

VOLUME 1, Part A:
General Aspects

Preface

In February 1993 the Council of Ministers has set the political goal to achieve a 90 % reduction of dioxin emissions from known sources by the year 2005 as compared to the reference year 1985. To achieve this ambitious aim an inventory of all relevant emission sources and an estimate of the total emissions in the member states is required. This allows to direct abatement measures to the most important sources of dioxins and furans.

During the EU Council Conference on 28. and 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 Federal Ministry for the Environment offered to take up the task of the leadership of a respective working group.

Following this proposal the EU Commission has since taken up the subject and DG XI committed this special research project to the North Rhine Westphalia State Environment Agency (LUA NRW) which started work in January 1995.

In the meantime a European directive limiting dioxin emissions from hazardous waste incineration plants has been enacted. Subsequent initiatives by the European Union to reduce dioxin emissions from other industrial plants may become necessary as the impact of dioxin emissions from certain industrial plants is far higher than from hazardous waste incineration plants. Due to the ubiquitous occurrence of PCDDs and PCDFs and their transport across borders permanent solutions can be achieved only by measures with far-reaching impacts.

Introduction

Dioxins and furans - structure and composition

The term "dioxin" is often used to denote a family of compounds known chemically as polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Each compound comprises two aromatic („benzene“) rings interconnected by oxygen atoms. In the case of PCDDs, the rings are joined by two oxygen bridges, whereas in the PCDFs, the rings are connected by a carbon bond and an oxygen bridge. Figure 1 depicts the basic structural formula of PCDDs and PCDFs, together with the numbering convention at the positions on the benzene rings where chlorine or other halogen atoms can be substituted.

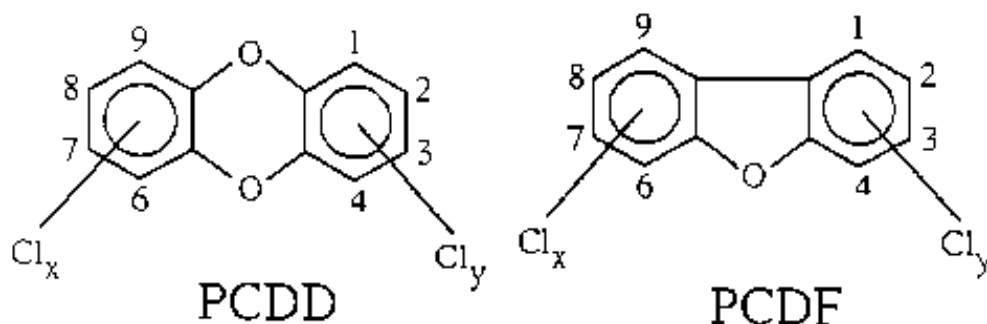


Figure 1: Chemical structures of PCDDs and PCDFs

Beside the polychlorinated compounds also dioxins and furans substituted by bromine are of certain interest. Particularly, fuel additives in leaded gasoline („scavengers“, <1; 2>) and flame retarding agents in plastics may form precursors of (partly) brominated dioxins and furans (PBDD/Fs) <3>.

Sources of dioxins

Not being produced intentionally for any purpose PCDD/Fs are formed as by-products in a number of chemical processes (e.g. production of chlorophenols) as well as in almost every combustion process in presence of precursor compounds containing carbon, oxygen, hydrogen and halogen atoms <4>. Therefore, PCDD/Fs are being emitted by various sources in differing amounts and mass flows. Even small changes in

the design of the equipment or process or a switch to a different substance that is entered into the process may result in considerable alterations of the dioxins concentrations in the waste gas, waste water or solid residues. For this reason no accurate estimate of the concentration that is emitted by a specific plant from the results of several measurements on similar plants is feasible. In most cases the unknown temperature profile and catalytic effects which take place in a de-novo synthesis account for the great uncertainty of the estimate.

The literature frequently distinguishes between primary and secondary sources of dioxins (see for instance 5). According to this distinction, which is quite uncommon in air pollution control, a source entering dioxins, which formed during a process, into the environment at a later time and/or at a site that differs from the site of development with waste water or residual matter belong into the category of secondary sources. For example, anthropogenic PCDD/F which are prevented from being emitted by waste gas cleaning processes may remain in absorbents and still get into the food chain and increase human intake if they are not destroyed. Another typical example for a secondary source is the copper industry with the dioxins-containing red slag left as waste product <6; 7> or the re-suspension of deposited, PCDD- and PCDF-containing particles by motor vehicles or the wind (the latter effect is suspected to be one reason for differences observed in most countries between estimated emission freights and measured deposition rates <8>).

Toxicological Aspects of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) constitute a group of chemical trace compounds which have become ubiquitous in the environment during the last century. Since some of the 210 different isomers/congeners have proven to be highly toxic or adverse to human health much effort has been spent in research on formation mechanisms, methods of analysis, toxicology and emission prevention. Following the toxicological findings are summarised since they are the key to understand why PCDD/Fs are of special concern in environmental pollution control.

General

Of all 75 dioxins and 135 furans the toxicity of very few of these substances has been studied in greater detail. The most extensive studies concentrated on the most toxic congener: 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD).

Pharmacokinetic and metabolism

The bio-availability after oral intake depends on the dose and carrier as well as on the congener. The amount of dioxins and furans resorbed after oral intake is bound to lipoproteins in the blood. PCDD and PCDF accumulate mainly in lipid tissue, liver and breast milk and pass the placental barrier.

On the molecular level the present model of the effect mechanism assumes that PCDD and PCDF are initially bound to cytosolic receptors of aromatic hydrocarbons (Ah receptors). The complex arising from this initial binding becomes associated with the dioxin responsive DNA elements and leads to an expression of certain genes. This in turn provokes an increased protein biosynthesis and induces the action of various cytochrome-p450-dependent monooxygenases. The resulting biological effects are seen to a large extent as the consequences of the acute and chronic exposure to dioxins and furans. However, all toxic effects observed to date in vivo, particularly the high acute toxicity of PCDD and PCDF, cannot be explained by the effect on the Ah receptor.

The elimination of PCDD and PCDF requires the metabolic conversion to polar derivatives. The elimination half-life depends on the degree of substitution of the individual congeners. In the case of 2,3,7,8-TCDD it amounts to between 5 and 10 years in humans.

Acute and chronic toxicity

For the evaluation of the toxicity of dioxins and furans animal studies and observations in man after 22 industrial accidents are available.

Present knowledge of the toxicity of dioxins shows that all effects observed in animals can in principle occur in humans as well. Because of strong differences in the effects of PCDD and PCDF between species and types the transfer of threshold values from animal experiments to humans is difficult. From observations after accidents or from epidemiological studies of workers no threshold values can be derived because the individual exposure to dioxins and furans can be rarely reconstructed in retrospect in exact amounts and because in most cases mixtures of various substances were involved.

Animal studies on the toxicity

In animal studies similar effects were observed whose intensity depended however on the species, subspecies, sex, age, dose and the congener. An intoxication was found to manifest itself by weight loss, chloracne, lipid infiltration into tissue, hepatomegalia, liver necrosis, porphyria, inhibition of the metabolism of vitamin A, lipid and hormones (mainly corticoid, thyroid and sex hormones), endometrioses, haemorrhages, thymus recession and death after several weeks of latency.

The L.D.50 for 2,3,7,8-TCDD varies between 0.0006 to 0.002 mg/kg body weight in guinea pigs and 1 to 5 mg/kg body weight in hamsters.

For 2,3,7,8-TCDD evidence of toxic effects on the immune and reproductive systems as well as of carcinogenic effects has been obtained.

In the animal experiments intake was almost exclusively enteral or dermal. No long-term inhalation studies have been conducted.

Observations in humans

In human tissue 15 of the 210 individual compounds could be detected. In all of them chlorine was substituted at position 2,3,7 and 8. The concentrations accumulated with age. More than 1000 cases of intoxication provided evidence of the acute human toxicity of 2,3,7,8-TCDD-containing mixtures of substances.

The most frequent symptom chloracne depends on the dose. The occurrence of mainly on skin that is exposed to light was found to be subject to large interindividual variation. In addition, hyperpigmentation, irritation of the mucous membrane and eyes, nausea, vomiting, damages of the liver parenchyma, pathological changes in the peripheral nervous system (neuropathy), inhibition of the porphyrin and lipid metabolisms with increases of the concentrations of the very low density and high density lipoproteins (VLDL and HDL), triglycerides, total cholesterol and phospholipids were observed.

The possibility of diabetic problems became apparent from the results of a study of US soldiers exposed to Agent Orange which was contaminated with 2,3,7,8-TCDD. However, this possible effect needs further clarification.

Long-term epidemiological studies point to a tumour promoting effect of 2,3,7,8-TCDD. This effect appears to depend on the duration of exposure, dose and congener.

No final conclusion can be drawn, however, because of the length of exposure to mixtures of substances found in reality to date.

Specific toxicity

Reproductive toxicity

While experiments with mice receiving 2,3,7,8-TCDD produced teratogenic effects such as cleft palate and hydronephrosis, embryotoxic and fetotoxic as well as lethal effects were prevalent in other animals. In vitro similar changes on human palatinal epithelium cells during the critical gestation stage were observed as have been seen in embryonal palatinal epithelium cells of mice. To produce this effect in human cells 200 times higher doses were needed than the 1000 to 3000 ng 2,3,7,8-TCDD applied to mice. Epidemiological studies in Seveso and Vietnam yielded no clear evidence of a teratogenic effect in humans.

Cases of rice oil poisoning in Taiwan in 1979 showed damages of organs and tissue of exodermal origin (e.g. skin, mucous membranes, nails and teeth) as well as inhibition of the psychomotor and intellectual development among intrauterine exposed children. The contribution of dibenzodioxins and dibenzofurans to these damages could not be determined due to the exposure to mixtures of substances. A reduction of female fertility and of the weight of male reproductive organs as well as a reduction of the number of Sertoli's cells and inhibition of spermatogenesis are reported from experiments with animals.

Mutagenicity

The majority of in-vitro and in-vivo mutagenicity tests conducted to date produced negative results. Only in lymphoma cells of mice point mutations were observed.

Carcinogenicity

Studies of cohorts exposed to TCDD-contaminated mixtures yielded evidence of an increase of the total tumour rate as well as of the incidence of pulmonary tumours and sarcomas. The tumour incidence increased primarily 20 years after the exposure. The epidemiological studies did not provide evidence of a dose-response relationship. The

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conforming results of the studies and the agreement of the results with animal experiments speak for a connection.

In animal experiments 2,3,7,8-TCDD was clearly identified as potent tumour promotor. Because no direct interaction of 2,3,7,8-TCDD with genetic material in the cell was observed 2,3,7,8-TCDD is classified as non-genotoxic carcinogen.

Studies on humans yielded no clear connection between TCDD exposure and tumour promotion because the studied persons were always exposed to mixtures of various substances. Therefore, the commission that issues the maximum permissible workplace concentrations in Germany classified 2,3,7,8-TCDD as clearly carcinogenic in animal experiments under conditions similar to conditions that may occur on workplaces (group III A 2).

Immunotoxicity

A dose dependent suppressive effect of 2,3,7,8-TCDD both on cellular as well as on humoral immune response was found in animal experiments. In humans, too, a decrease of the T lymphocytes in general as well as of certain T lymphocyte sub-populations were observed after intoxication with 2,3,7,8-substituted dibenzofurans. In addition, serum concentrations of the classes of antibodies IgA and IgM dropped significantly.

Tolerated PCDD and PCDF intake

Because no studies of the dose-response relationship in humans are available, it is necessary to use data from animal experiments in order to make quantitative statements on the health effects. The high doses applied in animal experiments make an extrapolation of the results of the experiments to the low dose range to which humans are exposed necessary. Such an extrapolation is fraught with uncertainties because the mechanism of molecular effects of dioxins and furans is not yet completely understood.

Due to the inter and intra-species differences of the toxicity of 2,3,7,8-TCDD to various target organs, the Environmental Protection Agency (EPA) in the USA has not yet put out a tolerance limit for whole-body exposure. In assessing the risk of 2,3,7,8-TCDD the EPA came up with a virtual safe dose of 6 fg/kg body weight per day. This dose is based on the carcinogenicity of 2,3,7,8-TCDD and provides protection from toxic effects as well. It is not a limit that is connected with protective measures. In an

reassessment which is to be revised currently, the EPA is studying the health hazards posed by the present background concentrations.

International Toxic Equivalents

Because humans generally are not exposed to 2,3,7,8-TCDD alone but to mixtures of various PCDD and PCDF congeners toxicity equivalence factors are used in the assessment of the toxic effects in general. PCDD and PCDF congeners with chlorine atoms in the 2,3,7 and 8 positions are of particular environmental concern, especially the tetrachloro Dibenzo-p-dioxin congener 2,3,7,8-TCDD which was released from the ICMESA plant at Seveso in 1977. Of the 17 PCDD and PCDF congeners with chlorine in the 2,3,7 and 8 positions, 2,3,7,8-TCDD is the most toxic, and by convention is assigned a toxicity rating (called a Toxic Equivalent Factor, or TEF) of 1.0. The remaining 2,3,7,8-positional congeners are then assigned lower TEFs, relative to that of 2,3,7,8-TCDD (see Table 5). The toxicity of a mixture of PCDDs and PCDFs, relative to 2,3,7,8-TCDD, can be expressed then by multiplying the concentrations of those 2,3,7,8-positional congeners present in the mixture by their respective TEFs. The resulting products are called Toxic Equivalents (TEQs), with units identical to that in which the concentrations of the individual congeners are expressed. The TEQ of the mixture is obtained by summing the individual TEQs.

Though a number of toxicity rating schemes had been developed (Table 5), the NATO/CCMS (1988) scheme has been adopted internationally. This TEFs are termed as International TEFs, or I-TEFs. The I-TEFs for the seventeen 2,3,7,8-positional congeners of PCDDs and PCDFs are presented in Table 5: for all other congeners that may be present in a sample a TEF value of 0.0 is assigned. The summation of individual TEQs for a mixture of PCDDs and PCDFs is termed the International Toxic Equivalent or I-TEQ of the mixture.

Model	Eadon USA	Northern System	NATO/CCMS
Year of publication	1985	1988	1988
dimensional term	„Eadon-TEQ“	„NTEQ“	„I-TEQ“
Congener			
2,3,7,8-Cl₄DD	1	1	1
1,2,3,7,8-Cl₅DD	1	0.5	0.5
1,2,3,4,7,8-Cl₆DD	0.033	0.1	0.1
1,2,3,6,7,8- Cl₆DD	0.033	0.1	0.1
1,2,3,7,8,9-Cl₆DD	0.033	0.1	0.1
1,2,3,4,6,7,8-Cl₇DD	0	0.01	0.01
OCDD/Cl₈DD			0,001
2,3,7,8-Cl₄DF	0.33	0.1	0.1
1,2,3,7,8-Cl₅DF	0.33	0.01	0.05
2,3,4,7,8-Cl₅DF	0.33	0.5	0.5
1,2,3,4,7,8-Cl₆DF	0.011	0.1	0.1
1,2,3,6,7,8- Cl₆DF	0.011	0.1	0.1
1,2,3,7,8,9-Cl₆DF	0.011	0.1	0.1
2,3,4,6,7,8-Cl₆DF	0.011	0.1	0.1
1,2,3,4,6,7,8-Cl₇DF	0	0.01	0.01
1,2,3,4,7,8,9- Cl₇DF	0	0.001	0.001
OCDF/Cl₈DF	0	0.001	0.001

Table 5 Toxic equivalence factors (TEF) used in different model systems

While this system is broadly accepted for its practicability there are certain limits giving rise to criticism: First, non-additive interactions of effects which are not mediated by the Ah receptor remain unaccounted. Secondly, it should be noted that the TEQ scheme is a measure of the toxicity of a mixture of PCDDs and PCDFs, whereas the transport, fate and uptake of PCDDs and PCDFs following their release to atmosphere depends on congener-specific physicochemical properties such as vapour pressure, potential for degradation, bioconcentration factor, etc. The relative proportions of the 17 congeners included in the TEQ scheme may alter from the time of discharge to the eventual uptake at the point of exposure, depending on the fate of individual congeners in the environment. Therefore for the purposes of assessing environmental effects subsequent to the release, it may be necessary to consider the fate and transport of each individual congener rather than as an aggregated TEQ. Hence it should be kept in mind that a high

PCDD/F emission level (if given in I-TEQ) does not necessarily correspond to high immission or exposure levels.

Consequences

According to the toxicological assessment the entry of dioxins and furans into the environment and into the human food chain needs to be reduced as a precautionary measure. The WHO regional office in Europe has set a limit for the total daily intake of 10 pg 2,3,7,8-TCDD/kg body weight which takes into account the general toxicity. In Germany tolerable daily intake values of 1 to 10 pg I-TEQ/kg body weight are in effect for PCDD and PCDF. Most experts on effects tend to agree that the tolerated daily uptake of polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs) by the population should not exceed 1 pg I-TEQ/kg body weight per day. However, the average uptake of dioxins and furans by the population at present amounts to between 2 and 3 pg I-TEQ/kg per day and exceeds this limit. Babies may even consume as much as 150 pg I-TEQ/kg with the mother's milk during the period of breast feeding.

Although 95 % of the PCDDs and PCDFs are ingested by humans with the food, it is assumed that most of the dioxins and furans enter the food chain from the air. Despite of that predominant share of deposition from the air, other sources - e.g. milk cartons, coffee filters, wooden constructions treated with PCP etc. which may be major contributors in some cases to the intake of PCDDs and PCDFs - need to be studied as well. Most environmental experts agree therefore that there is an urgent need to reduce the entry of dioxins and furans into the environment in order to protect the health of people.

This notion receives added support by the latest evaluation of the carcinogenic risk posed by dioxins and furans carried out by the United States Environmental Protection Agency. In the tentative report on this latest assessment the limitation of the daily consumption of PCDDs and PCDFs to 0.01 pg I-TEQ/kg-d is proposed in order to keep the estimated additional risk to 10^{-6} . This new assessment will increase political pressure to implement efficient abatement measures in spite of the still ongoing scientific debate.

The reactions of the various member states of the European Union to these risk evaluations differ widely. In some countries, such as Austria, Sweden and Germany, an emission limit of 0.1 ng/m³ I-TEQ has been set or is scheduled to go into effect for primarily waste incineration plants. In some countries, such as Luxembourg and the Netherlands, emission limits have been passed for other industrial plants as well, while in Germany all plants have been asked to reduce the emissions of dioxins and furans as far as possible according to the principle of minimisation for carcinogenic and highly toxic compounds. In the United Kingdom emission limits can be set by the respective authorities in individual licences.

In order to meet this requirement first abatement measures have already been initiated in industrial plants in which relatively high emissions of dioxins were measured in some member states, e. g. in the course of the monitoring programme which is in progress in the state of North Rhine-Westphalia (NRW).

After passage of the European directive which limits the emissions of dioxins from hazardous waste incineration (HWI) plants, a second initiative by the European Union to reduce the emissions of dioxins from other industrial plants is necessary because the entry into the environment by some of these plants is far higher than that by HWI plants. To date no concerted efforts have become apparent in Europe to reduce the emissions of dioxins under the same requirements for all industries in the member states. Since the PCDDs and PCDFs are ubiquitous in the environment and are transported across borders (e.g. through deposition, rivers or products) permanent solutions can be achieved only by measures which have far-reaching impacts.

Technical abatement measures

As with other pollutants the task of reducing the entry of PCDD/PCDF emissions from production facilities into the environment is generally tackled in two steps. In a first step measures are being taken which either keep pollutants or substances from which pollutants are being formed away from the plant or which inhibit or may be even prevent the formation of pollutants during the production process. Such so-called primary measures include the

- substitution of substances or additives
- modification of the operation of the plant
- changes of the design of the plant

When all these measures have been exhausted additional secondary measures are being implemented such as the installation of equipment which separates the pollutants from the substance flows. In order to reduce the emitted concentrations of PCDD/PCDF to below 0.1 ng I-TEQ/m³ both primary and secondary measures will be needed in the majority of cases. This stepwise approach proved to be economic. In principle, tertiary measures are feasible as well such as

- improvement of the discharge conditions
- limitation of the operation to certain times
- relocation of the plant to a different site

but these methods will not be taken into consideration in this context.

The application of secondary measures for reducing the emissions of dioxins requires an evaluation of all technical aspects of the collection process. Following parameters need to be considered:

- the collection efficiency
- the consumption of energy and raw material, the spatial requirements
- the disposal of residues (the influence on other environmental compartments)
- the operating reliability
- the availability of the waste gas cleaning facility.

A number of different techniques have been developed for the reduction of the emission of dioxins by secondary measures. They can be applied individually or in various

combinations and modifications. Presently they are mainly applied in waste disposal plants.

Primary measures

Following causes lead to the emission of PCDD/PCDF:

- PCDD/PCDF are used as input material or additives in a plant and leave the plant again as emission,
- PCDD/PCDF are formed in a process from precursors such as chlorobenzenes, chlorophenols or polychlorinated biphenyls,
- PCDD/PCDF are being formed in a process by a de-novo synthesis.

In cases where a substitution is not feasible the destruction of the PCDD/PCDF or of the PCDD/PCDF precursors entered into the process or the prevention of the formation of PCDD/PCDF belong to the other primary measures which can be pursued.

In order to destroy the PCDD/PCDF which were entered into a combustion chamber the combustion conditions need to be adjusted accordingly. By variation of following parameters the combustion process can be optimised:

temperature

residence time

O₂-concentration (CO, ΣC)

turbulence

Temperature, residence time and turbulence need to be considered jointly. Experiments have shown that more than 90% of the PCDD/PCDF are decomposed at a temperature of 800°C and a residence time of 1.5 seconds. ↗ At a higher temperature a shorter residence time suffices.

In addition, a sufficiently strong turbulence is required. This demand makes sense but due to different technical designs of the facilities it is hardly quantifiable. Turbulence is a flow condition characterised by irregular motion; adjacent flows are rapidly mixed with each other. Because the kinematic viscosity of a gas increases with rising temperature, turbulence will slow down. The demand to operate at a high temperature takes account of only part of the circumstances and thus can hardly achieve the desired goal which is the destruction of the PCDD/PCDF. It is necessary to find the optimum temperature for the given residence time that produces enough turbulence.

In order to avoid a de-novo synthesis it is necessary for the waste gas to pass the favourable temperature range of 500 to 200°C as fast as possible <10, 11>. It is to be expected that at temperatures above 200°C the PCDD/PCDF concentration in the cleaned gas rises markedly <12>. Considerable reductions of the PCDD/PCDF emissions can be achieved through reduction of the temperature level in the cloth filter. Studies by Vogg have shown that PCDD/PCDF can be formed even in electrostatic precipitators when the temperatures are between 215 and 260°C <13>.

The favourable conditions for a de-novo synthesis can also be inhibited by reducing the organically bound carbon as far as possible; in combustion processes a low carbon monoxide concentration and a low particulate carbon content are the parameters that help to prevent a de-novo synthesis.

Moreover, the operating conditions play an important role. In firing systems soot blowing needs to be mentioned in this context; process modification may lead to a notable reduction of the PCDD/PCDF emissions. The use of pure oxygen as combustion gas has the effect of producing a lower waste gas volume flow so that the waste gas cleaning equipment can be dimensioned in a smaller size. But this does not lower the PCDD/PCDF emissions <14>.

Inhibition

Attempts were made to inhibit the formation of PCDD/PCDF by limiting the catalytic effect of the metal compounds present in the waste gas through the supply of chemical substances to the combustion chamber or right behind the combustion chamber. The main intention was to suppress the Deacon reaction which produces Cl_2 by oxidation of hydrogen chloride. The Cl_2 is responsible for the chlorinating reactions in the further course of the process.

For inhibiting the catalytic actions of compounds in the waste gas sulphur compounds and amines are used for example. The supply of SO_2 prevents the formation of PCDD/PCDF by an additional reaction path which converts elemental chlorine into HCl <15> .

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In one experiment a slurry of 42% triethanolamine with 1 to 2% fly ash from an electrostatic precipitator was added. A 65% reduction of the PCDD/PCDF concentration in the fly ash could be observed <16> .

In spite of successful laboratory and field experiments in which reductions of more than 50% <17> were achieved inhibition of the formation of PCDD/PCDF has not become a widespread practice; the method requires that additional substances be applied which are frequently a burden to the environment and may cause problems in the waste gas cleaning equipment.

Secondary measures

Dust collector

It is feasible to remove particle bound PCDD/PCDF with a dust collector. At temperatures below 200°C the collection of particle bound PCDD/PCDF prevails over the de-novo synthesis. In a garbage incineration plant a collection efficiency of 67% could be achieved at a temperature of 180°C <18>. The frequently high PCDD/PCDF content in the collected dust can be reduced to very low values by the thermal procedure proposed by Hagenmaier <19, 20> Experiments studying the dust removal from waste gases at high temperatures (>400°C) to prevent the de-novo synthesis which takes place on the surface of dust particles when the waste gas is cooled and reaches temperatures of 400 to 200°C remained relatively unsuccessful <12> . Aside from the technical problems of removing the dust from the waste gas of garbage incinerators at high temperatures certain heavy metal salts could not be removed from the waste gas in sufficient amounts because of their relatively high vapour pressure so that this path of reducing the PCDD/PCDF emissions is feasible only in individual cases. The chances of a de-novo formation of PCDD/PCDF in the precipitator diminish with decreasing temperatures and shorter residence times. At temperatures below 200°C no significant novel formation of PCDD/PCDF is to be expected <21>.

The removal of particle-bound PCDD/PCDF from the waste gas coming from an iron ore sintering plant with a cloth filter which was temporarily installed behind the electrostatic precipitator for test purposes yielded a reduction of the PCDD/PCDF of 36 to 73% <22>

Spray absorber

Spray absorbers followed by an electrostatic precipitator or a cloth filter have been in use for many years in garbage incinerators for the reduction of PCDD/PCDF emissions. The absorbent (lime slurry) is atomised in the spray tower. The gas is first absorbed by the liquid phase and then by the solid phase. A temperature drop below a lower limit should be avoided to prevent clogging of the cloth filter due to crystal water adhering to CaCl_2 . With this method PCDD/PCDF collection efficiencies of approx. 60% are feasible provided an electrostatic precipitator is installed for dust collection.

By adding coke made from bituminous coal in a quantity of up to 500 mg/m^3 a much higher PCDD/PCDF collection efficiency of approx. 90% can be achieved [18]

Using a cloth filter instead of the electrostatic precipitator increases the residence time because the gas flow must also pass the dust layer clinging to the surface of the cloth filter. With this approach PCDD/PCDF collection efficiencies of around 97% I-TEQ are feasible [18, 23] .

Scrubber

Simple scrubbers such as those used for the separation of HCl and HF in garbage incineration plants proved to have a low PCDD/PCDF collection efficiency due to the low solubility of PCDD/PCDF in aqueous media. Only the particle-bound PCDD/PCDF are separated [12; 24]

The addition of activated coke to the scrubbing fluid improves the PCDD/PCDF collection efficiency somewhat to a value of about 50%.

Flow injection process

Carbon containing adsorbents can be used for the collection of PCDD/PCDF even at temperatures around 120°C because of the low vapour pressure of dioxins and furans which allows adsorption at such temperatures. Generally coke made from bituminous coal or activated coke made from anthracite is used as adsorbent. Since the use of carbon containing adsorbents always requires fire protection measures [23], experiments were conducted to substitute carbon by another adsorbing material. The use of zeolitic adsorbents turned out to be rather successful. Zeolites are naturally

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occurring or synthetically produced, crystalline aluminosilicates with porous structure whose micropores are suitable for adsorption of certain gas molecules. Natural zeolitic adsorbents are presently applied in a fluidised-bed reactor which has been installed in a garbage incineration plant to clean the waste gas. In spite of the low concentrations in the uncleaned gas a PCDD/PCDF collection efficiency of approx. 90% was achieved. Zeolites are also used as adsorbents in flow suspension processes as well as in discontinuously or continuously travelling-bed processes <18>. However, in these processes coke made from anthracite or from bituminous coal is most frequently used as adsorbent.

The recovery of the spent coke of any of the two types by thermal treatment in a so-called Hagenmaier drum at 450°C for 2 hours in oxygen-free atmosphere is feasible. <19>

The flow injection process is based on the injection of finely grained coke stemming from anthracite or bituminous coal mixed with limestone, lime or inert material into the waste gas flow with a temperature of approx. 120°C so that the material is suspended in the flow rather homogeneously. The added material is transported in the flow to the subsequent cloth filter where it settles in a layer on the surface of the cloth filter. The inert material which is added in an amount of more than 80% serves to take up the heat that is developed by the exothermic reactions involved in the adsorption process. It helps to prevent ignition of the coke. In order to make better use of the adsorption material part of it may be recirculated.

Flow injection processes are being used in Europe in a number of waste incineration plants for the collection of PCDD/PCDF, HCl, HF and SO₂. Due to the necessary high amounts of inert material the residual matter left from the process are considerable. With this process a PCDD/PCDF collection efficiency of 99% can be achieved.

In an incineration plant for wood waste (wood blocks from wood chopping, wood shavings, grinding dust, wood waste with remnants of lacquer and glues) the dust emission could be reduced to less than 10 mg/m³ with a cloth filter. The collection efficiency of the cloth filter for PCDD/PCDF amounted to 33% on the average when lime alone was injected into the waste gas flow before entering the cloth filter. The

addition of coke stemming from bituminous coal to the lime increased the collection efficiency to 72%. In the dust that collected in the cloth filter the threshold values for dioxins contained in the German hazardous substances act were exceeded by two orders of magnitude. The average concentration of PCDD/PCDF measured in the uncleaned gas amounted to 6 ng I-TEQ/m³ <22>.

Fluidised-bed process with adsorbent recycling

With regard to process engineering the fluidised-bed process lies between the flow injection process and the fixed-bed as well as travelling adsorbent-bed processes. The flue gas passes through the grate from the bottom and forms a fluid bed of coke stemming from bituminous coal and inert material with a temperature of about 100 to 120°C. As in the case of the flow injection process limestone or lime can be used as inert material. However, the amount of coke can be higher than with the flow injection process. The adsorbent is separated from the flue gas in a dust collector (cyclone or cloth filter) and returned to the fluid bed. Generally the adsorbent can be recycled several times so that it is feasible to collect other acid components such as HCl, HF and SO₂.

While activated coke adsorbs mainly PCDD/PCDF and heavy metals, HCl, HF and SO₂ are removed by the lime-containing inert material. This is in contrast to the discontinuously or continuously travelling bed process in which the acid components of the waste gas are also collected by the activated coke.

The advantage of the fluidised-bed process lies in the high residence times of the adsorbent and in its better use.

For this reason it can be assumed that the collection efficiency is notably higher than with the flow injection process <25>

Fixed-bed or travelling-bed process

In a fixed-bed or travelling-bed adsorber granulated coke stemming from bituminous coal (with diameters of 1 to 4 mm) or anthracite coke (with diameters from 4 to 5 mm) are being used as adsorbent. The coke moves slowly quasi continuously or discontinuously from top to bottom while the waste gas flows in perpendicular or

opposite direction to the direction in which the coke is moved. Fixed-bed or travelling-bed reactors can be designed either as cross-flow or parallel-flow reactors. The activated coke takes up pollutants during its entire residence time in the reactor, which may be as long as 4000 operating hours. The time period during which an effective exchange of substances takes place is in fixed-bed or travelling-bed processes about 10 times longer than in flow injection or fluidised-bed processes. PCDD/PCDF are collected to a depth of 20 cm <26> . Frequently it is not distinguished between fixed-bed and travelling-bed. The bed of activated coke of cross-flow fixed-bed adsorbers is not moved during the time adsorption takes place. The spent coke is withdrawn and replaced by new coke. In travelling-bed reactors the coke bed moves continuously.

The coke layer can be up to 1.5 m deep. The gas flow approaches the coke-bed with a speed of about 0.1 to 0.5 m/s.

In order to minimise the disposal problems with the spent coke and to optimise the collection of various other pollutants, the fixed-bed or travelling-bed reactor is designed to consist of multiple beds. In this case the coke layer which is less loaded with pollutants can be burned, for example, in the combustion chamber, while the lower amount of coke carrying a high pollutant load is subjected to thermal treatment according to Hagenmaier <19>.

Very high PCDD/PCDF collection efficiencies of more than 99.98% can be achieved with the fixed-bed or travelling-bed adsorber <26> .

Certain safety requirements need to be observed for the operation of the fixed-bed or travelling-bed adsorber such as CO measurements for early detection of hot spots and initiation of suitable protective measures <27>

Catalytic decomposition of PCDD/PCDF

Measurements in waste incineration plants provided evidence that the catalysts used in the selective reduction of the oxides of nitrogen in the flue gas suppressed the formation of dioxins by 85%. This proved that a single, adequately designed catalyst can be used in the removal of the oxides of nitrogen and dioxins <28>. In order to prevent clogging of the catalyst with coarse fly ash particles as well as to avoid rapid wear and closing of the pores by ammonium sulphate the catalyst for the destruction of PCDD/PCDF is usually

applied after all other cleaning stages and even in the case the flue gas has to be reheated again. The advantage of the PCDD/PCDF removal by catalysts is that no difficult disposal problems of residual matter have to be solved because no residues are left from the process. On the other hand the catalyst lacks the capacity of removing as wide a spectrum of pollutants as activated coke.

The catalysts installed after the electrostatic precipitators and scrubbers in the waste incineration plants in Vienna Flötzersteig and Spittelau reduce the PCDD/PCDF to levels that comply with the limit of 0.1 ng I-TEQ without any problems <29> .

Electron irradiation processes

As has been shown in the experimental plant TAMARA of the Nuclear Research Centre in Karlsruhe PCDD/PCDF compounds in the flue gas of waste incineration plants can also be reduced by electron irradiation. A reduction of the PCDD/PCDF by 99% could be achieved. The decomposition products are simple organic acids; the pressure loss and the specific energy consumption of the process are low. No large-scale application of the process has become known to date. A comparison of various secondary emission reducing measures is presented in Table 6 <18, 22, 23>:

Collection process	Absorbent or adsorbent	Collection efficiency*%)
Dust collector	dust collected in a filter	70%
Scrubber	bituminous coal coke	50%
Spray absorber plus electrostatic precipitator	lime slurry	60%
Spray absorber plus electrostatic precipitator	lime slurry plus bituminous coal coke in a quantity of approx. 500 mg/m ³	90%
Fluidised-bed process	zeolite	95%
Catalytic process	(NH ₃ or H ₂ O ₂)	95-99%
Spray absorber plus cloth filter	lime slurry plus bituminous coal coke in a quantity of approx. 500 mg/m ³	98%
Flow injection adsorption plus cloth filter	bituminous coal coke (200 mg/m ³)	99%
Fluidised-bed process	bituminous coal coke (80 mg/m ³)	99.9%
Fixed-bed or travelling-bed processes	anthracite coke	99.99%

Table 6 PCDD/F collection efficiencies of technical abatement measures

(related to I-TEQ)

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