INFLUENCES OF CL, CU AND BR ON THE FORMATION RATE OF PXDD/F DURING FUEL BED BURNOUT IN A GRATE FURNACE

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Introduction

Measurements above the fuel bed inside the combustion chamber of a pilot plant for municipal solid waste incineration showed significant formation of PCDD/F during the burnout process of solid waste on a grate. Under controlled combustion conditions, these PCDD/Fs were almost completely destroyed at high temperatures and long residence times already inside the combustion chamber where the flue gas burnout takes place. Only when the combustion process is disturbed high amounts of these PCDD/F are able to pass the furnace and lead to high concentrations in the raw gas in front of the flue gas cleaning system [1].

Based on the results from burning different fuel mixtures it was concluded that the burnout characteristic of the fuel bed and also the concentration of chlorine, copper and bromine in the fuel may have a significant influence on the formation rate of PCDD/F during fuel bed burnout. To investigate the effects of the elements Cu, Cl and Br on the formation of PXDD/F (X=Cl, Br) more in detail special experiments were conducted at our pilot plant TAMARA.

Experimental

During all test runs natural wood chips (Cl=600ppm, Cu=1.7ppm, Br<1ppm) mixed with swelling clay (Cl= 600ppm, Cu=120ppm, Br<1ppm) as inert material were used as model fuel to simulate municipal solid waste. This fuel mixture was characterized by almost constant heating values and low concentrations of the above mentioned elements of interest. The addition of

Cl (as pure PVC granulate), **Cu** (as fine dispersed Cu_2O) and **Br** (as fine dispersed KBr)

separately and in combination under constant combustion conditions will demonstrate the effects of these elements on the formation rate of halogenated dioxins and furans. The experimental program is shown in Tab.1

Tab.1: Experimental program

experiment no.	1	2	3	4	5	6
wood chips (kg/h)	175					
swelling clay (kg/h)	30					
Cu_2O (g/h)	-	50	-	50	50	50
PVC (g/h)	-	-	2000	2000	2000	-
KBr (g/h)	-	-	-	-	150	150

Since the heating value of the fuel was nearly unchanged by these additives the burnout process was practically unaffected. Therefore differences in the formation rates of halogenated dioxins and furans measured in the flue gas leaving the fuel bed could be attributed to the element concentrations contained in the fuel.
Sampling of the flue gas constituents including PXDD/F took place at several locations only a few cm above the fuel bed along the grate. Details of the furnace and the sampling procedure were described elsewhere [1]. The total mass flows of the halogenated dioxins and furans were calculated from the local concentrations and the local flue gas flows as shown in Fig.1.

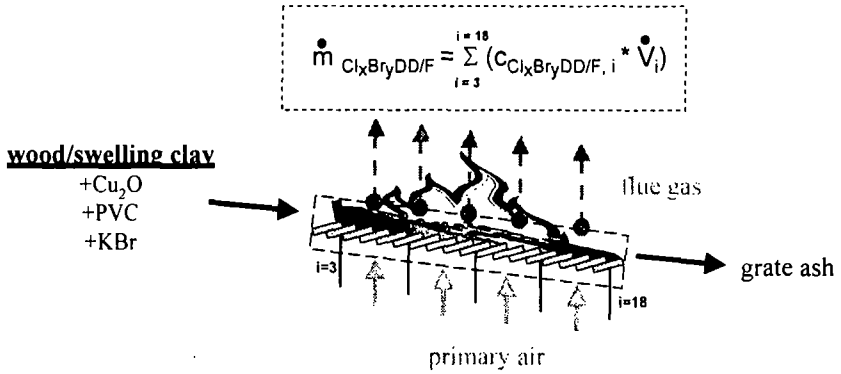

Fig. 1: Determination of the formation rate of halogenated dioxins and furans during fuel bed burnout

Results
The formation rates of PCDD/F at the experiments 1 to 5 are depicted in Fig 2. Both test runs burning wood chips (exp.1) and wood chips together with copper oxide (exp. 2) resulted only in negligible formation rates of PCDD/F.

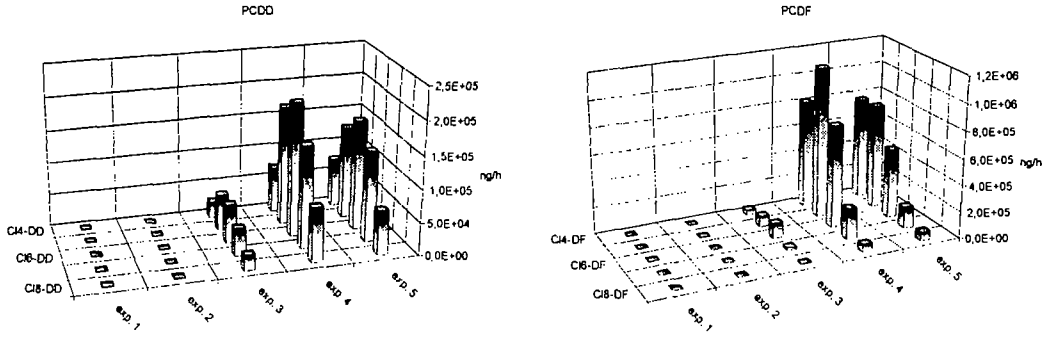

Fig. 2: Influence of Cu_2O and PVC on the formation of PCDD/F during fuel bed burnout

The experiment burning wood chips together with PVC (exp. 3) showed increased formation rates of PCDD/F. The highest formation rates were found when burning the wood chips together with PVC and copper oxide (exp. 4). When adding KBr together with PVC and Cu_2O a slight decrease

of the formation rate of the pure chlorinated dioxins and furans was observed. The homologue profiles were practically unchanged in both experiments.

Compared to exp. 2 where only Cu_2O was added the experiments with the combined PVC and Cu_2O addition (exp. 4 and 5) resulted in high copper concentration in the fly ash downstream of the boiler. This enhanced transfer of copper out of the fuel bed to the flue gas depends strongly on the chlorine content of the fuel [2] and indicates well the formation of copper chloride which can be volatilized easily at the high temperatures in the fuel bed.

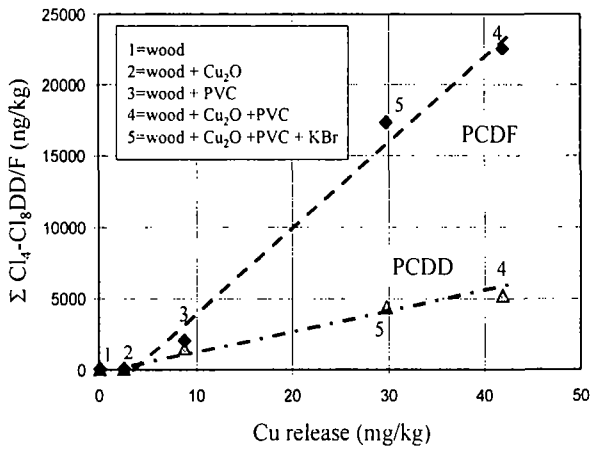

Fig. 3: Correlation of PCDD/F formation and Cu release from the fuel

The comparison of the copper release and the formation of PCDD/F showed a good correlation as shown in Fig. 3. This result agrees well with the findings of Lee [3] and Hatanaka [4].

Therefore it can be assumed that copper chloride affects the formation of PCDD/F during fuel bed burnout on two possible pathways :

- heterogeneous reactions of hydrocarbons [5] formed during fuel burnout [6]
- de-novo synthesis [7] from residual coke or from soot particles formed inside the fuel bed

The addition of KBr together with PVC and Cu_2O in exp. 5 resulted in high formation rates especially of mixed halogenated dioxins and furans as depicted in Fig. 4. Homologues more than 3 Br atoms were not detected. The formation rate of PCDD/F was nearly unaffected.

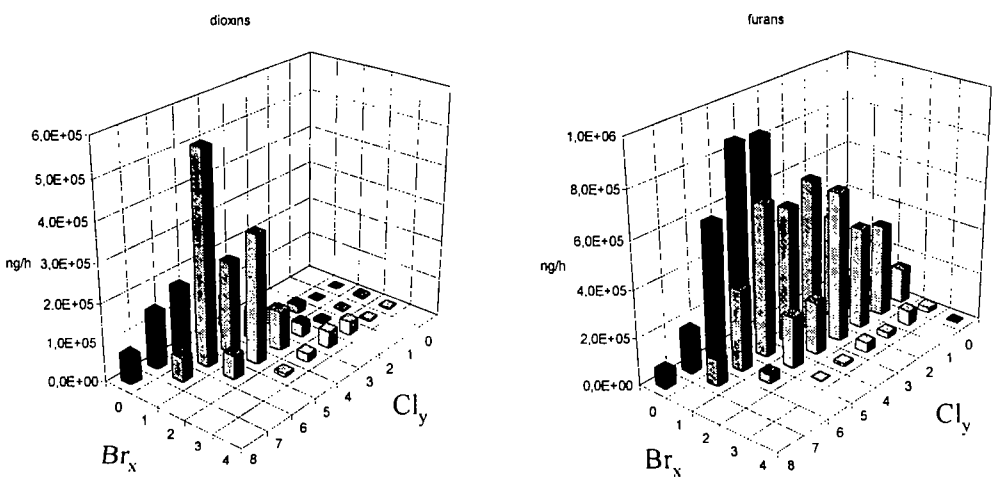

Fig. 4: Formation rates of Cl_xBr_y-DD/F burning wood together with Cu_2O, PVC and KBr

As shown in Tab. 2 the mole ratios of Cl/Br (A) for all PXDD/F formed during fuel burnout were found to be much smaller compared to the ratios of both elements contained in the fuel (Cl/Br=25) as well as of the acid gases HBr and HCl found in the raw gas downstream of the boiler (Cl/Br=29). From these results it can be concluded that bromine (from KBr) must be a more effective halogenation agent than chlorine (from PVC) in PXDD/F formation in the burnout process.

Tab.2: Cl/Br ratios of Cl_xBr_y-DD/F formed during fuel bed burnout (A) and in the raw gas (B)

	Cl_xBr_y-DD					Cl_xBr_y-DF				
x+y	4	5	6	7	8	4	5	6	7	8
Cl/Br (A)	7,5	5,7	5,3	5,0	7,3	4,2	5,0	7,0	5,8	8,8
Cl/Br (B)	20,1	27,3	19,0	12,9	59,0	8,4	20,6	22,1	29,4	40,3

The PXDD/F in the raw gas downstream of the boiler showed a much higher Cl/Br ratio (B). Since the PXDD/F formed during fuel bed burnout were nearly completely destroyed before leaving the combustion chamber the PXDD/F in the raw gas must be mainly formed inside the boiler section from older fly ash deposits [1]. The dominance of PCDD/F and their homologue profiles agreed well with experiments on the role of bromine in de-novo synthesis carried out by Luijk [8].

The addition of only KBr and Cu_2O (exp. 6) showed mainly the formation of PBDD/F during fuel burnout. The Br_2 and Br_3 homologues of the dioxins as well as of the furans were found to be dominant. Higher than 3 fold brominated compounds were not detected.

Summary

The investigations described above could be summarized as follows:

- If Cu_2O or PVC was individually present in the fuel only very small formation rates of PCDD/F were observed.
- High concentrations of copper combined with high concentrations of chlorine in the fuel lead to high formation rates of PCDD/F. The formation of PCDD/F correlated with the formation of copper chloride during fuel bed burnout.
- High concentrations of bromine, chlorine and copper in the fuel resulted in high formation rates especially of mixed Cl_xBr_y-DD/F. PCDD/F formation was nearly unchanged.
- KBr and Cu_2O addition lead mainly to formation of low brominated PBDD/F.

References

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