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Determination of Requirements to Limit Emissions of Dioxins and Furans

Report from the Working Group of the
Subcommittee Air/Technology of the
Federal Government/Federal States Immission
Control Committee

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Telefax: 030/8903 2285

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Elisabeth Schmid

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Preface

Measures to Reduce the Emission of Dioxins and Furans in the Federal Republic of Germany.

A central issue for the protection of human health and the environment will also be the reduction in future of the new inputs of polychlorinated dibenzodioxins and dibenzofurans, generally designated dioxins, into the environment. Effective measures have already been taken in Germany in recent years to fulfill this matter of concern. One example of this is the 17th Ordinance for the implementation of the Federal Imission Control Act (Waste Incineration Installations Ordinance). This ordinance applies to all installations in which certain waste materials in solid or in liquid form, or similar substances are incinerated. As well as strict requirements for an extensive range of air-polluting materials, it also lowers the emission-limit values for dioxins to 0.1 ng TE/m^3 in waste gases.

Against this background and commissioned by the Conference of the Ministers for the Environment and by the State Commission for Immission Control, it shall be investigated whether the limit values 0.1 ng TE/m^3 for emissions can also be applied to other emitting groups. In order to respond to this question, a working group has been set up under the direction of the Federal Ministry for the Environment. Other members comprise further expertise from Federation and State, as well as from the sciences and from measuring institutions. The information available on emissions of dioxins from installations which do not fall under the Ordinance for Installations for Waste Material Incineration, has been compiled.

Emphasis of the investigation was placed on large stationary industrial sources (installations subject to licensing in accordance with the Federal Immission Control Act); furthermore, the available information on domestic firing installations, dry cleaning processes and traffic was also compiled. The information is based on results from recent measurements. Pollution's from residues, in particular from filter dust, were also gathered. The individual processes with respect to their dioxin relevance and possible measures for their reduction, were investigated on the basis of the measurement results available. An evaluation of the measurements resulted into the classification of essentially three groups of installations according to the significance of their emissions:

a) Installations with an emission concentration of dioxins of less than 0.1 ng TE/m^3,
b) Installations with an emission concentration of dioxins of between 0.1 and 0.5 ng TE/m^3,

c) Installations with an emission concentration of dioxins of greater than 0.5 ng TE/m^3.

Included in group a) are power stations and combustion plants for fossil fuels, motorized or gas turbine installations for landfill gases, firing ovens for brickworks and building materials, cement furnaces, blast furnaces, oxygen top blowing converters, hot-blast cupola furnaces, hot-spelter galvanizers, aluminum smelters for predominantly pure materials, chemical plants, smoke-curing and green feed drying installations, domestic firing installations.

Belonging to group b) are shredder installations, installations for drying wood shavings, pyrolysis plants, installations for drying aluminum chips, thermal paint-stripping equipment.

Belonging to group c) are sintering plants, shaft furnaces for copper and lead, electric arc furnaces, aluminum smelters for impure materials.

Furnaces for the combustion of wood require special consideration as the emissions of dioxins greatly depend on the types of wood burned, the quality of the furnace and the dust collection fixtures installed. Untreated woods, good burn-out, good waste gas removal and effective separation result in emissions of less than 0.1 ng TE/m^3. Slightly higher emissions result from burning chipboard which has been manufactured using ammonium sulfate. Significantly higher dioxin concentrations are emitted if coated woods, wooden materials containing chloride and treated woods (e.g. with PCP, Lindane) are introduced into the combustion process.

The dioxin concentrations from cremation installations (crematoriums) range from 0.5 to over 10 ng TE/m^3.

The following concept of graduated requirements has been determined in order to limit the emissions of dioxins:

* Measures are not required for installations from which the emission of dioxins does not exceed the limit value of 0.1 ng TE/m^3.

* Installations with a waste gas volume flow of less than 5000 m^3/h are exempt from defining a limit value for their dioxin emissions. A minimization of the emissions shall however follow by the introduction of materials-related and process-related measures.

* For those installations which emit more than 0.1 ng TE/m^3 but less than 0.5 ng TE/m^3, it shall be determined on a case by case basis whether the defined limit value of 0.1 ng TE/m^3 for emissions is applicable as a target value. Case by case investigations shall take into consideration the dioxin carriage, the possibilities of recycling the residual materials as well as the expenditure necessary for implementing reduction measures.

* For those types of installation types with dioxin emissions exceeding 0.5 ng TE/m³, a target value of 0.1 ng TE/m³ is to be strived for by a pre-treatment of the materials, by conversion or optimization of the processes and waste gases transportation, as well as by the use of particularly effective waste gas purification technologies.

* Measures to reduce the emissions from wood combustion installations must be taken which shall depend on the power of the installation and the types of wood used. The target value here is 0.1 ng TE/m³.

Whether emission limitations for crematoriums need to be defined, is currently being investigated by the Federal States Committee on Pollution Control.

The results of this report form the basis for the decision from the Conference of the Ministers for the Environment from 24./25.11.1994. The resolution includes directives for emission restrictions and defines measures for the reductions of emissions (the wording of the resolution is attached as pages 4-6). The responsible local authorities of each Federal State must implement the decision. A swift implementation would contribute to a significant reduction in the intake of dioxins into the environment.

The following report is an official publication in German and has been adopted by the Federal Government/ Federal States Immission Control Committee. The publication in German has been issued by, and is available from, the publishers Erich-Schmidt.

43rd Conference of the Ministers for the Environment, 24th and 25th November 1994 in Chemnitz

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Agenda No. 24: Requirements to limit the emissions of Dioxins and Furans

subject: LAI (the Federal Government/ Federal States Immission Control Committee)

Resolution:

1. The Conference of the Ministers for the Environment have noted the report from the LAI.

2. The conference has determined that the dioxin emissions from
- a multitude of types of installations are, as a rule, less than 0.1 ng TE/m³, from individual types of installations considerably lower than this level,
- other types of installations are between approximately 0.1 and 0.5 ng TE/m³, and
- further types of installations exceeding 0.5 ng TE/m³, in some case even significantly greater than these levels.

3. The Conference of the Ministers for the Environment recommends the implementation of the following graduated plan to limit the emissions of dioxins and furans with regard to the current state of knowledge.

Furthermore, the requirements of the TA Air remain unchanged.

4. For those types of installations, from which the dioxin emissions do not exceed the limit of 0.1 ng TE/m³, further measures are not required. An increase of values from lower emissions to this limit is not however permitted.

5. For those types of installations having a waste gas volume flow of up to 5000 m³/h, a limit for the emissions for dioxins will not be defined as in the bagatelle regulation of the TA Air. A minimization of the dioxin emissions should however result from materials-related and process-related primary measures as well as optimizations in the waste gas purification techniques.

6. For those installations which emit less than approximately 0.5 ng TE/m³ but more than 0.1 ng TE/m³, taking into consideration

- the dioxin carriage (annual emission)
- the possibilities for recycling the residues and
- the expenditure for reduction measures,

on a case by case basis, it shall be determined whether an emission limit of 0.1 ng TE/m³ shall be applied as a target value.

7. For those types of installations with emissions exceeding 0.5 ng TE/m³, a target value of 0.1 ng TE/m is to be strived for by measures for the pretreatment of the materials utilized, by conversion or optimization of process operations and waste gas removal as well as by the implementation of particularly effective waste gas purification fixtures for dioxins in the course of a case by case investigation.

8. With regard to the recycling of wood and wood rests can be excluded, which in particular contain substances with chlorine (especially ammonium chloride), or are coated with materials containing halogenorganic substances, an optimization for wood-firing installations is to be carried out

- for installations up to 2.5 MW of the combustion and of the waste gas transportation as well as for the conventional dust deposits,
- for installations exceeding 2.5 MW, a particularly effective deposition of dust shall be installed as well as an optimization of the combustion and waste gas removal.

With regard to the recycling of wood and wood rests can be excluded, which in particular contain substances with chlorine (especially ammonium chloride), or are coated with materials containing halogenorganic substances, particular waste gas purification techniques shall be considered for wood-firing furnaces; in the course of a case by case investigation, a target value of 0.1 ng TE/m³ in the waste gas is to be strived for combustion plants of 1 MW and greater.

9. The LAI is requested to check, whether a special emission limit for dioxins and furans shall be defined for creation installations.

10. The Conference of the Ministers for the Environment recommend a rapid implementation of the above measures for new installations.
For the modernization of existing installations, appropriate interim time periods shall be foreseen for the accomplishment of the minimum target values, whereby, those installations with high dioxin mass flows should be modernized with a particularly high priority. The assessment of the time periods shall take appropriate times into consideration for the planning, installation and implementation of effective measures for emission reductions and which are expected to also result in an increase in the knowledge from the investigations currently being conducted.

11. Supplementary to the requirements placed on installations subject to licensing, the Conference of the Ministers for the

Environment explicitly point out the potentially higher dioxin emissions from those installations which are not subject to licensing. In particular those for solid fuel domestic firing installations in which improper materials utilized, such as waste packing materials, plastics or old paper are also burned, and can result in higher levels of dioxin in the waste gases. More information to the public on this subject is considered required with the objective of ensuring that only those materials are utilized which are approved.

12. With regard to the emissions of polybrominated and mixed-halogenated dioxins and furans, the Conference of the Ministers for the Environment have determined that only few results are available.

The use of compounds containing bromine shall be avoided as much as possible. For the implementation of process-related and waste gas measures to minimize the emissions of polychlorinated dioxins and furans, the effective reduction in polybrominated and mixed-halogenated compounds will be approximately proportional.

13. The conference of the Ministers for the Environment has noted that EU is concerned with the problems of dioxin emissions from industrial installations, and that Germany has offered to take over the chairmanship for the generation of the EU report. The Conference of the Ministers for the Environment has assured the Federal Minister for the Environment to support him in the accomplishment of this important assignment.

Protocol Note Hessen, Bremen, Sachsen-Anhalt

The Conference of the Ministers for the Environment considers the intended interpretation of the existing statutory regulations beyond the definition of a uniform statutory limit value for dioxin emissions of 0.1 ng/m^3 as being necessary for all industrial installations with mass flows, which are comparable to those from waste incineration installations, as far as this is possible according to the state of technology.

Report from the Working Group of the Subcommittee Air/Technology of the the Federal Government/ Federal States Immission Control Committee:

Determination of Requirements to Limit the Emissions of Dioxins and Furans

Sub-Division Page

Note: 4th BImSchV is the abbreviation used throughout this report for the Fourth Ordinance for the Implementation of the Federal Immission Control Act.

1. Mandate

The Federal Government/ Federal States Working Group DIOXINS, commissioned by the Conference of the Ministers for the Environment has requested the the Federal Government/ Federal States Immission Control Committee (LAI) to investigate the extent to which the emission limits of the Ordinance on Incineration Installations for Waste and Similar Combustible Substances (17 BImSchV) of 0.1 ng TE/m^3 for dioxins and furans can be applied to other emitting groups (e.g. installations for recycling metals, wood-burning furnaces). During the 77th conference of the the Federal Government/ Federal States Immission Control Committee which convened 06./08. May 1991, the subcommittee "Air/Technology" proposed that the emission limits for dioxins be worked out for the respective installations. The subcommittee recommended in an interim report to the LAI, based on the minimization rules in accordance with items 2.3 and 3.1.7 of paragraph 7 TA Air, to limit the emissions of dioxins and in individual cases of furans within the scope of reasonability, by as much as possible; a target value of 0.1 ng TE/m^3 should be strived for The LAI took note of this interim report during its 79th conference which convened 07./09. October 1991 and requested the subcommittee to compile emission values for installations with dioxin and furan emissions of relevance in an extensive report, and to determine the limit values for these emissions.

The conference of the subcommittee "Air/Technology" which convened 04./06. November 1991, requested that a working group be set up by the Federal Ministry for the Environment, to prepare and compile the available information. This working group should comprise representatives of the States, in particular experts from State Offices or Institutes as well as further expertise. The report shall also include the emissions of polybrominated and mixed-halogenated dibenzodioxins and dibenzofurans.

The preliminary report from the working group "Determination of Requirements to Limit the Emissions of Dioxins and Furans, Status April 1993" was noted on 10./12. May 1993 by the LAI and presented to the 41st Conference of the Ministers for the Environment on 24./25 November 1993 in Saarbrücken. This report was noted by the Conference of the Ministers for the Environment and commissioned the LAI at the same time to update the report with respect to the more recent knowledge available, to investigate again the possibilities of implementing the measures called out in the resolution under consideration of the current state of knowledge, and to report on the results of these investigations to the 43rd Conference of the Ministers for the Environment in the autumn of 1994.

2. Explanatory Working Procedure

The working group constituted on January 28, 1992. Experts from the Federation and the States, as well as from the Sciences and from Monitoring Institutes are represented in the Working Group (attachment). The work was supported by contributions from further specialist institutions as well as from experts from the Federal Ministry for the Environment.

The concept and the working procedure of the working group were defined during the first meeting.

Types of Installations

- Installations which are subject to licensing and having dioxin-related emissions shall be investigated; to this end, emission standards and measures for their reduction shall be described as comprehensively as possible.

- Installations in which waste and substances similar to waste are incinerated, or could be incinerated as well, shall be included (e.g. power stations, incineration installations of approx. 1 to 50 MW, cement works). Results from measurements shall also be included here if waste or substances similar to waste are incinerated alongside conventional fuels.

Those installations shall **not** be considered on an individual basis which are already subject to extensive control by the 17th Ordinance on the Implementation of the Federal Immission Control Act. As well as waste incineration installations, these also include furnaces for burning cable, dross incineration furnaces, thermal soil-extraction installations, thermal container-cleansing installations (refer also to the resolution of the Federal Government/ Federal States Immission Control Committee from 12./14. October 1992 regarding the "queries arising from the interpretation and application of the 17th Ordinance of the Federal Immission Control Act").

Further Sources

- Emission data and measures for emission reduction for those installations not subject to licensing (e.g. domestic firing installations, dry cleaning), will be also be used as available.

- Information regarding dioxin emissions from traffic and the appropriate measures for emission reduction will also be given superficially and for information.

Data Acquisition

In order to enable a differentiated evaluation of processes, emission data, causes of the formation of dioxins as well as measures for emission reduction, an extensive grid for the acquisition of the data has been worked out in which the measurement and operating data has been entered and forwarded to the Federal Ministry for the Environment.

Precedence has been given to the evaluation of the more recent data and from samples taken and analyzed in accordance with the principles of the proposed guideline VDI 3499 sheets 1 to 4. The results from reports published in accordance with paragraph 26 of

Federal Immission Control Act from State Offices/Institutes as well as from Monitoring Institutions have been used as much as possible.

As well as the foremost chlorinated dioxins and furans, the emissions of brominated and mixed-halogenated dioxins and furans shall also be included.

Information on the pollutions due to residues, from filter dust in particular, shall be given as well as on the immissions of dioxins from waste gases.

Causes and Reductions of Immissions

Furnaces for the incineration of waste are, regarding the formation and reduction of dioxin immissions, the installations which have been investigated the most. Even though these installations are not the subject of this investigation mandate, the scientific knowledge and operational experience gained from these are of great significance for the development and application of measures for emission reduction for other types of dioxin-pertinent installations. Thus for the general description of formation mechanisms and technology for the reduction of PCDD/PCDF immissions, particular emphasis is placed on the analysis and evaluation of results from waste-combustion installations. For an investigation of the applicability of these results to other types of installations however, the pertinent materials, construction and secondary operational conditions as well as their proportionalities have to be observed in particular.

Discussions of the Results with Associations and Expertise Institutions

The working group recognized the importance of involving primarily those associations potentially affected by the results in the checking of the data and in discussions on the technical possibilities for reductions. Considerations in this respect by the working group were presented during the conference of the subcommittee "Air/Technology" convened 25./26. May in Bonn. The subcommittee recommended that expertise talks with Associations affected and other offices from the Federal Ministry for the Environment be conducted with the participation of the working group. The expertise talks, in particular on the subject of metals with:

- the Association of German Iron Smelters (VdEH),
- the Metals Economic Society e.V. (WVM),
- the Association of German Smelters (VDS)
- The German Foundry Association (DGV),

and on the topic of wood-combustion furnaces with:

- the Association of Steam Vessel, Containers and Pipe Construction e.V. (FDBR)

- the VDMA Expertise Association of General Air Technology, working circle, Heating Technology Wood,
- the Wilhelm-Klauditz-Institution, Frauenhofer Working Group for Wood Research, Braunschweig,
- Institute for Technical Engineering and Steam Boilers of the University of Stuttgart,

took place on 25th and 26th November in Berlin. The results of these expertise talks as well as individual discussions with operators and manufacturers are taken into consideration in this report as far as possible.

Dioxin Seminar

An expertise seminar entitled "Dioxin Emissions from Industry, Traffic and other Sources - Emission Limitations and Reductions" was held on 24./25. February 1994 within the scope of the UTECH '94 by the Center for Further Education on Health and Environmental Protection, Berlin e.V. More than 100 experts from home and abroad took part in this congress, during which the important sources of dioxin, effective measures for the reduction of their emissions as well as possibilities to limit emissions were presented and discussed.

3. Input of Dioxins and Furans into the Environment

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) are present everywhere in the environment. These compounds are persistent, accumulative, ecologically toxic and toxic to humans. Dioxins and furans are not produced intentionally. They form exclusively as undesired side products from predominantly chemical and thermal processes. Standing foremost in their determination and evaluation are the chlorinated dioxins and furans. As well as the degree of chlorination, the positional isomerism has a significant influence of the properties of the compounds, and in particular on their toxicity.

Toxicity-equivalence factors have been used by different authors and institutions whereby the effectivity strength is given in comparison to that of 2,3,7,8-TCDD. In 1988, the NATO Committee on the Challenges of the Modern Society (NATO-CCMS) proposed the "International Toxicity Equivalence Factors" which has been widely accepted internationally in the interim and on the basis of which, the limit value in the 17th Ordinance on the Implementation of the Federal Immission Control Act of 0.1 ng TE/m^3 was defined, see Table 1.

If not noted otherwise, the following results are given in toxicity equivalents in accordance with the attachment to the 17th BImSchV.

Table 1: *Differing Systems of Toxicity Equivalence Factors based on 2,3,7,8 tetrachlorodibenzodioxin.* (International System and the NATO-CCMS correspond to the attachment of the 17th BImSchV)

Structure	TOXICITY EQUIVALENTS Eadon USA	Northern System	BGA D	International System, NATO-CCMS
2378-Cl_4DD	1	1	1	1
12378-Cl_5DD	1	0.5	0.1	0.5
123478-Cl_6DD	0.033	0.1	0.1	0.1
123678-Cl_6DD	0.033	0.1	0.1	0.1
123789-Cl_6DD	0.033	0.1	0.1	0.1
1234678-Cl_7DD	0	0.01	0.01	0.01
OCDD/Cl_8DD	0	0.001	0.001	0.001
2378-Cl_4DF	0.33	0.1	0.1	0.1
12378-Cl_5DF	0.33	0.01	0.01	0.05
23478-Cl_5DF	0.33	0.5	0.1	0.5
123478-Cl_6DF	0.011	0.01	0.1	0.1
123678-Cl_6DF	0.011	0.01	0.1	0.1
123789-Cl_6DF	0.011	0.01	0.1	0.1
234678-Cl_6DF	0.011	0.01	0.1	0.1
1234678-Cl_7DF	0	0.01	0.01	0.01
1234789-Cl_7DF	0	0.001	0.001	0.001
other Cl_4DD/F	0	0	0.01	0
other Cl_5DD/F	0	0	0.01	0
other Cl_6DD/F	0	0	0.01	0
other CL_7DD/F	0	0	0.01	0

As well as the polychlorinated compounds (PCDD/PCDF), the polybrominated and the mixed-halogenated dibenzo-p-dioxins and dibenzo-p-furans (PBDD/PBDF and PHalDD/PHalDF) are of significance. According to investigations available, there are no indications for big differences in the toxicities between the chlorinated and the brominated substitutes of this class of compounds; there is not however sufficient toxicological evaluation of the mixed-halogenated compounds, e.g. in terms of toxicity equivalence factors. The Federal Health Office has recommended using the same toxicity equivalence factors for brominated compounds as for the respective chlorinated compounds (refer to last column of table 1). The respective factors for tetra-, penta- and hexa- brominated dioxins and furans were published in the "First Ordinance to Amend the Hazardous Goods-Exceptions Ordinance" dated March 1994. Furthermore, the more rapid decomposition behavior of brominated compounds is to be pointed out. Brominated dioxins and furans can evolve and be set free during chemical or thermal processes in the presence of bromine compounds, for example from the carbonization of plastics with flame retardents containing bromine.

Regarding the present day residual pollutions and new intakes, the following areas are foremost; according to current knowledge, new intakes are predominantly the result of thermal processes. Further sources are the sewage sludge processing and the input via imported products.

Processes and Products from the Chemistry of Chlorine

PCDD/PCDF can evolve during certain production processes involving halogenated compounds. Above all, the input of the PCDD/PCDF into the environment can occur via the product and/or via the residual products from production processes.

The following processes in particular have been identified:

- *the production of 2,4,5-trichlorophenol*
The major side product which evolves is 2,3,7,8-TCDD. As of 1985, 2,4,5-trichlorophenol is no longer manufactured in the Federal Republic of Germany.

- *the production of pentachlorophenol (PCP)*
Since 1985, PCP has not been manufactured in the old states of the Federal Republic of Germany and is practically no longer used. The prohibition ordinance for PCP came into effect in 1989 and has been included in the Chemicals Prohibition Ordinance since October 1993. However, not insignificant amounts are introduced anew through the import of treated goods (e.g. textiles, leather goods, woods).

- *the production of polychlorinated biphenylenes (PCB)*
PCB's were regularly contaminated with PCDD/F; furthermore, fires involving PCB's (condensers and transformers) are sources of furans and dioxins. Since 1989, products containing PCB's may no longer be manufactured or be circulated as consumer goods.

- *chemical wood pulp and paper manufacture*
Chlorine bleaching during the sulfate wood pulp and paper manufacture was recognized several years ago as being a not insignificant source. Bleaching processes using elementary chlorine are no longer used in the Federal Republic of Germany. Larger quantities of chlorine-bleached wood pulp are however imported annually.

- *flame retardents for plastics*
Brominated diphenyl ethers, bromophenols and polybrominated biphenyls, which are used as flame retardents in plastics, can contain polybrominated dibenzofurans (PBDF) from manufacturing processes and can then be set free from the products. Should plastics containing flame retardents catch fire, high formation rates of PBDF can occur. The Association of the Chemical Industry declared the voluntary self-obligation in 1990, to give up the production and applications of polybrominated diphenyl

ethers for the German market. These compounds are virtually no longer used in practice. There does however exist a significant import potential from finished products such as electrotechnical appliances. the Federal Republic of Germany is currently striving to achieve a restriction of the applications for polybrominated diphenyl ethers in the EU as well.

- *manufacture of dyes*

The manufacture of dyes using chlorinated compounds as auxiliary agents has been identified as a source of new inputs of dioxins and furans. According to the results of recent investigations, phthalocyanin and bisazin dyes in particular, contained PCDD/PCDF as the starting materials for synthesis, whereby PCDD/F concentrations in the ppm range were confirmed in other studies of the latter group for chloranil. Synthesis paths for dye pigments on the basis of chloranil have been changed to use dioxin-free variants.

- *manufacture of vinyl chloride*

According to recent studies, very high dioxin contents have been found in the sludges which accumulate in the course of the treatment of waste water from the oxichlorination process for the manufacture of 1,2 dichloroethane (EDC) - a pre-product in the manufacture of vinyl chloride. The treatment of waste water is usually conducted in two stages. The metal sludges accumulating in the chemical step, which are mainly the catalytic metals copper and iron, had dioxin contents of as high as 4000.000 ng TE/Kg dry matter. The sewage sludges of the biological treatment stage showed very high dioxin levels as well at approx. 7.000 ng TE/Kg. Apparently, the carriage of fine particles from the chemical preparation stage into the biological stage is responsible here. Initial process-technical measures as well as the additional installation of effective filters between the chemical and biological stages have been introduced to reduce the dioxins in sewage sludges.

Thermal Processes

The formation of PCDD/PCDF is principally possible during combustion processes, as incompletely burned carbons as well as compounds containing chlorine are usually present. Accordingly, as well as in waste incineration installations, residual material incineration installations, power stations and furnaces subject to licensing, domestic firing installations shall also be considered.

A major source for the pollutions of PCDD/PCDF in the environment are the thermal processes in the metals sector, whereby there are larger bandwidths depending on the materials, processes, reduction technologies etc., which are employed. The types of installation are covered extensively in the report (see section 8.1.5).

Representative measurements of dioxin emissions from waste incineration installations have been carried out in the Federal

Republic of Germany. Based on the results available, an average waste gas concentration of around 8 ng TE/m³ in 1989 has been evaluated for existing waste incineration installations. Modern waste incineration installations using optimized combustion technologies as well as effective conventional waste gas purification techniques (e.g. fabric filters, electrostatic precipitators, scrubbers) have lower emissions of dioxins, at levels in the region of 1 ng TE/m³ and below. On account of the requirements of the Waste Incineration Installations Ordinance (17th BImSchV) which defines compliance with the very strict limit values of 0.1 ng TE/m³, the emissions of dioxins will be drastically lowered again.

4. The Formation of Dioxins and Furans during Thermal Processes

The incineration of waste is the thermal process which has been investigated the most to date. The following are known possibilities for the input or formation of PCDD/PCDF:

- Dioxins and furans already constitute components in the materials used and are either not completely or only partially converted. If an average PCDD/PCDF content of 50 ng TE/Kg in waste is assumed, then this (for a transfer into the waste gases without any decomposition) corresponds to an emission concentration of approximately 10 ng TE/m³ in the waste gases. All available results from investigations indicate however, that the dioxins and furans introduced with the materials utilized, are nearly completely decomposed during incineration.

- Dioxins and furans are formed from non-chlorinated organic materials in the presence of a chlorine source (De-novo synthesis). At temperatures of around 450 and to 250°C, the catalytic formation of chlorine from metal chlorides in the presence of oxygen is supposed to be the decisive starting reaction. In an oxygen-deficient medium, the decomposition of dioxins under otherwise identical conditions is to be observed during the course of a dechlorinating reaction.

The majority of PCDD/PCDF's found in filter dust and waste gases is formed mainly during the cooling phase within the waste gases system, which points to a certain domination of PCDD/PCDF formation according to the De-novo synthesis. As the conditions for De-novo synthesis prevail in many thermal processes, the knowledge gained from waste incineration installations also supplies valuable information for the solutions of the dioxin problems in other processes.

5. General Measures for the Reduction of Emissions

The measures for primary prevention or reduction of the formation of dioxins, as well as for secondary reduction of these can be differentiated between:

- materials-related primary measures,
- process-related primary measures,

- measures in the waste gases
- waste gas purification techniques
- procedures for treating the residues.

A large part of the experience with these measures has been gained from waste incineration installations.

Materials-Related Primary Measures

The following possibilities for the prevention or minimization of the formation of dioxins and furans come into consideration:

- avoidance of the use of additives containing chlorine or bromine (e.g. no usage of scavengers in leaded gasoline fuels, no usage of flame retardents containing bromine in plastics, no usage of the addition of hexachloroethane as a cleansing and degassing agent in aluminum smelting);

- Exclusion, screening or reduction of the materials utilized which contain chlorine or bromine (not applicable in practice for waste incineration installations; a screening or a pre-treatment could come into consideration for the recycling of secondary metals);

- modification of the materials utilized by the addition of chemical compounds. This could be achieved for waste incineration installations by the addition for example, of sulfur compounds or of lime into the combustion compartment as well as by the addition of inhibitors (amongst others, now known are preliminary studies using amines);

- pre-treatment of metallic materials utilized.

Process-Related Primary Measures

- optimized combustion technology for incineration installations (e.g. sufficiently high temperatures, sufficiently long residence times, sufficient oxygen, thorough admixing of the gases, firing control without cold streams); optimized burn-out of grate slag and fly ash, low carbon contents in fly ash and residues;

- materials and product-adapted smelting processes for the recycling of metals (e.g. avoidance of pyrolysis processes; salt-free smelting processes - applicable only in certain cases).

Reduction of Dioxins in Waste gases

The formation of dioxins in the waste gas can be reduced by the following measures; the experience from the incineration of waste in particular is available:

- the addition of inhibitors (limited degree of efficiency, observation of possible side reactions);

- the use of hot gas dedusters (corresponding trials in the incineration of waste):

° ceramic filters or cyclones for temperatures of between 800 and 1000 °C; only pilot trials to date, e.g. observe the problems of contamination;
° particle collecting at temperatures of around 450°C; cyclones, in particular hot gas electrostatic precipitators;

- quenching by the addition of water, provided the reduction of emissions takes precedence over the use of thermal energy;

- avoidance or reduction of fly ash deposits in the waste gases; requirements in accordance with the 17th BImSchV (appropriate waste gas routing as well as optimized cleaning of boilers, heating surfaces and waste gases).

Application of Waste Gas Purification Techniques

The following purification techniques can be employed in waste incineration installations as well as in other installations to a certain extent:

- catalytic oxidation; extended SCR catalysts (use of TiO_2 catalysts);

- adsorption methods using activated charcoal/coke or open-hearth cokes for the following reactions:

-- fixed bed and moving bed reactors,
-- entrained flow and filter layer techniques,
-- circulating fluidized bed,
(comparable efficiency as with entrained flow reactor);

- H_2O_2 oxidation methods;

- Waste gas scrubbing procedures using optimized fine scrubbers.

Dust removal using particularly effective fabric filters can reduce the concentrations of dioxins above all at waste gas temperatures of < 150°C due to the collection of dioxins which are bound to particles. The use of fabric filters usually results in values which are more favorable than, for example, electrostatic precipitators although other studies do not indicate any significant advantages of the fabric filters.

With the entrained flow technique and the addition of open-hearth coke or activated coke/lime or limestone mixtures and subsequent fabric filtering, the limit value of 0.1 ng TE/m^3 for emissions from waste incineration installations can usually be met with a margin. This technique has, for the first time, been put into operation on a large scale at the hazardous waste incineration installation located at Schöneiche near Berlin. Further installations using this method have started up operations. The entrained flow technique can be operated in existing installations following a relatively simple modification; for example HCl/HF separation according to the (pseudo) dry adsorption method. Approx. 2 % of active charcoal is added to the limestone additive. Additions of up to 35 % open-hearth coke are known. A mixture of products results as the residual substance, the disposal possibilities for which have to be investigated on a case by case basis; methods for the treatment of residues are in the development and trial stages, as well as in operation to some extent. The amounts of occurring residues containing dioxins depend on the configuration of the installation and can be kept particularly low when two-stage processes are used. More recent concepts are also based on the internal return and combustion, or on an external combustion of the contaminated residues.

If the installation works with high carbon contents or if only coke or coal is used, measures for the protection against explosion must be taken. Sources of ignition must be avoided for example, or inert materials (e.g. limestone) must be added, as described above.

For fixed bed techniques using open-hearth coke or activated charcoal, the waste gases must be pre-cleaned with respect to particles, HCl, HF, SO_2. Dioxins and furans as well as other organic substances are removed by the post-cleaning of the waste gases from residual amounts of these substances as well as for mercury. Disposal of the charged coke is necessary whereby burning is the prime alternative which is available. The method has a relatively high requirement on space ($V = 0.1 \ldots 0.2$ m/s). Particular precautions as well as surveillance measures are needed to prevent a self-ignition. Open-hearth coke (approx. DM 375 to DM 400 per tonne) has an economical advantage over pit coal activated charcoal (up to DM 7,000 per tonne). The first installations utilizing the fixed bed technique have gone into operation at the extraction center in Ruhr/Herten and at the waste incineration installation in Düsseldorf.

A method of cleaning by which there is no collection and storage of the deposited dioxins, but rather by which the dioxins are nearly completely destroyed, is the catalytic oxidation using TiO_2 catalysts in the temperature range 250°C to 350°C. Knowledge on the decomposition of dioxins, which was gained from the catalytic NO_x waste gas purification (SCR technique) was specifically developed further here. In pilot trials, efficiency rates for the decomposition of dioxin of 90 % and higher were achieved. Corresponding equipment has been put into operation in waste incineration installations (e.g. Wien-Spittelau and Stuttgart). Equipment operating according to this procedure is under construction at other waste-incineration installations.

Dioxins and furans are catalytically decomposed using gaseous hydrogen peroxide by the H_2O_2 oxidation technique. To this end, hydrogen peroxide, which is soluble in water, is admixed into the hot flow of waste gases using a binary nozzle, whereby it evaporates and is subsequently converted in a reactor filled with catalyst. The degree of decomposition exceeds 98 % for PCDD, the decomposition of PCDF's is between 95 and 98 % on average. The first technical installation will be put into operation at the end of 1996 behind the waste incineration installation at Dow Chemical Germany in Stade.

With scrubbing methods using optimized fine scrubbers, the fine dust particles are removed by spraying circulating water into the waste gas flow. After the scrubber, the waste gas passes through efficient droplet separators. A technical installation working on this principle is in operation at VOEST-ALPINE in Linz.

The following aspects deserve particular mention for the thermal processes in the production of metals:

- The waste gases should be collected as completely as possible, whereby particular attention should be paid to the charging processes.

- Non-combusted components in the waste gases (in dust form as well as in gaseous form) shall be avoided as much as possible by optimized process operations, combustion and, if necessary, passage through an afterburning installation.

- Admixture of the entrained/false air (e.g. air for cooling the waste gases) should be avoided as far as possible, in order to obtain small volumes of waste gas by which particle deposits in the flue gas can be prevented more easily, and by which more economical and efficient waste gas purification equipment can be operated as well for the selected removal of dioxins.

- The use of pure oxygen or oxygen-enriched air in place of atmospheric air is under consideration for the near total reduction of the specific waste gas volume flows of different thermal processes in the metals sector.

- A significant reduction of the dioxin emissions can often be achieved by the use of particularly efficient particle removers, e.g. using fabric filters especially in conjunction with the admixture of additives to waste gases.

Techniques for the Treatment of Residues

The treatment of residues (containing dioxin) is to be pointed out in particular. Differing techniques can be used, e.g. for the filter dusts from waste incineration installations:

- The catalytic treatment of filter dust in the lower temperature range under the oxygen deficiency conditions (equipment at a waste incineration installation in Stuttgart);

- The treatment of filter dust scrubbing techniques, e.g. according to the 3R-Process (Rauchgas = flue gases, Reinigung = purification, Rückstandsbehandlung = residue treatment), by which the filter dusts, following extraction of the heavy metals using hydrochloric acid, are returned to combustion for thermal destruction of their organic materials and of the dioxins in particular; the hydrochloric acids are accumulated from the acidic scrubbing of waste gases (a variation of this procedure is in operation in Switzerland);

- Numerous filter dust vitrification techniques;

- Recycling techniques as for example the manufacture of alinite cement;

- Solidification techniques for immobilizing the dioxins.

A large scale technical application has not yet been realized for techniques in the items 2 to 4.

6. Measurement and Monitoring of Dioxin and Furan Emissions

Sample-Taking

The taking of samples is carried out according to the set of VDI Guidelines 3499 sheets 1 to 4, "Measurement of Dioxins (Emission Measurements)". The individual systems for taking samples differentiate in particular in the ways and order that the elements deposited. Utilized are:

- Dilution methods
  (sheet 1, proposal March 1990)

- Condensation methods
  (sheet 2, proposal March 1993)

  Condensation methods with cooled probes
  (sheet 3, preliminary proposal 1993; response anticipated by the end of 1994)

- Polyurethane Foam methods
  (PUR Foam method, sheet 4, preliminary proposal 1993).

In the referenced VDI guidelines and proposals, the analytical procedure characteristics are described for concentrations of 1 ng TE/m² and greater. For concentrations of 0.1 ng TE/m³ and below, the corresponding procedure characteristics are currently being worked out Europe-wide within the scope of the CEN. Even though, as shown by detailed investigations, the procedures as described in the VDI guidelines can also be applied for this range of low concentrations.

For solid substances (filter dust, boiler ash and drosses) samples are taken according to the State Working Group on Waste, Guideline PN 2/78. According to this procedure, a minimum of ten representative samples is to be taken each day for solid substances, which are then combined to a collective sample and.

milled to a particle size of 0.1 to 0.2 mm. 25 to 50 g of sample are currently required for an analysis.

Sample Preparation

A careful multi-step preparation and cleaning of the sample is necessary prior to the analysis, in order to remove accompanying substances which could distort the analysis, and to reduce the analytical volume containing the dioxins and furans. Reference is made to the VDI guidelines.

Analytical Techniques

The analytical technique is described in detail in the VDI Guideline 3499 sheet 1 for waste gases as well as for solid samples.

For identification and quantification purposes, the fractions are either analyzed separately or investigated as a collective sample. After separating using quartz capillaries, mass spectroscopy is used for the qualitative and quantitative analyses.

Preparation of Euronorms

Euronorms are in preparation at the European level through the CEN as commissioned by the EU Commission. The TC 264 "Air Quality" (Office: Commission for Clean Air in VDI and DIN) has prepared preliminary proposals for sample taking, extraction and cleansing, as well as for identification and quantification. These Euronorms shall be available by the end of 1994.

Considerations of the Analytical Limits for the Calculation of the Toxicity Equivalence Values

If there are no dioxins found by a certain sample-taking and analysis technique, then the question is to be raised, as to how the toxicity equivalents are to be estimated for comparison purposes with the emission values in the calculation.

In accordance with the definition in the 17th BImSchV, the calculation of the toxicity equivalents for congeners for values lower than the detection levels (minimum < 5 pg/m^3 per congener) is to be calculated as the value zero, i.e. they are not taken into consideration. In case an emission limit is to be monitored, which, because of a mixed calculation, is less than 0.1 ng TE/m^3, a measurement and analytical technique with a particularly low detection level shall be selected. The detection limit of the individual congener should explicitly defined for all measurements (refer to the response on questions of doubt on the interpretation and application of the 17th BImSchV, page 61/62; resolution of the the Federal Government/ Federal States Immission Control Committee of the 82nd Conference on 12/14.10.1992 to agenda item 5.2.1).

The emission data compiled in section 8 does not always include detection limits. In the majority of cases, the detection limit has been taken into consideration to the fullest extent in the calculation of the toxicity equivalence values.

7. Regulations to Limit the Emission of Dioxins and Furans into the Atmosphere.

7.1 National Regulations in accordance with the Federal Immissions Control Act (BImSchG)

Many regulations for the BImSchG include general or quantitative requirements for the restriction of dioxin and furan emissions:

- First General Administrative Regulation for the Federal Immission Control Act (Technical Instructions on Air Quality Control - TA Luft) dated 27.02.1986.
No. 3.1.7 paragraph 7 defines a general law to minimize dioxins:

"For organic substances, which decompose with difficulty and are easily enriched and which are of high toxicity or which cannot be classified into any of the above three classes on account of other particularly harmful effects on the environment (e.g. polyhalogenated dibenzodioxins, polyhalogenated dibenzofurans or polyhalogenated diphenyls), the emission mass flow while is to be limited as much as possible within the scope of reasonability. As well as waste gas purification, the measures of technical processes in particular as well as measures which effect the properties of substances used and products are to be taken".

As the 2,3,7,8 tetrachlorodibenzodioxin is unambiguously classified as a carceogene according to the classification in part III A of the MAK (maximum working concentration) list, the minimization regulation of the TA no. 2.3 is applicable to the same extent.

- First Ordinance for the Implementation of the Federal Immissions Control Act (Ordinance on Small Firing Installation - 1. BImSchV) dated 15.07.1988 (BGBl. I page 1059).
In accordance with section 3 paragraph 1, only certain fuels are permitted (e.g. untreated wood, or treated wood provided it is not coated or does not contain wood-protecting agents or is not coated with materials containing halogenated organic compounds). Their use and proper operation according to the state of technology will minimize the emissions of dioxins extensively.

- Seventeenth Ordinance for the Implementation of the Federal Immissions Control Act (Ordinance on Combustion plants for Waste and similar Combustible Materials - 17th BImSchV) dated 23.11.1990 (BGBl. I page 2545).
With this ordinance, a uniform Federal Emissions limit for polychlorinated dibenzodioxins and furans was established for the first time. The 17th BImSchV includes many requirements, in order to not only reduce the formation of dioxins and furans in installations, but also to limit the emissions in total:

- The central issue is the emission limit value of 0.1 ng TE/m³, which in most cases is only possible by the installation of special additional waste gas purification equipment (refer also to section 5). With regard to an indisputable control of the limit values, the requirements are defined according to sample-taking and analytical procedures.

- Installations in which waste or similar combustible substances are burned as well are also covered by the ordinance. The definition of the emission limit for dioxins and furans is by use of a mixed calculation.

- A lower CO limit value as well as requirements with regard to a good waste gas burn-out (e.g. minimum temperature, minimum dwell time) are flanking regulations for the reduction in the formation of dioxin.

- The measures to reduce fly ash deposits in boilers and in flues also serve to significantly reduce the formation of dioxin.

- Nineteenth Ordinance for the Implementation of the Federal Immissions Control Act (Ordinance on Chlorinated and Brominated Compounds as Additives in Fuels - 19th. BImSchV) dated 17.01.1992.

The so-called Scavenger Prohibition Ordinance became law on 25.07.1992. In support of paragraph 34 of BImSchG, the use of chlorinated and brominated additives in leaded gasoline is prohibited. Thus the major path of input via chlorine and bromine in the engine is sealed as regards the formation of dioxins and furans.

7.2 EU Regulations

- Presentation to the Council of Ministers of a Guideline for the Incineration of Hazardous Wastes.

A proposal for a EU Guideline covering the combustion of hazardous waste was adopted by the Council of Ministers on June 28th 1993 (published with Document 8306/93 ENV 236 dated August 3, 1993). The requirements contained in the document correspond essentially to the 17th BImSchV. In particular, a guideline limit for dioxins and furans of 0.1 ng TE/m³ was adopted. The guideline proposal foresees that this value must be met as a limit value for new installations as of January 1, 1997. Transition regulations are foreseen for existing installations.

- Working group for the preparation of a guideline for the combustion of wastes not classified as hazardous:

Under the chairmanship of the commission, a working group is currently preparing a proposal for a guideline covering the combustion of non-hazardous wastes. The guideline shall also replace both guidelines currently in existence which cover new and existing installations for Municipal wastes. A preliminary proposal presented by the commission includes a limit value of 0.1 ng TE/m³ for dioxins and furans which is supported by Germany.

7.3 Memorandum from the German Government to the EU Council

During the EU Council Conference on 28/29. June 1993, the German Delegation presented a memorandum to the council covering the difficulties of dioxin emissions from industrial sources with the objective of compiling the knowledge available in the member states, evaluating it and demonstrating the possibilities of limiting the emissions.

The commission has since taken up the subject; it intends to set up a working group in the near future under the leadership of a member state. The Federal Ministry for the Environment has offered to take up the task of this leadership.

8. Emissions and Reduction Measures for Installations as well as for Automobiles

In accordance with the accuracy of the measurement methods, the results obtained can only be given in terms of a certain figure. The measurement reports transmitted and evaluated often include measurement results in which more digits are given than those which correspond to the accuracy of the measurements. The results have been - as transmitted - accepted. A subsequent rounding up or down has not been undertaken for the purpose of this report.

8.1 Installations subject to licensing (4th BImSchV)

8.1.1 Power Stations (no. 1.1. of the 4th BImSchV)

General Process Description

In power stations and heating power plants, a process of steam power for the generation of electrical energy and heat is operated using fossil energy carriers, in particular coal, but also oil and gas. Brown coal and mineral coal are nearly always burned in dust or in fluidized bed firings. Hard coal dust firing is operated at temperatures below the ash softening point (dry ash removal = dry firing) or above the ash softening point (liquid ash removal = melting chamber firing). Brown coal dust firing is carried out exclusively as dry firing.

Downstream waste gas purification equipment installed must be operated in very narrow temperature ranges for technological or material reasons. Depending on the numbers, type and installation of the waste gas purification equipment, the waste gases are partially cooled and then heated again a number of times.

Fuels

In the old Federal States, approximately 40 million tonnes of hard coal, 100 million tonnes of brown coal and approx. 1 million tonnes of oil are used at the present time and are foreseen in heating power plants for the future. By comparison, the amounts currently used in the new States are relatively low at 1 million tonnes of each. The power station use of brown coal for the generation of electricity here wall fall back from approx. 135 millions tonnes in 1989 to a forecasted 70 to 80 million tonnes (and possibly even less) by the year 2000.

Furthermore, other fuels such as e.g. old oil or sewage sludge will be fired in small amounts as well. (For orientation purposes: the total annual quantity of recovered old oil amounted to approx. 0.25 million tonnes at the end of the 80's, sewage sludge amounted to approx. 2.35 million tonnes dry matter).

Emission Standards

Emission standards for dioxins and furans are given in table 2; the values refer primarily to installations in the old Federal States.

For coal-fired power stations, an emission concentration in clean gas is given with a bandwidth of 0.0001 to approximately 0.02 ng TE/m^3. These statements also apply for heating power plants which are fired with heating oil EL or with coal dust. There are two measurement values included in table 2 by which the 2,3,7,8 substituted dioxins and furans necessary for the TE calculation were below the detection levels.

A further discussion of these values, e.g. a dependency on the type of firing equipment, is not possible from the data material available. In total, lower dioxin concentrations arose, and which were significantly less than 0.1 ng TE/m^3. Furthermore, this statement is not restricted as the detection limits are not mentioned in these results and are not given as values which are below the detection limits.

On account of the comparatively low dioxin and furan emissions from power station firings, these installations usually give the assurance of a good burn-out of the waste gases and furthermore, there is not the necessity for the implementation of special measures for emission reduction.

Table 2: Dioxin Emissions from Power Stations and Heating Power Plants

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits ng TE/Kg	N m^3/h	Remarks
Hard Coal Power Plant used oil for test purposes 2 test runs (I/II)	I) hard coal		5.2; 5,4/5		0.001-0.002 0.003-0.008 0.004-0.006	0.003-0.004	0.3-3	203000; 197100	1) in front of FGD-plant 2) in front of coke adsorber 3) in front of catalytic converter
	with used oil 1,7-2,7 t/h		5.4; 5.3/5		0.006-0.017 0.021-0.087 0.005-0.013	0.004-0.022	2-9	187800; 199500	1) - " - 2) - " - 3) - " -
	II)hard coal		6.9/5		0.003 0.001 0.0001	0.0001	21	197200	1) - " - 2) - " - 3) - " -
	with used oil 3,6-4,8 t/h		6.7/5		0.002-0.0015 0.0001-0.0002	0.001-0.002	18-20	205000	1) - " - 2) - " - 3) - " -
Hard coal power plant	hard coal (Ruhr coal)	a) 775 MWth b) 733 Mwth 745 MWth 743 Mwth 741 MWth	6.5/5 6/5 6.5/5 7.5	4		0.0001-0.0007 < 0.003 < 0.003 < 0.005 < 0.003		986000 990000 981000 1,000000	normal operation without FGD-plant/with Denox-plant with FGD-plant/without Denox-plant without FGD-plant/without Denox-plant

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
Power Plant	hard coal	a) 523 Mwth	6.3/5 5.7/5 6.7/5 5.5/5	4		< 0,002 < 0,002 < 0,002 < 0,002		1270000 1270000 1240000 1250000	normal without FGD-plant/with Denox-plant with FGD-plant/without Denox-plant without FGD-plant/without Denox-plant
- " -	hard coal	b) 63 Mwth	6.1/7 4.6/7 8.7/7	3		0,014 0,009 0,011	15	39400 68100 46700	H_20 conditioned, Ca(OH)$_2$ additive, fabric filters
- " -	coal		5.7				2-7	< 1000000	FGD-plant
- " -	hard coal	a) 254 Mwth	7.8; 8/5	2		0,0044 0,003		380000	E-filter SO$_2$-spray absorber (drypac) fabric filters
- " -	hard coal	a) 254 Mwth	7.1/5	1		0,018		360000	FGD-plant, SCR
	hard coal and 8 % paper rests	- " -	- " -	1		0,012		- " -	- " -
Power Plant (coal dust firing with additional fixtures)	hard coal (80 %) sewage sludge (5-10 %) liquid residues (1-3 %) soot (3 %)	a) 856 Mwth b) 85-100%	7.8/5	1		2.3.7.8-TCDD < 0,012		689000	E-filter Regavo, sodium sulfite scrubbing
		70-75%	7.6/5	1		2.3.7.8-TCDD < 0,012		512000	

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
power station (coal dust-firing)	brown coal	a) 280 Mwth b) 280 Mwth	7.5/6	6		all < 0.002 detection limit: 1pg		440000	Denox-plant, E-filter lime milk - FGD-plant
power station	brown coal	a) 760 Mwth	8.6/6	8		0.0001-0.0054		1,000000	E-filter
power station	brown coal	280 Mwth	a) 7.5 b) 6	6		< 0.0002		440000	Denox-plant, E-filter, FGD-plant-scrubber
- " -	brown coal wood shavings	280 Mwth	a) 7 4 b) 6	2		< 0.0002		427000	Denox-plant, E-filter, FGD-plant-scrubber
heating plant	heating oil EL	a) 397 Mwth	3.7/3	3		< 0.005		252000	Denox, FGD-plant, E-filter
heating plant	coal dust					0.0004		311000	Denox, FGD-plant, E-filter
power station (coal dust firing)	hard coal (Ruhr coal conveyor) heating oil EL								
block 2		b) 67-81%	7 1-7.5/6	1		0.01		267000	E-filter, fabric filters
block 3		b) 67-88%	7.4-8.6/6	1		0.008		249000	FGD-plant, Denox-plant
power station	brown coal	a) 455t steam / h	/6	3	0.05	0.04		500000	electrostatic precipitator, FGD-plant
power station	hard coal	no values.	/5	3		0.013	21	203000	heating oil EL

8.1.2 Combustion plants (no. 1.2 or 1.3 of the 4th BImSchV)

8.1.2.1 Combustion plants for Wood

General Process Description and Fuels

The fuel wood can differ very much in terms of forms and properties. Bulky wood, shavings, remainders from chipboard and other types of wooden materials, untreated wood, coated with substances either containing or not containing chlorinated organics, or treated with wood-protection agents, are several classification criteria.

The chlorine content of untreated wood is usually about between 0.001 and 0.01 % by weight. The chlorine content of bark lies significantly higher in the range of 0.01 to 0.02 % by weight. depending on the location, even higher chlorine contents can be found in untreated wood and barks in certain cases. Chipboard can have chlorine contents of up approx.. 0.2 % by weight depending on the constitution of the binding agents. Significantly higher values are to be found in wood materials which contain PVC constituents.

The requirements of the 17 BImSchV regarding combustion also apply to preservation agents to the extent that they are used to coat wood or wood rests or are constituents of wood.

As far as coatings for wood and wood rests consist of halogenated organic compounds, the respective combustion plants for wood are to allocated to nos. 1.3 in the attachment to the 4th BImSchV; installations of 1 MW and higher are subject to the formal, and the smaller installations of 100 kW to 1 MW to the simplified approval procedures.

Wood-based materials (chipboard, fiber board, plywood and other types of glued wood) as well as coated, painted or covered wood may, provided wood preservation agents are not used or are not a constituent thereof, or coatings which do not consist of halogenated organic compounds, be only used in furnace equipment with a nominal heating power of >/ 50 kW and only in at wood processing plants or in the wood processing; combustion plants which are operated using these types of wood as fuels are not subject to licensing for combustion heating outputs of up to 1 MW.

Emission Limits

Results of investigations are available for the following installations

- vertical cyclone firing
- cyclone injection firing
- distillation gas generator with downstream cyclone burner
- sloping grate firing

- chip firing (large-scale and pilot installations)
- shaft firing
- pre-furnace firing
- combined grate/coal dust firing
- fluidized bed firing
- underfeed furnaces.

The results for existing furnace constructions are compiled in table 3. Some installations not subject to licensing have also been included in the table. These are commercial installations and are designated in the table. Fluidized bed furnaces as well as investigations from a pilot plant for the combustion of wood containing wood preservation agents are covered separately.

Table 3: Dioxin Emissions from Wood-Firing Installations

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas	 Clean Gas	 Filter Deposits	Waste Gas Volume Flow	Waste Gas Treatment	Total Chloride Materials Utilized
					ng TE/m³	ng TE/m³	ng TE/Kg	N m³/h	Remarks	ppm
Vertical cyclone furnace *	chipboard rests (Cl: 0.05-0.08 %) solid wood chippings	a) 800 Mwth	4-8/11	6	0.039 0.075 0.024	0.006-0.021 0.003-0.006 0.007-0.003		full load 1350 partial load 1030 low load 890	waste gas return E-filter addition of lime to fuel	
Cyclone injection furnace 1	chipboard rests	a) 9.33 MW	7-10/11	4	0.02-0.08	0.14-0.6 0.08-0.14		full load 12300 partial load 7240	fabric filter (150-170 °C)	800-1300
Cyclone injection furnace 2	a) mixture of untreated wood + chipboard	a) 11 MW b) 90-100% load	6.7-10.1/11	2		0.006-0.034		16160-17660	E-filter	
	b) untreated wood			2		0.004-0.007				
	c) $(NH_4)_2SO_4$ - hardened chipboard			2		0.027-0.084				
	d) $(NH_4)_2SO_4$ - hardened chipboard + PVC			2		0.297-0.368				
Sulfur gas generator with cyclone burner (pilot plant) **	untreated wood	a) 300 kW b) 184; 250	9.7/11	2		0.039 0.027			cyclone, details of fuel, particles and ash table 4	
	wood fiber board coated with PVC	a) 300 kW b) 245 kW	8.0/11	2		0.042 0.318			cyclone, details of fuel, particles and ash table 4	
	wood treated with PCP and lindane	a) 300 kW b) 300 kW	7.9/11	2		0.639 0.232			cyclone, details of fuel, particles and ash table 4	
	demolition wood	a) 300 kW	9.9/11	2		0.12 0.17			cyclone, details of fuel, particles and ash table 4	
Sloped grate furnace	heating oil EL (pre-heated), wood shavings	a) 4.5 MW 2x b) 2.8 MW 1x	16.75/11	2		0.27 0.11		5300	fabric filters	

* commercial installation not subject to licensing

** installation not subject to licensing for certain types of materials utilized. For the use of wood/wooden materials, provided they are not coated with or do not contain wood preservation agents, or coatings do not consist of compounds containing halogenorganic compounds, the installation is subject to licensing requirements.

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks	Total Chloride Materials Utilized ppm
chip furnace	a) bark b) bark (with very low lindane content)	a) 16 MW	10.6-13.3/13 2.2-14.5/13	1 1		0.0005 0.0007	38.3	no values.	E-filter	
chip furnace	a) bark b) bark (with very low lindane content)	a) 2 MW	no values. no values.	1 1		0.0153 0.0322		no values.	cyclone	
chip furnace/pilot plant**	a) wood chippings b) wood chippings with PVC granules (Cl content 0.26 %)	a) 50 MW	no values. no values.	2 1		a) 0.992 (full load) 0,051 (partial load) b) 4.276 (partial load)		no values.	no values.	
shaft furnace (hand-charged) pilot operation**	mixture of untreated wood, non-coated, coated (PVC, melamine resin) chipboard (Cl content approx. 0.005 - 0.09 %)	a) approx. 50 MW	approx. 8-17/13	2		0.443-1.39		130-140	without	
pre-oven furnace*	pressed natural wood	a) 230 MW	16.7-19.3/13	2		0.453-0.697		560-630	cyclone	100-170
(combined roasting/dust firing	mixture of untreated wood, chipboard (Cl content approx. 0.03 %)	a) 25 MW (roasting) b) 14 MW (dust firing)	7.9-10.8	2		0.145-0.162		43300-44300	E-filter	

* commercial installation not subject to licensing

** installation not subject to licensing for certain types of materials utilized. For the use of wood/wooden materials, provided they are not coated with or do not contain wood preservation agents, or coatings do not consist of compounds containing halogenorganic compounds, the installation is subject to licensing requirements.

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	Crude Gas ng TE/m³	PCDD/F Content Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks	Total Chloride Materials Utilized ppm
underfeed furnace 1 (pilot plant)) **	a) mixture of untreated wood + chipboard	a) 230 kW b) 50% load	14.7-18.7/13	2		0.151-0.458		590-660 (at nominal load)	cyclone	
	b) untreated wood			2		0.242-0.398				
	c) (NH$_4$)$_2$SO$_4$ - hardened chipboard			2		0.179-0.547				
	d) (NH$_4$)CL - hardened chipboard + PVC			2		2.26-3.3				
	e) (NH$_4$)$_2$SO$_4$ -hardened chipboard + PVC			2		4.46-9.82				
underfeed furnace 2	chipboard - veneer rests	a) 3.5 MW b) 50-70% load	9.5-11.6/11	2		0.00-1.55		2400-3200	E-filter	
underfeed furnace 3 *	mixture of untreated wood + chipboard rests	a) 117 kW b) 60-70% load	15.9-16.5/13	2		0.24-0.939		250-270 (at nominal load)	without	
fluidized bed furnace	PVC coated wood rests materials	a) 3.1 MW	9.5/11	3		0.0014		5400	CaCO$_3$ in fluidized bed H$_2$O vaporization cooler fabric filters open-hearth coke rector	
		b) 2.2 MW				0.0011 0.0010 (without detection limit)				
wood-firing furnace * (underfeed)	solid wood chipboard of approx. 30 mg Cl/Kg	a) 345 kW				2.3			none	
wood-firing furnace * (underfeed)	solid wood chipboard of approx. 100 mg Cl/Kg	a) 200 kW				0.667			none	

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Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas	 Clean Gas	 Filter Deposits	Waste Gas Volume Flow	Waste Gas Treatment	Total Chloride Materials Utilized
					ng TE/m³	ng TE/m³	ng TE/Kg	N m³/h	Remarks	ppm
underfeed furnace	treated wood rests (painted, pickled wood/wooden material rests)	0.97 MW		3	8.8	5.8		1500	fabric filters; addition of lime, intermittent (trial operation)	
- "-	- " -	- "-		3	3.1	0.6		1500	fabric filters; addition of lime, open-hearth coke, intermittent (trial operation).	
solid-firing (grate with top burn-up residue, manual fuel intake) *)	pine wood billets	a) 58 kW	17.5/13	2		1.515		410	cyclone	37
			16.4/13			0.892		320		16
solid-firing (grate with top burn-up residue, manual fuel intake) *)	poplar wood billets	a) 70 kW	11.1/13	2		0.130		130	none	27
			10.1/13			0.048		110		19
solid firing (grate with top burn-up residue, manual fuel intake) *)	briquettes from sawing, milling planing chips as well as sawdust from coated and uncoated chipboard and wood	a) 70 kW	13.1/13	2		0.867		140	none	586 417
			12.8/13			0.0664		140		
solid firing (grate with top burn-up residue, semi-automatic charging via chutes) *)	saw gate shavings and chippings from veneer rests	a) 400 kW	14.9/13	2		0.0392		2100	none	55
			14.8/13			0.020		2000		58

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Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment	Total Chloride Materials Utilized
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks	ppm
solid firing (underfeed furnace) *)	chippings from large slabs and logging wood	a) 800 kW	12.3/13	2		0.097		1600	cyclone	60
			12.4/13			0.041		1600		125
pre-oven firing with sloped grate (fuel intake via endless screw) *)	(chippings from resin-pressed wood (beech/phenol resin and wood rests)	a) 35 kW	11.2/13	2		0.0120		120	none	30
			11.0/13			0.0047		120		40
solid-firing with grate feed (fuel intake via endless worm) *)	chippings from resin-pressed wood (beech/phenol resin and wood rests)	a) 960 kW (full load)	15.1/13	2		0.0022		2300	cyclone	36
			15.1/13			0.0080		2300		34
		a) 810 kW (partial load)	15.8/13	2		0.0014		1700		31
			15.7/13			0.0045		1700		31
solid-firing (grate feed with fuel intake via shaft)	chippings from chipboard and fiber board rests (coated and uncoated	a) 2.3 MW	19.0/11	2		0.670		11000	cyclone	101
			19.0/11			0.590		10600		140
a) solid-firing (grate feed with fuel intake via shaft) b) dust injection	a) chippings from chipboard rests, wood rests and bark b) sawdust	a) 11.9 MW	14.3/11	2		0.0278		25500	cyclone	133
			15.1/11			0.0297		27500		118

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Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment	Total Chloride Materials Utilized
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks	ppm
solid-firing (grate feed with fuel intake via endless worm)	sawdust, sawing shavings and board rests from hard-fiber board manufacture	a) 6 MW (full load)	11.5/11 11.5/11	2		0.296 0.233		11200 11000	E-filter	58 113
		(partial load)	11.7/11 13.6/11	2		0.045 0.143		7100 8500		88 57
solid-firing (underfeed furnace and injection furnace	sawdust, sawing and milling shavings (predominantly beech)	14.9 MW	9.8/11	2		0.009		17000	E-filter	38
			10.5/11			0.003		17000		57
solid-firing (solid injection via sloped grate))	sawdust, planing shavings and chippings (predominantly from beach, some glued, wood rests)	1.6 MW	15.9/11	2		0.071		6500	EFB-filter	369
			15.8/11			0.052		6500		339

* commercial installation not subject to licensing

** installation not subject to licensing for certain types of materials utilized. For the use of wood/wooden materials, provided they are not coated with or do not contain wood preservation agents, or coatings do not consist of compounds containing halogenorganic compounds, the installation is subject to licensing requirements.

Vertical Cyclone Furnaces

The vertical cyclone furnace is a modern low-emission installation for the combustion of wood with a furnace thermal output of approx. 800 KW. Measures have been implemented on the furnace as well as on the waste gas side to reduce the emissions(amongst others combustion compartment design, graduated air intake for combustion, waste gas return, E-filter). The air for combustion is blown tangentially into the combustion compartment in order that a thorough admixture and a high dwell time of the firing gases in the combustion compartment will be achieved. The good burn-out conditions are shown by the low CO emissions (approx. 70 mg CO/m^3 with respect to 13 % O_2).

Crushed chipboard remains are used as the fuel (chlorine content: approx. 0.05 to 0.08 %; nitrogen content approx. 3.5 %).

Cyclone Injection Firing 1

The investigated cyclone injection firing with downstream large-scale post combustion compartment enables a low-emission operation with good burn-out conditions. Measures have been implemented on the furnace as well as on the waste gas side to reduce the emissions (waste gas return, graduated air admission, fabric filters). A thorough admixture and a high dwell time of the firing gases in the combustion compartment are achieved by the tangential admission of air into the burner muffle. The high burn-out degree is reflected by the low CO and total C emissions (40-60 mg CO/m^3 at full power, 70-115 mg/m^3 at partial power, total C concentrations < 3 mg/m^3 with respect to 11 % O_2). The combustion compartment temperatures lie in the range of around 600 to 900 °C. Above all, chipboard remains with a chlorine content of 0.07 to 0.13 % by weight are used as the fuel.

The PCDD/F concentrations in the waste gases are given in table 3. There is a significant increase of the PCDD/F concentrations determined in the waste gases from crude gas to clean gas. A conclusive reason based on the information available cannot be given, as the operating temperatures of 150 to 170 °C for the fabric filters are significantly lower than the relevant temperature range for the formation of dioxins. The deposition of particles in the waste gases as well as a slow cooling of the waste gases in the temperature region of approx. 450 to 250 °C could be considered as possible explanations.

Cyclone Injection Firing 2

The 11 MW installation investigated is in accordance with the progressive status of technology as is the cyclone injection furnace 1 previously described, and enables a low-emission operation. A downstream filter is used for the removal of particle from the waste gases. As well as the customary fuel mixtures of untreated wood and wooden material remains, untreated spruce and ammonium sulfate hardened chipboard rests without or without added PVC were used. The good burn-out ratios are indicated by the very low CO emissions in certain cases (on average between 6 and 64 mg CO/m³, with respect to 11 % O_2 in the waste gases respectively, for PVC use of up to 190 mg CO/m³). Increased CO concentrations in the range of 540 to 700 mg/m³ resulted however from the use of $(NH_4)_2SO_4$ hardened chipboard, which is presumably attributable to an unsuitable particle size for the fuel. A considerably lower level of 0.1 ng TE/m³ than the limit for emissions was determined for the use of untreated wood together with the mixtures of fuels which are customary for operation.

The use of chipboard with constituent PVC gave the highest PCDD/F concentrations (approx. 0.3 - 0.37 ng TE/m³ with respect to 11 % O_2).

Distillation Gas Generator with downstream Cyclone Burner

The temperature in the sulfur gas generator was between approx. 400 and 600 °C, the corresponding burner temperature was between approx. 1,100 and 1,200 °C. As well as the PCDD/F contents in the waste gases, the dioxin contents in the substances used, in the cyclone particles and in the ash were determined. These are given in table 4 as a dependency on the fuel substances.
This installation is a pilot plant which would also explain the higher emission levels of HCl.

The influence of the substances utilized on the dioxins emissions is visible from the results available. Whereas the emissions increase significantly during the transition from untreated wood to wood coated with PVC and to wood treated with PCP, remaining however at a still reasonable level, a considerable increase occurred in particular in the deposited cyclone particles from the addition of PVC. Combustion of wood treated with PCP and lindane resulted in increased levels for CO by comparison with other the measurements.

Table 4 Dioxins from Fuel, Clean Gas, Dust and Ash, Distillation Gas Generator with Cyclone Burner (Pilot Plant), Volume Flow 250 N m^3/h

Fuel	PCDD/F Emissions (ng TE /m^3)		Chlorine content (Fuel) in %	PCDD/F Contents (Fuel) in ng TE/Kg	HCL Emission (mg/m^3)	Particle Emissions (mg/m^3)	PCDD/F Contents in ng TE/Kg	
							Ash	Cyclone Particles
untreated wood	0.04 0.03		0.004 0.006	0.5	0.5 2.4	9 22	30	30
PVC coated wooden fiber board	0.04 0.32		0.30 0.31	2	95.5 645.3	32 138	3300	23300
PCP/lindane treated wood	0.64 1) 0.23 1)	significantly higher CO values by comparison to the other measure ments	1.0 1.2	350	199.7 102.5	32 28	1300	9200
old timber from the disposal of building demolition remains	0.12 0.17		0.10 0.08 260	67 260	36.5 64.9	20 49	100	1000
	1) CO approx. 60-70 mg/m^3 otherwise approx. 10 mg/m^3							

Sloping Grate Firing

The installation investigated can be operated with heating oil EL as an alternative. For the use of wood shavings, the combustion compartment was preheated by an ignition burner up to the operating temperature before being switched over to firing the wood shavings. The boiler temperatures were between 700 and 1,000 °C. After cooling, the waste gases were cleaned using fabric filters. The relatively high variation range of the CO emissions (9 - 1850 mg/m^3) and the total C emission (2 - 48 mg/m^3) indicate that the installation was not set to an optimum.

Chip Firing (Large-Scale Installations)

The chip-firing furnaces investigated (16 MW, 2 MW) used untreated bark as well as bark slightly treated with lindane. All values measured are significantly less than the 0.1 ng TE/m^3 level and indicate that the emissions of PCDD/F are not appreciably influenced by the presence of wood which has been treated with lindane. The initial chlorine content of the substances used was only slightly increased by the lindane treatment (approx. 0.00001 % by weight of lindane in the wood), whereby the amount of lindane included was exceptionally low. The lindane contents are usually at least 50 times higher.

The extremely low emissions of PCDD/F from the one installation are, by comparison to those of the other installation (see table 3), particularly attributable to the better burn-out conditions and the more extensive particle collection (E filtering).

Chip Firing (Pilot Plant)

Wood chips as well as chipped wood with PVC granules were used in the 50 KW pilot plant. The chlorine content of the substances used was increased by a factor 3 to 0.26 % by weight on account of the addition of the PVC. Correspondingly high emissions of PCDD/F resulted from the investigation with PVC addition (4.3 ng TE/m^3); whereby a shift in the emission transfer to the particle proportion of the waste gases could be determined. The relatively high PCDD/F emissions at full load operation but without the addition of PVC (approx. 1 ng TE/m^3) are, by comparison with the above referenced installations, attributable to the unfavorable burn-out conditions and an insufficient dust removal.

Shaft Firing

The shaft firing furnace investigated which had a combustion thermal output of approximately 50 KW, was charged by hand using a mixture of untreated wood, coated (melamine resin, low amounts of PVC) and uncoated chipboard. The unfavorable burn-out ratios are documented by very high CO emissions (CO half hourly average values of up to 8700 mg/m^3 with respect to 13 % O_2). A fixture for the collection of particle from the waste gases is not present.

Pre-furnace firing

The pre-oven furnace with a combustion thermal output of approximately 230 KW was fired with pressed parts of untreated wood. A cyclone for the deposition of particles is downstream from the boiler. The relatively high CO emissions for the pre-furnace systems (half hourly average values of up to 1470 mg/m³ with respect to 13 % O_2) and high O_2 contents (approx. 17 - 19 % by volume) indicate that the installation is not set to an optimum with the correspondingly resulting unfavorable burn-out ratios.

Combined Grate/Coal Dust Firing

The installation investigated was a combination of furnaces for coal dust and feed grate firing (combustion thermal output for grate firing: 25 MW; for coal dust burner: 14 MW). The particle was removed from the waste gases by a downstream E filter.. A mixture of ammonium sulfate-hardened chipboard and untreated wood was used as the fuel, whereby approximately 20 - 30 % of the fuel is fired using the coal dust burner (wood sawdust). The chlorine content of the fuel mixture was approximately 0.03 % by weight. The installation showed good burn-out ratios (CO half hourly average values < 40 mg/m³) and an extremely good deposition of particle (particle emission < 1 mg/m³).

Fluidized Bed Firing Installation

The PCDD/F contents in the waste gases for differing fuels are given in table 5. Whereas in all cases for the crude gas the PCDD/F concentrations are extremely low, they are two powers of ten greater in the clean gas. The use of waste wood produces PCDD/F concentrations - in the crude as well as in the clean gas - of the order of a magnitude higher than from the use of forest wood or demolition wood. The De-novo synthesis comes into consideration here as a formation reaction. It could be supported by the C_6 ring structure of constituents in wood, cellulose and lining.

Table 5 Dioxin Emissions from a Fluidized Bed Firing Installation for Wood

Materials Utilized	PCDD/F Content			
	Crude Gas			Clean Gas
	upstream of boiler ng TE/m³	upstream of economizer ng TE/m³	upstream of scrubber ng TE/m³	ng TE/m³
Temperature °C	830-726	312-283	242-235	68-52
Waste Wood 1)	0.035	1.16	1.22	1.17
- " -	0.034	4.7	5.1	4.18
Forest Wood	0.007			0.12
Demolition Wood 2)	0.004			0.1

1) wood remains of all types (old furniture, orange boxes, coated and paint wood, cut wood)

2) from the demolition of old buildings.

Underfeed Firing 1

The use of different fuels in the automatic charging of underfeed furnaces with a combustion thermal output of about 230 KW with downstream cyclone deposition of particle was investigated. As well as the customary fuel mixtures of chipboard and untreated wood cuttings, untreated spruce wood shavings, ammonium sulfate and ammonium chloride-hardened chipboard remains as well as ammonium sulfate-hardened chipboard remains containing PVC were used.

The investigations were conducted at 50 % load and comparatively unfavorable conditions of combustion. The CO emissions were in the region of about 1200 to 3800 mg/m^3 with respect to 13 %O_2 in the waste gases, and for using PVC up approx. 6900 mg/m^3.

The lowest PCDD/F emissions were found from the use of untreated wood and for a mixture of chipboard and untreated wood chippings (approx. 0.15 - 0-45 ng TE/m^3 with respect to 13 % O_2 in the waste gases). Significantly higher levels were found when chloride-hardened chipboard was used (2.26 - 3.3 ng TE/m^3) and PVC additives (up to approx. 9.8 ng TE/m^3).

Underfeed Firing 2

The underfeed firing furnace investigated with a combustion thermal output of 3.5 MW was fired with chipboard and veneer wood rests. Downstream E-filtering removed the particles from the waste gases. The installation was run for two days with differing conditions of combustion for the measurements. Whereas PCDD/F concentrations in the waste gases of approximately 1.55 ng TE/m^3 from relatively unfavorable burn-out ratios (CO emissions approx. 760 mg/m^3 with respect to 11 % O_2 in the waste gases) were determined on the first day, PCDD/F values of 0.99 ng TE/m^3 were obtained on the second day of measurements from a more favorable setting of the installation CO emissions approx. 140 mg/m^3).

Underfeed Firing 3

The mechanically charged installation with a combustion thermal output of 117 KW was fired with natural wood pressed parts from milling, planing and sanding shavings. A fixture to remove particles from the waste gases was not present.
The measurement runs were conducted at loads of approximately 60 - 70 % and gave PCDD/F concentrations of approx. 01.94 and 0.24 ng TE/m^3 respectively for differing burn-out qualities with CO emissions of approx. 1800 and 690 mg/m^3 with respect to 13 % O_2 in the waste gases.

Pilot Plant for the Combustion of Wood containing Wood Preservation Agents

The pilot plant consisted of a 35 KW pre-oven furnace. The emission characteristics of wood treated with organic, and with inorganic wood preservation agents were investigated in comparison to those of untreated wood. The results for the untreated wood and chipboard, as well as for whited which had been treated with organic wood preservation agents containing chlorine, are compiled in table 5a. the investigations were conducted for good and to some extent for bad conditions of combustion. With a good burn-out, the CO emissions were usually in the range of between 70 and 150 mg/m^3 (up to 275 mg/m^3 for untreated beech), for a bad burn-out, CO emissions in the range of between 600 to 900 mg/m^3 were recorded with peak values exceeding 1000 mg/m.

Table 5a: PCDD/F emissions from a pilot plant for the combustion of wood containing wood preservation agents, with respect to 13 % O2, in ng TE/m^3 (including limits of detection).

Combustibles	Conditions of Combustion	
	good	bad
spruce (untreated)	0.012-0.013	-
beech (untreated)	0.036-0.046	0.145
chipboard (industrial) 1)	0.05-0.063	
chipboard (laboratory) 2)	0.186	
spruce with lindane	0.056	1.362
spruce with PCP	0.1	4.113
spruce with Dichloroflouride	0.26	1.78
spruce with Endosulfan	0.11	0.38
spruce with Chlorothalonil	0.14	0.85

1) hardened with ammonium sulfate
2) hardened with ammonium chloride

Table 5a emphasizes that using treated wood results in, as expected, higher dioxin emissions than from using untreated wood. Whereas the PCDD/F emissions for good conditions of combustion for untreated wood are significantly lower in some cases than the emission level of 0.1 ng TE/m^3, this limiting level could not be met when the organic protection agents investigated are used with the exception of one agent. With the use of chipboard hardened with ammonium sulfate (Cl content approx. 60 mg/Kg), a slightly higher PCDD/F level was given in comparison to the use of untreated wood. The combustion of chipboard manufactured in the laboratory and hardened with ammonium chloride (Cl content

Table 6. Dioxin emissions from Combustion Installations

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
heavy oil firing	heavy oil	no values	6.2/3 7.0/3 7.2/3	1 each		0.016 0.003 0.020		30500	no values
zone-feed grate 1)	natural gas with wood, paper, cartons, filter paper	a) 9.0 MW b) 73-84%	12.6-14.4/11 11.7-13.6/11	4		2.5-4.2 3.44-5.02		approx. 13000	E-filter
(fluidized bed furnace 2)	natural gas/heating oil EL and chipped bark, fibrous materials	a) 39.2 MW b) 80%	6.2/11	3		0.05 0.06 0.07	8.2	56000	E-filter, quenching and gas scrubbing
combustion installation 1)	paper, folders	a) 2.75 MW	12.7; 13.4/11	2		1.49; 2.0		5400	Afterburning chamber
fluidized bed furnace 1)	fiber remains, old paper remains, auxiliary burner: natural gas or heating oil	a) 42 t steam/h 39.2 MW b) 29.2 t steam/h	7.3/11	1	0.042	0.03	270.8	61500	E-filter, scrubber auxiliary burner not operated during measurements
	fiber residues	a) 42 t steam/h 39.2 t MW b) 38.4 t steam/h	5.9/-	1		0.03		41400	E-filter, scrubber auxiliary burner not operated during measurements
	drum residues fiber residues	a) 42 t steam/h 39.2 MW b) 26,3 t steam/h	6.2/-	1		0.01		39444	E-filter, scrubber auxiliary burner not operated during measurements

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
combustion installation [1] for residues with staged furnaces	slop, bio-sewage	a) 9.4 MW b) 5 MW	15.6/11	3		0.614 0.479 0.581		19900	afterburning burner 2-stage scrubber
mixed firing [1]	natural gas, sulfate spent liquor, bio-gas, trapping agents	a) 18.5 t steam/h	no values	1		0.04		101000	E-filter
fluidized bed furnace	coal		3.4-4.4/7					44000-60000	fluidized bed with limestone, fabric filter
	with paper sludge					0.002			
	without paper sludge					0.0013			

1) requirements of 17th BImSchV to be observed
2) installation closed down in the interim

8.1.2.3 **Firing of landfill gases**

General Process Description

Landfill gases are produced by aerobic and anaerobic, formation, decomposition and leeching processes of wastes from the landfills. Studies of their composition show a considerable potential for the emission of organic as well as inorganic air-contaminating substances, such that their acquisition and combustion (recycling) is necessary In 1991 according to surveys conducted by the Federal Ministry for the Environment, around 66 % of all landfills in the old Federal States were equipped with installations for collecting gases, each which being capable of collecting 30 to 50 % of the landfill gases formed.

As landfill flares produce increased residual emissions of environmentally harmful substances as a result of incomplete combustion, motorized installations and combustion muffles have instead been installed to reduce the emissions and to utilize the landfill gases burned. A generator is installed downstream of each of the motors to produce electricity; the usual outputs are between 200 and 250 KWel per motor.

Landfill muffles utilize the thermal energy of the gases in combination with the boilers to generate steam. The gases are fired at temperatures of 900 to 1000 °C and minimum residence times of 0.3 seconds within the closed combustion compartment.

Systems are also combined whereby the motor exhaust fumes are further fired, e.g. they are admitted to the firing muffles.

Substances Used

Investigations have shown that the composition of landfill gases at any one installation is relatively constant, although considerable differences can be given from landfill to landfill. The following substances in landfill gases are present in the following relative orders of magnitude:

- aromatic hydrocarbons 150 to 1,100 mg/m^3
- halogenated hydrocarbons 1 to 24 mg/m^3 (figure 3.1.7, class II)
- vinyl chloride and benzene 9 to 29 mg/m^3
- sulfur dioxide 7 to 135 mg/m^3
- halogenated hydrocarbons according to III b of the MAK (maximum working concentrations) list 1 to 29 mg/m^3.

(from "Presentation of the Results and Methods from an Investigation Program on Landfill Gases with Respect to the Requirements of Emission Protection", Hessian State Institute for the Environment, 1991, booklet 127).

8.1.2.3.1 Combustion Installations (no. 1.3 of the 4th BImSchV)

Results from emission measurements conducted in landfill muffles with waste heat boilers are compiled in table 7.

The levels for dioxin emissions are generally significantly lower than 0.1 ng TE/m³. They indicate good admixture and burn-out conditions in the muffles.

Two measurement results are with values of approx. 0.28 ng TE/m³ higher whereby one of these values can at least be attributed to an operational fault as being the cause.

Emission standards of 0.1 ng TE/m³ can also be expected from continual operation at optimized firing without any additional measures.

Table 7 Dioxin Emissions from Landfill Muffles (Reference Oxygen Content 3 % O_2 by volume)

Installation	Output a) long distance thermal/electrical output b) measured	Temperature °C	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Clean Gas ng TE/m^3	Waste Gas Volume Flow N m^3/h
Landfill gas Muffle	b) 3.5 MW	1350	2.2-2.9; 2.4-3.6	2	0.001; 0.001	2490; 2660
Landfill gas Muffle	b) 5.1 MW	1200-1250	5.5-6.7; 5.5-6.6	2	0.002; 0.002	2600; 2900
Landfill gas Muffle	a) 3.5 MW	730-1050 960-1000	3.2-8.7; 3.1-4.9	2	0.281; 0.048	1470; 1390
Landfill gas Muffle	a) 3.5 MW	1200-1250	2.4-2.5	2	0.049; 0.017	3300; 3020
Landfill gas Muffle	b) 7.1 t steam/h	no values	4.5	1	0.275 1)	6890
Boiler Installation	a) 1.89 MW b) - " -	-	4.2	1	0.006	1600

1) operational fault

8.1.2.3.2 Combustion Engine Installations (no. 1.4 of the 4th BImSchV)

Emission levels of dioxin for landfill engines are given in table 8.

Landfill engines - usually lean engines - produce dioxin concentrations in waste gases which are lower than 0.1 ng TE/m² at nearly all the installations which were measured.

8.1.2.3.3 Turbine Installations (no. 1.5 of the 4th BImSchV)

Emission values for an installation (nominal power 320 KW) are available. Dioxin emissions in the partial load region are with 0.16 and 0.4 ng TE/m³ in clean gas, higher than in the full load region with 0.063 ng TE/m³, which would apparently depend on the less favorable conditions of combustion in the partial load region.

Waste gas volume flow for the installation at nominal power is approximately 10,000 N m³/h.

Table 8: Dioxin Emissions from Combustion Engine Installations (Reference Oxygen Content: 5 % O_2 by volume)

Installation (no. of engines)	Engine Power (electrical) a) nominal b) measured	Cl content landfill gas mg/m³	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Clean Gas ng TE/m³	Waste Gas Volume Flow N m³/h
Landfill gas Engine (2)	b) 450 kW each	105; 126	6.45; 6.55	2	0.047; <0.0009	1800; 1900
Landfill gas Engine (2)	b) 200 kW each	15.8; 34.2	6.45; 6.7	2	0.0027; 0.0018	850; 850
Landfill gas Engine (2)	b) 450 kW each	61-80	7.1; 7.0	2	0.016; 0.0044	1890; 1830
Landfill gas Engine (2)	b) 218 kW each	12; 14	6.4; 6.2	2	0.063; 0.019	1140; 1160
Landfill gas Engine (2) with Muffle	b) 450 kW each	64; 61	3.2; 4.1	2	0.011; 0.0071	4470; 4270
Landfill gas Engine (2) with Muffle	b) 450 kW each	64; 61	4.6; 4.5	2	0.0044; 0.0062	4750; 4600
Landfill gas Engine (2) with Muffle	b) 450 kW each	105; 126	3.0; 2.95	2	0.0009; 0.0009	4600; 4500

Installation (no. of engines)	Engine Power (electrical) a) nominal b) measured	Cl content landfill gas mg/m³	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Clean Gas ng TE/m³	Waste Gas Volume Flow N m³/h
Landfill gas Engine (NO VALUES.)	no values	no values	6-7	4	0.03-0.2	< 2000
Landfill gas Engine (1)	a) 250 kW	no values	5.9	3	< 0.0015; < 0.0016; <0.0013	770
Landfill gas Engine (3)	a) 365 kW	20.8; 22.3	no values	3	0.007; <0.01; 0.024	1300; 1250; 1000
	a) 365 kW					
	a) 460 kW					
Landfill gas Engine (4)	b) 130 kW		5.5	3x3	0.0033; 0.0046; 0.0062	420; 430; 410; 550
	b) 139 kW		6.4			430
	b) 140 kW		5.4		0.0025; 0.0012; 0.087	410
	b) 180 kW		6.4		0.0007; 0.003; 0.004	550
Landfill gas Engine (3)	b) 250 kW	no values	no values	2x1	0.203; 0.0237	1250; 1100
Landfill gas Engine	a) 120 kW	no values	no values	1	0.083 (including detection unit)	113
Landfill gas Engine (1)	a) 430 kW b) 420; 430 kW	20-25	6.2-7.4	5	0.004-0.036	1954-1962
Landfill gas Engine (2)	a) 269 kW	102.6	5.29	4	0.001-0.006	1170

Installation (no. of engines)	Engine Power (electrical) a) nominal b) measured	Cl content landfill gas mg/m^3	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Clean Gas ng TE/m^3	Waste Gas Volume Flow N m^3/h
Landfill gas Engine (2)	a) 274 kE each b) -		6.5	3	0.003; 0.007; 0.017	2 x 1008
Landfill gas Engine (2)	a) 279 kW each - " -		4.8-6.4 5.4-5.8		0.001-0.004 0.016	3100 - " -
Landfill gas Engine	a) 500 kW			3	0.125	1000
Landfill gas Engine	a) 300 kW			1	0.1	1700
Landfill gas Engine	a) 279 kW b) 250 kW			1	0.2	1250
	a) 279 kW b) 240 kW			1	0.03	1100
	a) 279 kW b)250 kW			2	0.019	1160
Sewage Gas Engine	a) 1650 kW b) 1350 kW		9.6	1	0.03	6200

8.1.3 Installations for the Manufacture and Processing of Stone and Earths, Glass, Ceramics, Building Materials

8.1.3.1 Installations for the Manufacture of Cement (no. 2.3 of the BImSchV)

General Process Description

The most import raw materials for the manufacture of cement are limestone and clay or a calcareous clay in which both components are already naturally mixed. The components are milled, dried and subsequently fired in a rotary furnace to cement clinkers. Depending on the type of preheating of the material, it is differentiated between grate and cyclone preheating, whereby the starting materials are preheated to 800 °C. The raw materials pass through the rotary furnace towards the flame. In the hottest zone (sinter zone), the material being fired reaches temperatures of around 1450 °C; the most important reactions in the production of the cement clinkers take place here. After cooling, the clinkers are milled together with gypsum to ready cement.

The waste gases which contain particles, are passed through an electrostatic precipitator in the mill-drying installation in combined operations. In direct operations, the waste gases are cooled in an evaporation cooler upstream of the electrostatic precipitator.

Substance Used

Raw materials for cement:

limestone, clay, marl, chalk,

Fuels and combustible materials:

coal dust, used oil, used tires, landfill gases, heating oil S and others.

Emission Levels

Table 9 includes the emission levels for PCDD/F as a dependency on the differing substances used in the manufacture of cement.

For all plants investigated, the variation of the fuels utilized - with one exception (0.24 ng TE/m^3) - in the PCDD/F contents in the clean gas, were found to less than 0.1 ng TE/m^3. The explanation for this is the extremely good conditions for burn-out as well as the very low HCl contents in the waste gases (alkaline medium).

Four investigation results available from ready clinkers show PCDD/F contents to lie within a bandwidth of the lower detection levels of max. 2.3 ng TE/Kg clinker (TE-BGA) whereby the values which are less than 1 ng TE/Kg dominate.

8.1.3.2 Installations for the Firing of Limestone (no. 2.4 of the 4th BImSchV)

General Process Description

As well as different types of shaft furnaces, which is the classic kiln for the manufacture of fired limestone, rotary furnace kilns are also in operation in some cases.

The modern ring shaft kilns where there is a particular arrangement of the burners at two levels, the limestone and the firing gases in the upper two firing zones are forwarded in opposing directions, and in the lower section in the same directions, in order to guarantee an effective heat transfer. The firing process takes place at temperatures of around 1000 to 1100 °C. Coal has since been nearly completely substituted by liquid and gaseous fuels.

The waste gases are, after having released their thermal energy to the materials being fired and the atmosphere of combustion, cleaned by the use of fabric filters.

Substances Used

Limestone
fuels and combustible materials:
coal, heating oil, gas, used oil.

Emission Levels

PCDD/F emissions from lime-firing processes, in particular those utilizing used oils are given in table 10.

The concentrations of clean gas given are less than 0.1 ng TE/m^3. An influence of the fuel used (with or without used oil) cannot be concluded from the results available for shaft kiln constructions.

Table 9· Emission levels from Rotary Furnaces in the Manufacture of Cement (Reference Oxygen Content: 10 % by volume)

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m^3	 Clean Gas ng TE/m^3	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m^3/h	Waste Gas Treatment Remarks
Rotary Furnace[1]	coal, used oil (20 % of long distance heat output) bentonite	a) 3000 t/d	11.5-13.5	6		0.002-0.24	1	350000-387000	E-filter (140°C)
Rotary Furnace[1]	coal, used oil (up to 1000 ppm PCB) 10 % of long distance heat output	a) 1400 t/d	5.4-7.6	14		< 0.085		90000-102000	E-filter (170°C)
Rotary Furnace	coal dust	no values	5.8	9		0.004-0.02		< 250000	E-filter
Rotary Furnace	brown coal, landfill gas	a) 1100 t/d	8.9	1		< 0.024		60800	E-filter
Rotary Furnace[1]	coal used oil tires heating oil	a) 3150 t/d b) 96%	8.0; 8.9; 6.9	3 1,2 combined operation 3 direct operation		0.0146 0.019 0.035	40	approx. 220000	E-filter
Rotary Furnace[1]	coal used oil + tires (50 % of long distance heat output)	b) 93-99%	7.1-10	6		0.003-0.02		90000	E-filter
Rotary Furnace[1]	coal dust used oil + tires (50 % of long distance heat output)	b) furnace I 81-86% furnace II 90-96%	8.5-12	6		0.007-0.01		100000	E-filter

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
- " (recent measurement)	coal dust used oil + used tires (50 % of long distance heat output)	furnace I 960 t/d	8.7	1		0.002		approx. 105000	E-filter
		furnace II 960 t/d	13.1	1		0.006		approx. 105000	E-filter
Rotary Furnace[1)]	coal, used oil + tires (50 % of long distance heat output)	a) 3150 t/d b) 91,4%	8.8-9.5	3		0.016-0.033 (TE-BGA)		approx. 240000	E-filter
Rotary Furnace[1)]	coal used oil + tires (60 % of long distance heat output)	a) 3150 t/d b) 2800 t/d	8.4	2		0.001 0.017		approx. 225000	E-filter (cumulated operation)
- " -			7.0	1		0.002		approx. 203000	E-filter (direct operation)
Rotary Furnace[1)]	coal, used oil	a) 1500 t/d	6.5-7	3		0.0045-0.0059 (TE-BGA)		approx. 200000	E-filter
Rotary Furnace[1)]	coal, used oil, used tires	a) 3000 t/d	8.4	3		0.006- 0.021		approx. 225000	E-filter
Rotary Furnace[1)]	coal, tire cuttings, solvents	96 t/h		3		0.043; 0.016 0.008		approx. 120000	E-filter

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
Rotary Furnace[1]	coal, tire cuttings			3		0.0064		112000	E-filter
Rotary Furnace	coal	125 t/h		2		0.012		217000	E-filter
Rotary Furnace[1]	brown coal, used oil (50 % of long distance heat output)	1650 t/d	10-11%	3		< 0.001 each		180000-270000	E-filter (direct operation)
			12-13%	3		< 0.001 each			E-filter (cumulated operation)

[1] requirements of 17th BImSchV to be observed

8.1.3.3 Installations for the Manufacture of Glass (no. 2.8 of the 4th BImSchV)

General Process Description

On account of the differing areas of application and the corresponding demands on the glass quality, numerous raw materials are used in the manufacture of glass. The most important raw materials are sand, limestone, dolomite and soda. In addition to these, purifying, coloring and clarifying agents are employed.

Continuous or periodically-operating melting kilns are used for the manufacture. The melting temperatures are around between 1450 and 1650 °C. Natural gas and heating oil serve as the primary types of fuel used; there are also kilns which use electricity as the (additional) source of heating.

The emissions can not only arise from the mixtures but also from the fuels utilized. Depending on the composition of the raw materials, purifying agents and fuels, in particular NO_x, SO_x, fluorinated and chlorinated compounds and heavy metals are emitted together with the waste gases.

The sorption by hydrate of lime followed by subsequent collection of particle (usually electrostatic precipitators or fabric filters) has proven effective in reducing the emissions of sulfur dioxide and fluorinated compounds. Nitrogen oxide emissions be reduced as well by employing primary and secondary measures.

Materials Used

Sand, limestone, dolomite, soda, purifying, coloring and clarifying agents.

Fuels:
natural gas, heating oil.

Emission Levels

The levels of dioxin emissions are given in table 11 and are less than 0.1 ng TE/m³.

8.1.3.4 Installations for Firing Ceramic Products (no. 2.10 of the 4th BImSchV) here: Bricks

General Process Description

Bricks are predominantly manufactured from clays and materials containing clay (slate clay, marl, loam). In some cases, porosity agents (polystyrene foam, sawdust, gettering agents) are added to the raw materials to increase the porosity, and these agents then release sulfurous gas in the preheating zone at temperatures of between 200 and 400 °C. These are then to be converted in the course of the process by suitable admissions of gas into the hot zones of the kiln or by an external afterburning. Bricks are fired in tunnel kilns at temperature of between 900 and 1100 °C.

Heating oil and natural gas are generally used as the fuels. As far as emissions of gaseous inorganic chlorine and fluorine compounds as well as sulfur dioxide are to be reduced by waste gas purification, continuous-layer filtering using calcium carbonate or, in certain cases, by the injection of calcium hydroxide into the waste gases in conjunction with a particle collection by fabric filters is employed.

Materials Used

Clay, materials containing clays, possibly leaning or porosity agents.

Fuels:
heating oil, natural gas.

Table 10: Dioxin Emissions from Lime Kilns

Installation	Fuel	Output	Operating / reference oxygen content	Number of measurements	PCDD/F Content Crude Gas	 Clean Gas	 Filter Deposits	Waste Gas Volume Flow	Waste Gas Treatment Remarks
		t/d	% by volume		ng TE/m³	ng TE/m³	ng TE/Kg	N m³/h	
Ring shaft Furnace[1)]	heating oil S	175	9.2	1		0.035		16700	fabric filters
	heating oil S used oil	180	8.1	2		0.046 0.029		- " -	- " -
	used oil	180	8.1	1		0.043		- " -	- " -
Ring shaft Furnace[1)]	used oil	175	12.0-12.4	3		0.019 0.008 0.018		24000	fabric filters

[1)] requirements of 17th BImSchV to be observed

Emission Levels

The formation of dioxin is possible on account of the reaction of hydrocarbons with the chlorine from the natural raw materials and from the fuels.

The PCDD/F emissions from brick kilns are given in table 12.

The given concentrations for dioxins and furans in clean gas are as a rule less than 0.1 ng TE/m^3.

From operational practice, higher levels are also known, e.g. from the use of certain porosity agents (such as de-inking gettering agents). With regard to meeting a target level of max. 0.1 ng TE/m^3, particular reduction measures (e.g. post burning of sulfurous gases) may be necessary.

Table 11 Dioxin Emissions from Installations for the Manufacture of Glass

Installation	Fuel	Output a) long distance thermal/electrical output b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas	Clean Gas	Filter Deposits		Remarks
					ng TE/m³	ng TE/m³	ng TE/Kg	N m³/h	
Manufacture of container glass	fuels: heating oil/natural gas 200 mg Cl/Kg	680 t/d (3 lines)	9.7-10.1/9	3		0.01; 0.01 1 value operational error		63,000	dry sorption using lime, E-filter including waste gases from hot-air tempering
manufacture of quartz glass including pilot plants (several small furnaces)	$SiCl_4$, SiO_2, Cl_2, HCl, freon			2		0.086 0.074		9,300	wet scrubbing
cross-fired trough with regenerative air pre-heating for soda lime glass	fuel: natural gas	82 t/d		3	0.003-0.015	0.0016	1.9	10,700	E-filter

Table 12: Dioxin Emissions from Brick Firing Kilns (with respect to 18 % oxygen by volume)

Installation	Fuel Porosity agent	Firing Capacity / temperature t/h °C	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
Tunnel Kiln	heating oil S sawdust limestone	10.9 960	14.3	1		0.0013		11100	additional burner in pre-heating zone
Tunnel Kiln	heating oil S 60 % landfill gas 40 % sawdust limestone	12.4 960	17.2	1		0.0047		20400	- " -
Tunnel Kiln	natural gas paper sludge	6.5 850	17.8	3		0.0084 0.0084 0.00094		15500	furnace-internal carbonization gas after-firing
Tunnel Kiln	heating oil S and EL sawdust limestone	- 960	15.7	1		0.01		15000	carbonization chamber furnace-internal carbonization gas after-firing
Tunnel Kiln	heating oil S and EL landfill gas sawdust limestone	- 960	15.7	1		0.01		15000	- " -
Tunnel Kiln	natural gas no porosity agents	1070	17.1	2		0.027 0.020		15000	none

Installation	Fuel Porosity agent	Firing Capacity / temperature t/h °C	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
Tunnel Kiln	natural gas sawdust trapping agents	10 t/h 980	9.7	1		0.041		8800	carbonization gas return dump layer filter
Tunnel Kiln I and II	I) heating oil S liquid gas sawdust polystyrene limestone powder	- 960	18.7-19	3		0.046 0.019 0		36300- 37300	additional burner in pre-heat zone
	II) as above sawdust polystyrene recycled polystyrene paper sludge	960	18.7-19.5	3		0.344 0.049 0		33100- 25300 29900	- " -
Tunnel Kiln	natural gas	approx. 1030	16.2	1		0.0037 (TE-BGA)		13000	fluor-cascade adsorber (jura lime)
Tunnel Kiln	brown coal briquettes spruce wood shavings	65.3 t/d 900 °C	18	2		0.01-0.02		5170-5630	none
Tunnel Kiln	heating oil EL sawdust paper sludge	2/1000	16.4	3		0.010 0.009 0.011		4300	none

Installation	Fuel Porosity agent	Firing Capacity / temperature t/h °C	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow N m^3/h	Waste Gas Treatment Remarks
					Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits ng TE/Kg		
Tunnel Kiln	polystyrene sawdust for porosity		16.8	2		0.004; 0.005		30900	carbonization gas return
Tunnel Kiln	de-inking trapper paper trapper polystyrene	8 t/h	17.2; 16.3; 16.5	3		0.362; 0.108 0.107		5000	none

8.1.4 Asphalt-Mixing Installations (no. 2.15 of the 4th BImSchV)

General Process Description and Materials Used

Bitumen road construction materials are manufactured in asphalt-mixing installations. The main steps of the process are:

- charging the dry drum and drying the mineral substances,
- mixing the mineral substances with bitumen in the mixer,
- filling the mixed material into loading silos.

The main sources of emission of air-contaminating substances are the drying drum and the mixer.

The drying drums are heated by gas, oil or brown coal. The waste gases from the drying drums as well as from the mixers are cleaned to a greater extent by fabric filters and a preliminary upstream collection of particles by inertial forces deposition is usual.

Diffusion of particle emissions is reduced by encapsulation of relevant sections of the installation. Materials used along with mineral materials of differing grain sizes, are bitumen and binding agents containing bitumen as well as additives (organic or mineral fibers, polymers, dye pigments, adhesion improvers). Construction asphalt not containing tars is also used in certain cases.

Emission Levels

The measurement values available (table 13) are lower than 0.1 ng TE/m^3.

Table 13: Dioxin Emissions from Asphalt-Mixing Plants (with respect to 17 % O_2 by volume)

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
Asphalt-mixing plant	used asphalt 50% bitumen B 80 fuel: heating oil EL	a) 177 t/h	13.6	3		0.03 0.02 0.01		34000	fabric filters
Asphalt-mixing plant	natural grit gravel sand, max. 60 % construction asphalt heating oil / butane gas	a) 180 t/h b) 175 t/h	13.7	3		0.0013 0.0012 0.0007		36200	fabric filters
Asphalt-mixing plant	asphalt 30 % bitumen B 80 basalt grit, and, heating oil EL	a) 150 t/h	17-19	2		0.016 0.005		50000	fabric filters

8.1.5 Installations for the Manufacture and Processing of Steel, Iron and other Metals

8.1.5.1 Installations for the Roasting, Smelting or Sintering of Ore (no. 3.1 of the 4th BImSchV)

8.1.5.1.1 Sinter Installations in the Steel and Iron Industries

General Process Description and Substances Used

By sintering, the shredding of fine-grained, smeltable ores, iron ore in particular, to compact lumps by heating nearly to the melting or softening point is understood. Melting tendencies at the grain boundaries lead to a caking of the material.

Iron ores in the Federal Republic of Germany are agglomerated on conveyor sinter installations, the conveyor belts of which can be as big as 4 m in width and 100 m in length. The fine ore to be sintered is moistened and fed on to the circulating grid together with coke slack and additions such as limestone, quick lime, olivine or dolomite. The carbon contained in the mixture burns with the aid of the air sucked through the grid into the mixture, whereby the shredding is accomplished by the heat which is thereby released.

Chlorine compounds can enter into the sinter installation means of the additive cokes slack as well by the ore from its natural chloride contents. Furthermore, returned materials such as certain filter dust, scale and sludges from waste water treatment, which are added to the materials to be sintered, which can also increase the chlorine content of the substances used. This is reflected in the waste gases from sinter installations which contain inorganic gaseous chlorine compounds up to emission standards of the TA Air of 30 mg/m3 expressed as hydrogen chloride.

Table 14: Dioxin Emissions from Iron Ore Sintering Installations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
Iron ore sintering plant 1)	iron ore and additional materials			4		11.55		approx. 502000	E-filter
- " -	- " - 2)			6		2.45		- " -	- " -
Iron ore sintering plant 1)	iron ore and additional materials			3		43.2		approx. 680000	E-filter
- " -	- " - 2)			10		2.51		- " -	- " -
Iron ore sintering plant 1)	iron ore coking duff		19	1		1.9		1,000,000	E-filter
Iron ore sintering plant 1)	iron ore and additional materials (e.g. roll scale. E-filter particles, return-waste)	a) 375 t/h	16.3	3	2.075 2.30 1.99	2.28 2.37 2.27		approx. 500,000	E-filter
				1		2.1			

1) these values could not be reproduced from repeated measurements in varying conditions of operations and it must be assumed that a peculiar situation existed for these measurements

2) renewed measurement: additional materials (and to some extent the operating conditions) changed

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits ng TE/Kg	N m^3/h	Remarks
Iron ore sintering plant 1)	iron ore and additional materials	a) 260 t/h final product	14.8-15.9	5		5.2-14.1		approx. 300,000	E-filter
		- " -	- " -	5		2.2-12.2		- " -	E-filters and fabric filters
Iron ore sintering plant 1)	iron ore and additional materials	a) 390 t/h final product	16.4	1		2.56		584,000	E-filters
Iron ore sintering plant 1)	iron ore and additional materials	a) approx. 500 t/h final product			1.07 1.22 1.37	0.83 1.06 1.49		753,839	E-filters
particle-removal from chamber of a sintering plant				4		0.0109		217,000	E-filters
particle-removal from chamber of a sintering plant				3		0.619		439,000	E-filters
loading sintering plant	final product			4		0.0007		131,000	fabric filters
loading sintering plant	final product			3		0.0016		152,000	fabric filters

Emission levels

Emission levels for sinter installations are given in table 14. The majority of measured values lie today by around 2 ng TE/m³. In the past, significantly higher emission levels (from one installation as much as 43 ng TE/m³) were measured at certain installations. Sinter installations have large volume flows and constitute one of the largest sources of dioxin emissions of the present day.

To reduce the emissions, primary measures have been taken which are predominantly related to the substances used, e.g. avoiding the use of highly contaminated rest materials. Amongst others, these measures have lead to considerable reductions in the emissions from the above referenced installations with the very high emission levels and within a short space of time. The mechanisms for the formation of PCDD/F are currently being investigated more closely in a study program from the Rhine-Westfalian Technical High School in Aachen.

The installment of fabric filters downstream from an electrostatic precipitator (present) in the waste gases has been sponsored by the Federal Ministry for the Environment within the scope of an investment program to reduce environmental pollutions. This measure lead to a considerable reduction in the particle emissions, the effectivity of which with respect to a reduction in the dioxins is currently being investigated more closely. The preliminary measurement results available to date comprise a wider range (see table 14). To limit the dioxin emissions, according to experience gained from waste incineration installations as well as from other installations in the metal sector, the addition of sorption agents (mixture of limestone and coal/coke dust) is foreseen upstream from the waste gases. The reduction in emissions shall be further supported by process-related measures for sintering (e.g. return of waste gases in some cases). The loaded adsorbents which occur shall also be utilized in the process, whereby a enrichment of the dioxins shall be prevented. *)

*) This contribution will be updated in accordance with the status of this project and results of investigation as they become available.

Furthermore, a special scrubbing method has been developed for sinter installations in Austria. Emission levels of < 0.1 ng TE/m³ were achieved in a pilot plant in 1992. By this method, the waste gases from sintering processes are pre-quenched, the dioxins leached out in a downstream high-performance scrubber and subsequently separated by a high-efficiency drip deposition process. Rest materials occurring are currently returned to the sintering process. Initial investigations of a large-scale plant resulted in a reduction from 2.5 to 0.2 to 0.5 ng TE/m³.. A further reduction can be reached by supporting measures on the process side or by the addition of suitable adsorption agents (addition of brown coal cokes/coal slack/in front of the E filter and scrubber).

8.1.5.1.2 Installations for the Sintering or Roasting of Materials containing non-ferrous Metals

Ore concentrate containing non-ferrous metals have predominantly high sulfur contents. These are processed in sintering installations and/or roasting kilns, if required with the addition of other fine-grained materials containing non-ferrous metals (e.g. sludges containing non-ferrous metals with the greater proportions of additives such as lime, sand etc., which serve as slag formers, as well as projectile retention sands which serve as substitutes, lead sulfate sludges).

According to measurement values available, dioxin contents of < 0.1 ng TE/m³ of waste gases are reached for plants in the non-ferrous metals industry according to information from the Metal Trade Association e.V.

8.1.5.1.3 Installations for the Sintering of Special Materials

There are installations in which residual materials are sintered. Very high emissions of dioxin concentrations have been reported from one installation (47 ng TE/m³). By changing the substances used, the dioxin emissions could be reduced by approximately 50 % within a short space of time. Within the scope of an accompanying measurement program, it is currently being attempted to reduce the dioxin emissions by primary measures (e.g. further changing the substances used). (This plant is licensed in accordance with no 3.,1 of the 4th BImSchV).

8.1.5.2 Installations for the Production of Pig Iron or Non-Ferrous Crude Metals (no. 3.2 of the 4th BImSchV)

8.1.5.2.1 Installations for the Production of Pig Iron

Pig iron is recovered by blast furnace processes. There are a few results available on dioxin contents of the waste gases and these are given in table 15. The values measured are significantly lower than 0.1 ng TE/m³.

8.1.5.2.2 Installations for the Production of Non-Ferrous Crude Metals

General Process Description and Materials Used

Of the non-ferrous crude metals recovered, the particularly significant metals are copper and lead on account of the amounts recovered and the relevance of the emissions.

Production of Copper

The production of copper from primary raw materials is predominantly from the use of ores and concentrates. As well as these however, secondary materials/recycling products are increasingly being used, for example scrap materials. sulfidic ores are mainly processed according to the flash smelting technique. The hereby produced copper matte (copper content approx. 60 %) is furnace-blasted to blister copper (copper content approx. 95 %) in the matte converter and processed in the anode kiln to anode copper (approx. 99 %); the subsequent refining process is conducted by electrolysis.

Table 15: Dioxin Emissions from Installations for the Production of Iron

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
Blast Furnace (wind generator)		a) 600 t/d	4-6	3		0.03 0.029 0.004		70000	no values
Blast Furnace (wind generator)		a) 9000 t/d b) - " -	10-12	3		0.037 0.038 0.021		329200	depositor whirler scrubber
Blast Furnace (casting shed particle removal)		a) 9000 t/d		3		0.0015 0.002 0.002		700000	fabric filters
Blast Furnace (casting shed particle removal)		a) 600 t/d		2		0.002 0.004		91400	wet E-filter

Secondary raw materials such as oxide materials for example can also be processed in shaft kilns to copper matte or coarse copper. Blister copper is produced from copper matte in the matte converter and anode copper is produced from this in the anode kiln or, from coarse copper in the anode shaft kiln, as well as in the foundry kiln.

Scrap alloys are preferentially used in used metal converters and the copper thus recovered is transferred to the anode kiln. Scrap copper can also be processed directly in the anode kiln.

Emission Levels

Dioxin emission levels from extraction plants for crude copper are compiled in table 16.

Extraction of Lead

During the extraction of lead from primary raw materials, the sulfidic ores and concentrates in roasting and sintering installations are desulfurized and shredded and are reduced together with returned materials containing lead (e.g. return slack) and flue ash in shaft kilns to raw lead. In recent years as a replacement for this multi stage emission-intensive process, the environment-friendly QSL technique was developed. The QSL technique (named according to the initials of its inventors, Queneau, Schumann and the company Lurgi) is a continuous direct lead smelting process, by which the autogenic Roasting-Reaction-Smelting of intermediate substances containing sulfur and the carbothermic reduction of the bound lead oxide take place in a reactor. The raw lead is subsequently refined whereby the elements antimony, arsenic, copper, bismuth, zinc, tin and precious metals contained ion the lead, are separated in several process stages. Reverberator furnaces, rotary Reverberator furnaces and smelting crucibles are used.

Table 16: Dioxin Emissions from the Production of Crude Copper

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
shaft furnace (old installation)	coke, slack, copper slag, fine material containing copper, scrap iron	a) 1.8-7.5 t/h	14.5	1		9.67	18200 (TE-BGA)	30700	fabric filters
shaft furnace	slag, ashes, filter deposits (up top 30 % Cu), lime, sand	3x160 t/d	approx. 18	10	secondary hoods 1.3	2.3-6.2 beginning of 1989 one furnace 27.6; 29.5 end of 1989 1.5-2.0	900	3x60000	fabric filters
experimental crucible furnace	materials containing plastics	a) 300 kg in 6-8 h	20.2 20.7		3.5 1.3	2.0 0.1	7600 41000	22000 23000	fabric filters
converter	liquid copper, scrap brass, slag, coke, gas	a) 2000 t/a 7-10 t/lot	no values	1		0.57	4200 (TE-BGA)	116900	fabric filters
converter	liquid black copper with relay scrap	no values	no values	no values		0.26 (TE-BGA)		35000	fabric filters for injection into desulfurization plant
	without relay scrap					0.16 (TE-BGA)			
primary copper kiln for converter operation	matte of copper, scrap containing copper Cl content; max. 8 % Br content: max. 5 %		low is converted nearly completely					max. 300000	several E-filters scrubbing, coolers with SO_2 removal and conversion to H_2SO_4
	excluding plastics			2		0.001 (BGA)			
	with telephone scrap			2		0.0013 (BGA)			
	without telephone scrap			6		0.0058	10		

Installation	Materials_Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits ng TE/Kg	N m^3/h	Remarks
anode kiln (flame furnace)	black copper, recycling copper copper beech wood	a) 62500 t/a	11.7-16.4	1		1.09		10000	no waste gas treatment
anode kiln (flame furnace)	crude copper with thermally treated scrap					0.99 (TE-BGA)		81500	fabric filters with lime injection
	with mechanically treated scrap					0.41 (TE-BGA)			
experimental furnace (Velmede furnace)	electronic scrap (circuit boards, cards etc.)	100 kg/h	no values	1 each		1.4 TE-BGA		2000	fabric filters
						0.7 TE-BGA		2000	quench upstream of fabric filter
						0.003 TE-BGA		2000	quench upstream of fabric filter and activated coke filter (load layer)
anode kiln (flame furnace)	blister copper Cu- refining material Cu- brass	a) approx. 310 t/h/lot			secondary hood gas		cooler dust 1350 filter particles 310 secondary hood filter dust 9560		cooler fabric filter mixed chamber
	Zn-black copper and others	A) install, melt down	15.8	2	0.071 0.038	0.447 0.169		43000	
		B) refineries	14.7; 15.2	2	0.05 0.05	0.178 0.087		41000	
		C) pole	15.7; 16	2	0.041 0.053	0.209 0.148		40000	
		D) cast	13.4; 12.9	2	0.041 0.055	0.04 0.045		13000	

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
electric furnace	copper secondary raw materials and recycling materials	no values	no values					approx. 20,000	fabric filters for high SO_2, scrub and cooling installation, contact installation
	a) without recycling material b) with PE/PP c) with PVC				0.026 0.031 0.033				
converter	matte of copper additional materials computer scrap	a) 70 t/h	11	3		0.0047 0.0028 0.001		196,000	E-filter, scrub and cooling installation, contact installation additional emissions of brominated dioxins
suspended melting furnace	copper concentrate	a) 70 t/h							
	a) without sewage sludge granulates		10.5	1		0.0068		205,800	E-filter, scrub and cooling installation, contact installation (Esse)
	b) with sewage sludge granulates		9.4-9.9	1		0.00008		199.700	
- " -	copper concentrate	a) 70 t/h							- " -
	a) without		5.2	2	0.018; 0.035;	0.0001		84,100; 84,000	downstream of suspended melting furnace - E-filter)
	b) with PE/PP		4.1	2	0.027; 0.004;	not detectable		83,700; 81,900	
	c) with PVC		5.3	2	0.196; 0.3	- " -		84,800; 80,500	

An important secondary raw material is used storage batteries which, following a mechanical processing predominantly in drum kilns, are processed Further secondary materials (such as scrap, cable lead, lead ash) are also processed in different versions of the drum kiln.

Emission levels

The dioxin emission levels from the extraction of crude lead are given in table 17.

Emissions from the Production of Crude Copper and Crude Lead

The clean gas concentrations in waste gases from installations for the manufacture of crude copper or crude lead lie in the region of several Pico grams TE/m³ up to 2 ng TE/m³; for an old plant and for a further plant prior to modernization, higher values of up to 10 and 29.5 ng TE/m³ were also given respectively. This range can be explained by the large differences in the materials used in the differing aggregates and in the different operational processes. General correlations between types of emission and operation of the installations cannot be concluded from the condensed investigation results available. As only individual natural gas values are available, the efficiency and effectivity of the applied treatment of waste gases can also only be estimated on a case by case basis. Thus, for example, an oxygen injection in the region of the top of a shaft furnace lead (attachment 2 in table 16) leads to a reduction in the emissions by a factor of 15 to 20, but this measure alone could not realize the target value of 0.1 ng TE/m³.

The pilot furnace listed in table 16, in which smelting work and afterburning are realized together in the furnace (use of pure oxygen, temperatures exceeding 2000 °C, residence times exceeding 2 seconds), resulted in very low PCDD/F levels from under 0.1 ng TE/m³ in the waste gases from employing effective secondary measures such as quenching the waste gases in from of the fabric filters and downstream activated coke filters. These results however cannot be simply applied by transferring to other processes.

The shaft kiln included in table 17 (attachment 1) has since been shut down, the processing of the materials used is now carried out in an electric kiln. Very low emission levels for dioxin of less than 0.1 ng TE/m³ are achieved with QSL installation with its integrated process concept. It is planned for a lead re-smelting plant currently in operation, to reduce the levels of dioxin emissions by quenching the waste gases in the natural gas circulation followed by cleansing them using fabric filters and a downstream activated coke filter.

Reduction Measures

There are only a few concrete plans at the present time for additional reduction measures which have been publicized in this field. The industry is conducting internal investigations.

Fundamentally, the following measures are suitable, to achieve a far-reaching reduction of the dioxin emissions:

- pre-sorting of scrap,

- quenching the hot waste gases (provided the emission reduction has precedence over the recycling of heat),

- the use of oxygen or of air enriched with oxygen, for the firing process (not only in view of an improvement of the burn-out of the waste gases but also to minimize the volumes of waste gases to be treated,

- downstream purification of waste gases through a solid bed activated charcoal filter or through a fine current or filter layer reactor under the addition of activated charcoal or open-hearth coal dust. A minimization of the dioxin emissions with the goal of achieving a level of 0.1 ng TE/m^3 is strived for.

- downstream waste gas purification by catalytic oxidation.

The following of the above listed measure are being applied in practice:

- oxygen injection in shaft kilns for the extraction of copper which lead to a reduction in the extremely high levels of as much as 1 ng TE/m^3,

- alteration of installations with the objective of reducing the residence times in the critical temperature region in the waste gas system to suppress the De-novo synthesis.

Table 17: Dioxin Emissions from Installations for the Production of Lead and Lead Alloys

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m^3/h	Waste Gas Treatment Remarks
shaft furnace	particles containing lead and slack	no values	16.6	2 each				42000	fabric filter
	without polyethylene					0.52; 0.66	3100		
	with polyethylene					0.58; 0.58	2600		
short drum furnace	batteries, used lead, coke, soda, sodium chloride	no values	no values	no values	load, melt down, reduce, draw off	0.18 0.09		39000 31000	fabric filter
lead drum furnace	lead ashes/used batteries and scrap cable containing lead	no values	no values -			0.27		2x22000	addition of brown coal coke and hydrated lime (1:1) to process gas and afterburning in waste gas
	old battery lead, lead ash					0.22 0.14		2x22000	fabric filter with additional additive
flame furnace	old charging battery lead	9.3 t/h	20.3			0.022		54000	fabric filters
flame furnace	waste containing lead					0.276		5400	
QSL plant	ore concentrates, coal, additional materials	10.8 t/h		2		0.043 0.004		12000	hot-air E-filter (temperature range 350 - 400 °C)

8.1.5.3 Installations for the Production of Steel and for the Melting of Cast Iron (no 3.3 of the 4th BImSchV) including the Drying of Steel Chips

General Process Description

Scrap steel and iron are used for the production of steel or the production of iron, cast iron, malleable cast iron ands steel iron. Correspondingly different are the demands on the usage of the scrap and the processing involved.

Today in the converter process (oxygen-blast technique), 20 % scrap steel is added to the pig iron. When melting the scrap, the temperature of the molten bath rises from values of between 1300 °c and 1450 °C (liquid pig iron) to temperatures of between 1600 °C to 1750 °C (molten steel). Trace and associated elements are slagged off or are transferred as particles or vapors into the waste gases. The process is operated as a batch (discontinuous) process.

Solid substances used in the electric arc furnace (scrap, ferrous alloys, iron slurry) are melted predominantly by electrical energy which is inputted via the electrodes, as well as by fossil energies in the presence of oxygen. Electric arc furnaces have currently a capacity of up 200 tonnes; the duration of heat is in the region of 1 to 4 hours.

Cast iron substances in foundries are produced in cupola furnaces, induction crucible furnaces, revolving tubular kilns or electric arc furnaces. The cupola furnace is a shaft furnace and is the melting aggregate which is used the most in iron, malleable iron and steel foundries. The top of the furnace is loaded with steel, foundry scrap and pig iron as well as cokes and other additional materials. The molten cast iron is staked out from the bottom. Principally two types of cupola furnaces are to be differentiated: the cold-air cupola furnace with a melting-down power of approximately 8 tonnes per hour and with upper furnace-opening extraction as well as the hot-air cupola furnace with a melting-down power of more than 8 tonnes per hour and a lower furnace-opening extraction. The hot-air cupola furnace is operated with pre-heated air (500 to 600 °C). The volume current of waste gases from cold-air cupola furnaces is about 3000 m^3/t molten iron; for hot-air cupola furnaces it is around between 1200 to 1500 m^3/t. The crude gas particle contents amount to 10 to g/m^3.

The waste gas is purified using fabric filters, electrostatic precipitators or scrubbers; in hot-air cupola furnaces, the gases at the furnace opening are burned in the recuperator which is independently heated, and used for the generation of hot-air.

Substances Utilized

It is differentiated between own scrap and external scrap depending on the abundance. Normally, the domestic abundance can be divided as follows (simplified):

Unalloyed scrap

Used scrap
  used steel scrap
  shredder scrap
  old packets
  cast iron scrap

Unused scrap
  unused steel scrap
  new packets
  steel shavings
  casting shavings

Alloyed scrap
Circulation material from the production of cast iron.

There are also the following materials which are used:

- limestone
- coke or coal
- supplementary materials
- alloying elements.

Principally, the requirements which are placed on scrap depend on the qualities to be produced as well as on the emissions expected, not only with respect to the protection of ground and water, but also to maintaining the quality of the air. These requirements are assured on a cases by case basis by an extensive Quality Management in the scrap and recycling industry. Requirements are for example, adhering oils, greases and miscellaneous foreign substances.

Scrap, which does not fulfill the requirements is not used. This is particularly true in the steel industry.

Scrap processing techniques are covered in section 8.1.5.6.

Emission Levels

The dioxin emission levels from iron and steel smelting plants are compiled in table 18.

Table 18: Dioxin Emissions Levels from Iron and Steel Smelting Plants

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	Crude Gas	PCDD/F Content Clean Gas	Filter Deposits	Waste Gas Volume Flow	Waste Gas Treatment
					ng TE/m³	ng TE/m³	ng TE/Kg	N m³/h	Remarks
oxygen blast converter	scrap excluding plastic	180 t/lot	20.7	1		0.089		630000	E-filter secondary particle deposit
	scrap including plastic 1st lot 3 t; 7 subsequent lots without			2		0.076 0.017		646000 671000	- " - - " -
	scrap including plastic 1st lot 5 t 7 subsequent lots without			1		0.018		649000	
blast steelworks with 3LD converter	fine scrap ores, fluxing agent, lime	a) 180 t /lot			0.124 0.192 0.085	0.0090 0.0291 0.0128	1020	615900	E-filter secondary particle deposit
converter blast steelworks	pig iron	b) 1092 t/4 lots	20.9	3		0.032 0.033 0.004		570000	fabric filters
oxygen-blast steelworks with 3LD converter	a) new scrap b) mixed scrap c) foreign scrap	a) 140 t/lot		1 each	a) 0.077 b) 0.119 c) 0.050	0.026 0.045 0.040	6	165000	E-filter secondary particle deposit
oxygen-blast steelworks with 3LD converter	steel scrap (circulation scrap, new scrap, used scrap)	a) 150 t/ lot		3	0.917 1.7 2.66	0.024 0.042 0.063	5300	912068	fabric filters secondary particle deposit increasing proportion of non-metal contaminations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m^3	 Clean Gas ng TE/m^3	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m^3/h	Waste Gas Treatment Remarks
electric arc furnace	hoop-steel new scrap with waste-furnace scrap	a) 50 t/lot	20.9		3.6		7100	220000	fabric filters plant closed down
	with shredder scrap				0.099		3600		
	with shearing scrap				0.19		4500		
electric arc furnace	60 % clean scrap 40 % dirty scrap	a) 85 t/lot							fabric filter 4th cover opening
	without scrap pre-heat		18.9; 18.9	2		0.7; 2.3		68000; 68000	
	with scrap pre-heat		19.0; 19.2	2		5.6; 9.2		68000; 68000	
electric arc furnace	shavings, sheeting, castings, packets, demolition scrap	a) 2x65 t/lot	21	3		0.013$^{b)}$	1600	P = 76000	4th cover opening + shed with fabric filters P = primary waste gases S = secondary waste gases a) construction steel b) quality steel c) optimization (improvement of extraction and particle deposit of waste gases, installation afterburning, accelerated cooling)
				3		2.9$^{a)}$	160	P = 45000	
						0.2$^{c)}$		P = 85000	
				3		0.013		S = 650000	
electric arc furnace	scrap, used metals	a) 185 t/h	20.5			0.93		940000	fabric filters
	without pre-heat					0.5			
	with pre-heat					1.04			
electric arc furnace	shredder scrap	a) 185 t/h	20.6	3		0.267; 0.159		1040000	primary waste gas afterburning, quenching and with secondary waste gases to fabric filters
	steel scrap					0.236			
	chips, sheeting			2		0.13; 0.104		1100000	

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas			Waste Gas Volume Flow	Waste Gas Treatment
					ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
electric arc furnace	a) standard	a) 140 t/lot		1 each	P: 0.89	0.24	276	P: 120000	fabric filters
	purchased and own scrap, partly PE/PVC-coated and others	100 t/h			S: 0.49	0.0225		S: 380000	fabric filters P = primary waste gases S = secondary waste gases
	b) setup, clean conversion scrap, scrap containing cobalt	b) 150-160 t/ lot			P: 0.77 S: 0.015	0.2 0.01			P = primary waste gases S = secondary waste gases
	c) purchase and own scrap, partly PE/PVC, grease-chips, empty oil drums (worst case for measurement purposes only)				P: 3.91 S: 0.224	0.809 0.056			
	d) alloyed, non-allayed scrap				P: 0.66 S: 0.01	0.246 0.026			
electric arc furnace (for steel casting)	steel scrap circulation material, pig iron, alloyed materials	a) 6.1 t/h				0.0028 0.0035 0.0045	175	54143	fabric filters
electric arc furnace	sponge iron, new scrap, steel chips, used scrap, demolition scrap and others	a) 100 t/h			0.127 2.156	0.013 0.016		1.160.000	primary waste gas afterburning, quenching, with secondary waste gas to fabric filters
electric arc furnace	company scrap, purchase scrap/ shredder, light purchased scrap	100 t/h			0.02 0.02 0.41	0.01 0.01 0.04	74	520000	fabric filters
hot-air cupola furnace	steel scrap, casting scrap, coke, lime, additions	b) 38 t/h	11 4; 12.7		0.26	0.048	176	59400	fabric filters recuperator

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
hot-air cupola furnace	crap, circulation material, coke, lime, additions	a) 38,5 t/h	1.2-2.8	3		0.001-0.006		40000	fabric filters recuperator
hot-air cupola furnace	steel scrap, circulation material, coke, limestone	a) 60 t/h		2	0.07 0.01	0.005 0.001	1380	59.000	desintegrater recuperator
rotary drum furnace	circulation material, casting breakage, steel	a) 6 t/lot b) 5.4 t/lot	15.4-16.1			0.135		1200 (Oxygen burner)	fabric filters
rotary drum furnace	FeSi (containing Mg), machinery casting breakage, steel scrap, pig iron, and others, slight organic contaminants in brass	b) 2 t/h	19.6		0.901 0.036 0.466	0.627 0.574 a) 0.135	470 500	18200 19600 21800	cyclones, fabric filters a) short furnace switch-off due to overheating of filter
cold-air cupola furnace	pig iron, steel, casting breakage, circulation material, coke, limestone	a) 6-7 t/h b) 5.5 t/h		3		0.531 0.309 0.696	4850	17400	cyclone, fabric filters
cold-air cupola furnace	machinery breakage, pig iron, steel circulation material, coke, limestone	a) 4-5 t/h		3		0.0793 0.077 0.058	958	14341	dust pre-filter fabric filters
induction crucible furnace	contaminated steel scrap, pig iron, circulation material, additions	a) 19.5 t/h		2	0.032 0.077	0.003 0.003		240,000	fabric filters

The emission concentrations from hot-air cupola furnaces and converter steelworks lie significantly lower the 0.1 TE/m³. By comparison, electric arc furnaces, cold-air furnaces and rotary tube furnaces emit higher emissions of dioxins and furans in some cases. They amounted to as much as 9.2 ng TE/m³ for an electric arc furnace no longer operated today in Germany, which used preheated scrap. Dioxin concentrations from electric arc furnaces for secondary productions of steel lie within a range of 0.01 to 0.3 ng TE/m³ according to results from dioxin measurement programs from the Federal Ministry for the Environment. It should hereby be taken into consideration that the concentrations are lowered through mixing the primary waste gas with the outgoing air from the plant buildings. For the majority of the electric arc furnaces being operated in Germany, the joint removal of dust from primary and secondary waste gases is customary. For installations in which the treatments of the gas flows are conducted separately, the primary and secondary waste gases are designated with P and S respectively in table 18.

Levels higher of up to 0.8 ng TE/m³ have also resulted when substances used are melted down which have high contents of organic and chlorine contaminants. The tendency of the dioxin formation to depend on the degree of contamination in the substances utilized is supported by the levels found in the waste gases (up to 4 ng TE/m³). This underlines the significance of measures which are based on the substances utilized.

For measures related to the technical processes employed, the question is for example, to improve the removal of the waste gases in order to suppress the so-called De-novo synthesis as much as possible. One important measure is to lower the specifically high amounts of waste gases. Further measures could include the separate acquisitions of the waste gases of the 4th cover opening for the thermal afterburning with energy recycling (as well as the addition of oxygen) with subsequent particle-removal using fabric filters.

Furthermore, the emissions when loading and discharging, could be registered separately and also be treated separately.

In an electric arc furnace which utilized scrap steel, the reductions in the dioxin emissions by the addition of brown coal coke dust as the adsorption agent in the waste gas flows with subsequent separation using fabric filters (entrained flow filter layer techniques) were investigated. The arc furnace was operated for the investigations not only without, but also with, preheating of the scrap. In all cases, the degree of deposits for dioxins and furans exceeded 97 % which resulted in clean gas concentrations of 0.05 ng TE/m³ and lower. With regard to fire and explosion protection, particular precautions have to be taken. Further practical trials are necessary prior to a generalization. The charged adsorbents were treated externally.

In the iron and steel industry (not only for operators but also for the plant construction companies), further intensive investigations are being conducted to evaluate the effectiveness and the expenditure of the different techniques which are possible for emission reductions.

Other measures for a reduction in emissions include new recycling techniques for steel (e.g. melting of scrap steel in shaft furnaces and subsequent refining in converters), whereby these considerations have to be further investigated with respect to their practical realization.

Drying of Steel Chips

To date, results from an investigation for the drying of steel shavings are available, by which the oils in emulsions adhering to steel chips are removed in a calcining drum at approximately 250 °C. The calcining drum is heated using heating oil, the smoke and sulfur gases are extracted at the drum entrance and carried to post-burning. There were no dioxins or furans detected in the clean gas.

8.1.5.4 Installations for the Smelting and Refining of Non-Ferrous Metals (no. 3.4 of the 4th BImSchV)

8.1.5.4.1 Aluminum

General Process Description and Materials used

A) *Secondary Aluminum Production in Rotary Furnaces*

For the secondary production of aluminum, plants are operated for the preparation, smelting and refining of materials containing aluminum such as scrap, chips, and dross. Preparation plants are milling and grading plants for dross, drying installations for chips coated with oils, lubricants and separation agents, paint-stripping plants for scrap and in particular for shredder scrap. Rotary drum or hearth furnaces are used to melt down the aluminum scrap and the materials containing aluminum. Typical melting temperatures are around 700 to 750 °C. The waste gases have temperatures of typically 1000 °C for a normal operation. The burner is off when the materials are loaded; at the temperatures which then govern, an assured destruction of halogenated organic components is not given. The aluminum which is melted down in the smelting plants is usually treated further in converters to refine and alloy it, or to heat-treat it. Smelting furnaces have melting capacities of between 0.5 and 0.7 tonnes per hour. In rotary drum furnaces, the re-melt process is carried out under a layer of salt. The greater part of the contaminants introduced is collected by the salt such that it forms salt slack. Slat slack is further processed to molten salt, aluminum and impure aluminum oxide.

In order to keep the amounts of salt slack as low as possible, recycling materials are processed by mechanical means as much as possible so that the amount of salt required is kept to a minimum.

Alloying metals such as copper, magnesium, manganese, zinc are added in the converter, refined with chlorine gas and nitrogen and kept hot. The aluminum alloys are subsequently cast into bars or directly processed in molten form in the foundry.

B) Secondary Production of Aluminum in Open-Hearth Smelting Furnaces

In modern multi-chamber open-hearth smelting furnaces, clean grade materials used such as wrought alloys are melted down without salt. These furnaces have a preheating of the scrap of up to 400 °C and a post-burning of the waste gases. They are particularly economical from an energetics point of view; they are however only for the use of wrought alloys.

c) Miscellaneous Aluminum Smelting Installations

For using molten aluminum from aluminum electrolysis in aluminum works and for melting material returns and blank scrap, open-hearth furnaces are used for keeping the materials hot, refining and casting into rolling ingots and bars.

Purification of Waste Gases

The waste gases from smelting furnaces can contain gaseous inorganic chlorine and fluorine compounds in particular, in addition, the waste gases from converters contain chlorine gas. Furthermore and depending on the materials used, chlorinated organic materials can be included by the adherence of paints, lacquers, oils and greases which can lead to dioxins and furans by their incomplete combustion.

The waste gases from smelting furnaces and converters are usually removed together; the amounts of waste gases are usually in the region of between 15,000 and 20,000 m^3/tonne of aluminum.. Depending on the materials which are utilized, the crude gases can contain up to 150 mg/m^3 of particles, 100 mg/m^3 of gaseous fluorine compounds, 250 mg/m^3 chlorine compounds (up to 10 g/m^3 in the converter waste gases), and 5 mg/m^3 of chlorine gas. The waste gases from dross processing and from the processing of chips are usually removed separately. They contain mainly particles and organic substances.

The most widespread method for the purification of waste gases from melting furnaces and converters is the dry sorption technique for the deposition of HCl and HF using fabric filters. Hydrated lime as the sorbent is administered to the waste gas flow. Pilot and demonstration plants by which hydrated lime - admixed with activated cokes or open-hearth cokes - is added to the waste gases, have begun operations.

The emissions of organic substances (no. 3.1.7 TA Air) are low when the materials utilized in the melting furnaces contain only low amounts of organic materials, as for example in paints, lacquers, greases and oils. The waste gases from installation for the drying of chips are usually purified by a thermal post-burning and fabric-filtering. Waste gases containing particles from dross processing plants are also passed through fabric filters.

Table 19: Dioxin Emissions from Aluminum Smelting Installations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas	Clean Gas	Filter Deposits		
					ng TE/m³	ng TE/m³	ng TE/Kg	N m³/h	Remarks
drum furnace	Al scrap and return material	a) 7.5 t/h b) 7 1 t/h	20.3	2		0.86; 1.22		125200	hydrated lime fabric filters
drum furnace with converter (single measurements for orientation)	Al alloys Cl_2-N_2 gas treatment		19	1		7.02		95100	hydrated lime fabric filters
drum furnace with converter	shredder-casting-Al shavings, sheet packets Cl_2gas treatment	b) 1.25 t/h	18.7	3		0.19-0.27		41300	hydrated lime fabric filters
drum furnace (2 sets of measurement)	Al scrap	a) 3.8 t/h	I) 16.8-18-7	3		3.6-10.7		42700-48400	Venturi scrubbers with lime milk injection
			II) 18.0-18.6	3		0.76-2.1		48500-53800	
drum furnace with converter	slags, sand casting, die-casting, wire wastes and others	no values	17.7-18.3	3		0.58-0.61		15000	hydrated lime fabric filters
drum furnace with converter	Al scrap Cl_2 gas treatment	a) 2x2.5 t/h	19.0	3		0.65-1.99		40300	hydrated lime fabric filters
drum furnace with converter	Al scrap (chips, shredder, slag, castings) Cl_2 gas treatment	no values	20.4	3		0.07; 0.57; 3.72		35500	hydrated lime fabric filters

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
drum furnace with converter	Al scrap Cl_2 gas treatment	no values	19.6-20.0	3		4.86; 7.74		38500-39300	hydrated lime fabric filters
drum furnace with converter	Al chips (with oil) dross, castings, salt		20.6-21					50000	hydrated lime fabric filters
normal operation not with loader	15 % chips 40 % slag 45 % casting			1 2		0.79 0.38; 0.37			
not with draw-off						0.85			
operation max. emissions, loading	40 % chips 30 % slag 30 % castings			2		0.35; 0.31			
draw-off				1		0.37			
drum furnace with converter	Al scrap Cl_2 gas treatment	no values	18.8	3		3.76; 5.17 13.74		41400	hydrated lime fabric filters
drum furnace	Al chips Cl_2 gas treatment	a) 6 t/h	18.7	3	furnace waste gas	7.4; 9.5 9.5		75700	hydrated lime fabric filters
drum furnace, converter, warmer-oven	Al chips	no values	20	3	hood waste gas	0.07; 0.11 0.16		47050	hydrated lime fabric filters
2 drum furnaces + installation for drying chips	scrap containing Al Al chips	6 t/h + 2.5 t/h	18.6	2		3.3; 1.6		17400	hydrated lime and 8 % activated charcoal fabric filters
2 drum furnaces	Al scrap slag	no values	19.5	3		3.34; 3.88 5.80	6700; 4600 16600	128200	hydrated lime fabric filters

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
hearth trough kiln	Al scrap with adhesions, no salt	a) 3 t/h	11	1	4.6			6870	afterburning
hearth trough kiln prior to optimization	Al scrap together with AL melt	a) 14.3 t/h	17.2; 19	2	0.18; 1.05	0.13; 0.68		70000	hydrated lime fabric filters
hearth trough kiln (after optimization: improved feeding availability of materials, sorting of contaminants),				3	0.019 0.015 0.066	0.016 0.007			
two-compartment heath kiln	Al scrap	a) 2.8 t/h	18.8-20.6	2		0.19: 0.19		41000	hydrated lime fabric filters
smelting and casting furnace	Al scrap	b) 2 t/h	12-15	2		0.06-0.09		5000	no treatment of waste gases
induction furnace	Al scrap, Cl_2-Ar gas treatment	a) 20 t/h	20.6	1		0.008		34300	hydrated lime fabric filters
induction furnace	Al scrap (blocks, chips)	a) 0.8 t/h	no values	2		0.18; 0.29		20500	cyclone, fabric filters
6 drum, 1 induction, 1 melting down furnace, 6 converters	Al scrap shredded chips molten lacquers Cl_2 gas treatment	a) all furnaces 126t all converters 135 t	19.3	1		2.9		103300	hydrated lime fabric filters

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
Al smelting plant	Al chips, smelting AL Cl_{org} <200 mg/Kg Cl_{inorg} 35 mg/Kg	no values	19.7	3		0.02; 0.05 0.23		84500	hydrated lime fabric filters
different furnaces	Al returned material	a) 3 t/h	20.1	1		0.029		27500	fabric filters
2 drum furnaces 4 converters	Al scrap (chips, slag, outdated model, beer drums and others)								hydrated lime fabric filters
a) burner Gas/air mixture		b) 2.2 t/h	19	4	42.2	9.1	11100	40350	
b) oxygen burner rotary drum furnace		b) 2.7 t/h	19.4	4	82.1	11.6	18300	34000	
rotary drum furnace	Al scrap (chips, slag, sheet and others)					after step 1, step 2		7200 (in crude gas)	two-step, addition of sorption agent, cooler, fabric filter 1, addition of sorption agent 2, fabric filter 2
a) burner with gas/air		1 t/h	16.6		16.9	1) 1.37 0.49 2) 2.69 0.07			1) lime only in steps 1 and 2 2) lime only in step 1, lime - brown coal coke mixture in step 2
b) burner gas/air + oxygen injection		1.18 t/h	16.8		8.6				
c) oxygen burner + oxygen injection		1.5 t/h	20		36				

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m^3	PCDD/F Content Clean Gas ng TE/m^3	PCDD/F Content Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m^3/h	Waste Gas Treatment Remarks
2 rotary drum furnaces, converter (oxygen burner)	Al scrap (chips, slag, sheeting, castings, salt)	a) 1.15 t/h	19.9	20	18.47	0.014		15319	two-step, fabric filters, sorption agent: lime-coke-mixture
converter	Al scrap	15 t/h				1.15		94000	fabric filters
melting-casting furnace	Al scrap	27 t/h				1.25		33000	fabric filters
rotary drum furnace + converter	Al pellets Cu cooler sheet packets	a) 1.25 t/h	19.5	2		0.28; 0.8		36330	fabric filters

Emission Levels

Table 19 includes the emission levels for PCDD/F as a dependency on the type of furnace, the materials utilized and the waste gas purification techniques employed.

There are many measurements of dioxin and furan emissions from aluminum smelting plants which are documented within the scope of this report. The measurements available can only however describe a bandwidth. Waste gases from differing processes are often combined; further statements are to be concluded from a more exact analysis and knowledge of the secondary conditions of each respective case.

The emission levels for smelting plants in the secondary aluminum industry lie in the region of approx. 0.01 to approx. 14 ng TE/m^3. There are dependencies on the smelting aggregates, materials utilized and on the waste gas purification techniques employed.

In pilot and demonstration projects such as those within the scope of programs from the Federal Ministry for the Environment, the effectiveness of a number of measures to reduce dioxins has been investigated.

The results show that conventional purification techniques (usually the injection of lime hydrate and downstream fabric-filtering) for example in drum or open-hearth smelting furnaces are not adequate, as a rule, to meet the level of 0.1 ng TE/m^3.

By the use of oxygen burners in place of the customary natural gas - air burners in rotary drum furnaces, not only could a lowering of dioxins be expected, but also a reduction of the waste gas volume flows from the higher flame temperatures and a higher turbulence in the combustion compartment. This however was not confirmed in practice and there was even the tendency towards a worsening in the PCDD/F emissions. Further studies on the results of this are necessary and in particular, construction and technical process measures concerning the rotary tubular furnaces should follow for adaptation to the changed burner techniques, e.g. a better method of sealing the furnace.

An oxygen injection, used in conjunction with customary natural gas burners, which was introduced into the waste gases in the opposite direction to the waste gas flow, resulted in a reduction in the contents of organic hydrocarbon compounds in the waste gases and to a lowering of the emissions of polychlorinated dioxins and furans.

As secondary measures in the waste gases, improvements in the particle deposits were investigated, for example by filtering through surface coated filter media and changes in the sorption agents (amounts, proportions of activated cokes of brown coal cokes) as well as a multi-stage method of deposition.

In summarizing it could be found that with a single and multi-stage fabric-filtering installation and with the addition of lime hydrate with 10 % and higher proportions of active cokes/brown coal cokes, a degree of deposition for PCDD/F from more than 99 % and emission concentrations of 0.1 ng TE/m³ could be realized.

The following, other or continuation of the following measures can also be considered:

- Minimization and separate removal and purification of differently contaminated waste gas flows (for example converter gas/hooder gas),

- extensive avoidance of particle deposits in the waste gas channels and thereby the rapid passage at the same time through the critical temperature zones,

- improved pre-treatment of scrap aluminum shredders by using swim-sink separation techniques and grading through whirling stream depositors.

In accordance with the resolutions from the Minister Conferences of the Oslo and Paris Commissions from 21./22. September 1992, hexachlorethane shall, gradually and accordingly to a stepped plan, no longer be used in the aluminum industry sector:
- by 31.12.1992 for the hitherto major applications in the secondary aluminum industry,
- by 31.12.1994 for all applications in the secondary aluminum industry and including integrated foundries in the primary and secondary aluminum industries.

As a supplement, it should be pointed out that a EU proposal from the Commission to amend the guideline 76/769/EWG on the subject "Restrictions of bringing into circulation, and the application of certain hazardous materials and preparation" is currently under consultation. It is foreseen in this proposal (doc. III/3197/92-Rev. 1 Add. 2) amongst others, to prohibit the use of hexachloroethane in the aluminum industry; exempted from this however, shall be foundries with a maximum melting crucible volume [of 500 to 600 Kg] for a limited time period [until the end of 1988].

The treatment of the molt is to carried out according to the state of technology, for example with a nitrogen - chlorine mixture in the ratio of between 9:1 to 8:2, gas injection equipment for fine dispersion and nitrogen pre- and post-flushing and vacuum-degassing. For mixtures of nitrogen and chlorine, dioxin emissions concentration of around 0.03 ng TE/m³ were measured (as compared to values of > 1 ng TE/m³ for treatments with chlorine only) in a pilot plant.

The dioxin/furan contents of filter dusts are in the region of between 1000 and 10000 ngTE/m³, and in some cases even higher.

8.1.5.4.2 Copper

General Process Description and Materials Utilized

In smelting installations for copper and copper alloys, copper from the fused mass electrolysis (MANTAS, pig) and suitable scrap is also used as well as refinery copper which is extraction by the aqueous electrolysis of anode copper(so-called Cu cathodes). Alloy melting uses preliminary alloys of the respective alloying elements or even the metals themselves and usable scrap metals. The melting down is carried in shaft furnaces, drum furnaces or induction furnaces using oil, natural gas or electricity. The use of strongly contaminated scrap is not permitted because of the only limited possibilities of purifying the molt. The molt is purified by poling with fresh wood for the purpose of removing the oxygen, as well as by overheating the molt for the prevention of undesirable, easily vaporizable metals and metal oxides.

Emission Levels

In table 20, the emission levels of PCDD/F are compiled as a dependency on the type of furnace, materials utilized, operating conditions and techniques of waste gas treatment. The bandwidth of the reported dioxin concentrations in clean gases between 0.003 and 1.77 ng TE/m³.

One possibility of reducing the dioxin emission from shaft furnaces with hot entrances is the post-burning of the waste gases through the addition of oxygen.

A further possibility exists in the application of the fine stream technique (injection of lime/coal mixtures) into the waste gas flow with subsequent particle deposits in fabric filters. A corresponding approval procedure is shortly before its adoption. In as far as emissions limits < 0.1 ng TE/m³ can hereby be achieved can only be determined after completion of a large scale trial. The filter dusts loaded with dioxin/furan which occur, could be used in other installations from the same operating company.

Table-20: Dioxin emissions from Copper Smelting Plants

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
cathode shaft furnace	copper cathodes electrolytic copper with additional copper chips containing machining emulsions	a) 9 t/h	19.9	1		0.32		19300-23100	no treatment
			19.3	1		0.35			
anode shaft furnace	blister copper anode copper	no values	17.8 20.3		full load kept warm	1.77 0.032	13000 11500	115000 40800	fabric filters
	scrap, silver, natural gas								
wide bar furnace	cathodes, scrap, operating conditions	a) approx. 140 t/a					cooler particles		
		A) add, melt down	16.3; 16.0	2		0.06 0.05	350 filter deposits 90	43000	cooler, fabric filters
		B) refining	16.2; 16.3	2		0.097 0.061		40000	
		C) pole	18.1; 18.8	2		0.058 0.077		42500	
		D) cast	18.3; 18.2	2		0.053 0.041		28500	

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
rotary drum short furnace (Thomas Furnace)	used cathodes, copper returns, pole wood, charcoal	no values	20	1		0.023	1300	18700	cyclone, fabric filers
rotary drum furnace	red soot, brass, bronze	a) 10 t/lot	20.1, 20.2	2		0.05; 0.066		14700; 15200	afterburning, cooler, fabric filters
smelting furnace 2 Essen (experimental)	high tension lines (copper)	no values							
	without charcoal			2	5.8; 9.0			14700	
	with charcoal		20.5 -	2	6.8; 7.2			16400	
	untreated chips		20.8	2	14.3; 46.9			65000	
	dried chips			2	1.0; 1.2			45000	
	waste sheet (from customer)			2	0.7; 2.2			33000	
	own returns			2	0.2; 0.1				
						1.2; 0.5		158000; 164000	fabric filters
melting and casting furnace	copper alloys	a) 19.5 t/h b) 18.0 t/h	20.4	3		0.013 0.026 0.027		50000	cyclone, fabric filters
melting and casting furnace	copper/brass alloys	-	20.8	3		1.01 1.22 1.05		158000	cyclone, fabric filters
melting and casting furnace	copper/brass alloys	-	20.5	3		0.53 0.55 0.53		164000	cyclone, fabric filters

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
melting plant, foundry	brass (chips with adhering oil)	a) 780 t/h	20.8	2		0.005 0.003		200000	fabric filters
die cast foundry	brass, circulation brass with adhering oil, $BaCl_2$ as separating agent		no values	1		0.19		32560	no values
die cast foundry	brass alloys					0.019		49600	fabric filters
melting plant	red soot, brass, bronze		20.0			0.164 0.259		15000	fabric filters

8.1.5.4.3 Miscellaneous Installations for the Melting and Casting of Non-Ferrous Metals

The respective values measured are given in table 21; they lie within a range from 0.004 to 0.36 ng TE/m^3, i.e. values exceeding 0.1 ng TE/m^3 were found for certain plants for the smelting and casting of non-ferrous metals.

Table 21 Dioxin Emissions from Installations to Refine, Melt and Cast Non-Ferrous Metals

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits ng TE/Kg	N m^3/h	Remarks
hearth kiln (mixed tin plant)	mixed oxides from furnaces and converters, Cu-dross, soda, coke (2 operating condition)	a) 11 to 18 t/lot	18.6, 18.8 19.0; 19.4	2 2		0.011 0.06 0.03 0.01	plate cooler deposits 19 filter compartment 29	approx. 33000	cooler with fabric filters
	tin-lead mixed oxides								
induction crucible furnace	non-ferrous metals (Co, Ni, Cr)	a) 4.5 t/lot b) 4.42-4.47 t/lot	approx. 21	1		0.193		11200	cyclone
induction melting furnace	brass			2	0.6 1.36	0.33 0.36			fabric filters
smelting plant			20.7	2		0.013 0.0045		16753	fabric filters
smelting plant 1	silver	0.5 t							
smelting plant 2	precious metal returns	0.2 t							
hoist-crucible furnace	silver alloys	0.15 t							
zinc smelting plant	crude and used zinc	19 t/h		3		0.097		53400	fabric filters
zinc smelting plant	scrap zinc, zinc waste	6 t/h		3 3		0.0417 0.121		22300	fabric filters
magnesium smelting plant	scrap magnesium	0.5 t/h		3		0.203		5923	fabric filters

8.1.5.5 Installations for Hot-Dip Galvanizing (no. 3.9 of the 4th BImSchV)

General Process Description

For the prevention against rust, iron is coated with protective metallic layers, in the case of hot-dip galvanization with zinc layers. During this, the iron and steel parts to be galvanized are passed through pickling, rinsing baths and degreasing as well as for any subsequent surface treatments, through flux baths. The parts are then dipped into molten zinc (temperature approximately 450 °C) whereby metal zinc is deposited onto the surface of the parts. As the treatment baths on the one hand consist to a certain extent of acids and salts which contain chlorides (hydrochloric acid, ammonium chloride, zinc chloride), and the galvanization quality on the other side depends strongly on the grease and oil contents, the temperatures which occur in the molten bath suffice for a possible formation of dioxins and furans.
The gases from zinc baths which are extensively encapsulated to state of the art technology, are extracted and usually purified using fabric filters.

Materials Utilized:

- iron and steel parts, contaminated with oils and greases,
- pickling baths: predominantly hydrochloric acid,
- flux baths: alkaline/acidic degreasing agents in aqueous solutions.

Table 22 shows the emission levels for PCDD/F in relation to the operating conditions during hot-dip galvanization.

Table 22: Dioxin Emissions from Hot-Dip Galvanizing

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements		PCDD/F Content		Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
molten dip method	iron-steel parts HCl, $ZnCl_2$, NH_4Cl, Zn	b) 4- 5 dips/hour, > 1 t/h full load of extraction unit	approx. 21	1		0.008	2850	7720	fabric filters
- " -	- " -	b) 4- 5 dips/hour, full load of extraction unit	approx. 21	1		0.01	3810	13520	fabric filters
- " -	- " -	b) 4- 6 dips/hour, full load of extraction unit	approx. 21	1		0.007	2150	21590	fabric filters
- " -	- " -	b) 4- 6 dips/hour, full load of extraction unit	approx. 21	1		0.132	9614	24560	fabric filters

The dioxin emission concentrations from the installations investigated were lower than 0.13 ng TE/m³ in the majority of cases. For the measurement of the slightly higher value of 0.13 ng TE/m³ in the protocol, a defect in the fabric filter is suspected. The higher dioxin filter dust contents do however indicate a greater potential for formation by comparison with other installations investigated.

Dioxin and furan emissions apparently occur almost exclusively particle-bound. For installations which are operated using housed-in zinc baths and upstream degreasing stages, the waste gas purification using fabric filters generally appears to suffice as a measure to reduce emissions.

8.1.5.6 Installations for the Shredding of Scrap (no. 3.14 of the 4th BImSchV)

General Process Description

The processing of car wrecks and accumulated scrap in the Federal Republic of Germany (Stand September 1991) comprised of 45 installations in operations. These are divided into 27 shredders, 10 crushers 'zerdirator', 2 grinders 'kondirator' and 6 mills. The total processing capacity of these installations reaches 1.5 million tonnes per year on a single shift basis. The main task of these processes is the reduction in size of these materials into loadable dimensions as well as a separation of the materials. A dioxin emission potential exists on account of the materials utilized (plastics, oils, heavy metals) and the temperatures involved which principally suffice for the respective formation conditions.

Shredder Installations

Shredder installations are constructed according to the hammer mill principle in which rotating hammers break up wreck parts into smaller pieces over a anvil-type edge. As well as cars (50-80 %), light accumulated and mixed scrap (e.g. cookers, refrigerators) are also processed. Large scale shredder installations, which as well as shredding installations, also have separating fixtures and can process car wrecks without any pretreatment, i.e. with the engine, axles, gearbox, upholstery and tires.

A significant proportion of the vaporizable materials are already extracted by particle collection fixtures during the shredding process. The shredded scrap waste still present is conveyed to separation drums or wind sifters for further separation, after which an electromagnetic drum separates the steel scrap from the non-ferrous metals and other course contaminants (wood, rubber, plastics etc.). Finally the resulting non-ferrous metals are graded according to type on a sorting belt. Optimized swim-sink separation techniques and (following further shredding) swirling current separation techniques have been developed for aluminum shredder scrap in particular, which result in relatively well-sorted metal fractions.

Waste gases from shredder installations are generally extracted from virtually encapsulated shredding equipment and carried to waste gas purification fixtures consisting of high performance cyclone depositors and swirling current wet particle removers.

In refrigerated shredders, the scrap is cooled by liquid nitrogen (-196 °C) prior to shredding; these shredders are not currently used on a large scale.

Scrap Mills

These mills consist of milling houses with vertical walls in which a mower with a vertical axle is pivoted on both sides. Small sized scrap is put through further shredding; the material separation is as in shredding installations.

Emission levels

Individual measurement levels from shredding installations, which are given in table 23, lie in the region of 0.1 to 0.4 ng TE/m^3. Process-related primary measures are only applicable to a limited extent on account of their installation-specific operation. Emission reductions can be realized today in particular by means of waste gas purification equipment. Principally, the use of optimized Venturi scrubbers (possibly with the addition of active coke) can be considered. Measures related to the materials utilized will be increasingly put into application. In accordance with the requirements of the TA for Shredder Residues (proposal), a pretreatment (drying and disassembly) shall be carried out; accumulated scrap and car wrecks shall be shredded separately. In future and from the virtually complete disassembly of old cars, a recycling of resource materials could lead to a appreciable bypassing of the shredding installations and in particular of the problem materials containing chlorine.

Table 23: Dioxin Emissions from Scrap Processing Installations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas	 Clean Gas	 Filter Deposits	Waste Gas Volume Flow	Waste Gas Treatment
					ng TE/m³	ng TE/m³	ng TE/Kg	N m³/h	Remarks
hammer mill	scrap cars (90-95%) white scrap (5%)	20 t/h	no values	3		0.11; 0.112; 0.2		26800	cyclone deposit Venturi scrubber
rotor mill	mixed scrap (old cars, receptacles, sheeting)	56-65 t/h	20.4	4		0.19; 0.24 0.4; 0.43		93100	cyclone deposit, swirling flow wet deposit
shredder	old cars and mixed scrap	no values		3		0.032		87000	cyclone
shredder	own scrap containing non-ferrous metal	18 t/d		2		0.249; 0.039		27400	spray scrubber cyclone

8.1.6 Installations for the Manufacture of Chemical Products (no. 4.1 of BImSchV)

The results from dioxin emissions from installations for the manufacture of chemical products are also given. Not covered however is the possible input of dioxins into the environment via the products which are manufactured; general information on this is given section 4. The dioxin contents from residues and side-products are not covered either, provided they are substances which are treated or further processed in internal circulation systems.

The PCDD/F emission values given in table 24 were measured in the waste gases from installations in which conversion processes with substances containing chlorine take place, possibly involving a subsequent thermal post-burning of the gases (post-burning)). In some cases (each of which designated as "plant with post-burning" in column 1), no further information on the chemical plant is documented.

The dioxin concentrations given in the clean gas are usually lower than 0.1 ng TE/m^3 although some values are higher. An exact check is necessary in such cases. As concentrations for not only for the crude gas but also for the clean gas are given for the installations 2 and 3 in table 24, the effect of the alkaline scrubbers used for treating the waste gases can be evaluated. As the clean gases in both cases are higher than those of the crude gases, there would appear to be trans-chlorination reactions preferentially with the higher chlorinated dioxins taking place in the scrubber, which are selectively enriched in the scrubber washings. This confirmed by a consideration of the total values for dioxins and furans respectively. The higher assessment of lower chlorinated dioxin in the TE concept leads then to these (slight) concentration increases

Table 24: Dioxin Emissions from Chemical Installations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
afterburning in EDC plant	waste gases from production of 1,2 dichloroethane		11	1		0.05 (2, 3, 7, 8-TCDD)		1300	no values
chlorinated-paraffine reactor	paraffin + Cl_2	no values	no values	1	1.09	1.7		145	scrubbing during "air-purging", otherwise combustion plant
chlorinated-paraffine (CP) reactor	n-paraffin + Cl_2	600 t CP/month	20.6		0.036 selective deposit higher chlorinated D.	0.051	washing soda before injection 2.7 ng/l after injection 4,1 ng/l, CP 0.1 ng/g		
chlorine-silane plant	FeSi + Cl_2	no values	21.0	2		0.015 0.09		no values	scrubber (NaOH, water)
burner for manufacture of high dispersion silicic acid	$SiCl_4$, H_2O, air	no values	no values	2		0.003; 0.009		no values	spray washer columns
afterburning behind the chemical plant	waste gases containing HCl (approx. 90 % HCl by volume)	b) 60-80 m^3/h process gas	5.4-6.4			3.6		510	waste gas scrubber (spay-jet scrubber)
plant with afterburning	waste gases containing chloro-aliphatic compounds and toluene and HCl	b) 60 m^3/h HCL, 40-70 g toluene/h	no values	4		0.042 (without toluene) 0.021 0.014 0.013		120	waste gas scrubbing in tower packing column
plant with afterburning	waste gases with chlorinated organic compounds	b) approx. 13000 m^3 waste gases/h	3.8	1		0.024		19600	alkaline gas-scrubbing
rotary tube furnace [1)]	kieselguhr with PER distillation residues	a) 450 kg/h	10.7-12.7	3		0.3 0.48 1.24		3120	afterburning, lime injection, fabric filters

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
afterburning after vinyl chloride production	waste gas from vinyl chloride production		7/11	1		0.4		17300	afterburning, gas-scrubbing (acid, alkaline columns)
HCl recovery in EDC plant	chlorinated hydrocarbon waste gases, liquid chlorinated hydrocarbon residues	a) 450 kg/h HCL	no values	3		0.07; 0.11 3.6		2660	alkaline scrubbing
- " - (repeat measurement)	- " -	a) 450 kg/h HCL	5/11	2		0.0312; 0.0541	96 150	3400	alkaline scrubbing
production of phenyl hydrazine, crude base	aniline, hydrochloric acid, sodium hydrogen sulfate, caustic soda	a) 4000 t/a	14.4-14.5	2		0.001 0.002		8134	wet deposit before and after afterburning, afterburning
residue combustion plant 1)	liquid residues	a) 12 t steam/h	5.5/11	3		0.025 0.021 0.023		8700	E-filter, suspended material-cassette filters
HCl recovery	waste gas contaminated with chlorinated organics, liquid residues	no values	3.3	1		0.084		25000	1.:2 stage scrubbing (acid wash for HCl generation, NaOH wash) 2.: drip deposit
			3.5	1		0.08			
Catalytic waste gas purification in EDC plant	waste gases from oxichlorination	no values	3.8/11	3		0.043 0.052 0.036		7500	cooler, scrubber
afterburning after vinyl chloride plant	waste gases and liquid residues		4-8/11	3		0.01; 0.005 0.004			

1) requirement of BImSchV to be observed

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
plant with afterburning	pesticides			2		< 0.005		5500	wet scrubber
plant with afterburning	adhesives containing chlorine			2		0.021; 0.036		26000	wet scrubber
soot production	high-boiling circulation or residue oils from refineries and hard coal tar processing	b) 2.0-3.2 t/h	9.3 9.0	1 1		0.001 0.002		85200 88300	fabric filter with downstream afterburning

8.1.7 Installations for the Manufacture of Chipboard here: Drying of Wood Shavings (no. 6.3 of the 4th BImSchV)

General Process Description

During drying, the moisture is removed from the wood shavings in directly-heated or in indirectly-heated drying equipment down to a residual water content of 2 to 3 % by weight. More modern shaving dryers have a chip throughput of up to 25 tonnes per hour and with a correspondingly high water valorization power. Depending on the dryer concept, the waste gases volume flow can be as much as 200,000 m³/h. The waste gases contain combustion products (from the combustion by direct-heating dryers), wood particles, vaporized substances from the wood as well as thermo-hydrolytic products from decomposition. A differing composition in the waste gases is given depending on the selection of the drying parameters used (e.g. temperature of the gas intake, moisture content of the drying gases, chip moisture and residence times of the chips in the dryer) as well as on the type of wood and their particle size distribution. A suitable selection of the determining magnitudes could significantly reduce the emissions of the air-polluting substances.

Materials Utilized

Wood shavings
Fuels: heating oil S or EL
  Natural gas
  Wood particle (e.g. chipboard sawdust, sawdust) bark and others.

Emission Levels

PCDD/F concentrations in clean gas from drying installations for wood shavings are compiled in table 25.

Table 25. Dioxin Emissions from Drying Installations for Wood Shavings

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/Kg	N m³/h	Remarks
drum dryer	wooden shavings, heating oil S, wood and brown coal dust	b) 1.03 t shavings /h	18.4	1		0.15		53000	cyclone
drum dryer	wooden shavings, heating oil S, wood dust (contains $(NH_4)_2SO_4$)	12 MW FWL	16.7	1		0.022		37900	cyclone
drum dryer	wooden shavings, heating oil S + wood dust		17-19	no values		0.15		< 80000	cyclone
medium layer shavings dryer	wooden shavings, heating oil El/S, wood dust, solid firing with bark	a) 28 t shavings/h	15.6	1		0.005		36400	cyclone
drum dryer	wooden shavings, heating oil S, wood dust	b) 20.8 t shavings/h	15	2		0.46; 0.52		52000	scrubber and spin deposit
tubular jet dryer	wooden shavings, heating oil S, wood dust	b) 13 t shavings/h	17	2		0.15; 0.15		41000	scrubber and spin deposit
tubular jet dryer	wooden shavings, heating oil EL, wood dust	b) 13.8 t shavings/h	17	2		3.15; 3.51		39000	scrubber and spin deposit
tubular jet dryer	wooden shavings, wood and brown coal dust, heating oil EL	a) 17 t shavings/h b) 100 % 70 %	14.5	4	0.031 0.085 0.068 0.049	0.018 0.025 0.024 0.031		100000	E-filter, wet scrubber

The clean concentrations given lie in the region of 0.005 to 0.052 ng TE/m³ for the majority of installations. A dioxin concentration in the waste gases from one installation was found to be 3.1 and 3.5 ng TE/m³ respectively. It is assumed for this installation that the emissions resulted from a contamination by old timber as the material utilized or by pentachlorophenol in the fuel and that the firing conditions in the combustion compartment were not ideal at the time. Appropriate investigations are not as yet complete. It can however be assumed that the hitherto customary cyclones for waste gas purification were no longer adequate. In order to meet the limit values for particles of 20 mg/m³, further measures are necessary for particle removal, and by which dioxins will also be deposited. Existing correlations principally apply as well to the manufacture of MDF - boards (MDF = Medium Density Fiber boards).

8.1.8 Installations for the Drying of Green Feed (no. 7.25 of the 4th BImSchV)

General Process Description and Materials Utilized

For the production of green feed for storage and for the manufacture of concentrates, green feed is dried in drying installations. Drum dryers are often used for this, by which the feed to be dried comes into contact with hot gases either in the same or in opposite direction and leaves the dryer through air locks after the moisture has been removed. The temperatures of the hot gases entering the drum can be as high as 800 °C.

The hot gases are most often generated in integrated or in separate firing chambers; the fuels used are heating oil S or EL, natural gas, a combination of both as well as with other combustible materials.

Emission Levels

Individual values for emissions of PCDD/F from green feed drying installations are given in table 26. The clean gas concentrations given are generally low and in the region of between 0.008 and 0.083 ng TE/m³.

Table 26. Dioxin Emissions from Green Feed Drying Installations

Installation	Materials Utilized	Output[1] a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	PCDD/F Content Clean Gas ng TE/m³	PCDD/F Content Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
drum dryer	green feed, heating oil S/EL	b) 11.8-24.4 t/h	17.3-18.7	3		0.0084 0.0126 0.0427		40500	cyclone
drum dryer	green feed, natural gas	b) 11.7-15.0 t/h	16.3-16.8	3		0.0196 0.024 0.083		30400	cyclone
drum dryer	green feed, wood/straw	a) 18 t/h b) 18 t/h	15.8-17.3	3		0.063 0.061 0.020		59100	cyclone

[1] output as amount of water vaporized per hour

8.1.9 **Smoke-Curing Installations (no. 7.5 of the 4th BImSchV)**

General Process Description and Materials Utilized

Smoke-Curing Installations in which 50 - 70 % of the present day meat and sausage products produced consist of smoke generators, smoke-curing chambers and associated waste gas fixtures. In the coke generator, wood, twigs, spices and similar materials are decomposed pyrometrically. The desired smoke quality is achieved by means of process control. Three common smoke generation techniques are practiced:

- friction smoke method,
- vapor smoke generation and
- glowing smoke method.

Curing smoke consists of a number of substances such as for example, phenols, acrylaldehydes, formaldehyde, polycyclic hydrocarbons, short as well as long chain organic Acids. Only a small proportion is however known qualitatively to date.

The composition of the smoke is determined prominently by smoke generation technique, the properties of the wood, the threshold temperature, the air intake as well as the conditioning of the smoke.

By the conventional construction of smoke-curing chambers, the curing smoke flows through the chamber by means of thermal ascension (e.g. Altona oven). More modern smoke-curing chambers are nearly all operated using circulating air such that the volume flow of spent gases is reduced by as much as up to 99 % as compared with conventional constructions. The average amount of smoke needed and the emissions are reduced accordingly.

The spent gas is generally purified by the following means:

- aerosol deposits using E-filtering or scrubbers or fleece filters,
- deposits of gaseous emissions by means of thermal post-burning or adsorption or catalytic post-burning.

Emission Levels and their Reduction

Individual results from dioxin measurements in crude gas gave values of up to max. 1.02 ng TE/m^3. In clean gas following waste gas purifications, the concentrations were down to as low as 0.1 ng TE/m^3. No dioxins/furans were found in other measurements taken.

The small data basis available permits only a cautious generalization. Dioxin emissions from some-curing installations would however appear to be very low.

The emission should be reduced in accordance with the LAI resolution from may 8, 1991 (see 77 conference of the LAI, May 06-08, 1991) by the application of following measures:

- Coupled to the requirements of the Meat Ordinance of the Food Regulations, only untreated wood shall be used for smoke-curing and the intake of chlororganic contaminants (which are present in particular by the use of wood with bark portions, needles, and needle wood cones) shall be avoided as much as possible.

- For hot and warm smoke-curing, the spent gas volume flow shall be reduced in order to permit the conditions necessary for the application of effective waste gas purification installations.

- The proven waste gas purification installations (thermal post-burning, catalytic post-burning, scrubbers, activated charcoal filter) should be optimized in their efficiency in conjunction with the processes operated.

8.1.10 Pyrolysis Installations (no. 8.2 of the 4th BImSchV)

General Process Description and Materials Utilized

In pyrolysis installations, organic materials are decomposed in the presence of oxygen and under thermal effects into gaseous, liquid and solids substances. Temperatures and process conditions depend on the materials utilized and the desired products, in general combustible substances (sulfurous gases, coke-type solids) or raw chemicals (e.g. from pyrolysis oils) are produced. The pyrolysis is carried out in chambers and rotary drums, and fluidized bed techniques are also know.

Dioxin Emission Levels

The dioxin emission levels from pyrolysis installations are compiled in table 27.
The are individual value in the range of between 0.055 and 2.6 ng TE/m^3.

Table 27· Dioxin Emissions from Pyrolysis Installations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits ng TE/Kg	N m^3/h	Remarks
pyrolysis installation	shredder material		< 0.5	4		0.7-2.6		< 10000	no values
pyrolysis installation	joined rubber-metal parts		no values/3	1		0.055		no values	pyrolysis gases are burned as well

8.1.11 Drying installations for Aluminum Chips (no 8.3 of the 4th BImSchV)

Preliminary Note

Drying installation for aluminum chips are usually secondary equipment of installations of no. 3.4 of the 4th BImSchV.

General Process Description

A thermal treatment of the turnings is often carried out to reduce the oily processing auxiliaries (machining, drilling suspensions) adhering to the turnings; circulation washing equipment is also used to clean the turnings.

The turnings are dried by the thermal fixtures in rotary drum dryers heated by gas or heating oil; the organic substances contained in the waste gases are extracted and purified in thermal post-burning fixtures. The waste gases are cooled and the particles removed by filtering. The formation of dioxins is possible as the oil-based contaminants adhering to the chips contain certain compounds in which chlorine is bound both organically and inorganically.

Materials Utilized

Chips, contaminated with oils

typical composition:

mineral oil content of the turnings: 11.4 g(Kg
inorganic chlorine compounds: 184 mg/Kg
organic chlorine compounds: 64 mg/Kg.

Emission levels

The levels of PCDD/F emissions from the drying of aluminum chips are given in table 28 for the different contaminants in the turnings.

From the results measured from installation 1 in table 28, an effect of the chlorine content of the turnings used on the PCDD/F contents in the waste gases, as the HCl content in the waste gases increases proportionally at the same time with the increase of the chlorine content in the turnings. The materials utilized should therefore have as low a chlorine content as possible for processing.

Table 28: Dioxin emissions from Installations for the Drying of Aluminum Chips.

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
rotary drum dryer, 4 sets of measurements per 3 measurements	Al chips, contaminated with oil, different lots with varying amounts of oil Cl content approx. 160 mg/Kg	b) 1.2 t/h	15.9-16.6	6		0.24-0.66		7630-9050	afterburning, cooler, fabric filters
	approx. 600 mg/kg	b) 1.1 t/h	14.6-16.0	6		3.1-3.8			
after rehabilitation	Al chips Cl content < 200 mg/Kg	1.0-1 4 t/h	18.18.3	3		0.1-0.16		13900-15700	hydrated lime, afterburning, fabric filters
rotary drum dryer	Al chips	b) 2.6 t/h	19.8-19.9	1		1.05		36400	afterburning, cyclone, cooler, fabric filters
rotary drum dryer	Al chips	a) approx. 3 t/h	17.1-19-0	7		0.37-1.11		11000-15000	afterburning, fabric filters
rotary drum dryer	Al chips		18.6	3		0.08-0.1		9000	afterburning, fabric filters

8.1.12 Installations for the Thermal Stripping of Paints (no. 10.20 of the 4th BImSchV)

Dioxin emissions at installations for the thermal stripping of paints are given in table 29. One installation gave emission concentrations which exceeded 0.1 ng TE/m³. This installation has however been closed down in the interim.

8.1.13 Crematoriums (no. 10.24 of the 4th BImSchV)

There are currently approximately 100 crematoriums in existence in Germany with very different capacities in some case, in which approximately 300.000 cremation services are carried out per year.

General Process Description

The cremation is carried out in furnaces which are fired using oil or natural gas. There also some which run on electricity. The coffin is forwarded into the furnace by a conveyor fixture. In a muffle fitted out with chamotte, the coffin is burned at temperatures of between approximately 600 and 900 °C and the remains are then transported to a post burning chamber located beneath where they are post-fired (minimum temperature 850 °C).

The cremation time is about 70 minutes. The average volume of waste gases is approximately 1200 N m³/h for gas and oil fired furnaces and approximately 600 N m³/h for electrically heated furnaces (each with respect to 11 % O_2 by volume).

The waste gases from the muffle in more modern installations are transported via the afterburning chamber and the recuperator and are subsequently purified by cyclones and fabric or electrostatic precipitators.

Table 29· Dioxin Emissions from Paint-Stripping Installations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measure-ments	PCDD/F Content Crude Gas ng TE/m³	 Clean Gas ng TE/m ³	 Filter Deposits ng TE/Kg	Waste Gas Volume Flow N m³/h	Waste Gas Treatment Remarks
paint-stripping plant	different paints with PVC		approx. 15.4	3		0.09 0.09 0.06		4210-4540	afterburning, waste gas scrubbing using Venturi scrubber and packed tower columns
paint-stripping plant	no paints containing PVC or chlorine on measurement days		approx. 8	2		1 4 24.8		450	afterburning plant plant closed down
paint-stripping plant	painted materials		3.8-5.8			0.055		300-530	afterburning
paint-stripping plant	painted materials	2.5 t/lot		5		0.0039		200	afterburning

Materials Utilized

Coffins entering into the firing process are of differing constructions (chipboard coffins, hardwood coffins). In the coffin itself, plastics, paper, planing shavings, sawing shavings etc. are used. Furthermore, there are also certain deodorizing substances which are used (amongst others 1,4 dichlorobenzene (PDCB)). In the interim, the use of plastics and deodorants have been virtually banned by appropriate restrictions.

Emission levels

The dioxin emission levels from crematoriums are compiled in table 30.
Reductions in the dioxin emissions could be achieved at crematoriums by measures relating to the materials utilized as well as by technical combustion and waste gas measures, whereby the first two measures should be given priority in their application.

Measures Relating to the Materials Utilized

The VDI Guideline 3891 "Emission Reductions - Crematorium Funerals" (8/92) are applicable to crematoriums; by following these recommendations, a considerable reduction in dioxin levels can be reckoned with. The halogen content (chlorine and bromine contents) in particular of the materials utilized could be thereby lowered drastically. The following requirements shall be fulfilled:

- avoidance of the use of plastics containing halogens and in particular, PVC shall not be used for inside the coffin,

- no application of wood treatment agents which contain halogens for the manufacture of the coffins (no addition of ammonium chloride to chipboard) and,

- no application of odor-blanketing agents which contain halogens (e.g. 1,4 dichlorobenzene), as well as

- a control of the decorations of the coffin.

Table 30: Dioxin Emissions from Crematorium Installations.

	Capacity	Temperature °C	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m³	PCDD/F Content Clean Gas ng TE/m³	Waste Gas Volume Flow N m³/h	Waste Gas Treatment
1	5 cremation per day	550-880	12-18	3		6.39 3.5 3.79	2290	afterburning compartment cyclone
2	12 cremations per day	550-800	8; 7-9	3		1.59 2.37 2.26	4400-5100	afterburning compartment cyclone
3	5 hardwood coffins 6 chipboard coffins 4 hardwood coffins	> 900	no values	3		$14.4^{1)}$ $4.02^{2)}$ $5.02^{1)}$	4100-5200	afterburning compartment cyclone, fabric filters
4	6 cremations	800	18.7	3		0.82 1.82 3.42	600	cyclone
5	2 cremations	800	no values	2		2.59 2.89	4000	cyclone
6	10 cremations, electric furnace	800	19.2	2		0.5 0.7	3000	no waste gas treatment
7	5-6 cremations per day	cremation chamber 650-1000 °C	15.5	3		1.05 1.39 1.05	4 x 2090	cyclone, fabric filters
8	6 cremations per day	waste gases: 333 cremation chamber 800 °C	12-20	3		3.42 1.82 0.82 (excl. MWG)	4,900-6,400	cyclone (12)

Installation	Capacity	Temperature °C	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content Crude Gas ng TE/m^3	 Clean Gas ng TE/m^3	Waste Gas Volume Flow N m^3/h	Waste Gas Treatment
9	2 x 40 KW 4-5 cremations per day per furnace	waste gas: 179	18.3	6		0.111 0.745 1.776 (based on 17 % O_2)	2900	electrostatic precipitator
10	5 cremations per day and furnace, 2 furnaces	1173 1083 (afterburning compartment)	17.2-20.0	3		0.756 0.415 0.669	7008	fabric filter
11	approx. 20 cremations per day and furnace, 3 furnaces	750 to 900 (afterburning compartment)	15-17	3		a) 1.07 b) 0.136 c) 0.295 and 1.013 (based on 11 % O_2)	3000	a) no restriction of materials utilized b) with restriction of materials utilized plus addition of lime c) with restriction of materials utilized and without addition of lime all with fabric filters
12	approx. 20 cremations per day and furnace, 3 furnaces	750 to 900 (afterburning compartment)	15-17	3		4.02 5.22 14.4	3000	fabric filters and without restriction of materials utilized
				3		0.72 0.95 2.0 (based on 11 % O_2)		with restriction of materials utilized (acceptance measurements)
				3		2.76 to 12.1 (with respect to 11 % O_2)		with restriction of materials utilized (special measurement)
13	no values		19	3	0.38	0.004	6700	bio-earth filter

1) Coffin material wood, other fittings unknown
2) Coffin material chipboard, other fittings unknown

Technical Combustion Measures

According to the results of the measurements at installations 11 and 12 in table 30, the measures relating to the materials utilized of primary measures of technical combustion are to be supported. These should be orientated towards the adaptation of the available oxygen to the needs which are given by the burning process and thus a general reduction of the amount of air available for the firing process. The thus associated further advantages of:

- a reduction of the additional combustion materials for the afterburning chamber,

- an improvement in the burn-out quality of the waste gases and,

- a reduction of the particle content in the crude gases in particular during the critical phases of the cremation process,

would be given.

As technical firing magnitudes, the afterburning temperature and the carbon monoxide and oxygen contents in the waste gases could be taken as a guideline.

Measures Relating to the Waste Gases

A particularly efficient method of particle collection is also recommended in addition to the numerous gravity deposition techniques (cyclones, multi-cyclones) operated for the purification the waste gases, e.g. using fabric filters to collect the dust-bound dioxins and furans.

Whether by means of restrictions of the materials utilized, or an optimization of the technical firing parameters or an extremely efficient particle collection, further secondary measures necessary for purification of the waste gases cannot be conclusively evaluated from the results which are currently available.

It must also be hereby taken into consideration that additional space would be required for further waste gas purification fixtures and that many of the older crematoriums are historic monuments and protected accordingly.

8.1.14 Miscellaneous Types of Installations

The miscellaneous types of installations are compiled in table 31 which are not classified according to 4th BImSchV and for which there are only one or two results available from measurements taken.

Table 31· Dioxin Emissions from Miscellaneous Installations

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m^3	Clean Gas ng TE/m^3	Filter Deposits	N m^3/h	Remarks
bitumen blast installation	bitumen		9.2; 9.9; 8.4 (reference O_2 content: 11% by volume)	3		0.0027 0.0043 0.0091		2650-3370	afterburning plant
drying plant	sewage sludge		12	4		0.05-0.11		< 40000	E-filter, afterburning
experimental fire installation	cable with approx. 40 % PVC, light concrete wall	13 furnaces, various combustion compartments	6-8			2.3.7.8-TCDD 0.16		15600	afterburning, alkaline scrubbing
pesticides technical center	chlorobenzene and others					only PCDF T_4CDF 1-3		5500	afterburning, alkaline scrubbing
painted wire production	wire, paints					0.005; 0.002		4700	cold afterburning

8.2 Installations not subject to licensing

8.2.1 Domestic Firing Installations

Domestic fireplaces have, as a rule and in comparison with combustion plants which are subject to licensing, a worse burn-out of the fuels and waste gases, especially for burning appliances for solid fuels. Measures for the emission reductions from the waste gases are not common for domestic firing installations.

On account of the large numbers of household equipment, domestic firing installations contribute noticeably to the total emission of air polluting substances. The numbers of household installation in the old Federal States are:

approx. 5 million solid fuel firing installations,
approx. 15.2 million oil-firing installations and
approx. 15.3 million gas-firing installations.

The situation in the new Federal States is characterized by a high proportion of single fire appliances for solid fuels. Approximately 50 % of apartments were equipped with separate coal furnaces in 1990. The conversion to modern heating installations is currently taking place at rates which are regionally different.

Extensive investigations on emissions of dioxins and furans from domestic firing installations for using the fuels natural gas H, heating oil EL, anthracite coal, hard coal, coal briquettes, brown coal briquettes and wood have conducted by the State Institute for Emission Protection of North Rhine Westfalia (published in the LIS Report no. 103 "Emissions of polychlorinated dibenzo-p-dioxins and dibenzo-p-furans from Household Combustion", publisher: State Institute for Emission Protection, Essen, 1992).

Commercial combustions typical for the fuels were carried out in a test fixture operated under defined conditions, and the emissions were measured.

The following emission factors based on relative amounts were evaluated for the different fuels (table 32); the measurement results from investigations with Lausitzer as well as with Middle German brown coal supplement the table:

Table 32: Quantity-related Emission Factors for Domestic firing installations

Fuel	Emission Factors *
Natural gas H	0.051 ng TE/m³
Heating oil EL	0.017 ng TE/m³
Anthracite	0.124 ng TE/m³
Hard coal coke	0.552 ng TE/m³
Brown coal briquettes	
- Rhine brown coal	0.125 ng TE/m³
- Lausitzer brown coal	0.51 ng TE/m³
- Middle German brown coal	0.78 ng TE/m³
Briquettes (hard coal)	0.365 ng TE/m³
wood	0.53 ng TE/m³
wood (open hearth)	0.19 ng TE/m³

* For values lower than the detection levels, TE values of zero have been taken in place of the values actually calculated.

The contribution of domestic firing installations to the total emission of secondary significance when approved fuels are used in proper operation, whereby there can be large regional differences. The relative contribution can increase however in future, should the emissions from other sources decrease as a result of emission-reducing measures.

Particularly on account of the high proportions of solid fuel combustion appliances in the New Federal Sates is here with higher contributions to emissions from these sources to be currently reckoned with.

Increased dioxin emissions result from when waste packing material is added to solid fuels. Even though it is prohibited, this can happen in private households. Due increasing disposal charges, it must be reckoned with that waste household materials are being burned in domestic firing installations. The use of wood with the addition of waste packing material lead to an increase in the dioxin emissions of 0.06 ng TE/m³ (exclusively wood) to 8 ng TE/m³ (respectively relative to 11 % O_2 by volume).

This tendency was confirmed by recent investigations in Switzerland by which up to 114 ng TE/m^3 (with respect to 13 % oxygen by volume) was found in the waste gases from domestic firing installations which burning domestic waste as well. Because of the chimney heights are low, such fire appliances can produce considerable loads into the immediate vicinity.

Corresponding loads are also possible when PVC coated wood and chipboard was well as ammonium chloride-hardened chipboard, each of which can occur as rest materials and are also burned in wood fired installations which are subject to licensing, e.g. in smaller commercial wood-processing operations. As particular secondary measures for emission reduction from these installations are not usually installed in such appliances (and also not proportionally), the reduction of the emissions should be reached by the consequential primary measures relating to the materials utilized, e.g. avoidance of halogenated plastics and auxiliary materials.

8.2.2 Dry Cleaning

Dirt's adhering to textiles are removed by treatment with organic solvents in chemical laundries. In accordance with the regulation of the 2. BImSchV, only the perchloroethylene (PER) out of all chlorinated solvents may still be used.

The laundering process comprises of the process steps washing and drying; the solvent is purified by internal distillation in the machine. The distillation residues are collected in drums and must be disposed of.

Investigations of the distillation residues from laundry shop cleaning show that considerable concentration of PCDD/F are present in the distillation residues. An average value of 256 ppb has been calculated for all samples taken; 90 - 95 % were hepta- and octa- chlorinated dioxins. The trichloroethane content of the PER used, the addition of cleaning auxiliary substances, the pH value of the residues, the location of the laundry and the instrumentation parameters of the laundry machines all have no influence on the formation of PCDD/F. Neither could an influence of the solvent (PER, halogenated hydrocarbons, hydrocarbons) be determined.

A variation of the goods to be cleaned was shown by brand new goods and working clothes by higher PCDD/F levels than for the clothing worn for outdoors. These higher concentrations could have two causes: they could originate from textile industry equipment or additives (e.g. dyes) in the clothing, or they could come from adsorbed dirt's. Material paths are being investigated within the scope of a R & D project. The balancing of the inputs and outputs of chemical laundries shows that the textiles worn dominate the input side. The output side occurs to 99 % via the distillation residue side. An emission of dioxins and furans in the atmosphere plays virtually no role at all.

Comparative dioxin inputs are to be expected for chemical laundries which use hydrocarbon solvents (hydrocarbon installations).

8.2.3 Installations for the Processing of PVC

There are only a few results available pertaining to the emissions from installations for PVC processing. The information is summarized in table 33. This table also includes results from individual measurements on installations for the manufacture of track-like materials on spreading machines and their respective drying fixtures (gelling channels), which, according to no 5.6 of the attachment to the 4th BImSchV, are subject to licensing. The dioxin formation from the differing process is very low in each case.

Table 33: Dioxin Emissions from Installations for PVC Processing

Installation	Materials Utilized	Output a) nominal b) measured	Operating / reference oxygen content % by volume	Number of measurements	PCDD/F Content			Waste Gas Volume Flow	Waste Gas Treatment
					Crude Gas ng TE/m³	Clean Gas ng TE/m³	Filter Deposits ng TE/kg	N m³/h	Remarks
calendaring plant for the manufacture of PVC foil	PVC granulates	no values	no values	2		0.001 0.003		19300-20100	none
pressing plant for processing PVC and plastic recycling material	shredded PVC insulation material	a) 500 kg/h b) 525 kg/h	no values	1		0.037			none, waste gases transferred via hoods/slits
coating plant for PVC	PVC	no values	no values	2		0.0001 < 0.0001		100000	extracted air from gelling channels, fiber-glass low bed filters
foamed wallpaper manufacture	soft PVC	a) 36-41m, wallpaper per minute	18	3		0.007 0.007 0.004		11870	afterburning

8.3 Motor Vehicles

Combustion engines in motor vehicles are also a source of dioxins and furans. An R & D project concluded in 1992 "Investigations on the emissions of halogenated dibendioxins and dibenzofurans from the operation of combustion motors using commercial operating fuels"" (Essers, Hutzinger, Hagenmaier) measured the dioxin emissions from motor engines which were operated using leaded gasoline, gasoline containing scavengers and unleaded gasoline, with and without catalytic converters as well as from diesel engines, with the objective of determining the total emissions of polychlorinated dioxins/furans of motor vehicle traffic. The highest dioxin/furan emissions resulted from the operation of the gasoline engine using leaded gasoline with scavengers, which emitted PCDD/PCDF of between 0.5 and 1.5 ng TE per Kg gasoline (TE according to BGA); as well as polybrominated and mixed halogenated dioxins and furans in addition. Scavengers (1,2 dichloroethane, 1,2 dibromoethane) have up to now been intentionally added to leaded gasoline. PCDD/PCDF emissions approximately 90 % lower were measured from operating vehicles with unleaded gasoline. Regulated 3-way catalytic converters reduced the emissions by a further 80 %. The following average specific emissions were determined:

gasoline engine, leaded 0.74 ng TE/l fuel
gasoline engine, unleaded 0.09 ng TE/l fuel
gasoline engine with catalytic converter 0.02 TE/l fuel
diesel engine 0.05 TE/l fuel
(without differentiating between motor cars and commercial vehicles).

A prognosis of the total emission for the Federal Republic of Germany (old Federal States) using figures for the fuel consumption from the Mineral Oil Economic Association for 1990 and the evaluated TE levels results in an annual total intake of PCDD/F into the environment of approximately 11 g TE/year from vehicle traffic. This is caused to approximately 70 % by gasoline engines which are operated using leaded fuel containing scavengers. The use of fuels containing scavengers has been prohibited in the Federal Republic of Germany since July 1992 (Ordinance on chlorinated and brominated compounds as additives in fuels - 19. BImSchV dated 17.1.1992 BGBl. 1 page 75). Without the use of scavengers and the widespread use of catalytic converters in gasoline engines hat brought about a considerable reduction in the PCDD/F emissions from motor vehicles. Estimations for 1992 already indicate a reduction in the emissions of approximately 50 % as compared to 1990.

8.4 Brominated and Mixed-halogenated Dioxins/Furans

Through the presence of brominated compounds (e.g. brominated hydrocarbons from fire prevention agents, hydrogen bromide), brominated/mixed-halogenated dioxins and furans can be produced from thermal processes, or halogen exchange reactions (bromine by chlorine) can take place.

As the toxicity of the produced brominated dioxins/furans does not principally deviate from that of chlorinated counterparts (see also the first Ordinance to amend the Hazardous Goods Exception Ordinance dated March 24, 1994, in which the same toxicity equivalence factors for tetra-, penta- and hexabrominated PCBD/F were published as for their chlorinated counterparts), they shall also be included in this report. Only 5 installations in total however (3 from the sector of copper extraction/processing, 1 crematorium, 1 paper impregnation machine) have been documented with respect to emission levels, refer to table 34.

Table 34: Emission of Brominated and Mixed-halogenated Dioxins and Furans from Installations

Anode furnaces for processing scrap copper	0.02 ng/m^3 PBDF/D, 4.4 ng/m^3 PBCDF/D
Copper matte converter for processing scrap electronics	approx. 0.160 ng/m^3 PBDF/D
Shaft furnace for scrap copper (clean gas)	48.6; 162.2 ng/m^3 PBDF/D
Trial furnace (crude gas)	1.28; 19.7 ng/m^3 PBCDF/D
Cremation installation 1)	4 - 32 ng/m^3 PBCDF/F
Impregnation machine for paper	0.02 ng/m^3 penta BDF

1) coffin configuration not known

As the toxicity equivalence factors for mixed-halogenated compounds have not been determined and only values for brominated dioxins and furans are available as summated values, no toxicity equivalents (TE) can be determined. In order to give a comparison for these summated values , it must be pointed out that for example, for waste incineration installations, 0.1 ng TE/m^3 correspond to between approximately 2 and 5 ng PCDD/F/m^3.

The occurrence of polybrominated or mixed-halogenated dioxins/furans during copper processing utilizing scrap copper can be attributed to the intake of contaminants from plastics containing flame inhibitors. The few results available are to be only understood as being an indication for further investigations and that a detailed discussion based on present results is not possible.

By applying technical process measures as well as measures on the waste gas side for the reduction of the emissions of polychlorinated dioxins and furans, the emissions of polybrominated and mixed-halogenated compounds will be minimized practically to the same extent.

9. Summary

A multitude of dioxin/furan measurement results has been presented for the preparation of this report and systematically compiled for evaluation of the characterization of the modes for emission from the installations observed.

In contrast to the first report, stand 1993, the state of the knowledge regarding dioxin emissions from industrial installations has improved. Programs of measurement have been concluded and new studies have begun in many Federal States.

The emissions can already be well characterized for the differing types of installations, in certain cases interrelations are seen between the materials utilized, process conditions and the effectivity of purifications techniques for waste gases containing dioxin concentrations. For many types of installations, the results from the measurements are however specific to the respective construction and the operation on the individual installation and cannot therefore be used for a generalized conclusion. The continuation here and to a certain extent an expansion of the investigations is necessary in order to recognize the interrelations better and thereby enable a more objective orientated implementation of reduction measures.

With regard to the task mandate, the respective mass concentrations in the waste gases have usually been given in this report (e.g. in TE/m³). Bulk assessments would be desirable or necessary for the evaluation of the relevance of the emissions of the differing sources with respect to the dioxin intake into the environment. These have not been possible for the majority of the sources on account of the small amounts of data available.

Recommendations are given as a rule in the subsequent statements, which are based on the mass concentrations. By the implementation of the recommended measures to reduce emissions for the individual installations, the reduction of the mass emission flow of PCDD/F shall take precedence over a limitation of emission concentrations; this shall be considered in particular for objective measures for reducing the product-specific volume flow of waste gases.

I.

For the different types of installations according to the current status of the investigation results for **installations subject to licensing** to the extent that they do not fall under the 17th BImSchV, the following statements can be made with respect to a limitation of the dioxin emissions:

1. **Power Plants** show dioxin emission levels which are considerably lower the 0.1 ng TE/m³. The results of measurements

taken are generally from installations located in the old Federal States and have been confirmed by the individual measurements available from installations in the new Federal States.

2. Only a few results are available for **incineration installations which utilize coal, heating oil or gas.** The use of heating oil or gas results in dioxin levels which are significantly lower than 0.1 ng TE/m³. This is also to be expected from the recycling of coal.

3. **Installations which incinerate wood** shall be considered on a differentiated basis and in relation to the materials utilized, the construction of the furnaces, the means of waste gas removal as well as the techniques for reduction. The intake of chlorine into the furnace is also present even with untreated wood (chlorine content between approximately 0.001 and 0.1 % by weight on average).

The recycling of untreated wood in wood-firing installations which have good burn-out ratios (e.g. the avoidance of CO peaks and cold streams, CO emission levels which are considerably lower, if possible, than the levels in no. 3.3.1.2.1 of the TA Air), with good waste gases removal as well as an efficient dust removal (e.g. using fabric filters or electrostatic precipitator) can result in the emission limit in the waste gases of 0.1 ng TE/m³ being fulfilled.

The recycling of chipboard which has been manufactured with the addition of ammonium sulfate, leads to slightly higher dioxin emission levels being found as a rule, in comparison to the use of untreated wood. A similar mode of emission is to be expected from using painted or coated wood (with the exception of halogenorganic coatings); specific investigations on this are not available.

By contrast, significantly higher levels of up to approximately 10 ng TE/m³ of dioxin emissions are measured with wood which has been coated with substances containing halogenorganics (e.g. with PVC), wooden materials containing chlorides (e.g. from the use of hardeners containing NH_4Cl or spreaders containing NaCl in the binding agents) and treated wood (e.g. with PCP, lindane).

There are different primary and secondary measures which are suitable for reducing the dioxin:

- the avoidance of the use of halogenorganic substances to coat or treat wood, as well as binding agent additives in wooden materials (hardeners, spreading agents).

The use of PVC for coating can virtually be dispensed with. As adhesive for gluing at edges, ABS (acrylnitrile-butadiene-stysrene) strip is available as an alternative; other chlorine-free plastics can also be used as alternative coatings.

in place of hardeners based on ammonium chloride, equivalent hardeners based on sulfate may only now be used in Germany according to the information which is available to us. The use of spreading agents containing chloride (e.g. NaCl) as the binding agent can also be dispensed with today as the binding agent additive in wooden materials.

- As far as PVC in installations for wood processing is used, a strict separation from those materials containing PVC is to be observed, with regard to the use of wood rests in wood-firing installations.

- Construction and operation of installations with regard to a good burn-out. This is characterized by a low CO and low total carbon levels in the waste gases as well as by low loss at reds heat of the solid combustion residues (value for CO lower than 100 mg/m^3 should be strived for during normal operations of modern installations).

- Optimized waste gas removal with regard to a minimization of particle deposits in the waste gases.

- Effective dust removal by for example the use of fabric filters or by electrostatic precipitator, even in smaller installations.

While observing the basic rule of proportionality, a graduated course of proceeding can be considered for limiting the dioxin emissions from wood-firing installations, which consists of the following components:

- As far as the use of wood and wooden material rests which contain additional substances containing chlorine or are coated with substances containing halogenorganic substances, can be excluded 1), a optimization for wood-firing installations up to 2.5 MW in the combustion and in the waste gas removal as well as in the conventional removal of particles is to be undertaken.

- As far as the use of wood and wooden material rests which contain additional substances containing chlorine or are coated with substances containing halogenorganic substances, <u>cannot</u> excluded, the implementation of special waste gas purification technologies for wood-firing installations shall be considered (e.g. fine stream or solid bed techniques) in addition to the measures mentioned above.

- A target value of 0.1 ng TE/m^3 in the waste gases is to be strived for installations of 1 MW and greater; checking on a case by case basis is necessary while taking into consideration the technical secondary conditions, the emission-reducing technologies, the residues as well as the relevant expenditure.

- Adequate transition periods shall be permitted for the modernization or for the replacement of existing installations.

1) These are, amongst others, untreated wood, painted, lacquered or coated wood (fuel no. 4 to 7.. 3 of the 1st BImSchV or fuels of the no. 1.2, aa) and bb) of the 4th BImSchV).

Further investigation programs are currently being conducted by the Federation and by Federal States. The results from these programs serve to deepen the knowledge for explanations as well as for the operation of more modern installations and the optimization of existing installations with the objective of achieving minimized emission levels of dioxins.

4. The recycling of **landfill gases in combustion muffles, in motors or in turbines** result in dioxin emission levels < 0.1 ng TE/m^3 being met by the waste gases.

5. The results presented with regard to the sectors **brick/building materials manufacture and the manufacture of glass** show dioxin levels of < 0.1 ng TE/m^3 as well, with a few exceptions however. These results can be attributed to, amongst others, the good burn-out conditions for the fuels investigated. The emission levels of dioxin from **cement rotary furnaces** are less than (in some cases significantly less than) 0.1 ng TE/m^3.

6. For several types of installations in the sector of **production and processing of metals,** levels of less than 0.1 ng TE/m^3 in the waste gases can, as a rule, be met without the implementation of particular measures, for example:

- in the iron and steel industries for blast furnaces, oxygen blast converters and hot-air cupola furnaces,

- in the non-ferrous metal industry in installations for hot-dip galvanization, in aluminum smelting installations (which as well as pure aluminum, also use lightly contaminated primary scrap to a certain extent) or for aluminum smelting in induction crucible furnaces in oil-fired or gas-fired crucible furnaces (for the use of ready alloyed ingot materials).

For many types of installations involving thermal processes for the production and processing of metals such as shaft furnaces for copper or lead, electric arc furnaces, sintering installations and aluminum smelting installations using contaminated materials, levels for dioxin emissions which considerably exceed 0.1 ng TE/m^2 often however are found; the levels for shredder installations also exceed 0.1 ng TE/m^3.

Installations for the production and processing of metals are, according to the results presented and also under consideration of the large volume flows of waste gases, one of the main sources of dioxin emissions in the Federal Republic of Germany. effective measure are to be applied to reduce these emissions of dioxin.

There are different primary and secondary measure for emission reduction which are suitable, whereby the primary methods which should be preferentially applied are:

- The chlorine and bromine intake into the installations can be reduced considerably by replacement of materials containing chlorine and bromine or by not utilizing them at all, and thereby improving the prerequisites for the reduction in dioxin emissions by, for example:

-- avoidance of cooling greases containing chlorine in the processing of metals,

-- avoidance of hexachloroethane in the aluminum foundry sector,

-- avoiding to a great extent the use of coatings containing halogens;

- the use of coke qualities with a low proportion of volatile organic substances in the sintering installations sector;

-- reduction in the use of open-furnace particles and roll scale mot high oil contents or unknown contaminants in sintering installations;

- the use of processing techniques to separate metals and plastics or to clean metals by for example:

-- extensive disassembly and sorting of plastic components during the wrecking of old vehicles,

-- cold decomposition of cable,

-- the use of swim-sink separation techniques and swirling current technologies;

- Use of technical process measures to optimize the operating parameters by, amongst others:

-- reduction of the volume flows of waste gases, for example by the use of oxygen burners, prime avoidance of the false intake of air, construction optimization of the installation housings,

-- extensive avoidance of threshold and pyrolysis processes,

-- realization of good burn-out conditions,

-- low-emission operating of sintering installations (e.g. optimization of the sinter conveyor rates),

-- integrated post-burning of the waste gases;

-- extensive avoidance of the deposits of particles on heat exchangers and in the waste gases as well as a rapid cooling of the waste gases (e.g. by quenching, provided the reduction of emissions takes precedence over the use of thermal energy);

-- the use of more efficient waste gas purification techniques, including treatment and recycling of the residues.

Often the primary measures are not sufficient to realize an emission level of 0.1 ng TE/m³. The application of addition waste gas purification methods can prove necessary in such cases.

For thermal process for the production and processing of metals can, under observation of the rule of proportionality, a graduated course of action can be implemented to limit the emissions of dioxins:

- for smaller installations with low waste gas volume flows of up to 5000 m³/h, a level for the emissions of dioxin, or a targeted value as laid down in the bagatelle regulation in no. 2.3 of TA Air can be disregarded.

A minimization of dioxin emissions should be accomplished by primary methods relating to the materials used and to technical processes employed as well as by optimizing the conventional techniques used to purify the waste gases.

The current knowledge could apply to the bagatelle regulations for aluminum foundries in particular; trial measurements for this sector are still outstanding.

- For installations with a waste gas volume flow exceeding 5000 m³/h, a reduction should accomplished by measures for the pretreatment of the materials utilized, by conversion or optimization of the processing as well as the removal of the waste gases and by the employment of particularly efficient waste gas purification fixtures. A target value of 0.1 ng TE/m³ in the waste gases should be strived for in the course of investigations on a case by case basis.

If a level of approximately 0.5 ng TE/m³ has already been achieved for the waste gases, it shall be investigated on a case by case basis under consideration of:

- the dioxin carriage in the waste gases (annual emission),
- the possibilities of recycling the residual materials and
- the expenditure for reduction measures,

the extent to which those further measures necessary to achieve the target value may be dispensed with.

With regard to the improvement in the state of knowledge through investigations being continually conducted as well as with respect to the time periods required for planning, installation and putting into operation the effective reduction measures, appropriate interim periods until the realization of the reduction objectives, are to be foreseen for alterations to existing installations.

Installations with high dioxin mass emissions should be modernized with the highest priority.

7. It can be assumed from the few results presented from **installations in the chemical industry**, that a dioxin emission level from 0.1 ng TE/m^3 for many types of installations can be met without the implementation of particular measures for reduction of dioxins. With certain types of installations, additional reduction measures could be necessary e.g. waste gas purification techniques.

8. For installations for **green feed drying** as well as for **smoke-curing installations**, the emission levels are as a rule less than or equal to 0.1 ng TE/m^3 and are fulfilled by the implementation of primary measures as well as by conventional methods of waste gas purification.

9. For **installations for drying wood shavings, pyrolysis installations, installations for the drying of aluminum chips as well as for installations for the thermal stripping of paints**, the presented results of measurements taken currently exceed 0.1 ng TE/m^3; additional waste gas purification measures are required in order to meet the target value of 0.1 ng TE/m^3 in installations in particular for the drying of aluminum chips and certain installations for drying wood shavings.

The proposed requirement concepts for installations for the production and processing of metals can equally be applied to these installations.

10. For **cremation installations**, the limitation of materials utilized, technical firing measures as well as an efficient deposition of particles will bring about significant reductions in the dioxin emissions (refer also to the guideline 3891 from VDI "Emission Reductions - Cremations).

At the present time and on account of a resolution of the Federal Government/ Federal States Immission Control Committee from 20.10.93 in Schwerin in a working group, proposals for uniform Federal Requirements are being consulted (as well as for the limitation of dioxin emissions).

II

For **installations not subject to licensing**, those solid fuel combustion installation are particularly dioxin-relevant:

For the combustion of approved solid fuels in domestic firing installations, the dioxin concentrations are as a rule </ 0.1 ng TE/m^3 for an orderly operation of the installation. Apart from this, it should be pointed out that on those fuels suitable for domestic firing installations may be used (untreated wood, coals,

briquettes and similar), and that wood rests (e.g. chipboard or old furniture) or waste packing materials may not be utilized.

The unallowed use of plastics, old paper, cardboard and similar substances in combustion appliances leads as a rule to higher emissions of dioxins. More information to the public is deemed necessary on the subject of this.

The continual modernization and conversion of smaller combustion installations results in a significant reduction in the dioxin emissions, in particular in the new Federal States.

III

There are only a limited number of results concerning the emissions of **polybrominated and mixed-halogenated dioxins and furans.**

The use of brominated compounds should be avoided as much as possible. By the implementation of technical process and waste gas measures to reduce the emissions of polychlorinated dioxins and furans, the emissions of polybrominated and mixed-halogenated dioxins and furans will be reduced at the same time and with approximately the same effectivity.

IV

Comparative measures to those in Germany should also be implemented in neighboring states in order that the far-reaching transportation of dioxins and furans be reduced and that the disadvantages thereby incurred in competition be avoided.

Attachment

Members of the Working Group "Dioxin Emission Standards"

Dipl.-Ing. Jochen Baldner	Lower Saxony Ministry for the Environment, Hannover
Dr. Günter Bröker	State Institute for Emission Control, Essen
Dr. Hans-Hermann Eggers	Federal Environmental Agency, Berlin
Dr. Christian Ehrlich	State Institute for Environmental Protection, Halle
Dipl.-Ing. Walter Eickhoff	Hessian State Institute for Environmental Protection, Kassel
Dr. Dirk Frank	Ministry for the Environment of the State of Rhineland-Palatinate, Mainz
Dr. Werner Funcke	Society for Workplace and Environmental Analysis, Münster-Roxel
Dr. Wolfgang Gnausch	State Office for the Environment, Potsdam
Dipl.-Ing. Heinz Gräfe	Saxony State Office for the Environment and Geology, Radebeul
Prof. Dr. Hanspaul Hagenmaier	Institute for Organic Chemistry of the University of Tübingen
Prof. Dr. Johannes Jager	Technical College, Darmstadt
Dr. Hans-Joachim Keller	Provis GmbH, Stuttgart
Dr. Brigitte Köpke	Environmental Authorities of the Independent and Hansa City of Hamburg, Hamburg
Dr. Michael Lange (Chairman)	Federal Environmental Agency, Berlin
Dr. Klaus Lützke	Rheinisch-Westfälischer TÜV, Essen
Dipl.-Ing. Konrad Maier	Bavarian State Office for Environmental Protection, Munich
Dipl.-Ing. Jürgen Mayer	Baden-Württemberg Ministry for the Environment, Stuttgart
Dipl. Ing Claudia Mitsch-Werthwein	Baden-Württemberg Ministry for the Environment, Stuttgart
Dipl.-Ing. Matthias Pilz	Thuringia State Institute for the Environment, Jena
Dr. Joachim Stach	Umweltforschungszentrum (Environmental Research Center), Leipzig/Halle GmbH, Halle
Dipl.-Chem. Michael Wilken	ITU Ingenieurgemeinschaft Technischer Umweltschutz GmbH, Berlin.