

## **Destruction of PCDD and PCDF in refuse incineration plants by primary and secondary measures**

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### 1. Introduction

Since Olie, Vermeulen and Hutzinger /1/ detected traces of polychlorinated dibenzo-p-dioxins (PCDD) in the fly ash and flue gas of refuse incineration plants in 1977, intensive development work has started, aimed at understanding the mechanisms of formation and at developing effective countermeasures.

The ensuing public discussion was governed by the assumption that refuse incineration was the major source of the pollution of the environment by PCDD/F's and related substances. Thus it became politically expedient to establish statutory emission limits for refuse incineration. In some European countries allowance has meanwhile been made for this necessity with the introduction of a dioxin limit for the waste gas of

0.1 ng TEQ/m<sup>3</sup> (STP, dry)

as the toxicity equivalent (TEQ) as per the NATO-CCMS calculation proposal /2/.

### 2. Sources of the ubiquitous presence of PCDD and PCDF

PCDD/PCDF's can occur as undesirable by-products:

- in the case of incomplete combustion in the presence of a source of chlorine
- in industrial chlorochemical production processes.

In considering what sources play a part in the pollution of the environment with PCDD/PCDF's a distinction should be made between sources which are responsible for continuous emission of new dioxins into the environment, the "primary sources" and those sources which are fed by earlier dioxin emissions, the "secondary sources".

It is difficult to estimate the emission of dioxins from the various primary sources since the available data are inadequate. Whilst for flue gas emissions from municipal refuse incineration plants large quantities of data are available, there have not been, as far as we know, any measurements made of PCDD/PCDF emissions from household heating systems. There are also not enough data on PCDD/PCDF emissions in secondary raw material processing. Both in the case of secondary aluminium production and in the case of steel production with the use of scrap PCDD/PCDF emissions have been detected.

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An attempt to assess the emission of dioxins from various sources in the Federal Republic of Germany (primary and secondary sources) over the last 20 years /3/ suggests that PCDD/PCDF flue gas emissions from municipal refuse incineration plants (RIP) only make up a small percentage (< 5 %) of the ubiquitous pollution of the environment with dioxins.

For the contamination of humans with PCDD/PCDF's the potential already present in the environment already appears to be of greater importance than the current new emissions. While ten years ago the emission of PCDD/PCDF's into the environment most likely occurred mainly via products containing PCDD/PCDF's it must be assumed that the present-day continuous new emissions are mainly from thermal sources (combustion/incineration).

Municipal refuse has a PCDD/PCDF content of about 50 ng TEQ/kg. Translated into the flue gas produced during incineration this produces 10 ng TEQ/m<sup>3</sup> of flue gas. If one disregards the fact that via the filter ash a considerable percentage of newly formed PCDD/PCDF's is additionally discharged, with a flue gas emission of 10 ng TEQ/m<sup>3</sup> PCDD/PCDF input and PCDD/PCDF output would be balanced. With an emission limit of 0.1 ng TEQ/m<sup>3</sup> and with additional PCDD/PCDF destruction in the filter ash municipal refuse incineration would become a considerable sink for the PCDD/PCDF's already emitted into the environment.

Given this background, techniques which are developed for reliable adherence to a boundary value of 0.1 ng TEQ/m<sup>3</sup> in RIP's are not only of interest for refuse incineration plants.

### 3. Primary measures

#### 3.1 Incineration technology with reference to dioxin minimization

Irrespective of the low share contributed by refuse incineration in the ubiquitous presence of PCDD/PCDF's in the environment, in the interest of a demand for the minimization of PCDD/PCDF's and related substances the technology of refuse incineration has been subjected to critical review. Now that Nottrodt, Düwel and Ballschmitter /4/ have shown within the scope of input variations that expensive measures for refuse sorting (e.g. sorting out of PVC) do not have any influence on PCDD and PCDF concentrations during incineration, the primary measures still available are:

- combustion technology, i.e. design and operation of firing systems aimed at minimizing the "products of incomplete combustion."
- boiler technology, i.e. influencing of re-formation mechanisms.

Extensive tests in refuse incineration plants confirm the findings of laboratory tests according to which, by means of suitable combustion conditions defined by

- the combustion temperature
- the residence time at appropriate temperature level
- the degree of turbulence in the flame,

the PCDD/PCDF concentration in the flue gas leaving the combustion chamber can be reduced to below the detection level. The fact that, despite these combustion conditions, high dioxin and furan contents can again be measured in the raw gas at the end of the boiler is attributable to two formation mechanisms during the cooling down of the flue gas:

- formation from chlorinated precursor compounds in the gaseous phase
- formation by de novo synthesis on the ash grains.

Decisive significance is attributed to the latter mechanism by Hagenmaier /5/, the de novo synthesis taking place in the low temperature range from about 250 °C to 400 °C in the presence of chlorine and/or chlorides, oxygen and organic carbon. Studies on a fluidized bed firing system operated on the test centre scale showed the residual carbon content of the ash /6, 7/ to be an important influencing factor, so that the specifications for the refuse firing system must be expanded as follows:

- reduction of the fly ash load from the firing system
- lowering of the residual carbon content in the fly ash in the temperature range of the de novo synthesis; below this temperature level this residual carbon can bring about an adsorption of PCDD/PCDF's.

Refuse incineration in the parallel-flow firing system (Fig. 1) meets these expanded firing system specifications. As against conventional firing system conceptions, such as counter-flow and centre-flow firing systems, owing to the furnace configuration a flame swirl is produced above the combustion bed; as a result of which all the products of gasification are forced through the hot flame at high turbulence.

In Ludwigshafen RIP two new incineration lines have been installed which meet the above mentioned widened specifications, i.e. are characterized by low raw gas dust loads - on average 1.6 g/m<sup>3</sup> (STP) - with residual carbon contents of only about 1 % /8/. Raw gas sampling yielded for the PCDD and PCDF concentrations at the end of the boiler, under varying operating conditions, values between 0.2 and 1.5 ng TEQ/m<sup>3</sup> (STP, dry). The observed influence of the lowering of the O<sub>2</sub> level combined with the primary air pre-heating is made clear in Fig. 1 with reference to the example of the distribution of homologues.

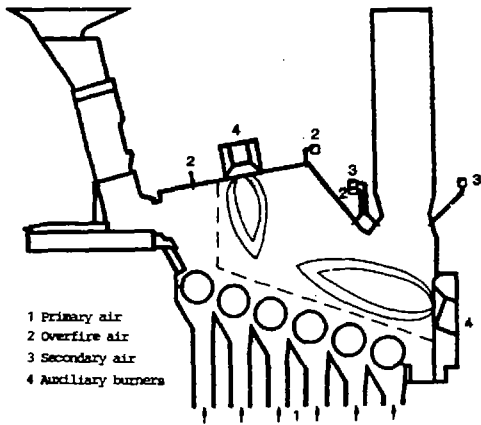


Fig. 1: Schematic representation of a parallel-flow firing system

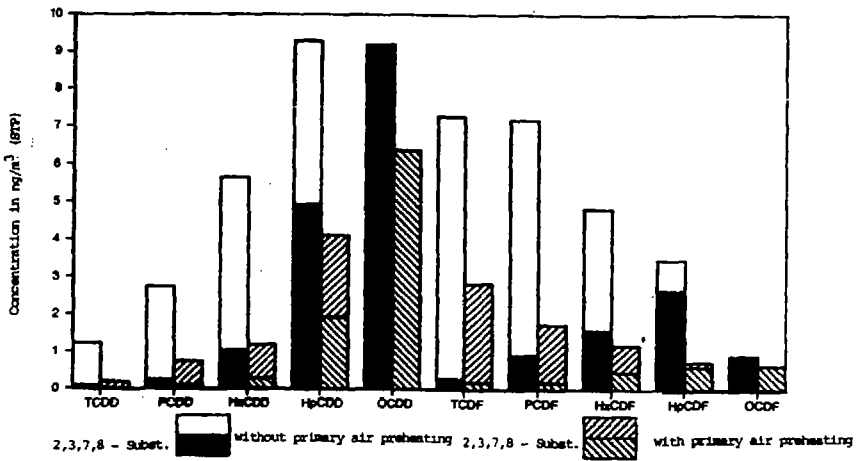


Fig. 2: PCDD/PCDF distribution of homologues at the end of the boiler in the Ludwigshafen RIP

### 3.2 Boiler engineering with reference to the lowering of dioxin levels

If the combustion and firing system measures have already proved effective, boiler-related measures - such as cleaning techniques or shock cooling by quenching - are currently still at the planning stage. The measures provided for in the refuse-fired boiler aim at suppressing the formation mechanisms occurring during flue gas cooling. A technology variant particularly attractive for the repair and modernization of old plants looks like being the use of inhibitors intended to counteract the formation process. Reduction rates of up to 95 % have so far been achieved in pilot plants / 9 /; however it has not yet been clarified what happens to the unreacted chemicals used.

A further interesting variant for the lowering of PCDD/PCDF emissions is put forward for discussion by Vogg et al. /10, 11/. In this case, by the addition of  $H_2O_2$  or  $O_3$  into the flue gas before the dust separator and at a temperature of less than 250 °C the re-formation mechanisms are to be suppressed. It also appears possible to carry out this chemical oxidation at temperatures above 250 °C in which case, in the presence of  $SO_2$ , partial  $SO_3$  formation can be expected. Vogg also reports that if an  $(NH_4)_2FeII(SO_4)_2$  solution were injected a remarkable reduction of the PCDD/PCDF concentration would be observed.

## 4. Secondary measures

Secondary measures aim at lowering the emissions of PCDD/PCDF's once they are formed to such an extent that limit values imposed are not exceeded. The possibilities described in sections (3.1) and (3.2) have, as far as our experience shows, not yet been sufficient to ensure adherence to this limit value.

For the secondary measures so far two fundamentally different technologies have suggested themselves:

- adsorption on a filtration material and subsequent destruction
- catalytic oxidation with direct destruction of the PCDD/PCDF's in the flue gas path.

### 4.1 Adsorption on activated carbon

Activated carbon is produced from materials with a high carbon content by driving off the volatile constituents and by possible subsequent activation. This process leaves behind a porous carbon structure with slight mineral occlusions and a high specific surface area which is suitable not only for adsorbing organic vapours such as benzene, toluene, chlorinated hydrocarbons and alcohols but in particular also PCDD/PCDF's /14/.

The usual raw materials used in the production of activated carbon are naturally hard coal and (Rhineland) lignite, the adsorbent obtained from the latter usually being referred to as A-coke or open-hearth furnace coke.

In the case of open-hearth furnace coke a distinction is to be made between two different grain size ranges which are brought into contact with the flue gas to be filtered in different ways: packed bed technique for an open-hearth furnace coke grain size of 1 - 5 mm and entrained flow adsorption (medium open-hearth furnace coke grain size: 40  $\mu$ m).

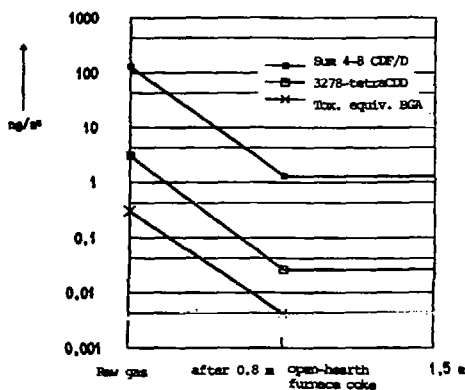


Fig. 3 PCDD/PCDF separation with open-hearth furnace coke in a 2,000  $\text{m}^3/\text{h}$  RIP pilot plant (acc. to Bewerunge/Ritter /6,12/).

Fig. 3 shows the results obtained in a pilot plant for the packed bed technique.

In the case of entrained flow filtration fine-grained open-hearth furnace coke, mixed with  $\text{Ca}(\text{OH})_2$  powder or  $\text{CaCO}_3$  powder is dispersed in the flue gas flow at temperatures between 110 and 160  $^\circ\text{C}$  and filtered off in the fabric filter. This technique has so far been used only in a hazardous refuse incineration plant in Schöneiche/GDR and it is reported /15, 16/ that with a mixture of anhydrous calcium hydrate and 2 - 5 % of open-hearth furnace coke, the PCDD/PCDF content in the flue gas is lowered from 1.5 - 4.2  $\text{ng TEQ}/\text{m}^3$  to  $< 0.1 \text{ ng TEQ}/\text{m}^3$ .

Common to the the packed bed and the entrained flow techniques is the fact that a residue containing PCDD/PCDF's is obtained. The North Rhine-Westphalian Ministry of the Environment [Ministerium für Umwelttechnik (MURL)] /13/ recommends that for its disposal this material be subjected to thermal after-treatment and then incinerated in the firing system of the respective refuse incineration plant.

#### 4.2 Catalytic PCDD/PCDF combustion

The technique of catalytic post-combustion is a common method of flue gas cleaning if organic trace substances are to be efficiently and cheaply eliminated from exhaust air/flue gas streams, i.e. oxidized to form  $\text{CO}_2$ ; the criterion of a low-cost method results automatically in comparison with non-catalytic (post-)combustion as the ignition temperature necessary for oxidation is considerably reduced by the presence of a suitable catalyst.

In the area of flue gas cleaning (flue gas is here to be defined as waste gas from combustion processes taking place with excess  $\text{O}_2$  as obtained in refuse incineration plants and fossil fuel-fired power stations) the usual process using the catalytic principle is that of Selective Catalytic Reduction (SCR) of  $\text{NO}_x$  by means of  $\text{NH}_3$ . The  $\text{TiO}_2$  catalyst materials used here mainly absorb  $\text{NH}_3$  which, by the withdrawal of oxygen from  $\text{NO}/\text{NO}_2$  (as well as from free  $\text{O}_2$ ) is oxidized to  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ; if  $\text{NH}_3$  is absent the same catalysts absorb  $\text{O}_2$  so that oxidizable substances (e.g.  $\text{C}_n\text{H}_m$ ,  $\text{CO}$ ) are combusted as a function of the catalytically lowered ignition temperature specific to the substance in question.

The economical application of catalysts for flue gas cleaning in the lower ppb range such as is necessary to achieve the value of  $0.1 \text{ ng TEQ/m}^3$ , has, however, not yet been described. Hagenmaier and Mittelbach report in /17, 18/ on the effectiveness of  $\text{DeNO}_x$  catalysts on a  $\text{TiO}_2$  basis for PCDD/PCDF oxidation in flue gases from refuse incineration plants at a catalyst service temperature

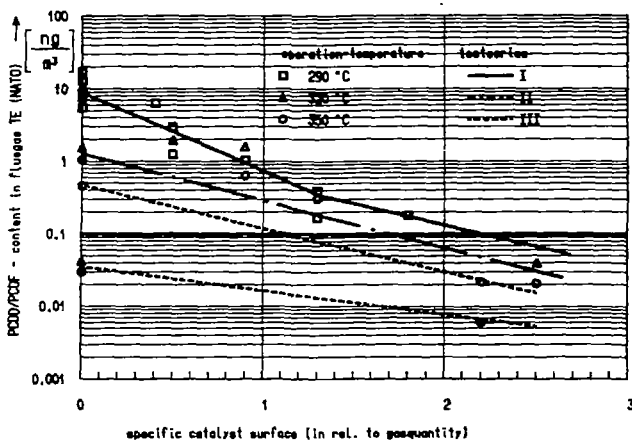


Fig. 4: PCDD/PCDF elimination on catalysts

of 270 - 350 °C. Fig. 4 shows the final contents achieved as a function of PCDD/PCDF initial concentrations and catalyst volumes. In the case of residence times of less than 1 second, with the initial values usual today final concentrations of less than 0.1 ng TEQ/m<sup>3</sup> can be achieved.

Making allowances for its residence time the catalyst is arranged after the conventional flue gas cleaning stage so that noxious substances such as ash, HCl, SO<sub>2</sub> now only pass into/onto the catalytic material in concentrations below the prescribed emission limit value. The particular advantages of this technology are:

- applicable immediately on an industrial scale without any further development work
- no PCDD/PCDF contaminated residues which would have to be handled within the refuse incineration plant operations
- simultaneously with PCDD/PCDF incineration, oxidative destruction of other products of incomplete combustion in the flue gases takes place - simple integration into the NO<sub>x</sub> reduction measure normally required according to the emission regulations by the increasing of the volume of catalyst.
- no additional safety measures necessary.

The second process feature mentioned is also extremely advantageous in the case of dioxin emission sources outside of the RIP area, namely when there is no incineration plant at the location of the flue gas cleaning equipment.

#### 4.3 Other measures

In conjunction with the intensive research being carried out on the subject of dioxin besides the above-mentioned techniques other approaches to lowering PCDD/PCDF emissions are being followed up, some of which have only been tested on the laboratory scale so far.

Further approaches are the refining of previous dust separation techniques. Besides the conceptual influence of having the lowest possible temperatures in the dust separator (< 250 °C) the following possibilities for exerting an influence are being examined:

Electrostatic precipitator:

HANAI et al. /19/ report on the increasing formation of numerous aliphatic and aromatic compounds from fly ash and HCl in a laboratory-scale electrostatic precipitator when the



electric power supply is increased. The cause is the formation of intermediate radicals which convert traces of carbon constituents of the fly ash to chlorinated hydrocarbons. In such a situation the use of electrostatic precipitators with a so-called voltage-pulse power supply gains in importance. With this technique the power supply can be throttled as a function of the electrostatic properties of the ash to 50 to 10 % of the non-pulsed power supply.

#### Aerosol separators:

Aerosol separators are ultrafine dust filters operated wet, i.e. using water at < 60 °C. Due to the increasingly stringent requirements for flue gas cleaning systems in RIP's such aerosol separators are being included in designs. Although PCDD/PCDF's are hydrophobic there are indications that this technique can be used for dioxin separation.

#### 5. Summary

The techniques and technical developments listed make clear that the aim to lower PCDD/PCDF emissions from RIP's to < 0.1 ng TEQ/m<sup>3</sup> is achievable. The solutions developed or being developed for this purpose render RIP's PCDD/PCDF sinks in the sense of substance cycles related to the national economy. Very probably the solution can, however, also be adapted to other dioxin emission sources.

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