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Behavior of Chlorinated Aromatic Compounds in the High–temperature Range of Waste Incineration Plants

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1. Introduction

It is known from many years of laboratory experiments that PCDD/F is generated from the carbon particles of the fly ashes from waste incineration plants at temperatures of 250 to 550°C (de novo synthesis) [1].

Own experiments on the dust separation by fabric filters in the raw gas of waste incineration plants demonstrated that a significant formation of chlorinated aromatic compounds in real systems with fresh fly ashes can be observed at a temperature above about 200°C already [2]. This formation in the low–temperature range (T=200 – 250°C) is based on the finely dispersed carbon particles of the fly ashes. An influence of gaseous precursors cannot be found in the low–temperature range [3].

According to measurements performed by several authors [4–7] in the furnace and boiler regions of waste incineration plants, the concentration of PCDD/F and other chlorinated aromatic compounds was rather high in the exhaust gas even at very high temperatures. Obviously, the temperature range of PCDD/F formation in the real exhaust gas of waste incineration plants is not identical to that obtained by the laboratory experiments on de novo synthesis.

Therefore, the following aspects were to be studied at the TAMARA [8] pilot plant:

- In which temperature ranges does a formation and/or decomposition of chlorinated aromatic compounds take place in the exhaust gas of a waste incineration plant?
- Is there an upper temperature limit of PCDD/F formation?
- Can PCDD/F formation be prevented by the use of a high–temperature deduster?

2. Experimental

To answer the above questions, several test series were carried out with exhaust gas samples taken at two different positions of the TAMARA plant. These exhaust gas sampling points are indicated in Fig. 1.

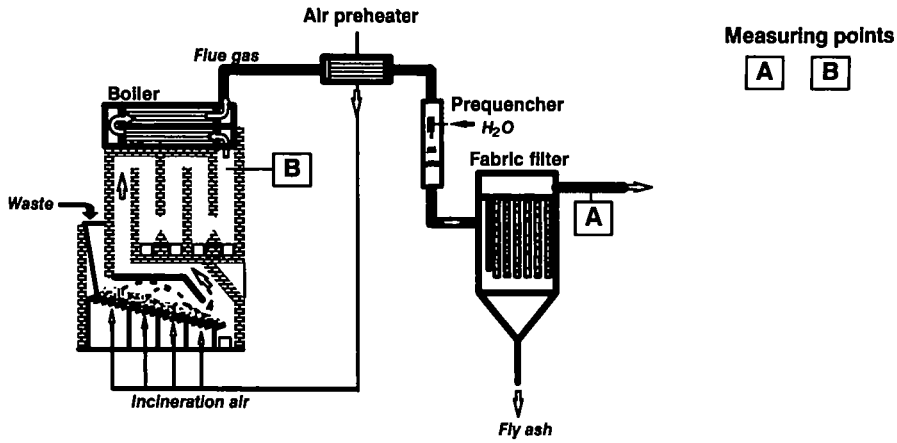


Fig.1: TAMARA flow chart and experimental positions

One gas sampling point was located downstream of the fabric filter for dust separation (A). Temperature of the practically dust–free exhaust gas amounted to about 180°C. The second sampling point was located in the last flue upstream of the horizontal boiler inlet (B). Here, the temperature is about 600°C with the mean fly ash concentration amounting to 300 mg/Nm^3.

The studies performed at both positions were based on relative comparisons of two simultaneous experiments using various bypass trains.

The position of the gas sampling probes were practically the same. The distance of the probe tips in the exhaust gas channel was about 5 cm. One sampling process was applied for reference measurement. The setup is represented schematically in Fig. 2.

The experiments were designed to determine the influence of the temperature in the hot gas section (HG measurement) on the concentration of chlorinated aromatic compounds under the following conditions:

- Use of various ceramic filter candles without fly ash
- Use of the empty housing without filter and without fly ash
- Fly ash filtration with selected filter elements

The major reference measurement components are a gas cooler at position B, a PTFE filter and a downstream adsorber (lignite carbon [9]). Cooling of the exhaust gas to 180°C in the gas cooler takes place within a period of about 65 ms. At position A, the reference section was reduced to the adsorber exclusively.

The second setup (HG measurement) consists of a heat exchanger (residence time <60 ms) and a heatable housing for temperature adjustment. The housing can be equipped with various ceramic filter candles. The setup downstream of the furnace corresponds to that of the reference measurement. By an exhaust gas volume flow of 1 Nm^3/h, the same amounts of fly ashes were ensured in all experiments at position B. Consequently, gas residence time in the filter housing decreased with increasing temperature. Depending on the temperature, mean gas residence time varied between 3.3 s (T=200°C) and 1.2 s (T=1000°C). The individual experiments had a duration of 3 hours each.

3. Results

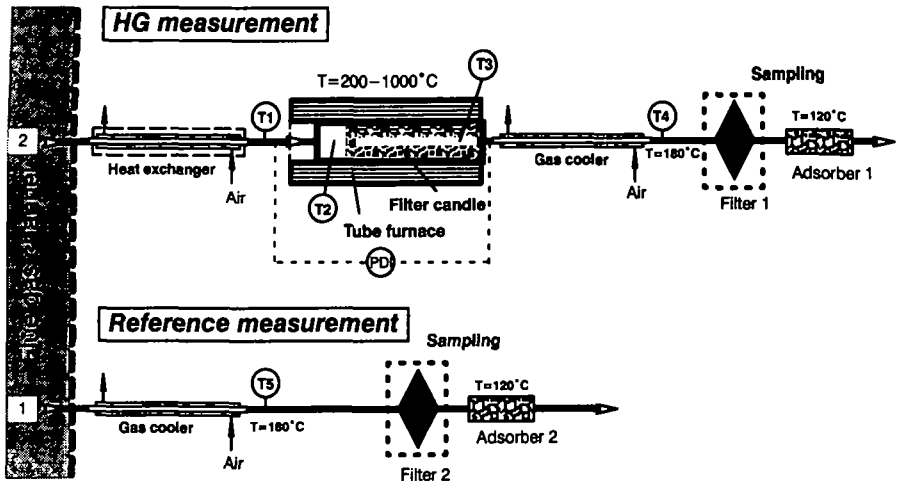


Fig.2: Experimental setup

The mean concentrations measured for the reference samples of chlorinated aromatic compounds in all test series are represented in Figs. 3 and 4 for both measuring positions.

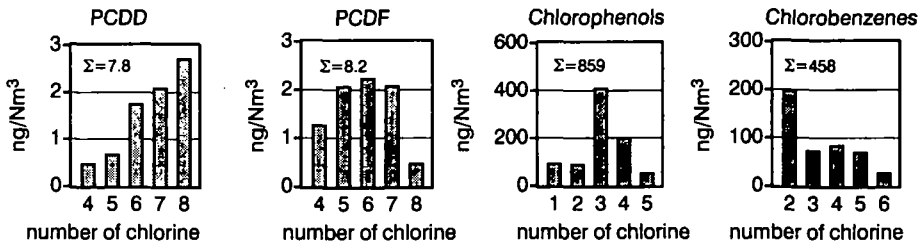


Fig.3: Reference measurement concentrations upstream of the boiler (mean values)

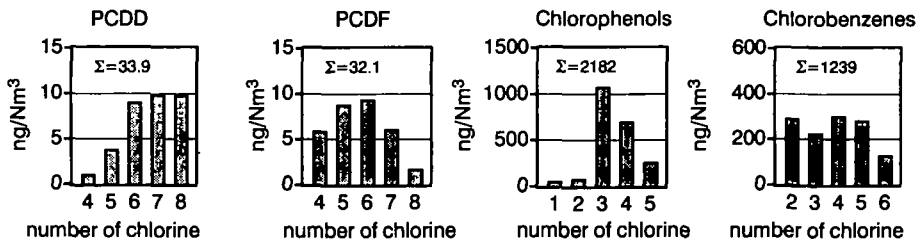
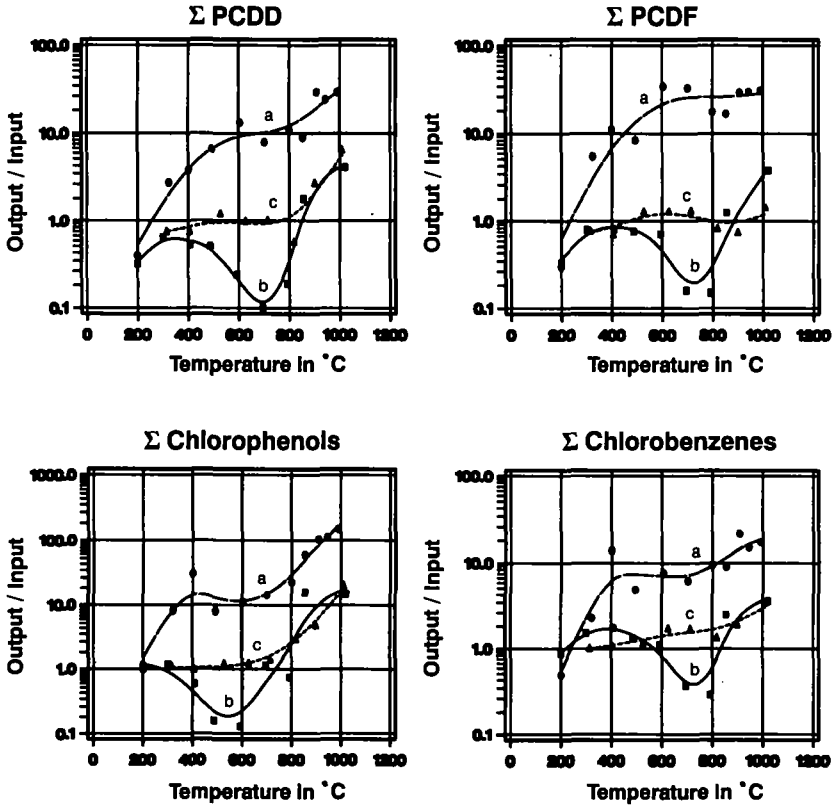


Fig.4: Reference measurement concentrations downstream of the fabric filter (mean values)

It is evident that significant concentrations of chlorinated aromatic compounds were found to exist at boiler position B at T=600°C. When comparing both positions, the concentration

downstream of the fabric filter is higher by a factor of about 3 – 4. This result confirms the measurements performed by Düwel [4] in the boiler range of a large–scale domestic waste incineration plant.

At position A downstream of the fabric filter, the influence of various hot gas filters (SiC and Al_2O_3 grain ceramics) and of the empty filter housing without fly ash on gaseous organic compounds was studied in the temperature range of 200 – 1000°C. Following the evaluation of these experiments, the aluminum oxide filter was preferred for use in the test series with fly ash filtration at position B. A survey of the integral values of the compounds investigated is given in Fig.5. Evaluation was based on a comparison of simultaneous samplings downstream of the HG system (output) and the reference measurement (input). The ratios (output/input) are plotted on the logarithmic scale as a function of temperature.



(a) Al_2O_3 filter with fly ash (position B)
(b) Al_2O_3 filter without fly ash (position A)
(c) housing without fly ash (position A)

Fig.5: Comparison of the test series

In the experiments with fly ash, a significant formation of chlorinated aromatic compounds took place above about 200°C, as expected. At first, the formation factors were found to increase rapidly up to a temperature of about 500°C. In the range of 500 – 800°C the formation

factor remains nearly constant. Further temperature increase then results in another rise of the formation factor especially for the chlorophenols. Even at filtration temperatures of 1000°C, considerable formation of chlorinated aromatic compounds takes place.

In experiments without fly ashes, a significant formation of chlorinated aromatic compounds was observed above about 800°C. The test series with the Al_2O_3 filter without fly ash yielded another temperature range of catalytic decomposition on the filter surface. Therefore, the following reactions must take place during hot gas dedusting:

- Formation from fly ashes (de novo synthesis)
- Heterogeneous gas/fly ash reactions
- Homogeneous gas phase reactions
- Reactions on the surface of the filter material.

On the basis of comparisons of the output/input ratios of all test series represented in Fig. 5, it can be determined qualitatively that the formation of chlorinated aromatic compounds predominates under the selected conditions in the temperature range of T<800°C in the presence of fly ash. In the high-temperature range of T>800°C, the formation mainly takes place from gaseous precursors. It must be noted that the mean residence time of the fly ash during filtration is about 1.5 hours, whereas the mean residence time of the exhaust gas amounts to some seconds only. Hence, a direct transfer of these results to processes in the boiler region of waste incineration plants is not possible.

4. Discussion

It was found out in the experiments that with increasing temperature up to 1000°C significant formation of chlorinated aromatic compounds takes place in the exhaust gas of a waste incineration plant. This result is in contradiction with laboratory experiments regarding the thermal stability of these compounds. PCDD/F was supposed to undergo nearly complete thermal decomposition between 800 and 1000°C at residence times of about 1s [10]. This discrepancy may be due to the fact that the data obtained in the laboratory experiments were determined in clean systems. PCDD/F was added to an inert gas and then passed through a heated tube reactor (quartz – capillary tube). Probably, wall effects (high surface/volume ratio) have not been taken into account sufficiently in these experiments [11].

By the experiments of Hesseling [12] on the use of hot gas filters for the prevention of PCDD/F formation in the temperature range of 500-600°C at a waste incineration plant, reductions of the TEQ concentrations by a factor of 1.5 to 8 were obtained as compared to filtration at 200°C. The limit value of 0.1 TEQ ng/Nm^3 was not reached. Compared to our grain ceramic filters, the ceramic fiber filters studied in this case have a much larger specific surface area. As a result, catalytic PCDD/F decomposition on the surface of the filter is much stronger.

Experiments by Fängmark [13] on the effect of high-temperature filtration at temperatures of up to 500°C in a laboratory-scale incineration plant led to high PCDD/F concentrations in the dedusted exhaust gas. Further formation in the downstream heat exchanger was not observed. The conclusions from the experiments described are in agreement with our own results. The formation of chlorinated aromatic compounds in the low-temperature range is mainly due to formation reactions from the fly ash.

By the measurements of Steinhaus [14] in the exhaust gas of a small incineration plant equipped with a ceramic hot gas filter at temperatures of 900°C, PCDD/F concentrations of up to 30 ng TEQ/Nm^3 were obtained. These high PCDD/F concentrations made an additional flue gas purification stage (carbon filter) necessary. The results gathered during practical use confirm our results, according to which PCDD/F formation cannot be prevented by hot gas dedusting.

5. Conclusions

The following conclusions can be drawn from the experimental studies on the behavior of chlorinated aromatic compounds in the high–temperature range and the comparison with literature data:

- The temperature range for the formation of chlorinated aromatic compounds in waste incineration plants ranges from 200°C to 1000°C. It remains to be found out by additional measurements, whether this result affects the operation of technical incineration plants.
- PCDD/F formation cannot be prevented by the use of a high–temperature dedus-ter in waste incineration plants.

6. References

1) Vogg, H., Stieglitz, L. *Chemosphere* 15 (1986), 1373–1378
2) Hunsinger, H., Kreisz, S., Vogg, H. *Chemosphere* 32 (1996), 109–118
3) Hunsinger, H., Kreisz, S., Vogg, H. *Chemosphere* 34 (1997), 1033–1043
4) Düwel, U., Nottrod, A., Ballschmieder, K. *Chemosphere* 20 (1990), 1839–1846
5) Akimoto, Y., Nito, S., Inouye, Y. *Chemosphere* 34 (1997), 791–799
6) Öberg, T., Warman, K., Bergström, J. *Chemosphere* 19 (1989), 317–322
7) Yamamoto, T., Inoue, S., Sawachi, M. *Chemosphere* 19 (1989), 271–276
8) Merz, A., Vogg, H. *Proc. of the Int. Conf. on Incineration of Hazardous, Radioactive and Mixed Wastes*, San Francisco, Calif., May 3–6, (1988) 1–11
9) Kreisz, S., Hunsinger, H., Vogg, H. *Organohalogen Compounds* Vol. 19 (1994), 231–234
10) Rordorf, B. F. *Chemosphere* 18 (1989), 1017–1024
11) Hasberg, W., Römer, R. *Chem.–Ing.–Tech.* 60 (1988) 435–443
12) Hesseling, W.F.M.; Smit, E.R. *Report–No. EWAB––9502; TNO–ME––95–037* (1995)
13) Fängmark, I., Strömberg, B., Berge, N., Rappe, Ch. *Chemosphere* 29 (1994), 1903–1909
14) Steinhaus, G., Dirks, F. *Proc. of the Internat. Incineration Conf.*, May 9–14, Houston Texas, (1994) 273–275