INVESTIGATION OF CHLORIDE TRANSFER AND OXYDATION AS PROCESSES IN THE
DE-NOVO-SYNTHESIS OF PCDD/PCDF ON FLYASH

L. Stieglitz, M. Eichberger, H. Bautz, W. Roth, J. Römer, D. Schild
Kernforschungszentrum Karlsruhe
Postfach 3640, D-76021 Karlsruhe, Germany

1. Introduction

The formation of organohalogen compounds from fly ash of municipal waste incinerators has been recognized as an important pathway for the release of polychlorinated dibenzodioxins (PCDD) and - furans (PCDF). The residual carbon from incomplete combustion was identified to be the precursor material for this so-called de-novo-synthesis. Based on laboratory experiments so far two basic reactions have been postulated to occur: a.) the metal-ion catalyzed transfer of chloride (halide) to the macromolecular structure of the carbon with the formation of carbon-chlorine bonds, b.) the oxidative degradation of these structures in the presence of oxygen and metal-ions (Cu^{2+}) as catalyst to carbon dioxide as the main product and volatile chlorinated aromatic compounds as by-products.[1] Besides PCDD/PCDF a variety of halogenated aromatic compounds are formed. These reactions are not restricted to incineration but are found to contribute in a series of thermal processes to the release of halogenated aromatics whenever carbon, chloride and special metal-ions are available, eg. in processing of copper ores and in metal recycling. The differentiation of the two processes " halide transfer - oxidation" with genuine fly ash is difficult. In this contribution data of the individual reactions are reported, obtained mainly by thermal treatment of model mixtures

2. Experimental

For the study model mixtures were prepared containing 4% activated charcoal, 7% chloride as KCl, 0,4 % Cu as $CuCl_2$ in Mg-Al-silcate. The mixture had a blank concentration of PCDD/PCDF < 1n/g for the single species, <20 ng/g for the sum of tetra- to octachloro spezies, and ca. 70 µg organic chlorine/g. Fly ash samples from a municipal waste incinerator were also included in the study. The samples were annealed in air at 150°, 200° 275° 300° 350°C, for the experimental details see [2]. The compounds volatilized were collected in a washing bottle containing toulene. After thermal treatment the residue was analyzed for total organic carbon, organic chlorine (TOX) and PCDD/PCDF and polychlorobenzenes (PClBz) and -phenoles (PClPh). The content of the washing bottles was analyzed for TOX and the compounds above.

SOU/FRM

3. Results and Discussion

3.1. The Formation of Organic Chlorine on Fly Ash and in Model Mixtures

Fly ash contains 500 - 900 µg/g organic chlorine (TOX). As can be shown by electron microscopic investigations the particulate carbon in fly ash appears to be fibers with an diameter of 10 - 15 µm with an distinct content of chlorine. Further analysis by ESCA confirmed a chemical state corresponding to a C-bond. For illustration an electromicroscopic overview of fly ash is shown in fig. 1a , with the carbon fibers in the center, in fig 1b the elemental composition of a carbon fiber is presented.
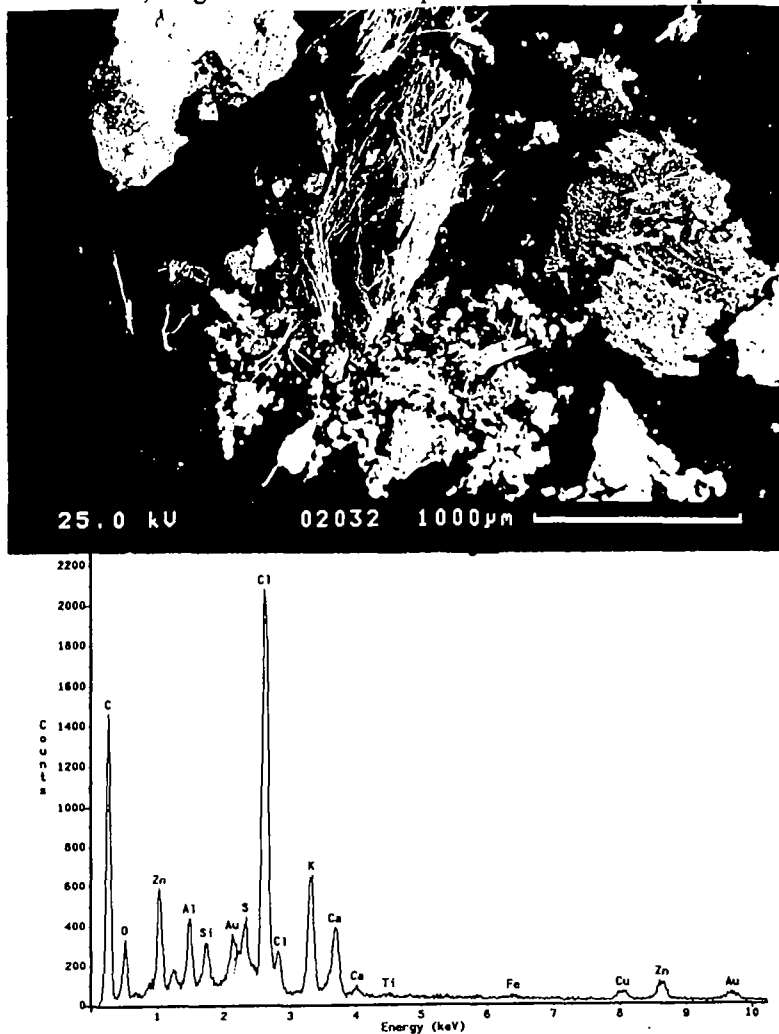

Fig. 1: Electronmicroscopic view (a) of fly ash with carbon fibers (center) and elemental analysis (b) with carbon and chlorine as main elements

Depending on temperature a fast increase in the model system is noted upon thermal treatment: At 150 - 200°C no change of the TOX (70 µg/g) is measured within the experimental errors. At higher temperatures a fast increase in the model system is observed upon thermal treatment:

The concentrations in µg/g acchieved are after

	5	10	15 min
at 275°C	98	136	266
at 300°C	126	236	300

From this it is apparent that in model mixtures starting with 275°C a fast transfer of the chloride to the carbon takes place. A saturation value for TOX is acchieved after longer reaction times (> 60 - 120 min): at 275°C ca. 350 µg/g, at 300°C ca. 700 µg/g and at 350°C ca. 650 µg/g. No reaction occurs in mixtures without Cu^{2+}, indicating the importance of Cu -ions as catalyst for the transfer of chloride. Similar reaction have been studied by Nonhebel in liquid systems.[3] The data compared with the corresponding results from fly ash samples are presented in table 1.

Table1: Behaviour of total organic chlorine (µg/g) in fly ash (FA) and in model mixtures (Mod)

temperature		reaction time (min)						
		0	15	30	60	120	240	360
275°C	Mod.	70	266	288	334	386	397	399
	FA	430	409	451	660	719	711	724
300°C	Mod	70	447	507	656	790	613	744
	FA	430	503	546	650	563	397	560
350°C	Mod	70	655	682	679	644	530	463
	FA	430	506	475	404	397	356	299

Except for the reactions at short times the general behaviour of TOX (sum of residual organic chlorine and volatile organic chlorine) in fly ash and in model mixture is similar: At 275 and 300°C slow increase in both systems occurs, whereas at 350°C a general decrease , probably due to oxidation and mineralisation to chloride is measured after 120 min reaction. From TOX only a fraction of 15 - 15% is extractable as EOX using hexane/cyclohexane.

3.2. Oxidative Degradation of Carbon and the Release of PCDD/PCDF

In previous studies the kinetics of carbon oxidation was described [2] by a combination of two first order reactions:

$$c_t = c_0 (a * e^{-k1t} + b * e^{-k2t})$$

Data of the carbon concentration upon annealing of model mixtures are listed in table 2.
As with fly ash, the reaction slows down after longer annealing and approaches a residual concentration. The parameters a,b and the reaction constants k1, k2 were evaluated. The reaction constants are comparable with fly ash data, a is 0.17 - 0.27, and b is 0.82 - 073, depending on temperature. The oxidation of carbon proceeds normally at 500°C. The presence of special catalysts causes a decrease to ca. 365°C as reported by Patrick, Walker 4) and McKee 5). Similar effects are responsible for the oxidation processes in fly ash. The influence of metal additves to carbon was investigated using differential scanning calorimetry (DSC). By this technique the sample (30 - 50 mg) is heated with a linear temperature program and the energy released recorded, yielding DSC curves, charakterized by the peak temperature (at maximum reaction) and the enthalpy.

SOU/FRM

Table 2: Decrease of carbon concentration (%) in model mixtures

°C	reaction time (min						
	0	15	30	60	120	240	360
275	3,1	2,8	2,74	2,57	2,51	2,64	2,44
300	4,4	3,9	4,0	3,8	3,3	3,1	2,9
350	3,1	2,37	2,	1,69	0,92	0,51	0,28

In table 3 the peak temperatures (heating rate 5 K/min) obtained with carbon-metal compound mixtures (ca. 4-5% Me) are presented. [6] The strong influence of metal additives is remarkable.

Table 3: Influence of metal-ion additives on the peak temperatures for the oxidation of carbon

Charcoal	544	CuO	508
Fe_2O_3	533	Cu	467
MnO_2	533	$CuCl_2$	411
$ZnCl_2$	496	$CuSO_4$	435
$NiCl_2$	452	CuF_2	456
$CoCl_2$	420	$CuBr_2$	315
		$CuCl_2*KCl$	308

The effect is especially pronounced for copper chloride which causes a drop of the oxidation temperature by ca. 200°C. With the complex $CuCl_2*KCl$ the lowest peak temperature is achieved with 309°C. The enthalpy is in the range between 21 and 24 kJ/g and relatively independent of the system. The corresponding data for fly ash are 347°C peak temperature and 22.9 kJ/g carbon. The investigation demonstrates the importance of the chemical composition of the fly ash for the oxidation process.

The degradation of the carbon is accompanied by the formation and release of volatile organohalogen compounds. The concentrations in the residues including the fractions volatilized are given as sums in table 4.
The results of table 4 can be compared with the TOX and the fraction of TOX calculated which is converted to the respective compounds: At 300° C the fraction of PCDD and PCDF is $7 - 9 *10^{-3}$ that of PClBz 3 - 4%. The ratio of chlorine:carbon in the residue after thermal treatment varies with temperature and reaction time (table 5). At 275 -300°C the atomic ratio chlorine/carbon lies between 3.1 and $5.8 * 10^{-3}$, with a slight variation with reaction time. At 350°C the Cl/C is increased by a factor of 3. Apparently the chloride tranfer and the formation of Cl-C-bonds is faster than the oxidative degradation of the carbon lattice.

Table 4. Formation of organohalogen compounds in model mixtures (ng/g)

temp.		0	15	reaction time 30	60	(min) 120	240	360
275°C	PCDD	<20	500	980	1250	2060	2400	3100
	PCDF	<20	700	1300	1700	3100	3000	4300
	PClBz	<20	8300	12500	17600	27100	31500	35000
	PClPh	<20	2060	1700	1200	360	370	400
300°C	PCDD	<20	1700	2500	6100	7900	8800	11600
	PCDF	<20	2500	3500	7300	9600	9600	13000
	PClBz	<20	12900	18400	29200	33000	39400	45100
	PClPh	<20	1200	1000	600	500	500	400
350°C	PCDD	<20	3200	4400	5700	4200	2100	730
	PCDF	<20	8400	11000	13000	12000	6000	3000
	PCBz	<20	44000	61000	69000	84000	90000	90000
	PClPh	<20	470	270	1000	270	480	100

Table 5 : Ratio of chlorine/carbon in model mixtures

temperature	30	reaction 60	time (min) 120	240
275°C	$3.6 * 10^{-3}$	$4.3 * 10^{-3}$	$5.2 * 10^{-3}$	$5.1 * 10^{-3}$
300°C	$3.1 * 10^{-3}$	$4.0 * 10^{-3}$	$4.6 * 10^{-3}$	$5.8 * 10^{-3}$
350°C	$9.2 * 10^{-3}$	$12.9 * 10^{-3}$	$16.5 * 10^{-3}$	$19.4 * 10^{-3}$

4. Conclusions

From experimental results with fly ash and model mixtures and the application of group parameters, combined with physico-chemical investigations such as DSC and electronmicroscopy/ESCA, a contribution to the mechanism of the de-novo-synthesis can be made and the following conclusions be drawn:

- Carbon in fly ash appears mostly as fibers. The presence of organic chlorine on the surface is distinct. The chlorine:carbon ratio as evaluated from the determination of organic chlorine and carbon (ca $5 * 10^{-3}$) does not represent the real elemental ratios on the surface. The chlorination degree of the carbon surface appears to be much higher.
- The transfer of inorganic chloride to the carbon matrix is catalyzed by Cu^{2+} and proceeds fast, within 10 - 15 min., measurably starting at 275°C.
- The oxidation of the carbon is slower than the chloride transfer and is the rate determining step for the formation of organohalogen compounds. It is also influenced by the presence of metal-ions, resulting in a decrease of the oxidation temperature. The strongest effect is from copper halides, especially in combination with adddtional chloride.

SOU/FRM

5. References

1. Stieglitz, L. , G. Zwick, J. Beck, W. Roth, H. Vogg, On the De-Novo-Synthesis of PCDD/PCDF on Fly Ash of Municipal Waste Incinerators, Chemosphere Vol 18, pp1219-1229, 1989.
2. Stieglitz, L. M. Eichberger, J. Schleihauf, J. Beck, G. Zwick, R. Will, The Oxidative Degradation of Carbon and its Role in the De-Novo-Synthesis of Organohalogen Compounds in Fly Ash, Chemosphere Vol 27, pp343-350, 1993
3. Nonhebel, D.C., Copper-Catalyzed Single Electron Oxidations and Reductions, Chem.Soc. (London), Spec.Publ. 24, 409 (1970)
4. Patrick, J.W., A. Walker, A Study of the Copper-Catalyzed Combustion of Carbon, Carbon 12, (1974), 507
5. McKee, D.W. A Copper-Catalyzed Oxidation of Graphite, Carbon 8,(1970), 131
6. Eichberger, M. Thermoanalytische Untersuchungen der Kohlenstoffoxidation in Flugaschen sowie in synthetischen Mischungen, Diploma Thesis, University Heidelberg 1992