

Dioxins in Waste Combustion – Conclusions from 20 Years of Research

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The Detection of Dioxins

In the year 1957 Sandermann, Stockmann and Casten published a paper on the pyrolysis of pentachlorophenol to look for new and effective wood preservers [Sandermann 1957]. They identified two pyrolysis products, the octachloro-diphenylendioxide and the respective tetrachlorinated compound. The first compound had no wood preserving properties, the second one looked promising. However, as the authors stated, 'since this compound caused heavy chloracne it did not invite to further investigations'.

Today we call this group of compounds dibenzo-p-dioxins (PCDD) and the tetrachloro compound they had synthesised, the 2,3,7,8 TCDD, became rather famous as 'Seveso dioxin'. One year after the Seveso accident [Buser 1982] Olie, Vermeulen and Hutzinger were the first to report about PCDD and the closely related group of dibenzofurans (PCDF) in filter ashes from three Dutch municipal solid waste incinerators [Olie 1977]. This finding initiated research activities around the world, but in several countries also violent public discussions concerning waste incineration.

The following description of dioxin research and its consequences for waste incineration will mainly focus on the contributions of Forschungszentrum Karlsruhe to disclose the formation path of PCDD/F.

Basic Formation Route

The research concentrated on reaction mechanisms which could be responsible for the formation of these compounds in waste incineration. Within 10 years the fundamentals of the synthesis of PCDD/F in waste incineration became clear. The main formation route was accidentally detected in 1985 during annealing experiments with filter ashes from a German waste incineration plant in a laboratory furnace for two hours under air atmosphere. As can be seen in Fig. 1 the concentration of PCDD and PCDF stayed almost constant up to 200 °C, however, at a temperature of 300 °C it increased approximately ten times [Vogg 1986]. At higher temperatures the PCDD/F concentration diminished again and the compounds were next to totally destroyed at 600 °C.

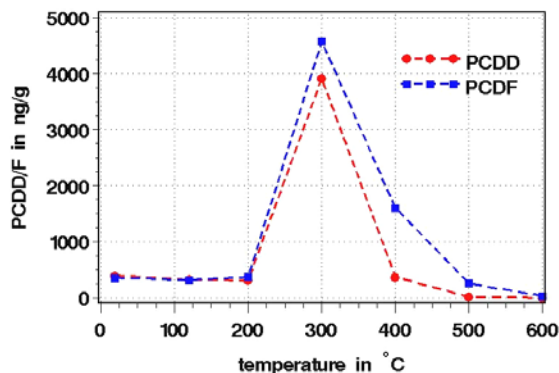


Fig. 1 Formation of PCDD and PCDF in fly ashes from waste incineration during annealing in air atmosphere

Detailed investigations of the reaction mechanism revealed within the next years that the basic reaction is a heterogeneous oxy-chlorination process [Stieglitz 1987 & 1989, Hagenmaier 1987, Hiraoka 1987, Vogg 1987 & 1989, Gullet 1990 & 1992]. The ingredients and conditions necessary to form PCDD and PCDF are

- products of incomplete combustion (PIC), e.g. soot,
- halogenides, mainly Cl^- , but also Br^- ,
- an oxidising atmosphere, and
- a catalyst, Cu salts being the most effective ones.

It was documented that along with the PCDD/F other chlorinated compounds like benzenes, phenols, biphenyls, and polyaromatic hydrocarbons were formed [Schwarz 1990]. Further experiments showed that the reaction starts to become noticeable at temperatures exceeding 200 °C (see Fig. 2) [Hunsinger 1994].

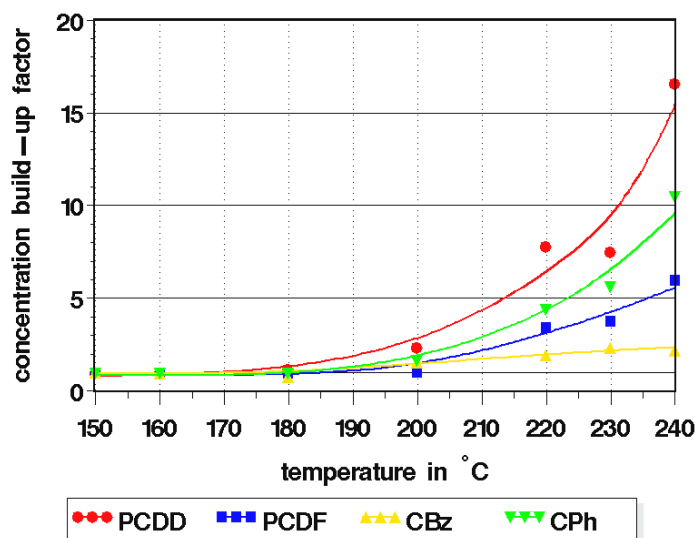


Fig. 2 Build-up factor of the formation of PCDD/F, chlorinated benzenes (CBz) and phenols (CPh) in the raw gas of a waste incineration plant as a function of the temperature

This slow reaction is called 'de novo synthesis' and takes mainly place in the dust deposits in the backend of the boiler and, if the dust removal system is operated at temperatures above 200 °C, also in this stage of the waste incineration plant [Vogg 1989]. Due to the high carbon content in the fly ashes back in the eighties the PCDD/F raw gas concentration downstream of the boiler was rather high, but the PCDD/F were almost totally adsorbed to the carbon particles in the fly ash. A good dedusting was a rather efficient removal step, but there were enough gaseous PCDD/F present which had to be taken care of by additional process stages like adsorption on charcoal [Dannecker 1990] or catalytic destruction [Hiraoka 1989]. These secondary measures and higher efforts in the abatement of all other pollutants were the main reason why in the early nineties the costs of waste incineration increased dramatically.

Head-end Techniques for Reduction

A careful analysis of the formation conditions revealed strategies to minimise the formation of PCDD/F by a number of so-called head-end measures which should in principle be effective without entailing additional costs [Vogg 1990 & 1991]:

- optimisation of the combustion control to achieve a better burnout and with that reduce the content of PIC in the raw gas, in the fly ashes and in the deposits inside the boiler,

- reduction of the gas velocity in the fuel bed to minimise the release of fly ashes from the bed,
- adequate cleaning of the boiler to minimise the deposition of fly ashes, and
- operation of the dust removal system at low temperature.

Such strategies are easily to accomplish even in existing plants and their application resulted in typical raw gas PCDD/F concentrations in the order of 1 ng(TE)/m^3 [Reeck 1991].

Influence of Cl and Br

Since halogens are essential for the formation of PCDD/F, halogen containing waste fractions like PVC or materials flame retarded by brominated compounds were blamed to enhance the PCDD/F formation in waste incineration. Extended experiments on the co-combustion of all kinds of waste plastics in the Karlsruhe TAMARA pilot plant for waste incineration pointed out that the addition of chlorinated materials does not increase the PCDD/F raw gas concentration provided a good burnout can be achieved. Experiments with high PVC input and also increased Cu inventory documented no significant influence of Cl or Cu on the PCDD/F raw gas level [Vehlow 1994]. Similar results were obtained in full scale experiments based on the TAMARA tests [Kerber 1994].

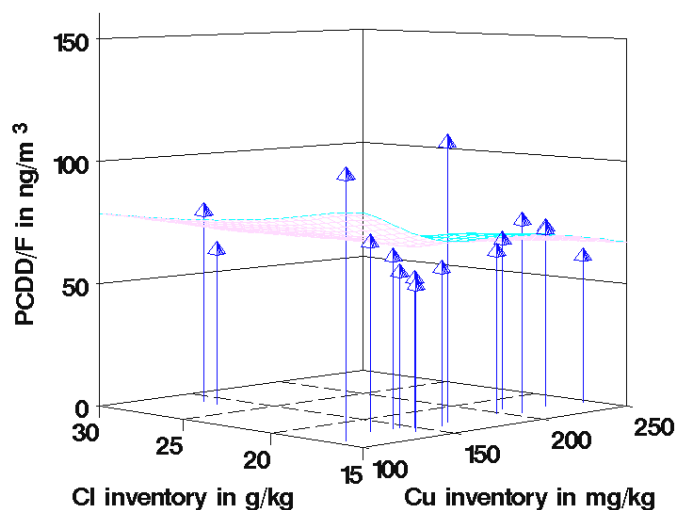


Fig. 3 Influence of Cl and Cu on the PCDD/F raw gas concentration in the TAMARA pilot plant

Another series of test campaigns in TAMARA focussed on the influence of Br on waste incineration. Test materials were flame retarded PUR and XPS foams and various types of plastic waste from electrical and electronic equipment (WEEE). All tests indicated that with increasing Br inventory in the waste the concentration of Br containing dioxins and furans increased. At the same time the concentration of purely chlorinated dioxins and furans was reduced. At a certain Br load, however, the concentration of mixed halogenated congeners levelled off. Mainly congeners with 1 or two Br atoms per molecule were analysed [Vehlow 1995 & 2000].

The compilation of all results in the left graph of Fig. 4 documents that the fraction of Br containing dioxins and furans can reach approx. 70 % of the total dioxin/furan inventory in the raw gas if the molar ratio of Br in the halogens exceeds some 30 %. The summarised concentrations of all halogenated congeners show a significant scattering but no correlation with the Br level in the waste (see right graph in Fig. 4).

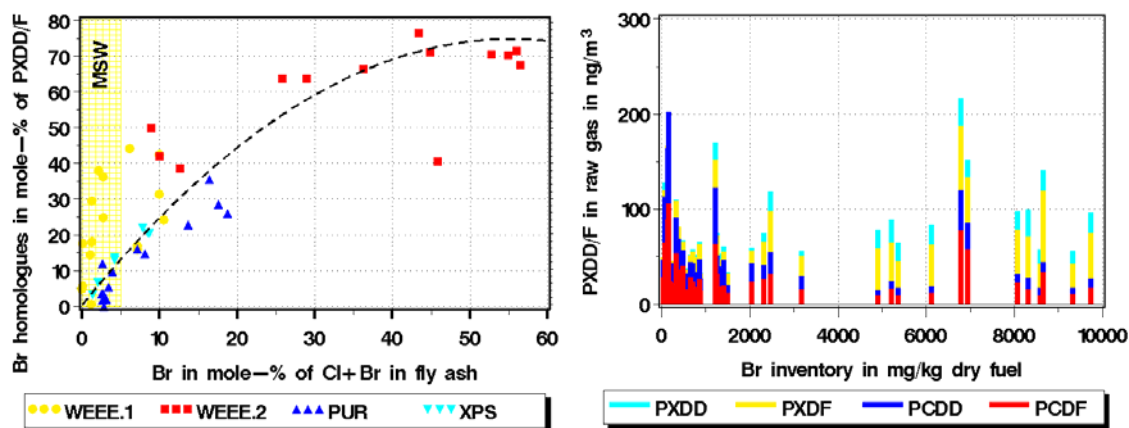


Fig. 4 Br containing dioxins and furans (PXDD/F) as a function of the molar Br share of halogens (left graph) and PXDD/F raw gas concentrations as a function of the Br inventory in the TAMARA pilot plant

These results, too, were recently validated in a full scale test but the results have not yet been published. All these results on the influence of halogens and catalysts give evidence that at normal combustion conditions the amount of PIC, of available carbon species, controls the formation of PCDD/F rather than other parameters and components.

Influence of Sulphur

Griffin published in 1986 the hypothesis that high sulphur dioxide concentration in flue gases suppresses the formation of PCDD/F in thermal processes by the reduction of elementary chlorine which is an essential intermediate reaction partner in the PCDD/F synthesis [Griffin 1986]. Experimental studies by various authors confirmed a low PCDD/F formation when burning fuels with high S/Cl ratios [Hagenmaier 1989a, Gullett 1992a, Lindbauer 1992].

From the point of view of the slow de novo synthesis an immediate influence of the SO_2 concentration in the flue gas is not very likely. To investigate this influence three parallel operated sampling trains were installed in the gas duct of a full scale waste incinerator which were controlled by the reading of a SO_2 monitor and were alternatively operated if the SO_2 concentration was below 150, between 150 and 250 or above 250 mg/m^3 (see left graph in Fig 5) [Hunsinger 2004]. The right graph in the same figure compiles the SO_2 concentrations analysed during one day.

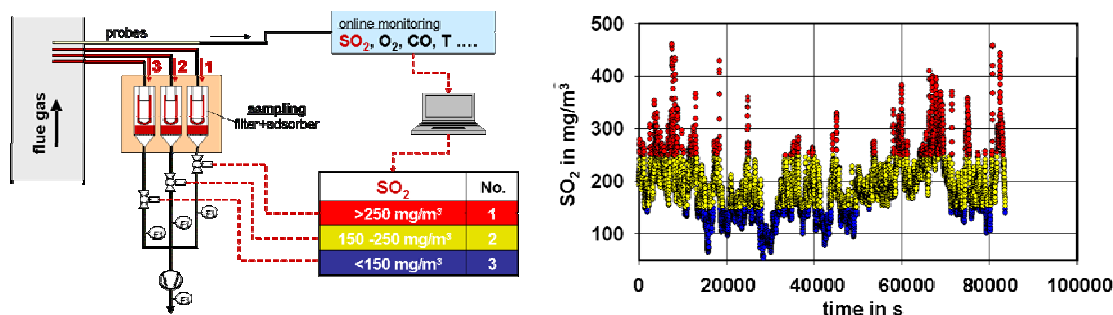


Fig. 5 PCDD/F sampling at 3 different levels of SO_2 (left graph) and SO_2 fluctuation during one day in a full scale plant (right graph)

Four sampling periods of 24 hours each were conducted which showed no significant influence of the SO_2 concentration on the PCDD and PCDF raw gas concentrations as can be seen from the results compiled in Fig 6.

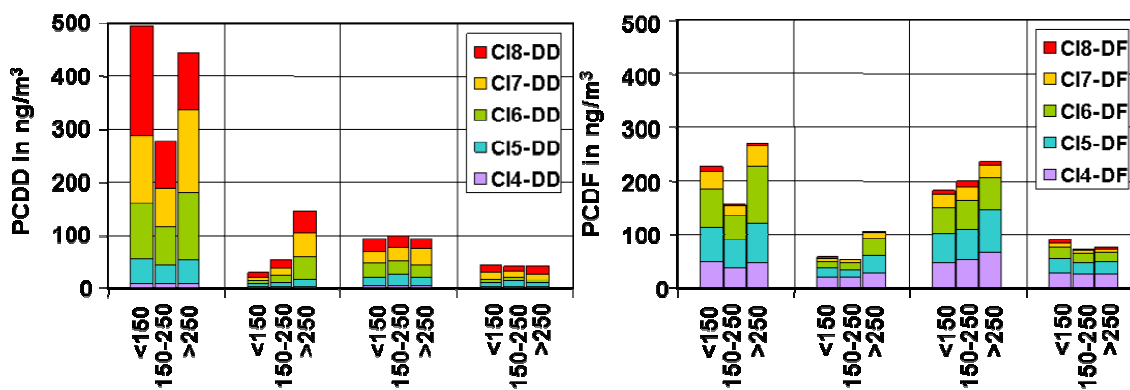


Fig. 6 PCDD (left graph) and PCDF concentrations analysed in four 24 h samples at 3 different SO_2 levels

The tests verify that the PCDD/F are not synthesised on the dust particles on their way through the boiler but that the reaction takes place in the bulk of the boiler deposits.

Further experiments were conducted in TAMARA with a long term elevated S/Cl ratio established by permanent sulphur addition to the fuel. The high SO_2 concentration in the raw gas caused an exchange of chlorides by sulphates and the fly ash chloride concentration dropped from the typical approx. 20 % down to < 0.3 %. It needed 15 hours of sulphur addition before this drastic reduction of chlorides in the fly ashes showed an effect: the PCDD/F concentration in the flue gases dropped slowly down by approx. 40 %.

The conclusion from these investigations is that in a waste incineration plant only a long term permanent change in the S/Cl ratio has an influence on the PCDD/F formation since it needs a long time before the chemical composition of the bulk material in the boiler deposits adopts its equilibrium to the changes in the fuel and/or in the gas phase.

Formation Inside the Combustion Chamber

The de novo synthesis is a complex system comprising parallel formation and decomposition reactions [Stieglitz 1988, Hagenmaier 1989]. This implies that even at high temperatures PCDD/F are formed, however, their lifetime is short and their analysis is difficult. The TAMARA pilot plant allows the sampling of flue gas inside the combustion chamber at a distance of few centimetres above the fuel bed. Such gas sampling experiments revealed a bi-modal distribution of PCDD/F in the gas with peak concentrations in those areas where still oxygen exists and the amount of organic compounds is already significant (see left graph in Fig. 7). The PCDD/F formed inside the furnace are characterised by a PCDF/PCDD ratio in the order of 10 [Hunsinger 2002].

These PCDD/F formed in the fuel bed are almost totally destroyed at the end of the post combustion area in the first flue. A quantification of the experiments is given in the right graph of Fig. 7. The concentration of the PCDD/F formed in the furnace went down by one to two orders of magnitude at the end of the first flue. Inside the boiler a new formation by the de novo synthesis takes place. These newly formed congeners have a PCDF/PCDD ratio in the order of one.

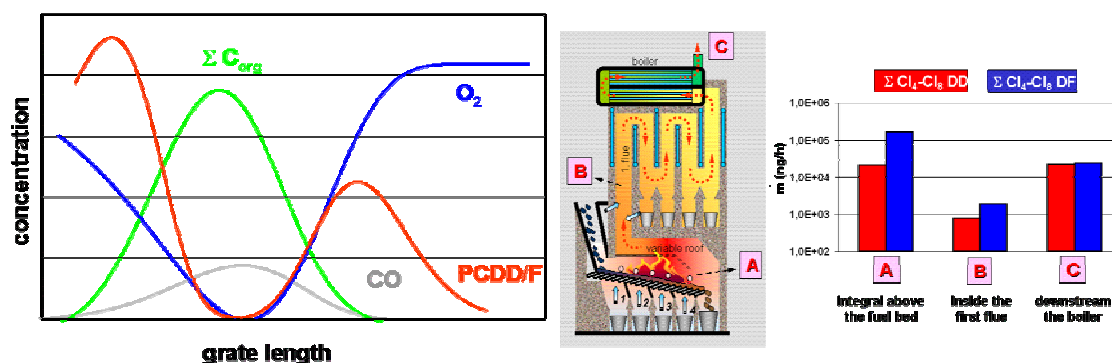


Fig. 7 Concentration profiles of oxygen, organic carbon compounds, CO and PCDD/F along the grate (left graph) and PCDD/F mass flow above the fuel bed, inside the first flue, and downstream of the boiler in the TAMARA pilot plant

Non-stationary Combustion Conditions

The above reported situation reflects stationary combustion conditions and a good combustion control. However, if the burnout in the combustion chamber is not complete, the PCDD/F formed in or above the fuel bed are not destroyed. They show up in the raw gas downstream of the boiler and increase the PCDD/F level there. Such situation can be recognised by a high PCDF/PCDD ratio. At the same time other PIC – e.g. soot – are deposited on the boiler walls and tube surfaces and are responsible for elevated PCDD/F during a certain period of time. This ‘memory effect’ has to be avoided and that means that non-stationary combustion conditions like failures in the control, in waste or air supply, and fast changes in the heating value of the waste need to be identified as soon as possible. A good indicator should be the CO concentration in the flue gas which is an unspecific indicator, but points out that the combustion is for any reason not complete.

A regular non-stationary event is the start-up and the shutdown of a waste incinerator. It has been experienced that during this phase much higher PCDD/F emissions can occur [Gass 2002]. The start-up has carefully been investigated in TAMARA which was first heated up with gas and wood chips before after 15 hours - when the gas temperature exceeded 850 °C in the post combustion area - waste was fed in.

The tests, the results of which are visualised in Fig. 8, were conducted analysing the major gas parameters online and taking consecutive raw gas samples of two hours each. The samples were analysed for soot and PCDD/F. The left graph of the figure shows a soot peak of 18 mg/m³ at the early beginning when the gas burner was started in the cold plant. In the second sample only approx. 2 mg/m³ were found and the following ones showed concentrations below 1 mg/m³. The PCDD/F measurements document a peak of 22 ng(TE)/m³ which starts four hours after the soot peak. The PCDD/F level in the raw gas decreased in the next sampling period down to approx. 10 ng(TE)/m³ and stayed there for another 12 hours. This implies that also for the first three hours of waste combustion no change in the PCDD/F concentration was detected before the PCDD/F concentration dropped down to ca. 4 ng(TE)/m³, a value which is typical for TAMARA raw gas at normal combustion conditions.

This behaviour can be explained by the temperature profiles in the boiler which are depicted in the right graph of Fig. 8. It has been pointed out above that the PCDD/F formation by the de novo synthesis has its peak around 300 – 400 °C. The shaded areas in the graph indicate the surface of the boiler within a temperature range between 200 and 500 °C. It is obvious that the PCDD/F peak in the second sampling interval fits exactly to the time when the area of the boiler in the sensitive temperature range reaches its maximum. Approx. 15 – 18 hours after start-up the boiler was in thermal equilibrium and especially the surface area where the tem-

perature ranged between 300 and 400 °C stayed stable. Once this condition was reached, the PCDD/F concentrations adjusted to the normal concentration level.

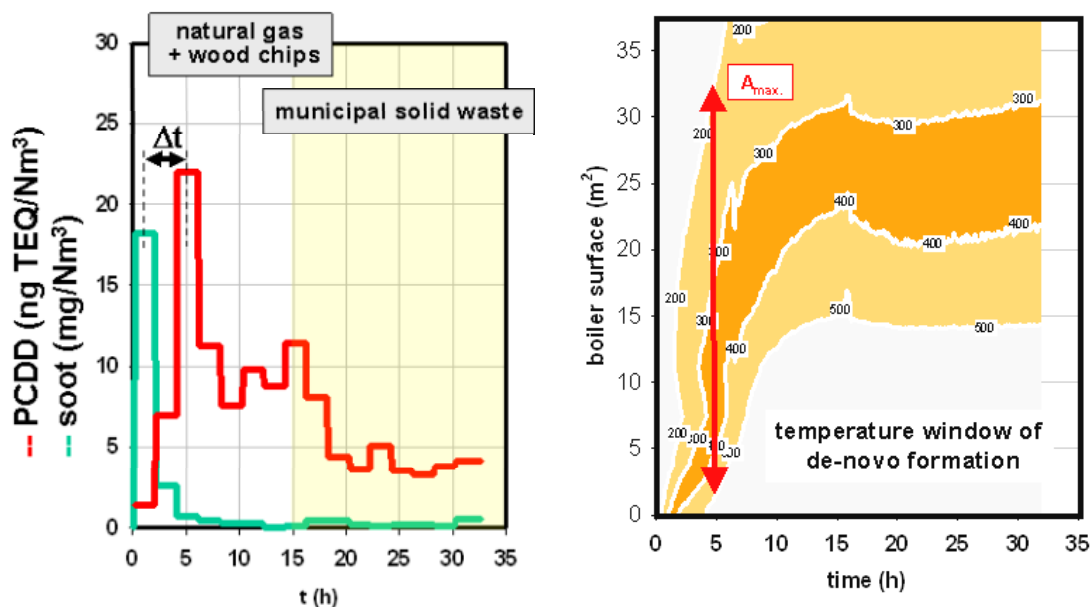


Fig. 8 Concentration of soot and PCDD in the raw gas of TAMARA during start-up (left graph) and momentary boiler surface in the PCDD/F formation temperature range during start-up (right graph)

The main conclusion from these tests is that a soot formation during burner operation has to be prevented. This soot will mainly be deposited in the boiler and serves as source for increased PCDD/F even if no waste is fed into the system. Although the boiler had been cleaned while the plant was out of operation there were obviously enough chlorides and enough catalytically acting heavy metal compounds in the remaining deposits to allow PCDD/F to be formed. In our test this period lasted for approx. 18 h.

Another recommendation would be to care for a fast and uniform heating of the boiler to minimise the surface areas of the boiler which stay in the sensitive temperature range of 200 – 500 °C.

State of the Art and Outlook

Almost three decades of research on the formation of PCDD/F in waste incineration have disclosed the major formation reaction mechanisms and their main parameters of influence. Since slightly more than 20 years Forschungszentrum Karlsruhe contributed to a great extent to the progress in this area which is not only of high scientific interest but is also a key topic in the ongoing controversial discussion of waste incineration.

Today we know:

- PCDD/F are mainly formed by the de novo synthesis in the back end of the boiler,
- optimisation of combustion control and burnout are suitable tools to reduce the PCDD/F level in raw gas and solid residues,
- filter systems should be operated at temperatures below 200 °C,
- increased halogen levels do not increase the PCDD/F formation as long as a good burnout is achieved,
- permanent high sulphur levels inhibit the PCDD/F formation,

- PCDD/F are also formed inside the combustion chamber but these congeners are destroyed in the post combustion area,
- instationary conditions have to be avoided.

The situation in terms of PCDD/F in a modern waste incinerator is schematically depicted in Fig. 9. The PCDD/F raw gas level downstream of the boiler can be kept below 5 ng(TE)/m³ which allows an easy compliance with the meanwhile almost worldwide found emission standard of 0.1 ng(TE)/m³.

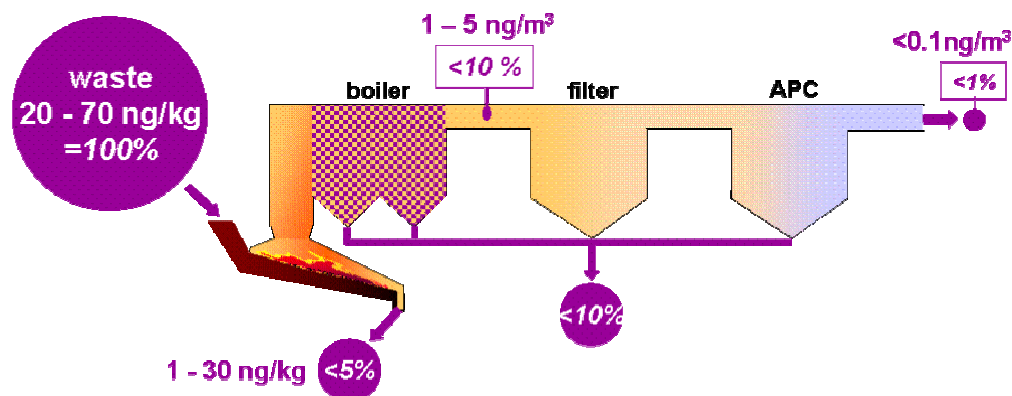


Fig. 9 PCDD/F in a state-of-the-art waste incineration plant

The main solid residue stream bottom ash carries PCDD/F loads which are not far above the typical concentrations found in Central European soil [Fiedler 1996]. Such low levels do not interfere with the utilisation of these residues e.g. in road construction which is practised in many European countries. Filter ashes and other gas cleaning residues are classified as toxic waste and require special disposal or inertisation measures.

In general it can be concluded that PCDD/F are no longer to be seen as a barrier to waste incineration. A negative impact on health or environment can be excluded if all technical knowledge is applied. However, the tendency to aim for 'zero emission' concepts and to limit the total PCDD/F emission from waste incineration will make technical upgrading of most plants necessary.

This is not that much a question of better abatement techniques but eventually a wide spread application of processes to inertise the gas cleaning residues. A respective process is high temperature ash melting which is common practice in Japan. Cheaper technologies are the 'Hagenmaier Process', the PCDD/F destruction at approx. 400 – 500 °C under air deficiency in a rotary drum [Hagenmaier 1987]. This process is partly used in Japan. Another method is the 3R Process which combines acid leaching of boiler and filter ashes with the effluents of the first scrubber and a recycling of the compacted leaching residues into the furnace of the waste incinerator for PCDD/F destruction [Vehlow 1990].

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