EMISSION CONTROL, ABATEMENT TECHNOLOGIES AND REMEDIATION

DECHLORINATION AND DESTRUCTION OF PCDD ON SELECTED FLY ASHES FROM MUNICIPAL WASTE INCINERATION

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Introduction

The highest load of PCDD/F from waste incineration are released, adsorbed, on fly ashes. Depending on the air pollution control devices, it amounts up to more than 90% of the total PCDD/F releases of an incinerator.

In Japan, "A New Guideline For Controlling Dioxin" was issued in 1997 including the aim to decrease the total PCDD/F release from all streams of municipal solid waste (MSW) incineration into the environment to below 5 µg TEQ per ton MSW[1]. This implies an additional treatment of fly ashes or the use of e.g. gasification melting technologies[2].

One option for the additional treatment is to subject the ashes to a melting process. Another possibility for the decontamination of dioxins in fly ashes is a low temperature treatment under oxygen deficiency[2].

While fly ashes catalyze under oxygen surplus around 250-450°C the *de novo* synthesis of PCDD/F, they catalyze in the same temperature window under oxygen deficiency the dechlorination-hydrogenation of PCDD/F and other chlorinated aromatic compounds[3]. This general property of fly ashes is already applied favorably in industrial scale plant operation for decontamination of fly ashes in Germany[4,5] and in Japan[6].

Fly ashes sampled in Japanese fluidized bed incinerators showed differences in the *de novo* formation potential compared to fly ashes from stoker incinerators[7]. This could be assigned mainly to the high pH of the ashes resulting from $Ca(OH)_2$ spray and the lower carbon content. Therefore, it seemed interesting for us to compare the low temperature destruction of PCDD/F on this fly ash, compared to a fly ash without the impact of $Ca(OH)_2$ spray.

Materials and Methods

Ashes. Two ashes were chosen for the comparison. One fly ash was sampled in a fluidized bed incinerator (FBI) using $Ca(OH)_2$ spray for removal of acid gases. The second ash was sampled in a stoker incinerator without using $Ca(OH)_2$ spray.

Pretreatment. To avoid the interference of the native PCDD/F present on the fly ashes, the ashes were pretreated under nitrogen atmosphere at 500°C for 3 hours to decompose the native Dioxins[8]. After this treatment, both fly ashes (FA) - FA1 (FBI with $Ca(OH)_2$) spray and FA2 (Stoker incinerator without $Ca(OH)_2$ spray) - were "Dioxin free" (Table 1). The elemental composition and the carbon content did not change by the treatment within the analytical error (Table 2).

Table 1: Amount of PCDD/F on "dioxin free" fly ash

ng/g	MCDD-OCDD	MCDF-OCDF	I-TEQ (NATO CCMS)
FA 1	0.087	0.056	0.001
FA 2	0.23	0.37	0.005

Table 2: Composition of the fly ashes before (FA1*/FA 2*) and after heat treatment (FA1/FA2)

%	CaO	SiO	Al$_2$O$_3$	K$_2$O	Na$_2$O	MgO	Fe$_2$O$_3$	ZnO	TiO$_2$	CuO	PbO	Cl	SO$_3$	P$_2$O$_5$	C
FA 1	38.0	13.5	9.5	2.6	3.4	3.5	4.9	0.8	1.7	0.74	0.45	18	3.2	2.2	0.86
FA 1*	37.6	10.1	7.4	4.9	5.1	2.3	4.3	0.7	1.5	0.66	0.50	19.3	2.6	1.8	0.69
FA 2	19.8	16.3	11.5	5.4	6.5	4.7	3.2	3.0	2.5	0.16	0.70	11.6	6.7	1.6	4.5
FA 2*	20.0	15.2	10.4	5.9	7.7	4.1	3.0	3.2	2.4	0.16	0.75	13.5	7.0	1.5	4.4

Experiments. For the experiments, the dioxin free ashes FA1 and FA2 were re-doped with 2000 ng OCDD/g corresponding to the amount of PCDD/F load of high contaminated fly ashes.
The ashes (0.5 g) were treated in a micro reactor. The reactor consists of a vertical Pyrex glass reactor connected to Nitrogen. For the experiments, the reactor was filled with N$_2$ and preheated to the respective temperature. The ashes were filled into the reactor and after 1 hour of heat treatment, the system was cooled to room temperature.

Extraction, clean up and analysis. The procedures for extraction, clean up and analysis is reported elsewhere[8,9]. MonoCDD (MCDD), diCDD (DCDD) and triCDD (T$_3$CDD/F) were analyzed by HRGC/HRMS on a DB17HT or a Sil88 column using a HP 6890 GC connected to a Micromass Autospec Ultima operating at a resolution of >10 000.

Results
The experiments were performed in the temperature range of 260°C-380°C. These range cover the temperature were Hagenmaier et al. performed their laboratory experiments[3] and the region of actual plants in operation[4-6].
The dechlorination of OCDD on FA2 is shown in Figure 1. The ash shows already at 260°C a considerable dechlorination potential and more than 70% of OCDD was dechlorinated. At 340°C, the maximum of dechlorinated PCDD shifted to DCDD and at 380°C, only 0.78% of the spiked OCDD was recovered as T$_4$CDD-OCDD.
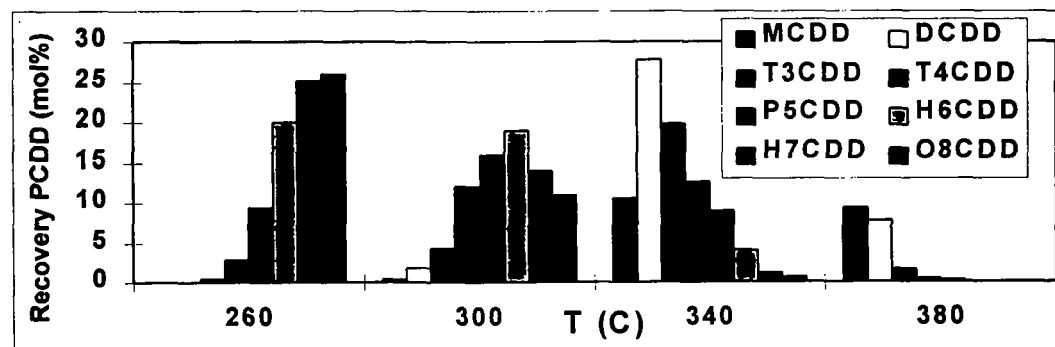

Figure 1: Low temperature treatment of OCDD on FA2 in dependence of temperature (1h)

When comparing the average chlorination degree of PCDD on FA1 and FA2 after the thermal treatment of OCDD, we find a lower average chlorination degree of the PCDD on FA2 compared to FA1 (Figure 2). Therefore FA2 exhibits a slightly higher dechlorination velocity for the PCDD in the whole examined temperature window.
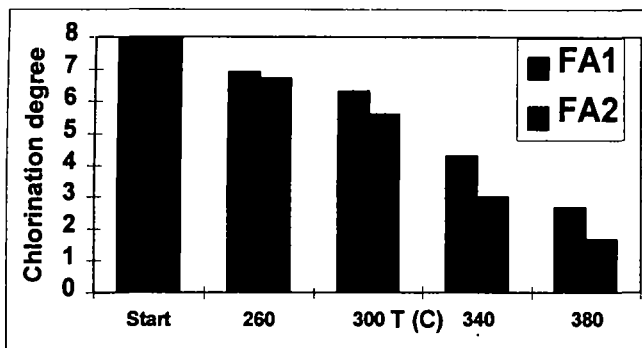

Figure 2: Average degree of chlorination measured for PCDD after the thermal treatment of OCDD (1h, N_2 atmosphere) on FA1 and FA2 between 260-340°C.

The destruction rates on the two ashes, however, showed the opposite behavior. Up to 340°C, FA2 exhibit only small destruction potency (Figure 3). After 1h heat treatment at 340°C more than 75% of the spiked OCDD was recovered on FA2 as MCDD-OCDD. With FA 1 under the same condition, less then 10% of the spiked OCDD amount were recovered as PCDD. At 380°C, the destruction increased considerably and less than 20% were found on FA2 mainly as MCDD and DCDD (Figure 1+3).

Considering only the important T_4CDD-OCDD (Figure 4), the recovery of both ashes at 380°C were below 1% (0.5% on FA1; 0.78% on FA2) of the spiked amount (Figure 4).
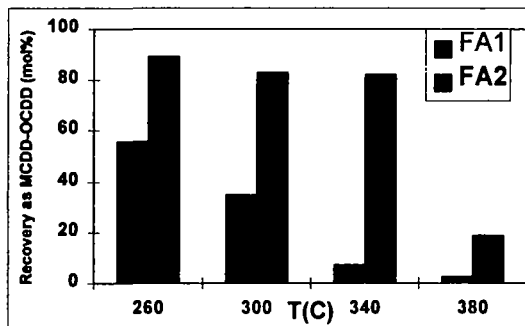

Figure 3: Recovery of total PCDD (MCDD-OCDD) on FA1 and FA2 after heat treatment at 260, 300, 340 and 380°C (1h, N_2-atmosphere)
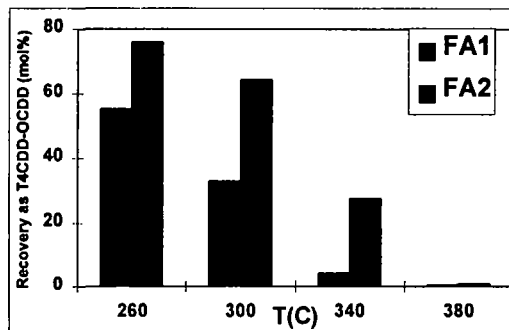
Figure 4: Recovery of T_4CDD-OCDD on FA1 and FA2 after heat treatment at 260, 300, 340 and 380°C (1h, N_2-atmosphere)

Discussion

As mentioned above, one difference of the two ashes are the use/non use of $Ca(OH)_2$ spray. This results for FA1 in a high pH of >12.3 while the pH of FA1 was <8. In our laboratory study on destruction of OCDD on model fly ashes with selected metal oxides, $Ca(OH)_2$ exhibit the highest destruction potency from the tested compounds[10]. Therefore, it seems to us most probable that this difference in ash composition cause the difference in destruction potency of these two ashes.

The procedure how the fly ash was fed into the micro reactor resulted in a small contamination with air. This was recognized due to *de novo* formation of PCDF during the dechlorination experiments with OCDD. FA2 shows here the higher *de novo* rates resulting from the higher

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carbon content and the lower pH. The low temperature treatment in the analogous experiments in sealed glass ampoules under "exclusion" of oxygen, did not result in a comparable formation of PCDF. Additionally, these experiments in the ampoules resulted in higher dechlorination rates compared to those performed in micro reactor (data not shown).

The dechlorination rate, destruction rate and *de novo* rate depend, therefore, on ash composition and the oxygen concentration.

The results from the micro reactor are in accordance with the actual performance in the industrial application with excellent PCDD/F decomposition in the temperature window around 380°C.

Therefore, the established experimental set up seems to be suitable for investigating the situation in real plant operation and it should be possible to optimize the process in respect to different ashes and operation conditions with the support of laboratory experiments.

Acknowledgment

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