

## THE OXYDATIVE DEGRADATION OF CARBON AND ITS ROLE IN THE DE-NOVO-SYNTHESIS OF ORGANOHALOGEN COMPOUNDS IN FLYASH.

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### Introduction

The metal-ion catalyzed transfer of chloride to the residual carbon of fly ash, followed by an oxydative degradation to CO<sub>2</sub> and volatile organochlorine compounds has been recognized as an important source for the formation of noxious compounds, such as polychlorinated dibenzodioxins (PCDD) and -furans (PCDF) in incineration plants.<sup>1</sup> In order to obtain a better understanding of the processes involved, the analysis of volatile compounds was accompanied by the determination of total organic chlorine (TOX), extractable organic chlorine (EOX) and by the investigation of the oxidative behaviour of carbon during the degradation, measured by differential scanning calorimetry.

### Experimental

Fly ash was thermally treated in air at 300°C and 400°C, with reaction times between 0.5 and 8 hrs. The analysis of PCDD, PCDF, PCI-benzenes and PCI-phenoles was performed by GC-MS. Additionally the residual carbon was determined according to M. Metzger<sup>2</sup>. The total organic chlorine and the extractable organic chlorine was measured by a method modified for the problem<sup>3</sup>. Differential scanning calorimetry (Netzsch Mod. 444) was applied to the annealed specimen.

### Results and Discussion

The influence of annealing at 300° and 400° C on carbon-, TOX-, and EOX-concentration is shown in table 1 together with the PCDD/PCDF concentrations. The degradation of carbon can be described by a combination of two first order reactions, differing by their reaction constants:

$$c_t = c_0 * (a * e^{-k_1 * t} + b * e^{-k_2 * t}),$$

for 300°C	a = 0.387, k1 = 0.0165 min <sup>-1</sup>
	b = 0.613, k2 = 0.0009 min <sup>-1</sup> :
for 400°C	a = 0.873, k1 = 0.0431 min <sup>-1</sup>
	b = 0.137, k2 = 0.001 min <sup>-1</sup>

c<sub>t</sub> being the carbon concentration at time t.

Table 1: Concentrations of Carbon, Total Organic Halogen (TOX), Extractable Halogen (EOX) and PCDD/PCDF in Fly Ash as a Function of Thermal Treatment

	reaction time (hrs.)					
	untreated	0,5	1	2	4	8
temperature 300°C						
carbon (%)	4,5	3,69	3,17	2,75	2,23	1,93
TOX (ug/g)	926	648	602	503	399	338
EOX (ug/g)	12,4	21,1	29,1	22,9	19,2	22,2
PCDDCDF (ng Cl/g)	0	747	366	n.d.	4021	4956
EOX/TOX (%)	1,3	3,3	4,8	4,6	4,8	6,6
TOX/C * 10 <sup>-3</sup> molar ratio	7	6	6,4	6,2	6,1	5,9
PCDD,CDF/C * 10 <sup>-3</sup>	0	1,15	6,1	n.d.	10,1	14,7
PCDD,DF/EOX * 10 <sup>-3</sup>	0	35,4	126	n.d.	209	223
temperature 400°C						
carbon (%)	4,5	1,84	1,29	1,27	1,05	1,03
TOX (ug/g)	926	320	137	149	142	145
EOX (ug/g)	12,4	63,7	43,7	40,8	35,4	25,6
EOX/TOX (%)	1,3	19,9	31,9	27,4	24,9	17,6
TOX/C * 10 <sup>-3</sup>	7	5,9	3,6	4	4,6	4,8

At 300°C after 2 hrs. 40% of the original carbon is oxidized, the main product being CO<sub>2</sub>.<sup>4</sup> Parallel to this, the TOX is decreased from 926 µg/g to 338 µg/g. During the thermal treatment the EOX is increased from 12.4 to 29.1 µg/g, followed by a decrease to a nearly constant level around 22 µg/g. From a combined study of the data, it is shown that the ratio EOX/TOX is increased during the reaction time from 1.3 % in the untreated sample to 4.8 - 6.6 % after annealing. The molar ratio of organic chlorine/carbon is unchanged during the annealing at 300°C at a value of 5.9 to 7 \* 10<sup>-3</sup>. The fraction of the organic chlorine represented by the PCDD/PCDF increases from 0 to 14.7 \* 10<sup>-3</sup>, the corresponding ratio to the EOX from 35 \* 10<sup>-3</sup> to 22%. The data referring to the behaviour of chlorobenzenes and -phenols are currently evaluated.

At 400°C a fast degradation down to residual carbon concentrations of 1.3 to 1.0 % is achieved already after 1 hr., accompanied by a decrease of the TOX to practical constant 145 µg/g. During the heat treatment the EOX/TOX values rise to 25 - 30%, indicating a higher degree of degradation into smaller molecules than in the 300°C experiment. The molar ratio TOX/C changes from 7 \* 10<sup>-3</sup> to values around 4 \* 10<sup>-3</sup> showing a preferred degradation of C-Cl-structures. Also the -

se experiments will be supported by the determination of the volatile organochlorine compounds (PCDD/PCDF, PCIBz, PCIPh).

**DSC-Measurements:** The oxidative behaviour of the carbon in the annealed samples was studied in the temperature range from 50 to 60 °C by differential scanning calorimetry (DSC). By this technique the sample is heated with a linear temperature program and the energy released recorded, yielding DSC curves characterized by the peak temperature (at maximum reaction) and the enthalpy. The data are presented in fig. : 1. In the untreated sample a single reaction is observed with a peak temperature at 347 °C and an enthalpy of 22.9 kJ/g carbon. During the experiment a shift of the peak temperature occurs, and additionally a second

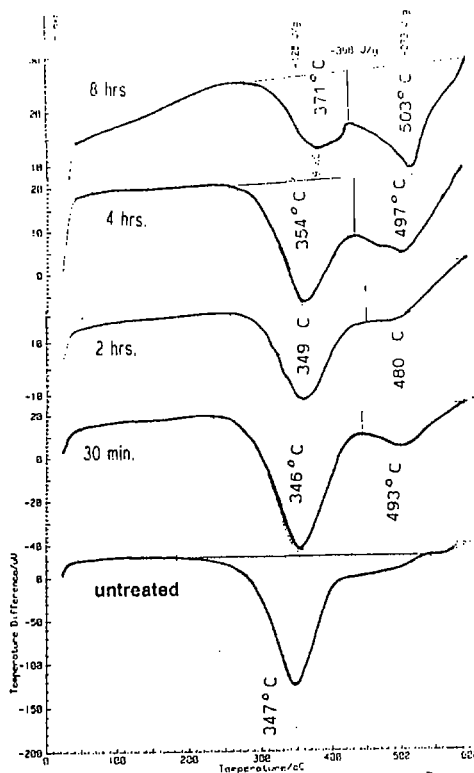


Fig. 1: DSC-Curves for Fly Ash Samples after Thermal Treatment at 300 °C

oxidation reaction is noted at 480 - 500 °C, its importance increasing with annealing time. The total enthalpy for the two reactions is constant at 22.3 +/- 1.3 kJ/g carbon for all samples, is, however, divided up between the two reactions. This appearance of an oxydation process at higher temperatures is the explanation for the slowing down of the carbon oxydation at 300°C.

### Conclusions

From the data it is concluded

- Fly ash contains appreciable concentrations of maromolecularly bound organic chlorine at levels of 900 ug/g, with only traces ( 1% relative) being extractable.
- Upon thermal treatment in air carbon is oxidized, leading to a decrease of the TOX, and a rise of the extractable fraction to 5% at 300° C and to 25-30% at 400° C.

- This degradation of the carbon is the source for the formation of a variety of volatile organic halogen compounds, such as PCDD/PCDF etc. and is an essential part of the de-novo-synthesis occurring on fly ash<sup>5</sup>.

### References

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