sources of unintentionally released PCB and PCDD/PCDF from a shredder plant turning end-of-life vehicles and waste from electronic and electrical equipment into various reusable fractions. An overview of a number of stack emission measurements of dibenzo-p-dioxins and dibenzofurans and unintentionally released polychlorinated biphenyls is given in table 3. The shredders are equipped with at least a cyclone filter system for de-dusting the flue gases. Flue gas flow rates are typically about 75,000 Nm³/h. All dibenzo-p-dioxins and dibenzofurans concentrations, except one, were below 0.1 ng TEQ/Nm³.



emission measurements	PCDD/F ng TEQ/Nm³	dioxin-like PCB (sum of 12) ng TEQ/Nm³
shredder 1	0.0098	0.048
	0.012	0.41
	0.0048	0.073
	0.0004	0.025
shredder 2	0.077	0.74
	0.043	1.06
	0.022	0.30
shredder 3	0.0088	0.171
	0.37	0.34
	0.025	0.73

(Source: François, F., Blondeel, M., Bernaert, P., Baert, R. 2004)

Table 3 Measured data for emission concentrations from shredder plants

Dioxin precursors which may result in the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) when burnt include polychlorinated biphenyls -containing condensers, polychlorinated biphenyls or chlorobenzene contaminated waste oils or textiles, and polymers containing brominated flame retardants (formation of polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzofurans (PBDF) as contaminants).

5. Recommended measures

An important best environmental practice is to strengthen the responsibility of the operators of shredders. An analysis should be undertaken to identify hazardous components and fluids with incoming material and to provide facilities to remove them before the shredder process.

It is crucial to control treated scrap, especially electric devices, transformers and condensers, which must be identified, dismantled and eliminated separately to avoid the introduction of polychlorinated biphenyls into the plant. This is also a measure to reduce the contamination of shredder residues by polychlorinated biphenyls.

Nevertheless, shredder residues are always contaminated and must only be disposed of in an incineration dedicated plant.

By dismantling and recycling big plastic parts, for instance bumpers, a considerable reduction of the remaining plastic fraction in the end-of-life vehicles and in the resulting shredder waste can be achieved.

By further treatment of shredder wastes, for instance by eddy current separation, a considerable proportion of the metals contained in the waste, such as copper and aluminium, can be recovered.

In order to achieve a higher proportion of recyclable fractions, the use of recyclable material and simple disassemblies should be encouraged in the stage of product design. This is not only valid for end-of-life vehicles.

6. Minimum technical requirements for treatment

Sites have to be constructed to prevent the contamination of soil, water and air. For this reason, appropriate storage facilities, including impermeable surfaces with spillage collection facilities; decanters and cleanser-degreasers should be provided, as well as equipment for the treatment of appropriate storage tanks for water, including rainwater. In addition, appropriate storage for dismantled spare parts, including impermeable storage for oil-contaminated spare parts, appropriate containers for the storage of batteries (with electrolyte neutralization on site or elsewhere), filters and PCB/PCT-containing condensers and appropriate storage tanks for fluids are necessary.

7. Primary measures

Fluids, like brake fluid, petrol, steering fluid, motor oil, coolants and transmission fluid should generally be removed from the end-of-life vehicle or other devices before shredding. This is especially applicable in the case of PCBs, which should be identified and removed from any device to be shredded. Specific attention should be given to transformers and condensers. Measures should include:

- The removal of batteries and liquified gas tanks;
- The removal or neutralization of potential explosive components, (e.g., air bags);
- The removal and separate collection and storage of fuel, motor oil and oil from other components;
- The removal of catalysts;
- The removal of tyres and large plastic components (such as bumpers, dashboards, fluid containers, etc.), if these materials are not segregated in the shredding process in such a way that they can be effectively recycled as materials.

8. Secondary Measures

Measures to prevent releases of persistent organic pollutants at shredder plants include:

- The advanced treatment of flue gas (with bag filters and activated carbon filters to remove both gaseous and particle emissions);
- The proper disposal of residuals and liquid shredder wastes containing a mixture of organic materials, heavy metals such as copper and, in many cases, polychlorinated

biphenyls and other chlorinated substances. Treating this waste in an inappropriate manner will lead to emissions of unintentionally released persistent organic pollutants. This is especially the case in open burning. Shredder wastes should be never burned in an open fire or in inappropriate facilities;

- The appropriate treatment of shredder waste is incineration in a facility meeting the requirements for best available techniques and best environmental practices. If such a facility is not available, disposal in a sanitary landfill may be preferred to other forms of disposal.

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Part III Source category (l): Smouldering of copper cables

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VI.L. Smouldering of copper cables

Summary

Scrap copper is often recovered by open burning of plastic coatings from electrical cable and wiring. Chemicals listed in Annex C of the Stockholm Convention are probably formed from plastic and trace oils with copper as a catalyst at smouldering temperatures between 250° and 500° C.

Best available techniques include mechanical cable chopping, stripping or high-temperature incineration > 850° C. A consideration is to set premium pricing for unstripped cables and wiring and encourage sending the feed material to copper smelters using best available techniques for treatment.

Performance levels associated with best available techniques are not applicable, as the smouldering process is not a best available technique or best environmental practice and should not be practised.

1. Process description

Smouldering of copper cables involves the open burning of plastic coatings from electrical cable and wiring to recover scrap copper and other constituents of the cablesThis process is labour intensive, and is performed by individuals or in small facilities without any abatement measures for air emissions. Smouldering is conducted in burn barrels or on open ground. No means of temperature control or oxygen addition are used to achieve complete combustion of plastic compounds.

The smouldering of copper cables is becoming prevalent in developing nations due to the recycling of computer scrap using manual methods. However, the process is not limited to developing countries and should be addressed on a global scale. Legislation has been implemented by many developed and developing countries to ban open burning, but the practice continues.

In the technical guidelines for identification and environmentally sound management of plastic wastes and for their disposal under the Basel Convention on the Control of the Transboundary Movements of Hazardous Wastes and Their Disposal it is stated: “Open burning is not an environmentally acceptable solution for any kind of waste” (UNEP 2002, p. 43). In addition, Decision VII/19 of the seventh meeting of the Conference of the Parties to the Basel Convention (October 2004) amended Annexes VIII and IX of the Convention to include new entries regarding the uncontrolled burning of plastic-coated cable scrap. The United Kingdom Clean Air Act states: “A person who burns insulation from a cable with a view to recovering metal from the cable shall be guilty of an offence … [and] shall be liable on summary conviction to a fine…” (Government of the United Kingdom 1993).

2. Sources of chemicals listed in Annex C of the Stockholm Convention

The formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) may occur with trace oils and the presence of chlorine from plastics in the feed material. As copper is the most efficient metal to catalyse PCDD/PCDF formation, the burning of copper cables may be a critical source of PCDD/PCDF emissions.

2.1 General information on emissions from smouldering of copper cables

Smouldering of copper cables releases various contaminants besides PCDD/PCDF, such as carbon monoxide (CO), sulphur dioxide (SO_2), polycyclic aromatic hydrocarbons, hydrogen chloride, heavy metals and ash. Incomplete incineration occurs because of the low burning temperature (250° to 700° C), resulting in the generation of hydrocarbons and particulate matter. Lead stabilizers, often included into the PVC polymer matrix of the plastic cable coating, are released during smouldering. Lead-coated copper cables are also burnt, releasing additional lead. Contaminants are emitted to air, water and soil.

2.2 Emissions of PCDD/PCDF to air

The incomplete incineration of chlorinated plastics causes PCDD/PCDF generation. Plastic coatings on copper cables consist mainly of polyvinyl chloride (PVC).

> "During combustion, various ring-structure hydrocarbon species (referred to as 'precursors') are formed as intermediate reaction products. If chlorine is also present, these species can react with each other to form PCDD/PCDF. The most frequently identified precursors are chlorobenzenes, chlorophenols, and chlorinated biphenyls. PCDD/PCDF may also be formed from the reaction of complex organic molecules and chlorine. Several studies have identified strong correlations between chlorine content and PCDD/PCDF emissions during combustion tests" (EPA 1997, p. 3–8).

Destruction of PCDD/PCDF requires temperatures above 850° C in the presence of oxygen (European Commission 2001).

3. Alternative processes to smouldering of copper cables

To prevent the generation of PCDD/PCDF, smouldering of copper cables should not be conducted. Alternative treatment processes to open burning are discussed below. The insulation material, for example PVC, may also be recovered by using these processes.

3.1 Cable chopping

Cable chopping allows for the separation of plastic coatings from cables without the generation of PCDD/PCDF through thermal methods (UNEP 2001). This process is able to treat cables of mixed type and different gauges. The products recovered are granulated copper and PVC.

Cable chopping involves the following steps:

3.1.1 Presorting

Presorting according to cable type is crucial for efficient cable chopping operations, providing maximum value from recovered scrap with easier separation of plastics. Sorting criteria include metal alloys (separating copper and aluminium cables), conductor diameter, cable length and type of insulation. Long cable lengths are sheared to < 1 m, while densely baled cable is broken up into loose streams. Treated cables can vary between thin gauge and 8 cm diameter. Unsuitable material such as superfine wire and grease or tar-filled cables should be removed.

> "In the past PCB was added to PVC for certain cable systems for high voltage applications to improve insulation performance and to certain low voltage cables as flame retardant. The presence of these cable systems should be determined before starting the recycling process" (UNEP 2001).

According to PCB data reported for Germany, most of the samples show contamination levels of 30 mg PCB/kg, with some reaching contamination levels of several hundred ppm and others with contamination levels < 10 ppm.

3.1.2 Cable chopping

Cable chopping is used to reduce long cable sections into acceptable size for the granulator. This process is optional in smaller facilities. Less filter dust is produced in comparison to cable shredding.

3.1.3 Granulation

Granulation is conducted to free metals from plastic insulation and jacketing. Fine granulation is necessary to achieve sufficient liberation of metals from the plastic. However, small amounts of metals will remain locked in the plastic and be lost as waste.

3.1.4 Screening

Screening can be used to ensure adequate liberation of metals by particle size separation. Oversize material can be reprocessed in the granulator. Metal particles can be recovered from the screen product by removal of lighter non-metallic particles using an aspirator. Dust collection and filtering should be conducted during screening.

3.1.5 Density separation

The recovery of metals is dependent on the efficiency of the separation technique and degree of liberation of the metal from plastics. Separation of metal particles can be conducted using density separation techniques such as fluidized bed separators. Dry electrostatic separators can provide increased recovery compared to density techniques.

3.2 Cable stripping

Cable stripping is a cheaper method for copper cable recovery than chopping, but at lower throughput. PCDD/PCDF generation is not of concern in this process. This technique is preferred in developing countries due to the lower cost. Presorting of cables should also be conducted before stripping according to metal type, insulation material, conductor diameter and length (UNEP 2001, p. 44).

Despite the lower production rate, copper can be completely recovered as no residual metal remains in the plastic insulation. Careful segregation by insulator type can produce waste material consisting of only one type of polymer, allowing for easier recycling of both the metal and plastic fractions.

Cable stripping machines can process only single strands of cable at rates up to 60 m/min or 1,100 kg/min with cable diameter ranging from 1.6 mm to 150 mm.

3.3 High-temperature incineration

High-temperature incineration should only be used for treating cable that cannot be recovered by chopping or stripping. Materials such as fine wire and grease- or tar-filled cables are burnt in controlled atmosphere incinerators to ensure complete combustion of plastics. Effective flue gas cleaning systems should be utilized (UNEP 2001, p. 46).

Furnace off-gases contain contaminants such as PCDD/PCDF, carbon dioxide (CO_2), sulphur dioxide (SO_2), hydrogen chloride and fluoride, and dust. Because PCDD/PCDF adsorb on particulate matter, dust should be collected using efficient methods such as fabric filters and recycled to the furnace. Post-incinerator afterburning and quenching should be considered if incineration is ineffective in eliminating PCDD/PCDF. SO_2 and hydrogen chloride and fluoride should be removed by wet alkaline scrubbing.

Incinerated scrap metal has less value due to oxidation from thermal treatment. A high potential for PCDD/PCDF generation exists with incineration. Cable chopping and stripping are preferred to high-temperature incineration as these processes are more economical and environmentally sound. Cable types unsuitable for chopping or stripping can also be treated in primary or secondary copper smelters.

4. Summary of measures

Table 1 summarizes measures for new copper cable recovery facilities.

Table 1. Measures for new copper cable recovery facilities

Measure	Description	Considerations	Other comments
Alternative processes	Various recommended treatment processes should be considered to replace open burning	Processes to consider include: • Cable chopping • Cable stripping • High-temperature incineration for material unsuitable for chopping or stripping	Incineration is considered to be a best available technique in configuration with suitable gas collection and abatement

Smouldering of copper cables should not be conducted as this practice generates PCDD/PCDF emissions. Open burning should never be considered as an acceptable means of waste treatment.

Guidelines and legislation against the smouldering of copper cables have been implemented at federal, state, provincial, territorial and municipal levels by many countries.

Examples of such guidelines and legislation include UNEP 2001; Government of the United Kingdom 1993; Government of Hong Kong 1996; Government of New Zealand 2004.

A consideration is to set premium pricing for unstripped cable and wiring to encourage sending the feed material for treatment in copper smelters using best available techniques.

Achievable performance limits are not applicable, as the smouldering process is not a best available technique or best environmental practice and should not be practised.

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Part III Source category (m): Waste oil refineries

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V.I.M. Waste oil refineries

Summary

Waste oil refineries are listed in Annex C of the Stockholm Convention as a source that has the potential to form and release chemicals listed in Annex C.

For the purpose of this guidance section, waste oils (or used oils) are defined as any petroleum-based, synthetic, or plant- or animal-based oil that has been used. Waste oils may originate from two large sources: industrial waste oils, and vegetable and animal waste oils. Among the industrial waste oils, three main oil streams can be identified: industrial oil (e.g. hydraulic oil, engine lubricant, cutting oil); garage or workshop oil; and transformer oil.

Waste oils have been found to be contaminated with polychlorinated dibenzo-p-dioxins,, polychlorinated dibenzofurans and polychlorinated biphenyls.. At present there is no available evidence that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans or polychlorinated biphenyls, are newly formed in waste oil refineries. The data available indicate that the polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans or polychlorinated biphenyls released from waste oil refineries or waste oil handling and management plants are from industrial, intentional production of polychlorinated biphenyls or chlorobenzenes that are present in the waste oils either by contamination in the synthesis process (of these chemicals) or have become contaminated during the use phase or earlier recycling processes. In this sense, waste oil refineries represent a distribution source of chemicals listed in Annex C rather than a formation source.

According to available information, waste oil management options include reuse or regeneration; thermal cracking; and incineration or use as fuel. It should be noted that dumping and open burning are also practised in many countries.

For information on waste oil disposal in incinerators or on use as fuel, the relevant sections of this guidance document should be consulted (sections V.A, waste incinerators; V.B, cement kilns firing hazardous waste; VI.A, open burning of waste; VI.C, residential combustion sources; and VI.D, fossil fuel-fired utility and industrial boilers).

1. Introduction

Waste oil refineries are listed in Annex C of the Stockholm Convention as a potential source of chemicals listed in Annex C. The information reported about waste oil refineries as sources of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) is very limited and further research is needed.

2. Waste oils

Waste oils include any petroleum-based or synthetic oil that has been used. Water, chemicals, metal particles and dirt become mixed in with the oil during use, degrading its properties until it must be replaced by new oil.

New oils are a mixture of a base oil (mineral or synthetic) and additives (15–25%). The type of base oil and additives determine the possibility of regeneration and the possible formation of PCDD/PCDF in waste oil refineries.

3. Occurrence of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) in used oils

Hagenmaier and Brunner (cited by Fiedler) analyzed new and used (after 10,000 km in cars fuelled with leaded gasoline) motor oils. At a limit of quantification of 0.05 μg/kg per congener, no polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans could be detected in fresh and used motor oils. However, highly chlorinated polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans or were detected in recycled oils, probably from used oils contaminated with pentachlorophenol and its sodium salt, which in Europe were used in the mineral oil industry. It must

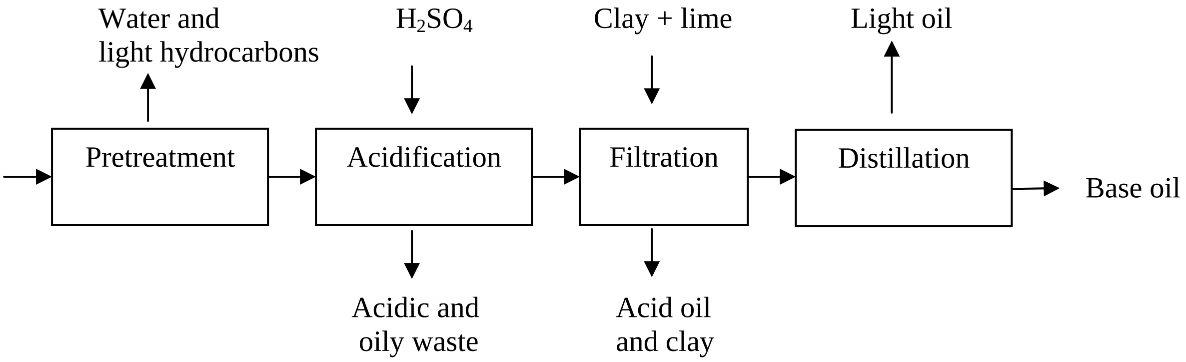
be noted that some of the additives used in modern lubricant oils contain chlorinated compounds and it is necessary to continue monitoring waste oils fed to refineries.

4. Waste oil refineries

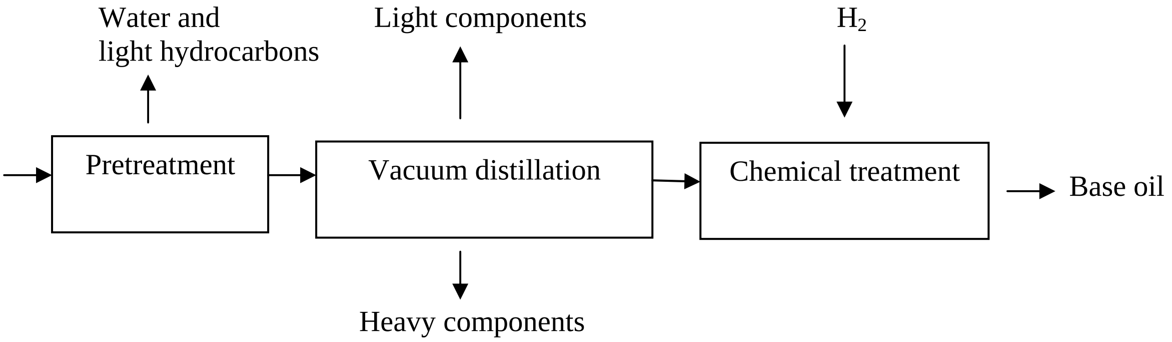
Waste oil refineries are designed to produce a base blending oil, some by-products and some wastes. The lighter parts of the by-products may be used as fuel; the heaviest, containing additives and carbonaceous species, may be used as a blending component in road surfaces.

Five technologies are representative of waste oil refineries:

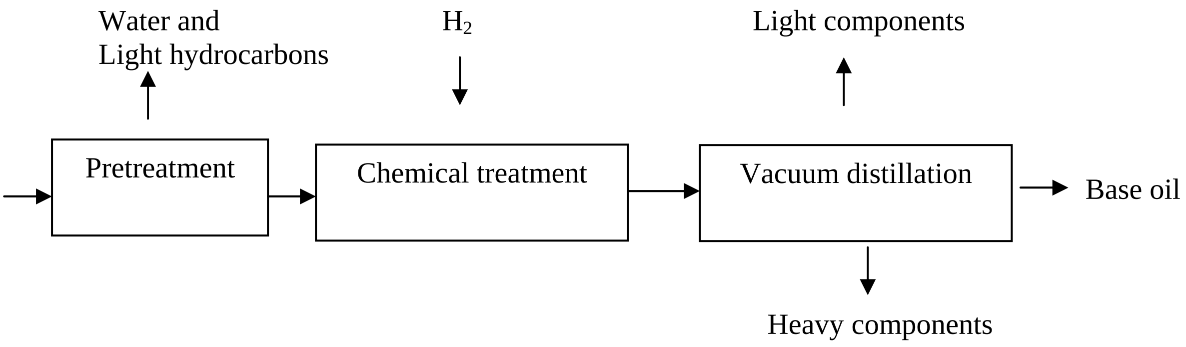
4.1 Vacuum distillation + clay treatment



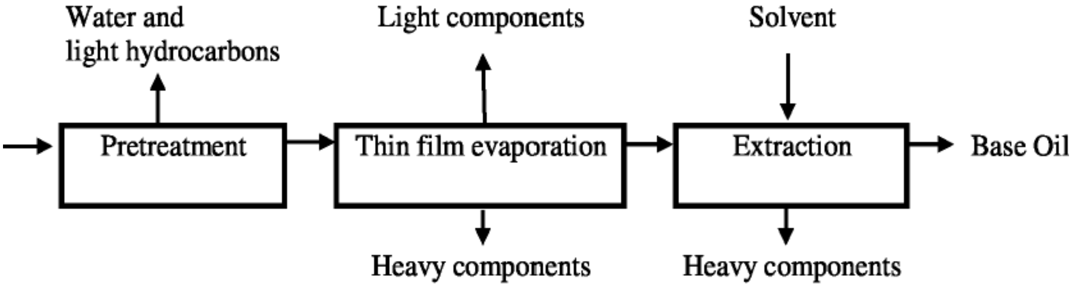
4.2 Vacuum distillation + chemical treatment



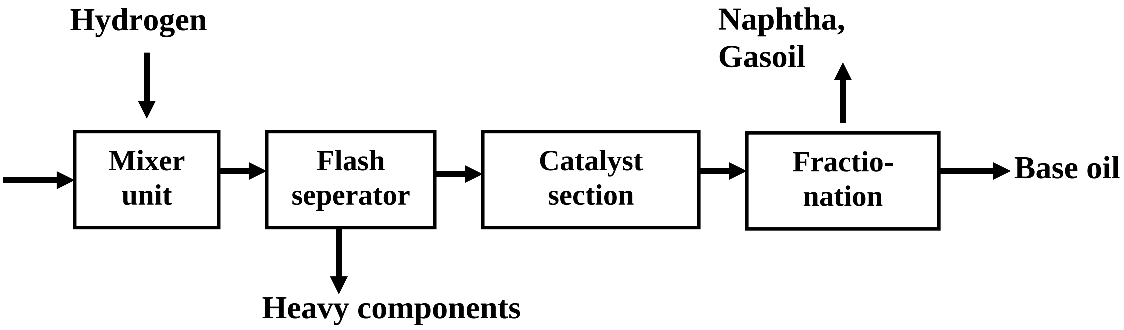
4.3 Hydrogen pretreatment + vacuum distillation



4.4 Thin film evaporation + extraction



4.5 Direct contact hydrogenation (UOP-DCH process)



5. Measures for reduction of polychlorinated dibenzo-p-dioxins,, polychlorinated dibenzofurans (PCDD/PCDF) and polychlorinated dibenzo-p-dioxins and polychlorinated biphenyls (PCB)

As previously indicated, PCDD/PCDF and PCB in oil base or residue from waste oil refineries emanate from contaminated waste oils. Therefore, one basic measure to reduce PCDD/PCDF and PCB emissions from such refineries is to only treat waste oils with low PCDD/PCDF and PCB concentrations.

The European Re-refining Industry Association (Groupement Européen de l'Industrie de la Régéneration; GEIR) recommend that the following waste oils be preferred for regeneration:

- Engine oils without chlorine;
- Hydraulic oils without chlorine;
- Non-chlorinated mineral diathermic oils.

6. Conclusions

- Waste oils have been found to be contaminated with PCDD, PCDF and polychlorinated biphenyls (PCB);
- At present there is no available evidence that PCDD, PCDF and PCB are newly formed in waste oil refineries;
- Waste oil refineries are a distribution source of chemicals listed in Annex C rather than a formation source;

- The waste oil treated in waste oil refineries must have a low content of PCDD, PCDF, PCB and chlorinated additives.

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