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

Formation of PCDD and PCDF – an overview[2]

Note by the secretariat

The annex to the present note contains a background paper on the formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) prepared by the secretariat of United Nations Environment Programme (Chemicals). The background paper is provided for the information of the Expert Group and is not intended to be exhaustive.

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[1] UNEP/POPS/EGB.1/1.
[2] This document has not been formally edited.

Formation of PCDD/PCDF

– An Overview

January 2003

D R A F T

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Formation of PCDD/PCDF – An Overview

Table of Content

Table of Tables

Table of Figures

1 INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) have never been produced intentionally but are unwanted byproducts of many chemical industrial processes and of all combustion processes. Enzymatic reactions that dimerize chlorophenols to PCDD/PCDF, *e.g.,* during composting or in sewage sludge, represent a biological source. However, in comparison to the chemical-industrial and combustion processes, biological formation seems to be negligible. In addition to the above mentioned primary sources, where PCDD/PCDF are formed in a process, PCDD/PCDF can be releases from so-called secondary sources (= reservoirs), *e.g.,* landfills, sewage sludge, contaminate sediments, *etc.*, where once formed in another process the contaminants re-enter the environment with or without human activity.

In industrialized countries, primary sources in the past of contamination of the environment with PCDD/PCDF were due to the production and use of chloroorganic chemicals, including the pulp and paper industry (through bleaching with chlorine gas). Once PCDD/PCDF were detected in emissions of municipal solid waste incinerators (MSWIs) (Olie *et al.* 1977), they became a key issue in the discussion of sustainable waste management and with time they became a management tool for any thermal process. A recent compilation of existing dioxin emission inventories (UNEP 1999) has shown that less than two dozens of countries have knowledge about the dioxin emission in their country. However, the compilation has also shown that the incineration of municipal, hazardous and medical waste is not always the sector with the highest dioxin emissions. Processes of the ferrous and the non-ferrous metal industries can be major emitters of PCDD/PCDF as well as the power generating sector, the manufacture of mineral products (especially when these plants are used for the co-combustion of hazardous waste) and others (NATO/CCMS 1991, Fiedler and Hutzinger 1996).

Since the first dioxin emissions have been identified and at any time when a "new" source has been discovered, attempts were started to reduce the emissions of these unwanted byproducts. In general, there are two approaches for release reduction: primary measures, which prevent the formation of PCDD/PCDF and secondary measures, which will remove and/or destroy PCDD/PCDF formed within a process or facility, to avoid release into the environment. The successful application of any of these two approaches requires understanding of the physical and chemical processes, which take place in any plant or process under investigation.

This paper briefly summarizes basic and major findings in the formation and options for the prevention of formation of PCDD/PCDF and/or their abatement [1].

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[1] Major parts of Chapters 1,2, and 4 are excerpts from: Literature Survey by Heidelore Fiedler (UNEP Chemicals, Geneva) and Hermann O. Nordsieck (BIfA GmbH, Augsburg). Work Package 2.2.2 in Research Project: MINIDIP - Minimization of Dioxins in Thermal and Industrial Processes: Mechanism, Monitoring, Abatement. Commission of the European Community, November 2001, ENV4 - CT97 – 0587

2   COMBUSTION AND OTHER HIGH-TEMPERATURE PROCESSES

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) are formed in trace quantities in combustion processes *via* two primary mechanisms (Gullett *et al.* 2001):

1- The so-called *de novo* synthesis in which PCDD/PCDF are formed from non-extractable carbon (C) structures that are basically dissimilar to the final product (PCDD/PCDF) (Stieglitz and Vogg 1987); and

2- Precursor formation/reactions (Dickson and Karasek 1987, Froese and Hutzinger 1996) via aryl structures derived from either incomplete aromatic oxidation or cyclization of hydrocarbon fragments.

More than twenty years of dioxin research has resulted in a multitude of papers dealing with parameters influencing the formation and/or the destruction of PCDD and PCDF. Today it is fair to say that despite all progress made in this field that THE formation mechanism is still to be discovered. Further, also there is still controversial discussion on mechanisms or conditions, which are dominating in the formation of PCDD/PCDF. Despite this somewhat unsatisfactory situation, chemists have long known that chemicals react along a limited number of elementary mechanisms. These basic mechanisms also apply to the formation of by-products such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans and high temperature processes as the incineration of all types of wastes, the generation of energy and heat from fossil and biomass fuels, the generation of metals and mineral products from natural resources or the recycling of ferrous and non.-ferrous metals from secondary resources.

2.1   Parameters Influencing Dioxin Formation

Basic chemistry books will show that very few if any, organic chemical present in any feedstock will survive direct contact with the flame. The principle relationship between the stability of an organic chemical, temperature and residence time is shown in Figure 1. As a general rule, it can be seen that thermally less stable compounds are destroyed at temperatures between 500 and 600 °C whereas thermally stable compounds, such as PCDD, PCDF or PCB require temperatures well above 800 °C to be destroyed.
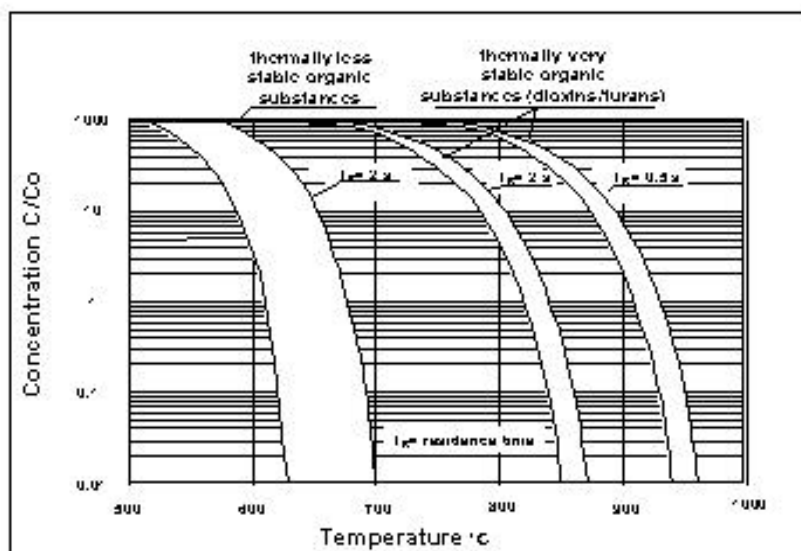
Figure 1:   Thermal stability of organic chemicals (taken from Hartenstein 2003)

2.2 Zone Model

Thus, the majority of the pollutants emitted *via* the stack from any thermal process must originate from chemistry occurring outside the flame.   Dellinger and Taylor (1998) established a "Zone Model" for combustors to classify types of reactions typical for each zone.   The main characteristics of the Zone Model are summarized in Table 1.   This Zone Model assumes that within each Zone the mechanisms of formation and destruction are relatively consistent.   Zone 1, the pre-flame zone, occurs at the front end of the device and is characterized by a wide range of temperatures, short residence times and low excess air conditions.   Because it occurs at the front end, this zone is not considered to be directly responsible for a very large fraction of emissions. Instead, it creates new reactants that react in further downstream zones.   The reactants formed are generated *via* several low energy pathways.   Zone 2, the flame zone, has high temperatures at which virtually all organic compounds present in the feed will undergo complete conversion to its most thermodynamically stable end-products, preferentially carbon dioxide (CO_2), water (H_2O), nitrogen oxides (NO_x), *etc*.   Although the flame zone does not generate significant organic precursors nor pollutants, it generates inorganic compounds such as NO_x and/or HCl, which in subsequent zones can be very important reactants.   Further, within the flame zone flow-paths of very poor fuel/air mixing to circumvent the hot flame can occur, which prevent complete destruction of organic molecules.   The high-temperature zone 3 is a chemistry-rich zone, where many types of high-energy unimolecular and bimolecualr radical-molecule reactions occur.   It is characterized by temperatures from around 600 to 1100 °C, residence times of a few seconds and both, oxygen-rich and oxygen-deficient regions.   Experiments indicate that the majority of the pollutant formation in this zone takes place in the oxygen-depleted pockets or poor waste-air mixing regions.   It is within this zone that most of the polycyclic aromatic hydrocarbons (PAH), heteroatom-containing polynuclear aromatics (PNA) and some higher molecular weight chlorinated hydrocarbons (CHC) are formed *via* radical-molecule, molecule growth pathways.   Zone 4, the quench zone, lies outside the combustion chamber; it is characterized by either rapid or gradual quenching of the gas

temperature. Residence times vary greatly, but can be as long as 10 s. Oxygen conditions also vary greatly from O_2-deficient conditions (due to combustion in upstream regions) to very O_2-rich conditions if air-in leakages occur. The quench zones have not be studied in much detail but especially laboratory experiments and pollutant's mass balance considerations strongly indicate that a large fraction of all types of combustion byproducts leaving the stack are formed in this zone. Zone 5, the surface-catalysis zone, exists at largely the same longitudinal point in the flue gas path as zone 4. However, zone 5 is fundamentally different from the other four zones as now, the effects on surfaces have to be considered. Reaction times can be he same as for zone 4 for entrained particles but can also last for several hours on deposited particles before re-entrainment occurs. The reaction times can be even longer if fixed surfaces are being involved in the reactions. As for the importance of the temperature: below 200 °C, there is not sufficient energy for activation of chemisorption and above 600 °C, most reactants will be desorbed. Whereas the formation of PCDD/PCDF in this zone has received quite high attention, the formation of other lipophilic pollutants has attracted less attention although their formation can be assumed. Most of the reactions taking place under these conditions, such as de novo synthesis of simple and more complex CHC, partial oxidation of hydrocarbons and CHC to form carbonyls, alcohols, organic acids, epoxides, *etc.* and nitration reactions to form a wide range of nitrogen-containing products. Most of these reactions will require the presence of a transition metal catalyst in addition to an adsorption site.

Table 1:   Dominant mechanisms of formation and destruction

No.	Zone	Reaction Conditions	Decomposition Mechanisms	Formation Mechanisms
1	Pre-flame	T = 200-1000 °C t_r<<1 s [O_2] 50 % excess air	Mechanism 1 mechanism 2 mechanism 3	Mechanism 1 mechanism 2 mechanism 3
2	Flame	T = 1000-1800 °C t_r<<0.01 s [O_2] 50 % excess air	Mechanism 3 mechanism 2 mechanism 1	Mechanism 2 mechanism 1 mechanism 3
3	High-Temperature Thermal	T = 600-1100 °C t_r = 1-10 s [O_2] = 50-100 % excess air	Mechanism 1 mechanism 2 mechanism 3	Mechanism 3 mechanism 2 mechanism 1
4	Gas Quench	T = 80-600 °C t_r- 10 s [O_2] = 3-9 %	Mechanism 1 mechanism 2	Mechanism 3
5	Surface Catalysis	T = 200-600 °C t_r<- 10 s to 10 min [O_2] = 3-9 %	Mechanism 4	Mechanism 4

Decomposition Mechanisms	**Formation Mechanisms**
1. Concerted molecular elimination	1. Concerted molecular elimination
2. Bond fission	2. Complex radical-molecule pathways
3. Bimolecular radical attack	3. Recombination and association mechanisms
4. Surface-catalyzed decomposition	4. Surface-catalyzed synthesis

The reaction pathways that are believed to occur in combustion processes are listed in Table 1: there are four destruction mechanisms of principal organic hazardous compounds (POHC) and four mechanisms to generate products of incomplete combustion (PIC) (Dellinger and Taylor 1998). The sequence of the mechanisms listed prioritizes the different mechanisms

according to the five principal zones.

2.2.1 Decomposition Mechanism 1 - Concerted Molecular Elimination Reactions

Concerted molecular elimination to form stable products is a unimolecular reaction and only involves the parent compound. In these reactions, the formation of PICs from a POHC is dependent only upon time, temperature and the Arrhenius parameters of the reaction. An examples of a 4-center process is the decomposition of pentachloroethane to tetrachloroethylene and HCl (where a fragile POHC is transformed into a thermally stable PIC. The decomposition of diethyl phthalate to phthalic acid and ethylene is an example of a 6-center reaction and should demonstrate that phthalates should not survive the conditions in an incinerator. These reactions normally have moderate activation energies, what means that normally temperatures below 700 °C and a gas residence times of 2.0 s are sufficient.

2.2.2 Decomposition Mechanism 2 – Bond Fission

Carbon-chlorine ruption is an example of bond fission, *e.g.* decomposition of carbon tetrachloride at temperatures of 700-800 °C. Bond fission is a significant mechanism only if the bond dissociation energy is higher than 85 kcal/mole. As a general rule it was found that

1. C-Br bonds are weaker than C-Cl bonds, which are weaker than C-H bonds in homologous molecules;

2. Increasing halogen substitution generally decreases the strength of the C-Cl(Br), C-H and C-C bonds;

3. When resonance-stabilized radicals are formed, bond strengths are drastically lowered.

2.2.3 Decomposition Mechanism 3 and PIC Formation Mechanism 2 – Bimolecular Radical-Molecule Reactions

Once destruction of the parent POHC has occurred and reactive radicals are formed, radical-molecule reactions will usually be the dominant pathway for POHC destruction and PIC formation. Hydroxyl radical are the dominant reactive species under most practical stoichiometric and oxidative conditions, while oxygen atoms (O) and hydrogen atoms (H) are the dominant reactive species under very fuel-lean and very fuel-rich conditions, respectively. Highly halogenated wastes can result in the generation of reactive halogen atoms, *e.g.* F•, Cl•, Br•, and I•.

2.2.4 Decomposition Mechanism 4 - PIC Formation Mechanism 4 – Surface-Catalyzed Reactions

These reactions have been intensively studied because of their implication in the formation of PCDD/PCDF. Studies of surface catalysis have shown that there may be more than one route of formation that include different roles for the surface. The proposed roles are:

1. A catalyst for condensation reactions of molecular, chlorinated PCDD/PCDF precursors: chlorinated hydrocarbons such as chlorophenols and chlorobenzenes are absorbed onto the surface where they undergo condensation reactions to form primarily PCDD and less amounts of PCDF.

2. A source of carbon as a reagent = de novo pathway: molecular oxygen and HCl react with the carbon in the flyash to form PCDD/PCDF in a complex series of steps;

3. A catalyst and/or mediative agent for chlorination of hydrocarbons: transition metals catalyze the chlorination of simple or more complex hydrocarbons that then act as a precursor for the formation of PCDD/PCDF

The dualism of surface-catalyzed oxidation has to be considered: metals can catalytically dechlorinate and oxidize organics at high temperatures as well as catalytically chlorinate organics at lower temperatures. The breakpoint between formation of PCDD/PCDF and its destruction will depend upon on the type of metal present, the nature of the site, the chlorine concentration, and the concentration of oxidizers such as O_2 and even NO_x.

2.3 Basic Consideration

The processes by which PCDD/PCDF are formed during incineration are not completely understood nor agreed upon. Most information about formation of PCDD/PCDF during combustion processes have been obtained from laboratory experiments, pilot-scale systems, and municipal waste incinerators (MSWI). Three possibilities were proposed to explain the presence of dioxins and furans in incinerator emissions (Hutzinger *et al.* 1985):
(1) PCDD/PCDF are already present in the incoming feed - *e.g.* estimates for municipal solid waste are 6-50 ng I-TEQ/kg waste - and are incompletely destroyed or transformed during combustion.
(2) PCDD/PCDF are produced from related chlorinated precursors (= pre-dioxins) such as polychlorinated biphenyls (PCB), chlorinated phenols and chlorinated benzenes.
(3) PCDD/PCDF are formed *via de novo* synthesis from chemically unrelated compounds such as polyvinyl chloride (PVC) and other chlorocarbons or are formed by burning non-chlorinated organic matter such as polystyrene, cellulose, lignin, coal, and particulate carbon in the presence of chlorine donors.

These basic findings led to the establishment of the "Trace Chemistries of Fires" (Bumb *et al.* 1980) and later on it was verified in a variety of thermal processes that PCDD/PCDF were present in all emissions - flue gases, bottom ashes, fly ashes, scrubber water. Although all three of the above mentioned possibilities can occur in large scale operations, recent results showed that options (2) and (3) dominate over option (1). The smaller probability as indicated in option (1) is due to the fact that with today's combustion and flue gas cleaning technologies and due to thermodynamic reasons, PCDD/PCDF are destroyed when incinerated at temperatures above 800 °C and sufficient residence times (*e.g.* 2 s as required in MSWI combustion). Today there is an agreement that the most important pathway for formation of PCDD/PCDF is when the flue gases are transported down the cooling zone at temperatures between 250 and 450 °C (Hutzinger *et al.* 1985, Bumb *et al.* 1980, Hutzinger and Fiedler 1993). Both, fly ash with its constituents - organic carbon, chlorides of alkali and earth alkali metals, metal activators, and catalysts (Stieglitz *et al.* 1989) - and dioxin/furan precursors in the gas phase play a role in the formation mechanism of PCDD/PCDF. In addition, parameters such as oxygen, water vapor, and temperature have to be taken into

account. In MSW-incinerators the preferred location to generate PCDD/PCDF are economizer and equipment for dedusting, *esp.* electrostatic precipitators (Vogg 1991, 1993, 1995).

Although much research was performed to study the formation of PCDD/PCDF in combustion processes, there is still no clear evidence, which mechanism is dominating and which parameters are important. There is some evidence that both, homogeneous reactions in the gas phase and heterogeneous reactions on surfaces of particles play a role to form these thermodynamically stable compounds (Hutzinger and Fiedler 1988, NATO/CCMS 1991). In addition, there are several indications that the mechanisms to generate PCDD/PCDF in the gas phase and in the particle phase are different. Within the following sections, some key-parameters are briefly summarized which have been identified to influence the formation of PCDD/PCDF in combustion processes.

2.3.1 Role of Temperature

Some early experiments were performed at high temperatures, when *e.g.* Rubey *et al.* (1985) studied the thermal stability of PCB and the formation of PCDF. The experiments clearly showed PCB (here: 2,3,4,4,5-pentachlorobiphenyl = 2,3,4,4',5-CB) are stable up to temperatures around 700 °C. With increasing temperatures, there is a decrease in the PCB concentration and an increase in PCDF formation. Preferentially, lower chlorinated PCDF (Cl_4DF) were formed with a maximum at about 750 °C. Further increase of the temperatures results in destruction of the newly formed PCDF.

Experiments to study the temperature dependence typically range from 180-550 °C and the formation of PCDD/PCDF in the heterogeneous phase at long residence times was evaluated. In 1986/85 using heated fly ash in a stream of air, Vogg and Stieglitz determined an optimum window for the *de novo* formation of PCDD/PCDF at temperatures 280-320 °C (Figure 2) (Vogg and Stieglitz 1986, Stieglitz *et al.* 1989, Vogg 1991). In subsequent experiments, Schwarz *et al.* found a second maximum around 400 °C for especially PCDF; for the PCDD the maximum was less pronounced (Figure 3) (Schwarz *et al.* 1990). As can be seen from Figure 3, PCDD were less stable than PCDF at higher temperatures. Such results are confirmed from large-scale operations, *e.g.* municipal waste incinerators, where more PCDF are present than PCDD.
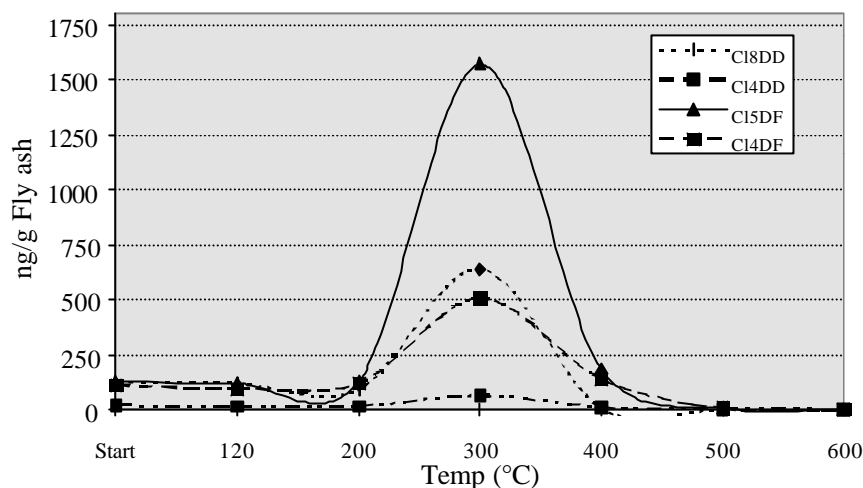
Figure 2.   Temperature dependence of formation of Cl_8DD, Cl_4DD, Cl_5DF, and Cl_4DF on fly ash (2 h annealing time) (Stieglitz *et al.* 1989, Vogg and Stieglitz 1986)
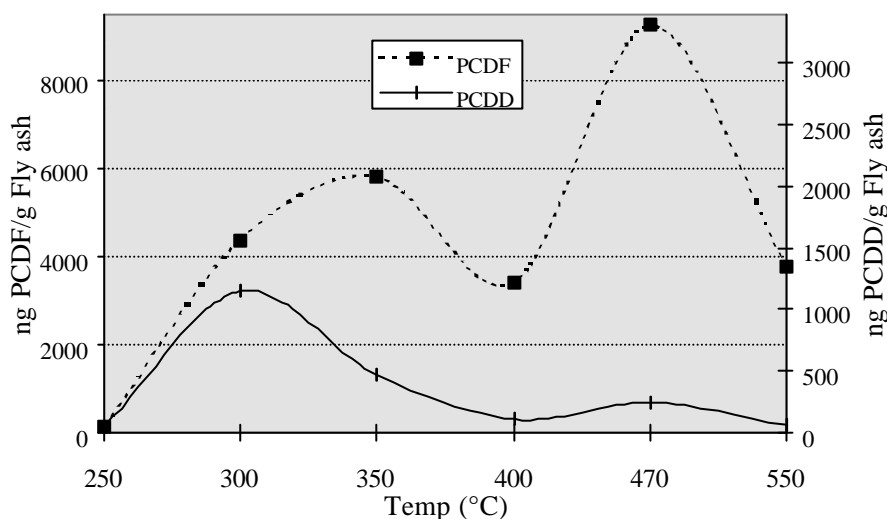
Figure 3:   Temperature dependence of PCDD/PCDF formation (2 h annealing time) (Schwarz *et al.* 1990)

2.3.2 Role of Temperature and Residence Time

For gas-phase reactions, Figure 1 also clearly shows that temperature is not the single limiting factor and the combination of two, *e.g.*, temperature and residence, is an important parameter for determining the efficiency of how organic substances are being destroyed. As a general rule: higher temperatures need shorter residence times of the gaseous molecules. As a consequence: it is up to the engineers to decide how to build and operate a plant.

2.3.3 Role of Precursors

Karasek and Dickson (1987) were the first to show that pentachlorophenol (PCP) serves as a precursor to PCDD when condensed over fly ash. From their experiments in a temperature range from 250 to 350 °C, the authors concluded that metallic constituents in the fly ash act as catalysts for the formation of PCDD. In more recent works, Milligan and Altwicker (1996a, 1996b) found that gas-phase 2,3,4,6-tetrachlorophenol was the most efficient precursor in PCDD formation. In addition, the newly formed PCDD were found desorbed in the gas phase and not adsorbed on fly ash. The measured conversions of chlorophenols to PCDD were in agreement with a model suggesting that two adjacent adsorbed precursor molecules dimerize to the product.

2.3.4 Role of Sulfur/Chlorine Ratio

In 1986, Griffin established a hypothesis to explain the formation of PCDD/PCDF as a result of the sulfur-to-chlorine ratio in the feed Griffin (1986). It is well known that combustion of fossil fuels like coal generates much less PCDD/PCDF than combustion of municipal solid waste. The hypothesis states that in coal there is a sulfur-to-chlorine ratio of 5/1 whereas in municipal waste the ratio S/Cl is 1/3. The latter ratio allows to form molecular chlorine according to the Deacon process catalytically driven by metals, *e.g.* copper. The molecular chlorine is considered to be responsible for the *de novo* dioxin formation according to the following equation (1):

$$CuCl_2 + \tfrac{1}{2}O_2 \rightarrow CuO + Cl_2$$
$$\underline{CuO + 2\,HCl \rightarrow CuCl_2 + H_2O}$$

$$2\,HCl + \tfrac{1}{2}O_2 \rightarrow H_2O + Cl_2 \qquad\qquad (1)$$
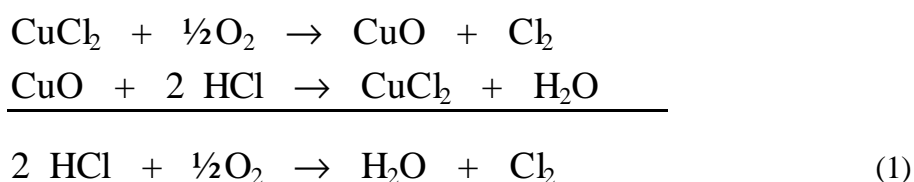
However, in fossil fuel with a surplus of sulfur over chlorine, molecular chlorine (Cl_2) will be "captured" according to equation (2) and formation of chlorinated aromatics does occur. In cases of fossil fuels, such as coal, crude oil, and gas, reaction (2) dominates over reaction (1).

$$Cl_2 + SO_2 + H_2O \rightarrow SO_3 + 2\,HCl \qquad\qquad (2).$$
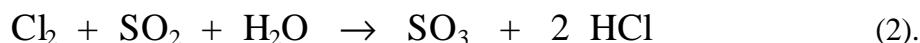
Similar S-to-Cl ratios as in coal are found in wood and sewage sludge.

In addition to the above mentioned theoretical considerations and observations from large scale operations, Lindbauer *et al.* (1992) found lower PCDD/PCDF concentrations when high-sulfur coal was added to the fuel. Recent results from Raghunathan and Gullett (1996) showed that in the presence of HCl relatively much PCDD/PCDF were formed; however upon addition of SO_2, the formation rate of PCDD/PCDF decreased. The authors determined a critical S/Cl ratio of 0.64. Further increase of S did not result in less dioxins and furans. As no congener- or homologue-specific correlation for the inhibition of dioxin formation could be established, the authors concluded that the depletion of molecular chlorine Cl_2, the active chlorinating agent, by SO_2 through a gas-phase reaction appears to dominate over the deactivation of the copper catalysts in fly ash (= inhibition mechanism) as previously reported (Griffin 1986).

2.3.5 Role of Chlorine Species

The influence of the chlorine species can be summarized that chlorination of aromatic com-pounds readily occur in the presence of Cl_2. Such substitution reactions do occur in the pres-ence of fly ash (heterogeneous phase, probably surface-catalyzed) as well as in the gas phase (homogeneous phase). At temperatures up to 250 °C, HCl does chlorinate chlorine-free dibenzodioxin, 1,2,3,4-Cl_4DD or toluene when adsorbed to fly ash. Without fly ash, Cl_2 was 4-times more efficient than HCl in chlorinating these compounds (Gullett *et al.* 1994). Gaseous chlorine (Cl_2) was found to be the most efficient chlorinating agent (Gullett *et al.* 1990).

2.3.6 Role of Oxygen

From laboratory, pilot-scale, and large scale experiments it was concluded that increasing oxygen concentrations from 0 to 10% resulted in increasing formation of PCDD/PCDF. The O_2 content pushes the Deacon reaction towards Cl_2-production and subsequently to formation of organochlorine compounds (Vogg *et al.* 1987). Under pyrolytic conditions (oxygen deficiency), dechlorination of PCDD/PCDF occurs at temperatures above 300 °C.

2.3.7 Role of Metals

When testing the efficiency of metals to catalyze formation of PCDD/PCDF, copper was found to be the most efficient compound (Stieglitz *et al.* 1989).

Recent studies have shown that small hydrocarbons such as acetylene and ethylene are readily chlorinated in the presence of cupric chloride or cupric oxide and HCl (Froese and Hutzinger 1993, 1996). The mechanism to reduce Cu(II) to Cu(I) and the oxychlorination of the newly formed Cu(I)Cl to reconvert to Cu(II)Cl_2 completes the catalytic cycle. The mechanism is very similar to the copper catalyzed Deacon reaction that converts HCl into Cl_2. With acetylene, however, the reaction is accelerated as the activation energy for the formation of Cu(I)Cl is reduced.

2.3.8 Role of Deposits and Other Parameters

Results from Kanters and Louw (1996) showed that in the absence of fly ash, deposits in the cooler ends of a municipal solid waste incinerator favor the formation of PCDD/PCDF and other PICs (products of incomplete combustion). The authors showed that catalytic processes caused by conditioned walls played an important role in the formation of PCDD/PCDF *via* oxychlorination at temperatures above 600 °C.

To complete this survey, some additional parameters should be mentioned that were reported to favor the formation of PCDD/PCDF in combustion processes. However, quantitative information is not available. From MSWI incineration it is known that humidity in the feed leads to poorer combustion conditions resulting in a poorer burn-out and higher concentrations of organic carbon in the fly ashes, thus favoring PCDD/PCDF formation. High copper concentrations in fly ashes generate higher PCDD/PCDF levels. An interesting finding is that the HCl concentration in the raw gases seems to be less important for the

formation of dioxins and furans than the content of inorganic chlorine in the fly ashes (Vogg 1991, 1993, 1995). Whereas the chlorine concentration in the gas phase is a result of the chlorine in the input, a saturation of the fly ashes seems to occur at relatively low chlorine concentrations; in other words: Once a saturation with Cl is reached on the fly ashes (occurring at relatively low chlorine input), formation of PCDD/PCDF occurs. As a result, high chlorine levels in the input do not increase the PCDD/PCDF concentrations in the emissions as the Cl concentrations on the fly ashes are independent on the chlorine in the feed. Most findings obtained in MSWI combustion can be transferred to other thermal processes.

3   WET-CHEMICAL PROCESSES

Historically, the first observations of contamination with PCDD and PCDF were from the manufacture of chlorinated phenols and their derivatives.   In particular, pesticides such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and pentachlorophenol (PCP) were highly contaminated with PCDD and PCDF.   High PCDF contamination was also found in polychlorinated biphenyls (PCB).

PCDD and PCDF can be formed in chemical processes where chlorine is involved.   The following processes have been identified as sources of PCDD and PCDF with a decreasing probability of generating PCDD/PCDF from top to bottom:

- Manufacture of chlorinated phenols and their derivatives,

- Manufacture of chlorinated aromatics and their derivatives,

- Manufacture of chlorinated aliphatic chemicals,

- Manufacture of chlorinated catalysts and inorganic chemicals.

For some of the processes the formation of PCDD and PCDF is implicit from the manufacturing process, *e.g.,* through direct chlorination (with chlorine gas) of phenols (in the presence of a metal catalyst) or through condensation of chlorophenates.   PCDD/PCDF contamination in chemicals that do not contain oxygen at the aromatic ring seems to result from purification processes such as distillation processes during synthesis or alkaline extraction.

The production of chlorine from alkali salts or brine utilizing graphite anodes has been shown to result in high contamination of the residues mainly by PCDF with lower concentrations of PCDD.   Contamination in the µg TEQ/kg range has been reported in electrode sludges.   For chemical manufacturing processes, the generation of PCDD and PCDF is favored if one or several of the conditions below apply:

- High temperatures (>150 °C)

- Alkaline conditions (especially during purification)

- UV radiation or other radical starters.

An example of a high-temperature process is the accident in Seveso: On July 20, 1976, a runaway exothermic process started in the reaction batch of a 2,4,5-trichlorophenol synthesis process at the ICMESA plant at Meda, Italy.   The temperature in the reaction vessel rose far above 200 °C, thereby producing a large amount of 2,3,7,8-TCDD (tetrachlorodibenzo-*p*-dioxin, 2,3,7,8-Cl_4DD).   Other results indicate that the critical temperature range starts at about 150 °C.

An example for the PCDD/PCDF formation potential under alkaline conditions present mechanistic studies on the formation of PCDD/PCDF from short-chain chloro-aliphatic compounds.   When trichloroethene (C_2HCl_3) is exposed to sodium hydroxide (NaOH) dichloroacetylene (C_2Cl_2) is being formed, which seems to be a key intermediate in the formation of PCDD/PCDF (NATO/CCMS, 1991).

Hydroxy radical donors such as Fenton's reagent ($FeSO_4/H_2SO_4/H_2O_2$) hydroxylate chloro-aromatic compounds such as chlorobenzenes and chlorinated biphenyls.   Finally, metal chlorides frequently used as catalysts in chemical synthesis processes may contain aromatic chlorinated compounds (*e.g.,* tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, octachlorostyrene, *etc.*) and thus precursors of PCDD/PCDF (NATO/CCMS 1991).

In pulp and paper, the presence of PCDD/PCDF results from the bleaching of wood (or other materials) with chlorine (gas) and/or chlorine derivatives.   Reducing the concentration of chlorine in the bleaching process by adding incremental charges of chlorine has reduced the amount of PCDD/PCDF formed.   To split the addition of chlorine has reduced the formation of unwanted byproducts including PCDD/PCDF.   The use of chlorine dioxide (ClO_2) in ECF (elemental chlorine-free) bleaching step(s) has considerable reduced the concentration of PCDD/PCDF in the final products (pulp, paper), in the effluents, and the sludges.   The presence of PCDD/PCDF in ECF bleaching may be due to impurities of Cl_2 in the ClO_2 (Fiedler *et al.* 1990).

4   DETAILED QUESTIONS

The topics addressed in the sections below are very heterogeneous, they address very different items, some of a very general nature, others very detailed and specific. Also the answers should be carefully considered and the nature of the recipient should be taken into account. There is a large difference in the needs of, *e.g.*, a party to a convention that has to fulfil reporting obligations by presenting its national emission inventory; a researcher who is interested in evaluating the latest detail in a possible chemical mechanism, an engineer with a task to find a technical or technological solution for a plant, a statistician to play with data and numbers and perhaps not much relevance to practical application or implementation. Finally, financial, technological, and occasionally geographical, social or ethical constraints may build up barriers higher than any scientific solution can imagine.

4.1   Inventories (National and Worldwide) and Data Branch Specific Data Together with Their Fingerprint

Presently, there exist about 20 national inventories, which report release of PCDD and PCDF into air. A few inventories address release to others vectors, such as water, land or with products and residues (UNEP 1999 and updated). Of the existing inventories, nearly all are from developed Northern hemisphere countries. Since that date, only two more inventory have been completed and published, namely for New Zealand (NZ 2000) and for Hong Kong SAR as a part of the People's Republic of China. The EU dioxin inventory has been updated in 2001 (EU, 2001).

Existing PCDD/PCDF inventories are not satisfactory as there is no harmonized methodology to compile inventories. Consequently, the existing inventories are neither complete nor comparable. Not all inventories consider all known sources, some examine only industrial sources and some are limited to a small subset of sources, there is no consistent means of handling and presenting data and some are out of date. This has led to the situation in which some inventories do not address potentially important sources of PCDD/PCDF, perhaps because there was insufficient information on a national basis, leading to the misleading conclusion that these sources are not significant and hindering the development of effective controls.

In all inventories annual releases are reported on a TEQ basis. However, presently, there are three TEF schemes applied in national inventory reporting: Nordic (one country; Sweden in its report; the other Nordic countries – Norway and Finland – do not specify but it can be assumed that they used the N-TEF scheme as well), WHO-TEF (one country - Japan since 1999) and I-TEF (presently still the majority of countries). The coming POPs Convention, however, will base dioxin and furan emission release inventories on the WHO-TEFs – and include the 13 coplanar and mono-ortho substituted PCB. Ion the other hand, the UN-ECE Convention, where are EU countries are signatories, utilizes the I-TEF scheme! This will cause a conflict in reporting requirements to governments. No country spends any effort to report or to collect information on non-2,3,7,8-substituted congeners. Once again, the estimates have an unknown uncertainty anyhow: there is an uncertainty on the

appropriateness of the emission factors applied and there may be an even higher uncertainty towards the activity rate in the country under consideration.

In the UK, there is an attempt to establish congener-specific emission data. The presentation given at DIOXIN'2000 by Alcock *et al.* (2000) left many open questions and such approach does not seem to be realistic.

Fortunately, the base for the US dioxin inventory is accessible as a EPA-report (US-EPA, 1997). Although coverage is not complete, emission patterns of various industrial processes are reported. An update has been published in recently (US-EPA, 2001).

One major drawback in inventory reporting is that many industrialized countries use a mix of national measured PCDD/PCDF data and emission factors from the literature. As these emission factors are given on an I-TEQ basis only, there is no chance for fingerprinting. And where is the need for fingerprinting in the inventories?

The aim of inventory making should be to have more countries reporting – also within EU Member States – and inventories should cover all known sources quantified on a TEQ-basis.

Guidance to establish dioxin and furan inventories were established by UNEP (2001) and UN-ECE (United Nations Economic Commission for Europe, EMEP/CORINAIR 2001).

4.2   Congener Profile and Toxic Congener Presentation Methods, PCA, HCA

Multivariate techniques have been used for the evaluation of quantitative structure-activity relationships (QSARs) and in toxicology to rank PCDD/PCDF congeners according to their toxic potency. The literature that was evaluated for this report does not address toxicological questions but deals with pattern recognition related to source recognition. Hierarchical cluster analysis (HCA) and/or principal component analysis (PCA) are mathematical tools that have been applied for evaluation of PCDD/PCDF. Such methods are easy to apply as the dioxin and furan analysis generally provides results in terms of 10 groups of homologues, 17 2,3,7,8-substituted congeners or as TEQ value, which is derived from the masses of the 17 2,3,7,8-substituted PCDD/PCDF congeners in relation to their toxicity factors. Therefore, each data set consists of several numbers, which can be placed into relation to each other or to a common denominator such as ΣPCDD/PCDF, TEQ, or others. In these ways, HCA and PCA have been used, *e.g.*, to compare sediment and soil samples with potential sources of release such as pulp mills, polychlorinated biphenyls (PCB) run-off or application of pentachlorophenol (PCP) in the timber industry (Fiedler *et al.* 1997). In this case like in others as well, where limited dataset were applied, both methods were able to distinguish between different matrices with known PCDD/PCDF contamination (*e.g.,* PCP, PCB, kraft pulp mill effluents) or other sources of environmental contamination (Wenning *et al.* 1993). In some instances, a specific PCDD/PCDF source could be correlated to an environmental sample, *e.g.,* the pattern of a U.S. brand of pentachlorophenate – and not he European brand - was found in sediment samples. Other common applications of relate soil or vegetation samples to combustion sources; *e.g.,* Schuhmacher *et al.* (1998), Grundy *et al.* (1997). Kjeller (2000) summarized the results of large datasets for source, spatial and temporal variation.

Early applications use PCA to study the formation pattern of PCDD and PCDF in for

example co-combustion of mixed waste plastics with coal (Ruuskanen *et al.* 1994). Later Gullett *et al.* (1998) evaluated the effects of combustion combustion parameters on the homologue profiles of PCDD/PCDF in pilot plants to simulate municipal solid waste incineration and co-combustion of coal. With multivariate analysis, 83 % of the variation of the profiles could be described and the operating parameters were found to have significant influence of the homologue profiles.

Despite these successful applications published in the scientific literature (and there are many more), there are some caveats to consider. The advantage of these multivariate methods should be used if there is good and valid data. However, PCA or HCA should not be used as the ultimate tools; they should not be over-engineered and over-interpreted.

When working with large datasets, the use of these methods looses its value as the samples will be spread all over the sheet. Difficulties also arise when the data have been generated by different laboratories with different performances towards sensitivity or selectivity. Also in different years, patterns may differ.

For low concentrations, the methods loose value: for example: if there is a low contaminated soil, which indicates a special pollution source, *e.g.*, due to evaporation. Although the optical inspection may give evidence that a source exists, *e.g.*, PCP-contaminated former timber site, "Kieselrot", *etc.*, the contamination may not be high enough to stand a "hard" mathematical evaluation and to dominate the overall pattern or profile.

It should also be taken in mind that PCAs with their complex set-up are hard to understand by laymen.

4.3   Gas Phase Condensation, Oxidation and (De-) Chlorination Reactions

When addressing formation pathways of PCDD and PCDF it should be taken in mind that most of these studies were performed at laboratory scale under well-controlled conditions to test a certain hypothesis. In full-scale operation and under routine conditions, these results should be put into perspective as the combustion conditions may be different and more complex reactions may take place due to less well-defined input materials, less stable experimental conditions, much longer operational times, and less well-maintained equipment. In real life, ageing of equipment, interferences by humans, mode of operation (*e.g.,* partial or full load) *etc.* may play role and result in the formation of unwanted byproducts such as PCDD/PCDF.

About 20 years of studying PCDD/PCDF formation mechanisms in combustion processes have proven the complexity of chemical reaction mechanisms involved. In terms of increasing complexity the following mechanisms have been identified (*e.g.,* Mätzing 2001):
−   Homogeneous gas-phase reactions of appropriate precursors;
−   Heterogeneous oxidation of carbon with PCDD/PCDF being formed as by-products even in the absence of organic precursors (*de novo* synthesis);
−   Heterogeneous reactions of gaseous precursors at (particulate) surfaces;
−   Heterogeneous and/or condensed phase reactions of particulate precursors;
−   Heterogeneous and/or condensed-phase reactions of both gas-phase and particle precursors.

Another further complication in the investigation of PCDD/PCDF formation mechanisms and the relative importance of gas-phase *vs.* heterogeneous reactions or precursor mechanism *vs.* de novo synthesis is given by the fact that there is an inherent dualism of formation and destruction of PCDD/PCDF, which occurs in the same temperature range and especially under real conditions in full-scale operation. The dualistic principle of formation and destruction is shown in Figure 4.
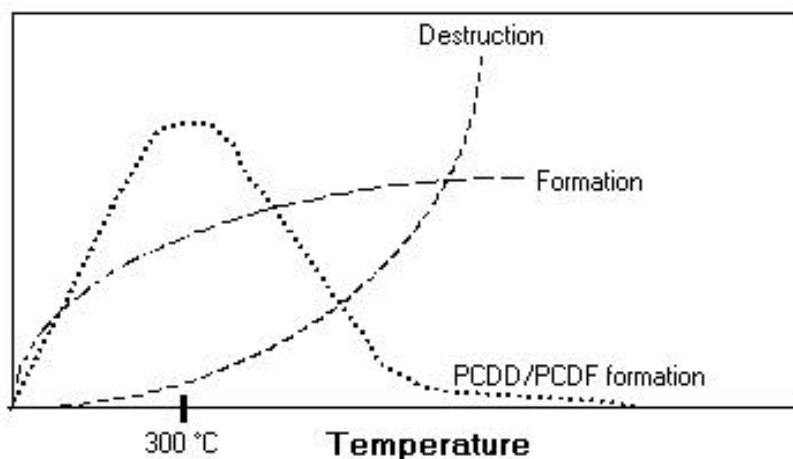

Figure 4:   The dualistic principle of formation and destruction of PCDD/PCDF (taken from Hartenstein 2003)

Shaub and Tsang (1983) developed a simple 13-step gas-phase reaction mechanism and a separate heterogeneous catalytic model of dioxin/furan formation to explain the concentrations of PCDD/PCDF found in the emissions of waste incinerators. They concluded that heterogeneous rates were much larger than homogeneous rates and that more rapid heterogeneous rates were necessary to account for the presence of the observed concentrations. Sidhu *et al.* (1995) found in their experiments with 2,4,6-trichlorophenol as precursor that the kinetic rates used in the gas-phase dioxin model by Shaub and Tsang were underestimated. These findings were confirmed by Huang and Buekens (1999). Finally, Grotheer and Louw (1996) verified in their study that homogeneous rates in the reaction mechanism proposed by Shaub and Tsang were indeed correct and that their experiments and those by Sidhu *et al.* could be interpreted in terms of a different gas-phase model incorporating phenoxy radical recombination as the key step in dioxin formation. Thus, none of the studies conducted have considered a detailed kinetic model with incorporation of reversible chemistry and must be considered preliminary. An assessment of present state-of-knowledge suggests that heterogeneous processes account for at least 2/3 of the PCDD/PCDF emissions from waste incinerators (US-EPA, 1998). Additional studies are needed to obtain more insight into these processes.

Correlations between chlorobenzenes and chlorophenols present as precursors in many combustion processes and concentrations of PCDD/PCDF in the emissions of waste incinerators have been studied. Although these two classes of precursors for PCDD and PCDF have been identified unambiguously, the relevant mechanisms that lead to the formation of these precursors are unknown (Kaune *et al.* 1998, Blumenstock *et al.* 1999).

Froese and Hutzinger (1993, 1996) demonstrated that PCDD/PCDF (and chlorobenzenes,

chlorinated phenols) can be formed from short-chain hydrocarbons such as acetylene, ethylene, or ethane, when exposed to an HCl-air mixture over various SiO_2/metal oxide surfaces. Although these experiments indicated a prominent role of surface-catalyzed reactions in formation of PCDD/PCDF, product yields were greatest at elevated temperatures (round 873 K) where homogeneous gas-phase reactions also occur. Furthermore, neither a plausible overall mechanism nor a detailed surface model was deduced from these empirical studies. Thus, key issues such as how these molecules adsorb on the catalyst, when and how chlorination occurs, how molecular growth proceeds, and why the products desorb from the surface remain unresolved.

Surface catalyzed molecular growth reactions form PCDD/PCDF. Two major pathways have been identified for the formation of PCDD/PCDF: precursor, *e.g.*, chlorophenols, and *de novo* synthesis whereby under the term "*de novo*" pathway all those reactions are considered where the formation of PCDD/PCDF originates from elementary carbon. In this reaction the specific formation pathway is not specified. In the other, the precursor pathway, formation of PCDD/PCDF starts from chlorinated benzenes or chlorinated phenols. These precursors may be present in sufficient quantities in the incoming feed, *e.g.*, in waste incinerators but may not be present in such amounts in other thermal processes that emit high concentrations of PCDD/PCDF. Detailed mechanisms had been proposed by Born *et al.* (1989, 1993) where PCDD formation occurs by phenoxy radical addition and Cl elimination at an *ortho* carbon of the phenol by forming an o-phenoxyphenol intermediate. Another formation route may involve a phenoxy radical-radical combination by oxygen-carbon coupling to produce the keto tautomer pf the phenoxyphenol. The radical-radical mechanism seems to be favored at lower temperatures. In both cases, the resonance-stabilized phenoxy-phenoxy radical is formed, followed by ring condensation either *via* 6-ring closure at another Cl-substituted ortho-carbon or *via* a 5-ring closure; the loss of a second Cl completes the formation of PCDD. Whereas the 6-ring pathway forms only one isomer (1,6), the 5-ring pathway produces a pair of isomers (1,6 and 1,9, Sidhu *et al.* 1995). The formation of PCDF follows a different mechanism whereby ortho-ortho coupling of phenoxy radical at unsubstituted sites form an o,o'-dihydroxybiphenyl intermediate *via* its keto-tautomer (Weber and Hagenmaier 1998); elimination of H_2O results in the PCDF.

The temperature dependence (300-900 °C) of the gas-phase formation of dichlorodibenzo-*p*-dioxin and dichlorodibenzofuran from 2,6-dichlorphenol and 3-chlorophenol has been studied in a flow reactor under pyrolytic, oxidative, and catalytic reaction conditions (Nakahata and Mulholland, 2000). The results show that at high temperatures the distributions of 1,6-DCDD and 1,9-DCDD from 2,6-dichlorophenol and 1,7-, 3,7-, and 1,9-DCDF from 3-chlorophenol were similar to the thermodynamically calculated distributions. However at low temperatures, the preferred formation of 1,6-DCDD and 1,7-DCDF demonstrated kinetic control. In the case of PCDD formation the results at lower temperatures are consistent with lower transition state barriers for 1,6-DCDD *via* either a five-member ring closure pathway alone that produces both isomers or a lower activation energy six-member ring intermediate pathway that produces exclusively the 1,6-DCDD. In the case of 1,6-DCDF formation, the results suggest that steric factors associated with geometries of phenoxy radical *ortho-ortho* carbon coupling play an important role in determining the distribution of DCDF isomers.

4.4   Metal and Particulate Catalyst Oxidative Carbon Breakdown, Condensation and (De-)Chlorination Reactions

The *de novo* formation mechanism has been studied in laboratory fixed-bed experiments only (Mätzing 2001).   The studies were carried out under well-controlled conditions to study the potential of PCDD/PCDF formation as a function of the inherent surface-catalyzing actions of the fly ashes or solid organic carbon in relation to parameters such as temperature, chloride or copper concentrations.   The basic result of all these studies is that PCDD/PCDF formation *via* the de novo mechanism just requires elemental carbon, gaseous oxygen and particulate chloride mixed together in a certain, quite narrow temperature range.   Other gaseous or particulate substances may affect the amount or the rate of PCDD/PCDF formed but there is no general agreement about the importance of certain ingredients.   However, it should be noted that the presence of copper has been recognized necessary for the formation of PCDD/PCDF as well.

4.5   Inhibition of Dioxin Formation by Means of *inter alia* Sulphur and Nitrogen Compounds

Addition of chemicals to prevent formation of PCDD/PCDF in incineration processes is a primary measure to reduce dioxin emissions from such processes.   Experiments on a labora-tory, pilot plant and full-scale basis have shown that nitrogen and sulfur containing chemicals are suitable inhibitors (Dickson *et al.* 1989, Addink *et al.* 1996). Pilot plant test have been performed (e.g. Lenoir, 1989). Few full scale applications are known, especially in Japan studies are on-going.   In Europe almost no application exists as the methods are not efficient enough to guarantee emissions securely below 0.1 ng I-TEQ/m³.

Ruokojärvi *et al.* (2001) studied the effect of urea as an inhibitor for reducing PCDD/PCDF concentrations in flue gases in a pilot scale plant.   Total PCDD/PCDF concentrations decreased by up to 74 %, the decrease being greatest for the highly (octa-)chlorinated congeners. Urea was added at a level of 1 % of the feed; the inhibition seemed to be independent of the fly ash particle size distribution.

Tuppurainen et al. (1998) reviewed mechanisms of inhibition of PCDD/PCDF formation and the destruction of these compounds.   The role of the so-called Deacon reaction has been well-established where the presence of sulphur in the feed material that enters a combustion plant will reduce the formation of PCDD/PCDF: in the presence of sulphur, the active agent (Cl_2) will be converted to HCl that is less likely to undergo aromatic substitution reactions to produce PCDD/PCDF or their precursors.   The second possible role of the sulphur is to react with the Deacon catalysts, *e.g.,* CuO to alter their ability to produce Cl_2; in other words to toxify the catalyst.   A third possibility will be that sulphur may sulphonate phenolic precursors, thus preventing chlorination by the Ullman reactions, or perhaps by forming the sulphur analogues of PCDD/PCDF, the dibenzothianthrenes and dibenzothiophenes, respectively.

Inhibitors injected into the combustion chamber or after the combustion chamber are strongly absorbed and react with active sites on the catalytic fly ash surface to form stable, inactive complexes with metallic compounds, thereby reducing or eliminating the catalytic activity of the metals or their oxides.   All molecules containing a lone electron pair, *.e.g.,* molecules containing nitrogen or sulphur, are suitable to form stable complexes with copper, iron, and

other transition metals. Also, alkaline chemicals can suppress PCDD/PCDF formation. The addition of limestone or calcium oxides prevents HCl decomposition and ammonia behaves similarly. The introduction of a suitable catalyst inhibitor should decrease the yield and change the distribution of PCDD formed on the fly ash. The addition of catalyst inhibitors containing amino- and hydroxy-functional groups to the fly ash surface greatly inhibited the catalytic activity of the fly ash. The best results have been obtained with organic amines (Lippert *et al.*, 1991), *e.g.,* ethanolamines, such as 2-aminoethanol and triethanolamine (Dickson *et al.* 1989), which have been used to block actives sites, probably through formation of copper nitrides.

4.6   Chemical and Catalytic Oxidation and Dechlorination of Dioxins

Catalytic oxidation, which results in the destruction of PCDD/PCDF to CO_2, H_2O and HCl in the flue gas are proven technologies to enable stack gas concentrations below 0.1 ng I-TEQ/Nm³. Weber *et al.* (1999) studied the decomposition of PCDD/PCDF with two commercially available V_2O_5-WO_3/TiO_2-based catalysts. TiO_2-based V_2O_5-WO_3 catalysts originally have been designed for the removal of nitrogen oxides (NO_x) by selective catalytic reduction (SCR) but it has been shown that they are very effective in the decomposition of PCDD/PCDF at the same temperatures as are used for the $DeNO_x$ reaction. In the last years, the commercial SCR catalysts have been optimized for the combined dioxin/NOx destruction. This was achieved mainly by increasing the oxidation potential of the catalysts by a higher vanadium content. In their study Weber *et al.* utilized a simplified testing procedures for the laboratory study of the catalytic destruction of chlorinated polycyclic aromatic compounds on commercial TiO_2-based V_2O_5-WO_3 catalysts in the temperature range 150-250 °C.

The results showed that both catalysts decompose these polycyclic aromatic molecules in the examined temperature range 150-310 °C with an efficiency of more than 95 %, the PCDD/PCDF (1,3,6,8-Cl_4DD, 1,3,7,9-Cl_4DD, 2,4,8-Cl_3DF) even to an extent of more than 98 %. However in the experiments carried out at 150 °C, 59-75 % of the PCDD/PCDF were found unchanged on the catalysts, while at 190 °C less than 7 % of the unchanged PCDD/PCDF were found on the catalysts after the experiments. Therefore, at temperatures below about 200 °C, polychlorinated aromatic compounds remain adsorbed on the catalyst for several minutes without being oxidized. At temperatures below 200 °C, the oxidizing potential of V_2O_5-WO_3 is obviously not sufficient to decompose polychlorinated aromatic compounds effectively.

Most of these aspects are relevant in the heterogeneous phase and are addressed in chapter 5. On a technical scale catalytic oxidation is commonly applied in air pollution control systems where catalysts to destroy PCDD/PCDF are used. On a technical scale, dechlorination under oxygen-deficient conditions are applied, *e.g.* in the Hagenmaier Trommel.

The thermal dechlorination process was originally developed by Hagenmaier *et al.* (1987). According to this hypothesis PCDD/PCDF in flyash will break down under the following conditions:

– Oxygen deficient atmosphere

– Temperature: 250-400 °C

– Retention time: approx. 1 hour;

– Discharge temperature of treated flyash: <60 °C.

The system (= Hagenmaier Trommel) is in full-scale operation at some German MSWI and in Japan. A pilot test plant in Japan has been described by Ishida *et al.* (1998). They used a reactor with a capacity of 500 kg/h; the reaction temperature stayed at 300-400 °C for 1-3 hours whereby the ash inlet and outlet temperatures were about 60 °C. N_2 gas was used to maintain O_2-deficient conditions. The results showed that PCDD/PCDF decomposition in the fly ash increases with increasing temperature of the fly ash. Optimal conditions were around 350 °C ash temperature and a residence time of 1 hour where 99 % of the PCDD/PCDF were destroyed.

4.7 Dioxin Reduction by Process–Related Measures, Influence of Oxidising/Reducing Conditions, Oxygen Level, Residence Time, Macro- and Micro-scale Mixing, *etc.*

Dioxin reduction starts with primary measures such as prevention. Therefore, when considering to build a new plant or start a process careful thoughts should be spend what to achieve and how to achieve. Considerations should be given to different technologies that achieve the same goal but do not release PCDD/PCDF (or other pollutants).

Also considerations, which are not dioxin-related may play an important role such as low waste technologies, energy efficiency, effluent-free processes (moving to closed circles), small stack volumes, *etc*. Many of these measures will result in lower PCDD/PCDF emissions although none of them is directly connected to PCDD/PCDF formation mechanisms.

Large plants may behave differently from small plants and laboratory experiments. And badly managed plants will have higher emissions than well-operated plants of the same type. For a large plant, it must be secured that operation from a permit point of view is guaranteed securely. Thus, very often primary measures such as pre-sorting of feed materials(especially in processes other than waste incineration), charging, geometry, *etc.* are accompanied by end-of-pipe technology to keep emissions safely below any legal limit value.

Especially in routine processes and in plants of all sizes, very basic requirements apply and have the large positive impacts. Such common place issues are:
- Ensure adequate operation and maintenance of the equipment at all times
- Keep all equipment in good working order and as designed operating conditions
- Train personnel with respect to understanding the implications of operating procedures
- Closely monitor and control the process
- Modify the existing equipment
- Avoid spills and accidental releases

4.8   Partition of Dioxins between the Gas and the Solid Phase, Vapour Pressure, Adsorption Isotherms, Diffusion Characteristics, Thermodynamic Data

This is a theoretical item with a practical application when designing and dimensioning equipment, *e.g.*, for flue gas cleaning after thermal processes. For some compounds, *e.g.*, less hydrophobic chemicals, the partition between particle and water phase may play a role.

Partition depends on several physical and chemical parameters and will vary case by case according to the environment and the chemical compound. For example, a particle-loaden environment will have more PCDD/PCDF adsorbed than a particle-free environment when the same congener will be forced more into the gas-phase than in the first case. Modelers call this fugacity. In any case and from a practical point of view, too much differentiation is not needed as no plant manager will run his equipment at the borderline to non-compliance. Therefore, order of magnitude estimates/numbers will be sufficient.

The practical and analytical needs to differentiate between particle and gaseous phases hardly exist at present as in present regulations, the total of the PCDD/PCDF emissions are limited. In most regulations, the emissions of PCDD/PCDF must be expressed as toxic equivalents.

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