The Influence of Elemental Sulfur on the De-Novo-Synthesis and the Oxidation of Residual Carbon on Fly Ash

R. Bechtler, L. Stieglitz, G. Zwick, R. Will
Institut für Technische Chemie, Bereich Physikalisch-Chemische Verfahren
Forschungszentrum Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany

1. Introduction

The metal-catalyzed oxidative decomposition of residual carbon on fly ash 3) leads to a large variety of compounds. In good approximation, the oxidation of the carbon can be described as a combination of two reactions 1). In the course of these reactions, a series of polychlorinated compounds are formed as by-products and released. In this paper the influence of different amounts of elemental sulfur on fly ash, added before thermal treatment, is discussed. The objective of this work was to investigate the change of the activity of the metal-catalyst, the kinetics of carbon oxidation and the chlorination potential of the fly ash by the presence of sulfur. Besides PCDD/PCDF, the influence on the formation of several other halogenated compounds was determined. Further on, the ability of sulfur to react with instable cracking products of the macromolecular carbon structure e.g. butadienes, styrenes, is discussed.

2. Experimental

Fly ash from an electrostatic precipitator of a MWI-plant was used in this study. The inhomogeneous material was ground and refluxed five times with cyclohexane and benzene, filtered and dried under reduced pressure (0,15 mbar) at room temperature for 48 hours. Then, 1 to 3% elemental sulfur was added to the fly ash. For the sample with 1% sulfur thermal treatment was performed for 30, 60, 120 and 240 min., the other samples for 120 min.. The samples were treated in a vertical quartz tube with a frit at the bottom using an ascending flow of wet synthetic air at 350°, 400°, 450°C, for more experimental details see 2). After thermal treatment and clean-up, the residual carbon was determined by total oxidation at 850°C and catalytic conversion to CO_2. The quantification occurs by infrared detection and the contents of carbonates was subtracted . The PCDD/ PCDF/ PCBz and some other polychlorinated compounds were quantified by GC/MS after clean-up and fractionation on alumina.

3. Results and Discussion

3.1 *Oxidative decomposition of residual carbon*

In previous studies, the kinetics of the residual carbon decomposition was described in good approximation 1) by a combination of two first order reactions:

$$c_t = c_0 \left(a \bullet e^{-k1 \bullet t} + b \bullet e^{-k2 \bullet t} \right)$$

The parameters a and b represent the initial fractions of the residual carbon (c_0) which are decomposed to CO_2 and volatile organic compounds. For the fly ash with 1% sulfur, a parametric regression of the measured concentrations of residual carbon after thermal treatment was performed and the reaction constants are given in table 1:

Table 1: Reaction constants for decomposition of residual carbon on fly ash with 1% elemental sulfur

temperature °C	a	k_1 min.$^{-1}$	b	k_2 min.$^{-1}$
350°C	0,51	0,067	0,49	0,0031
400°C	0,70	0,057	0,30	0,0048
450°C	0,80	0,050	0,20	0,0073

The differential scanning calorimetry of the fly ash samples with amounts of sulfur up to 3% shows, that the characteristic peak temperature at maximum reaction ist constant at 347°C. However, we determined the residual carbon of all samples after thermal treatment and found higher residual carbon concentrations with ascending amounts of elemental sulfur. Therefore we suppose, that the added sulfur has no influence on the peak temperature at maximum decomposition of carbon. However, the reaction constants of the kinetics of the residual carbon decomposition are changed (see 1)).

3.2 Formation of PCDD/PCDF/PCBz

After thermal treatment and clean-up of fly ash with different contents of elemental sulfur, a series of polychlorinated compounds are quantified. For a first contribution, we report about the effect on the formation of PCDD, PCDF and PClBz. With increasing contents of elemental sulfur, more PCDD/PCDF are formed. Further on, the formation of the PClBz in relation to the rest of quantified polychlorinated compounds is reduced. In table 2, some of the determined concentrations are presented.

Table 2: Formation of PCDD/PCDF/PCIBz in fly ash with different contents of elemental sulfur up to 3%, at 350°C, 400°C and 450°C total concentration after 2 hrs treatment (ng/g fly ash)

temp. [°C]	sulfur conc.	PCDD	PCDF	PCIBz
350	1%	2747	8151	76396
	2%	8404	10869	97652
	3%	7395	8325	41118
400	0%	638	4550	77639
	1%	2552	8755	47189
	2%	3883	6742	36666
	3%	5104	7491	34988
450	1%	675	4078	24950
	2%	948	3567	23455
	3%	1217	3300	21505

To compare the formation of PCDD and PCDF, the concentrations are transformed in molar values. In fig. 1, the ratio between the PCDD and PCDF formation is presented.

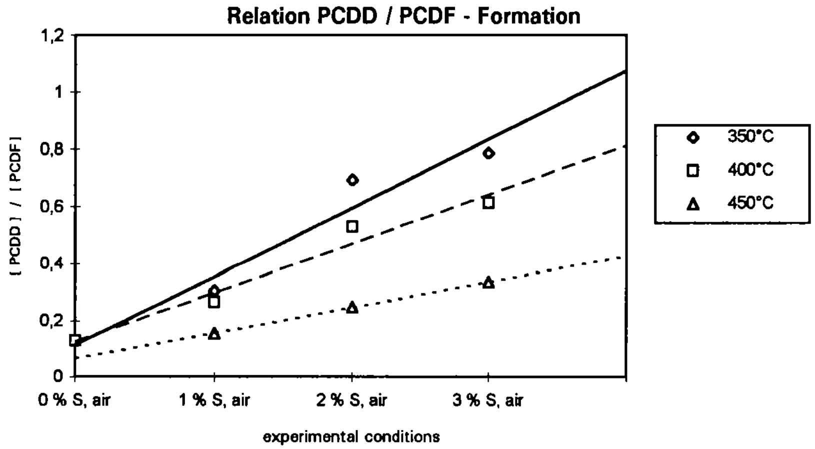

Fig. 1 : The molar ratio PCDD/PCDF, in dependence of different contents of elemental sulfur on fly ash

As seen from fig. 1, the ratio PCDD/PCDF is increased, with increasing contents of elemental sulfur.

3.3 Formation of Intermediate Compounds by De-Novo-Synthesis

Apart from PCDD/PCDF/PClBz, a series of other compounds is formed ²⁾. These compounds are aromatics with a vinyl- or butadienyl-group which are stabilized, by perchlorination. In detail, the compounds are hepta- and octa-chlorostyrene, decachlorovinylnaphthalenes, decachlorophenylbutadiene, decachlorooctatetraene and the dodecachlorobisphenylethenes (perchlorostilbenes). Their maximum of formation occurs after 60 min. reaction time. After that, the compounds react on the hot surface of the fly ash to other compounds, and after 240 min., only amounts in the range of the detection limit are determined.

Conclusions:

- By the addition of elemental sulfur to the fly ash before thermal treatment, an influence on the heterogeneous metal-catalyzed oxidation of the carbon 3) is observed. With increasing temperatures, the reaction constant k_1 of the fast reaction is reduced in the presence of sulfur. From this it is indicated that a diffusion controlled process is responsible for the first reaction. Parallel, the rate for the second reaction is higher than without sulfur and its importance increasing at higher temperatures. The transport of the reaction partners influences the kinetics of the reaction.
- Increasing amounts of sulfur on the fly ash lead to other compositions of the crack-products, and the formation of PCBz is reduced. With increasing sulfur content, the formation of PCDD is prefered compare to that of PCDF.
- Parallel to the formation of CO_2, the macromolecular carbon structure of the fly ash is decomposed to intermediate aromatic and aliphatic structures, which are stabilized by perchlorination.

References:

1) Stieglitz L., M. Eichberger, J. Schleihauf, J. Beck, G. Zwick, R. Will, (1993) „The Oxidative Degradation of Carbon and its Role in the De-Novo-Synthesis of Organohalogen Compounds in Fly Ash“ Chemosphere, Vol. 27, No. 1-3, pp 343-350

2) Bechtler R., G. Zwick, K. Hedwig, W. Roth, L. Stieglitz, (1995) „Formation of Polychlorinated Aromatic and Aliphatic Compounds on Fly Ash in the Presence of Sulfur“, Dioxin´95, Vol. 23, FRM pp 353-356

3) Schwarz G., L. Stieglitz, (1992) „Formation of Organohalogen Compounds in Fly Ash by Metal-Catalyzed Oxidation of Residual Carbon“, Chemosphere, Vol. 25, pp 277-282