Formation of Chlorinated Aromatic Compounds in the Raw Gas of Municipal Solid Waste Incineration Plants

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1. Introduction

In the temperature range of 200 to 240°C chlorine aromatics are formed during dust separation by fabric filters in the raw gas of municipal solid waste incineration plants [1]. The experiments performed at a large-scale waste incineration plant clearly indicated that the absolute carbon content of the fly ashes plays a minor role in the formation of chlorine aromatics in this temperature range. To study the influence of the fly ashes in more detail, additional experiments were performed at the TAMARA incineration pilot plant [2].

TAMARA is characterized by an excellent burnout of the fly ashes (C < 0.1%) and very low CO concentrations (<5mg/Nm^3) of the raw gas downstream of the boiler. Dust concentrations amount to 300-500 mg/Nm^3 only. The mean diameter of the particles is about 1 μm. Due to the low C concentrations in the fly ash and the resultant low adsorption capacity, >99% of PCDD/F is found in the gas phase.

2. Experimental

The experimental setups are represented schematically in Fig.1.

In test series 1, temperature was varied in the range of 180-240°C during raw gas dust filtration. Reference measurements at a constant filter temperature of 180°C yielded relatively constant levels of chlorine aromatics in the raw gas over the test period.

In test series 2, the formation potential of fresh fly ash was studied under air atmosphere. At first, fly ash was accumulated simultaneously on two filters at a temperature of 180°C (2a). Filter 2 was removed and analyzed. Filter 1 was heated to 240°C immediately after the dust collection phase and passed by a wet air flow (H_2O concentration=150g/Nm^3) (2b). A carbonized lignite (HOK) adsorber cartridge was installed downstream of the filter for sampling the gaseous chlorinated aromatic compounds [3]. Three consecutive samplings were carried out at the times 0-3h, 3-6h and 6-26h.

3. Results

In spite of the very low C concentration of the fly ash, the formation rates of PCDD/F and chlorophenols obtained in the TAMARA raw gas experiments at dust filtration temperatures of

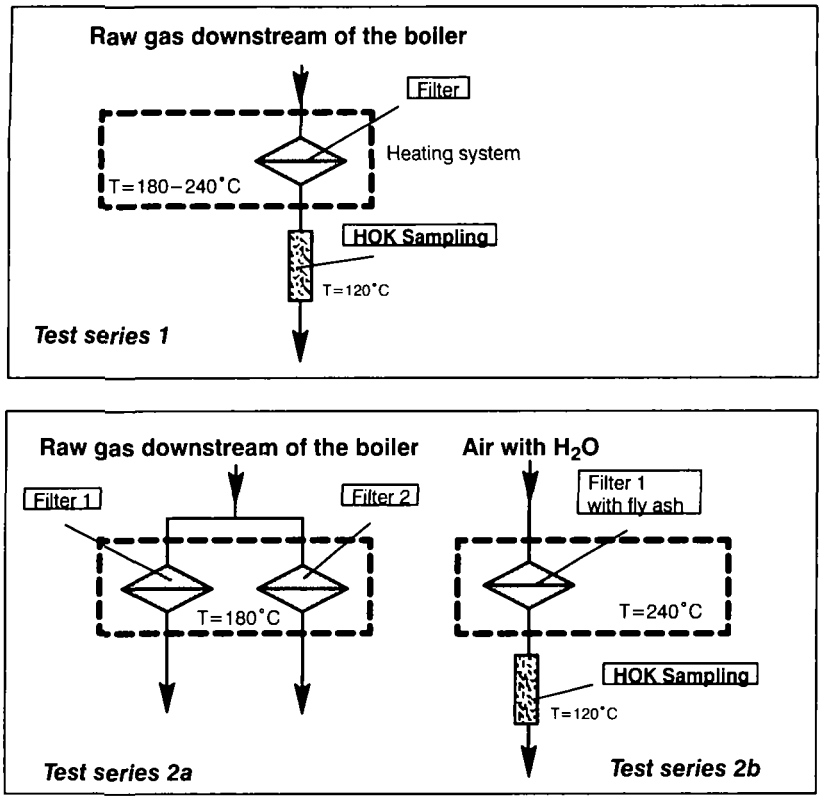

Fig.1: Experimental setups

180–240°C were similar to those of the large–scale plant [1]. The concentrations of chlorine aromatics measured in the TAMARA raw gas at various filtration temperatures are presented in Tab.1. In contradiction to the experiments at the large–scale incineration plant, however, significant formation of chlorobenzenes was found to take place in TAMARA.

Tab.1: Integral concentrations at various filtration temperatures

Temperature (°C)	ΣPCDD (ng/Nm^3)	ΣPCDF (ng/Nm^3)	ΣChlorophenols (ng/Nm^3)	ΣChlorobenzenes (ng/Nm^3)
180	63	47	5005	1172
200	326	70	8224	3772
220	601	203	13994	9038
240	939	300	17100	20008

By comparing the congenere profiles of the chlorine aromatics formed at 240°C in TAMARA and the large–scale plant, respectively, almost identical homologue distribution patterns were obtained. The normalized homologue distributions are represented in Fig.2.

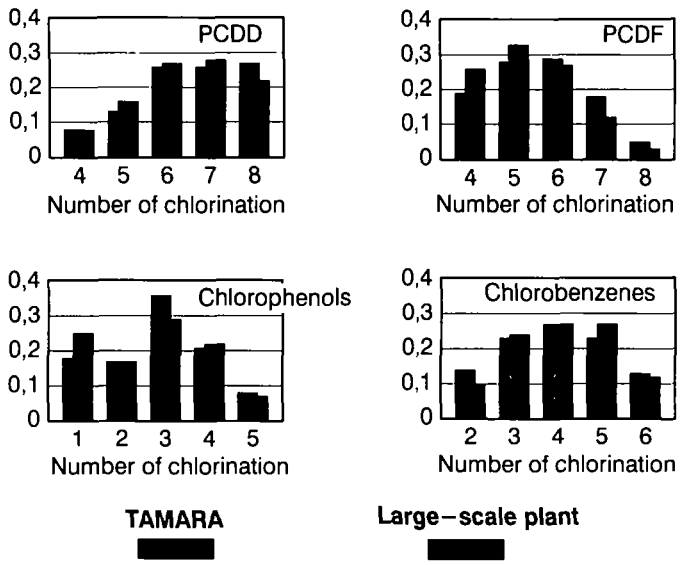

Fig.2: Normalized distribution patterns of the chlorine aromatics formed at 240 °C

In test series 2, as well chlorine aromatic compounds were formed at 240 °C. Tab.2 however points out that under air atmosphere formation rates are very low compared to that in a raw gas environment.

Tab.2: Comparison of the formation rates at various gas atmospheres (T=240 °C)

	ΣPCDD (ng/g*h)	ΣPCDF (ng/g*h)	ΣChlorophenols (ng/g*h)	ΣChlorobenzenes (ng/g*h)
Exp. 1 (raw gas)	1395	404	19245	29973
Exp. 2 (air, 0–3h)	18	11	2003	2741

When comparing the C concentrations of the fly ashes of filters 1 (2a) and 2 (2b), a slight decrease from 200 to 170 ppm was observed. However, this difference of the carbon contents of the fly ashes is within the limits of analytical error and does not allow any clear statements to be derived with regard to C balancing. It can be concluded from the test series 2 that the formation of chlorine aromatics has to be attributed to de–novo synthesis from the particulate residual carbon of the fly ashes as described by Vogg and Stieglitz [4].

By means of separate studies of the three individual experiments of test series 2b, it was found out that the formation potential of all classes of compounds investigated decreases significantly with increasing test duration. Since the C concentrations do not vary considerably during the tests, this has to be considered an indication of an "aging process" of the fly ashes.

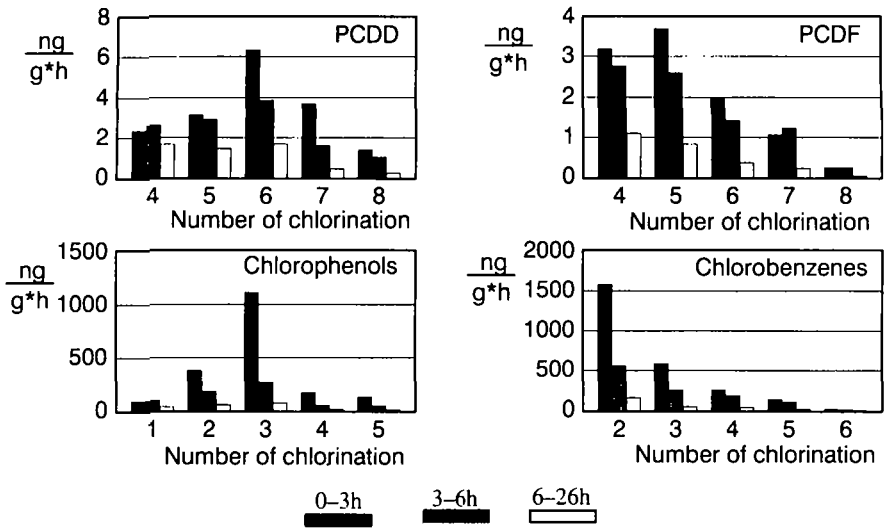

Fig.3: Formation of chlorine aromatics in a wet air flow (test series 2b)

4. Conclusions

As fly ashes with strongly varying C concentrations exhibit similar formation rates of chlorine aromatics in the temperature range of 180–240°C and formation from the carbon of the fly ash is negligibly small, formation reactions of chlorine aromatics have to be attributed to the composition of the raw gas. Experiments are currently performed in order to scrutinize the influence of various exhaust gas components.

5. References

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