

## PCDD/PCDF MEMORY EFFECTS IN A LABORATORY SCALE INCINERATOR

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### Introduction

Numerous studies in laboratory pilot incinerators focus on the understanding of the formation mechanism of PCDD/PCDF. In laboratory tests, incinerators are mostly operated only several hours and normally do not exceed half-day operations. In addition, the sampling time in laboratory (often not exceeding 1 hour) are typically lower than the measurement time required for full scale incinerators (4 to 8 hours).

For full scale incinerators it was found that disturbed combustion conditions can cause memory effects and result in long term emission of PCDD/PCDF for several hours<sup>1,2</sup>. Memory effects are, however, not reported for combustion tests performed on laboratory scales.

In this paper we present results on PCDD/PCDF formation using a laboratory flow reactor and demonstrate that difficulty in interpreting data may occur when memory effects are not considered.

### Materials and Methods

The schematic of the entrained flow reactor is shown in Figure 1. The flow reactor was connected to a stainless steel cooler and a filter. The temperature of the furnace was maintained at 1000 °C. The cooler was kept at a temperature around 175 °C and the temperature of the filter was kept below 70 °C. As combustion material we used a pyrolysis charcoal<sup>1</sup> with a chlorine content of 3 %. The ash content of the charcoal was 31.4 %, resulting in a chlorine content of the fly ashes of about 6 to 9 % which is in the range of the chlorine content of fly ash from municipal waste incinerators. The charcoal was fed via a micro feeder into the preheated furnace. The different air ratio  $\lambda$  (actual oxygen concentration/theoretical oxygen demand for complete combustion) were adjusted by changing the charcoal feeding rate. The total gas flow was kept constant in all experiments. PCDD/PCDF were analysed separately in the fly ash and in the gas phase. The clean-up procedures are reported elsewhere.<sup>3,4</sup>

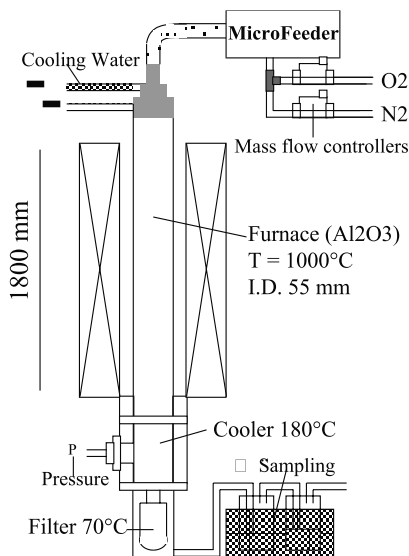
### Results and discussion

#### *PCDD/PCDF emission with change of the air ratio ( $\lambda$ )*

In one experimental series the air ratio was changed in 30 minute intervals. As starting air ratio we choose  $\lambda=1.4$  and increased the air ratio for the second sampling to  $\lambda=1.8$ . These air ratios are comparable to conditions in waste incinerators or coal boilers. For the third and fourth sampling we tested high air ratios of  $\lambda=2.5$  and  $\lambda=3.0$  respectively, which are normally not applied in incinerators or boilers. Fly ash was sampled during the respective sampling intervals and analysed for PCDD and PCDF. As expected, the combustion quality increased with increasing the air ratio: The ashes generated at an air ratio of  $\lambda=1.4$  and  $\lambda=1.8$  were black in colour indicating insufficient burn out while the ash at  $\lambda=3.0$  was grey.

<sup>1</sup> the charcoal was produced by pyrolysis of refused derived fuel (RDF).

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**Figure 1.** Schematic of the entrained flow reactor.

The PCDD/PCDF were practically all adsorbed on the fly ashes<sup>2</sup>. The PCDD/PCDF detected in gas-phase after the ash filter was low contributing less than 0.1 % to the total TEQ. Therefore the PCDD/PCDF adsorbed on the fly ash represent approximately the total PCDD/PCDF amount emitted from the flow reactor. Figure 2 shows the total PCDD/PCDF concentration and TEQ value adsorbed on the fly ashes. The TEQ from PCDD/PCDF in the fly ash ranged from 0.8 to 6.9 ng TEQ/g. The ratio of PCDF to PCDD was between 4 to 10. The PCDD/PCDF levels increased with increasing air ratio. The PCDD/PCDF concentration in the fly ash was below 1.5 ng TEQ/g during sampling at low air ratio of  $\lambda=1.4$  (0.9 ng TEQ/g) and  $\lambda=1.8$  (1.5 ng TEQ/g). While at high air ration  $\lambda=2.5$  (5.5 ng TEQ/g) and  $\lambda=3.0$  (6.9 ng TEQ/g) the PCDD/PCDF concentration were above 5 ng TEQ.

### *Time dependency of PCDD/PCDF emission with constant air ratios*

In a second experiment we kept the air ratio constant at  $\lambda=3.0$  (the condition were the highest PCDD/PCDF were detected in experiment 1 (Figure 1)). The experimental time was comparable to the first experimental series and the sampling time of the fly ash was 15 and 30 minutes respectively. Figure 2 shows the TEQ values and total PCDD/PCDF concentrations in the fly ashes of the respective sampling interval. Similarly to the first experiment, the PCDD/PCDF concentration during the 4 sampling intervals again differed considerably. The total PCDD/PCDF formed was between 0.5 and 4.1 ng TEQ/g. The PCDD/PCDF concentration in the ashes increased with experimental time (Figure 2). Further, the average PCDD/PCDF amount generated in this experiment was lower (2.4 ng/g) compared to the first experimental series (3.8 ng/g). Therefore, the higher combustion quality in this second experiment resulted in an lower overall PCDD/PCDF emission.

The increase of PCDD/PCDF emission with time was observed also in other experimental runs. Therefore the “correlation” of increasing PCDD/PCDF emission with increasing air ratio (Figure 2) in the first experimental series was only an artefact and actually depended on the experimental time.

<sup>2</sup> the high adsorption rate resulted from the low temperature of the dust filter and the high ash content (ca. 15 g/Nm<sup>3</sup>)

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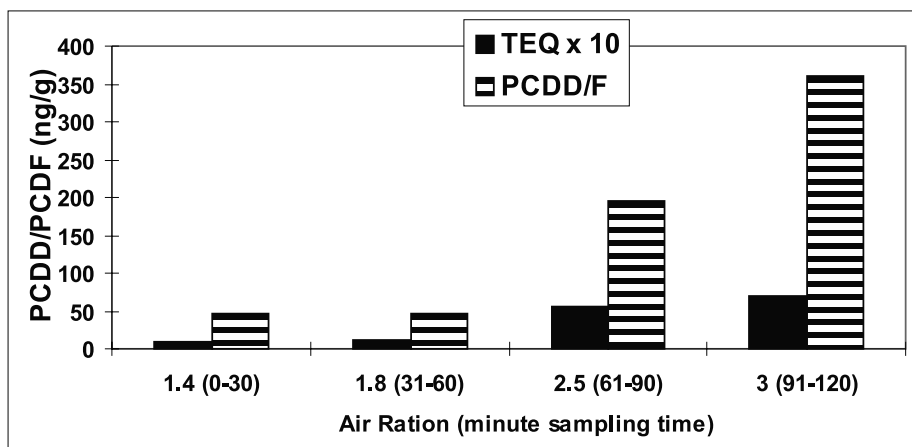


Figure 2. PCDD/PCDF amount in fly ashes in the experiment with different air ratio

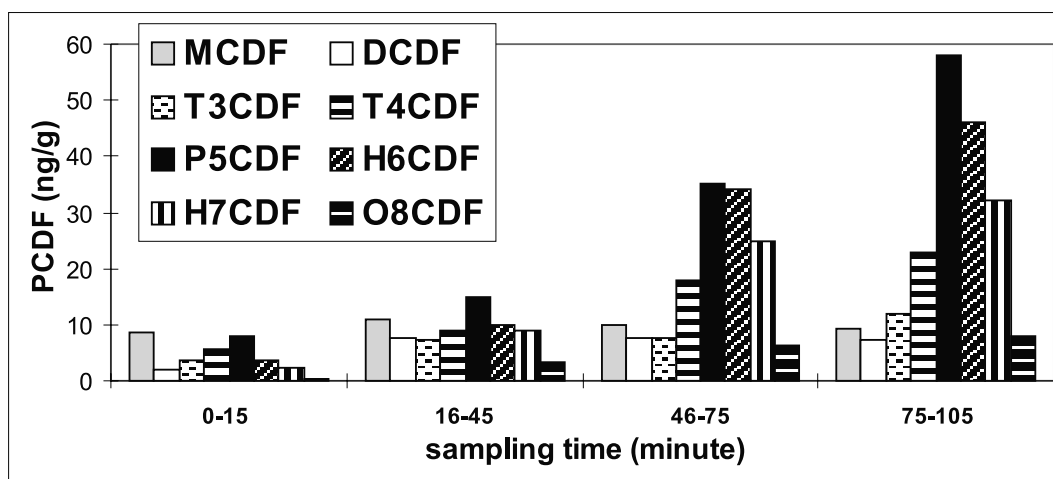


Figure 3. PCDF amount and homologue pattern in an experiment with constant air ratio (1 = 3.0).

### *Mechanistic aspects with respect to the observed time dependence of PCDD/PCDF emission*

The observed time dependence of PCDD/PCDF emission can be explained by considerations of dioxin formation mechanism. Recently Gullett<sup>5,6)</sup> and Wickström<sup>7)</sup> reported on a PCDD/PCDF formation in an entrained flow reactor “in one second” (in-flight formation)<sup>3)</sup> by assuming the residence time of the fly ash in the reactor equal to the gas phase residence time. For our experimental set-up, however, this rapid PCDD/PCDF formation rate can not explain the remarkable difference of nearly one order of magnitude for PCDD/PCDF concentrations observed in ashes sampled during the first 15 minutes and between 75 and 105 minutes (Figure 3). After the experiment we discovered that about 1

<sup>3)</sup> In another experimental set-up we could verify the possibility of a de novo synthesis within seconds.<sup>6)</sup>

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to 1.5 g ash (ca 10% of total fly ash) was attached to the wall of the vertical furnace and the cooler. The increasing PCDD/PCDF emission with increasing experimental time can be interpreted by a *de novo* synthesis of PCDD/PCDF on this attached ash in the minutes and up to hour range during oxidative degradation of the carbon included/adsorbed on these ash. The formation and final desorption of the PCDD/PCDF can result then in the observed increasing emission in the hour range. In this respect, the high PCDD/PCDF values in experiment 1 between 90 and 120 minutes at  $\lambda=3.0$  (6.9 ng TEQ/g) (Figure 2) can be explained by a memory effect: the low air ratio  $\lambda=1.4$  and  $\lambda=1.8$  in the first hour of the combustion test resulted in a higher carbon deposit in the reactor compared to the second experimental series (with constant high air ratio  $\lambda=3.0$ ) serving as a base for high PCDD/PCDF emission during the following hour (Figure 2).

## Conclusions

Memory effects for PCDD/PCDF emission can be observed in small scale incinerators. In a simple flow reactor (furnace, cooler and filter) the time frame of the memory effects were in the range of hour(s). Depending on the experimental set-up, the combustion conditions of hour(s) before the actual measurement can have a crucial impact on the emitted amount of PCDD/PCDF. This should be considered for experiments in laboratory scale facilities (as well as in large scale incinerators). Therefore short term measurements and experiments with a single measurement should be carefully evaluated and assessed.

In this respect it is interesting to investigate the differences in formation rates for different experimental set-ups/conditions and evaluate the relevance for large scale incinerators.

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