

Role of Basic Oxides on the *De Novo* Synthesis of PCDD/PCDF and the Influence of the Gas Phase Composition

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Introduction

The dioxin formation potential of fly ash samples from eight Japanese fluidized bed incinerators during heat treatment between 290-400°C in a stream of air was found to be very low compared to that of fly ash samples from European stoker type incinerators [1]. The low *de novo* synthesis potential under the conditions of this heat treatment could be assigned to a comparatively high calcium content, resulting in a rather high pH of the fly ash of 11.5 to 12.7 [1]. The suppression of PCDD/F formation by CaO spray was also reported in another laboratory study [2].

Injection of calcium oxide or calcium carbonate into the raw gas stream of waste incinerators is the favored method in Japan for the removal of acid gases (SO_x and HCl).

We found that in case of dust removal by electrostatic precipitators (ESP) operated at temperatures between 230-270°C, the major proportion of PCDD/PCDF formation takes place in the ESP after Ca-injection [3]. The question therefore arises why the inhibiting effect of calcium found in the laboratory experiments is not equally effective in the incinerators.

The difference between the laboratory experiment and the incinerators is the composition of the gas phase. We therefore investigated the influence of acidic gas phase and combustion off gases on the *de novo* synthesis of PCDD/PCDF on basic fly ashes and model fly ashes with basic oxides.

Materials and Methods

Major basic species present in fly ash are Al₂O₃, CaO, MgO (and the corresponding silicates).

The following model fly ash samples (MFA) were prepared:

MFA1: carbon free fly ash from a fluidized bed incinerator (21%Ca) + 2% activated carbon + 0.5% Cu as CuCl₂ + 5% Cl⁻ as KCl.

MFA2: basic aluminum oxide + carbon, Cu and Cl⁻ as for MFA1.

MFA3: silica containing 28% CaO + carbon, Cu and Cl⁻ as in MFA1.

MFA4: silica containing 15% MgO + carbon, Cu and Cl⁻ as in MFA1.

MFA5: silica + carbon, Cu and Cl⁻ as in MFA1.

MFA1 to MFA3 were prepared also by a modified procedure resulting in the samples MFA1a to MFA3a. For their preparation the aqueous slurry of ingredients described for the preparation of the model fly ash samples was adjusted to pH 5 by addition of diluted H₂SO₄ and dried.

In addition three fly ash samples from fluidized bed incinerators were included in the experiments. FA-1 and FA-2 stem from two older plants with poor combustion practice while FA-3 was sampled in a new FBI incinerator with good combustion practice.

For the flow experiments with combustion off gases, 1g paraffin was pyrolysed in small portions at 900°C in an air stream and the gas was passed through a bed of 2g fly ash (FA-3 (N₂)) at 300°C for about one hour. The heat treatment, the preparation of model fly ash samples (MFA) and the methods for extraction, clean-up and analysis of PCDD/PCDF have been described previously [1,4].

Results and discussion

Influence of Ca spray stop in fluidized bed incinerator 1

In a measurement campaign we evaluated the influence of calcium spray on the PCDD/F formation rates in FBI 1. During standard operation, calcium was introduced as CaCO₃ at 850°C resulting in basic fly ashes (pH 11.7) with a Ca content of 20%. Upon stopping the Ca spray we observed a minor increase (0-25%) of PCDD/F in the gas phase. If we include the PCDD/F amount adsorbed on the fly ash in the total PCDD/F mass balance, we could not establish any influence of the stop of Ca-spray in this incinerator upon PCDD/F formation.

Influence of basic oxides on the PCDD/F de novo formation potential of model fly ashes

The 4 model fly ash samples MFA1 to MFA4 including basic oxides show only a low *de novo* synthesis potential for PCDD/PCDF while MFA5 on silica-basis shows a high PCDD/PCDF formation potential (Table 1)

These results indicate that the heterogeneous catalysis of PCDD/PCDF formation is inhibited by the basic oxides. The model fly ash samples MFA2 to MFA4 which had been prepared in aqueous solution showed pH values from 9.3 (Al₂O₃) to 13 (CaO) (Table 1). They all show an inhibition of PCDD/PCDF formation to a similar degree which suggests that not the Broensted basicity of the oxides but rather the Lewis basicity is of importance for this effect.

After neutralization, the samples MFA2a and MFA3a showed a *de novo* synthesis potential for PCDD/PCDF equal to MFA5 while the PCDD/PCDF formation with MFA1a was slightly lower (Table 2). For a MFA based on alumina Schoonenboom and Olie also found a higher PCDD/F formation potential with the acid alumina [6]. The inhibitory influence of basic oxides upon the *de novo* synthesis can therefore be annulled by neutralization of the ash samples.

Table 1: *De novo* synthesis of PCDD/PCDF on model fly ash samples before (MFAx) and after (MFAx_a) neutralization

Sample	MFA 1	MFA1a	MFA2	MFA2a	MFA3	MFA3a	MFA4	MFA 5
ΣPCDD	148	678	50	2810	8	2388	46	2135
ΣPCDF	429	1519	171	10471	66	6220	26	5723
I-TEQ	15	48	8	406	2	238	0.9	182
pH	12.6	5	9.3	5	13	5	9.4	6.8

Influence of the gas composition on the de novo formation of basic fly ashes

1) Influence of HCl in the gas phase on model fly ashes and fly ash samples from fluidized bed incinerators

If HCl is added to the gas phase (1500 ppm) during the heat treatment of MFA1 one finds a PCDD/PCDF formation comparable to that of MFA1a (total PCDD 950 ng/g, total PCDF 1506 ng/g, I-TEQ 34 ng/g).

Heat treatment of fluidized bed fly ash samples (FA-1 and FA-2) which show no significant PCDD/PCDF formation potential in air at 300°C [1] yield 18 fold (8000ng/g) or 4 fold (9500ng) PCDD/PCDF concentration, respectively, when the gas phase contains 1500 ppm HCl (Tab. 2). After the heat treatment the pH of the samples was still >11. Therefore HCl does not act by neutralization of the fly ash itself but rather by acidic activation of the particle surface. With a third FBI fly ash (FA3), no significant *de novo* synthesis was found after the addition of HCl to gas phase (Tab.2). This ash sample originates from a FBI with good combustion practice (PCDD/F emission concentration below 0.1ng I-TEQ/Nm³ and less than 1ng I-TEQ/g in the fly ash). With this fly ash sample low carbon content therefore seems to be the second limiting factor.

So far it can not be decided whether during the heat treatment of fly ash the basic matrix inhibits the catalytic transfer of chlorine, the chlorine formation or the oxidative decomposition of the particulate carbon. In preliminary studies we found that basic oxides inhibit both the formation of chlorine and the decomposition of the carbon matrix.

Table 2: PCDD/PCDF concentration in FBI fly ash samples before (FAX) and after (FAX-T) heat treatment (1h, 300°C) in the presence of 1500 ppm HCl.

Sample	FA1	FA1-T	FA2	FA2-T	FA3	FA3-T
ΣPCDD	305	1570	2230	4580	16	14
ΣPCDF	170	6960	1140	6710	31	57
I-TEQ	4	102	23	117	0.55	1.8

II) Influence of combustion off gases on PCDD/F *de novo* formation of basic FBI fly ash

In Table 2 the dioxin formation potential of the fluidized bed fly ash samples are shown. With the inactive FA-3 we evaluated the influence of organic components in combustion gas (paraffin combustion). For these experiments we first removed the original PCDD/F by N₂ heat treatment. Further heat treatment of this "dioxin free" ash FA-3(N₂) in the presence of HCl (1000ppm) did not result in significant formation of PCDD/F (Tab.3). However, when the off gas from paraffin combustion is passed through a bed of FA-3(N₂) at 300°C formation of 2390ng PCDD/PCDF/g ash (29 ng I-TEQ/g) is observed. This proves that the low dioxin formation potential of FA-3 is indeed due to the low carbon content.

This combustion off gas seems sufficient to activate the catalyst. An alternative interpretation is that the "carbon source" or respective the precursor in the combustion gas do not require further catalytic activation for PCDD/F formation. But also when we assume that the carbon from the off gas do not need an additional catalytic break down as it is necessary for the unburned carbon in the fly ash or for the added activated carbon, at least for the chlorination step a catalytic transfer from the fly ash is necessary. The low degree of chlorination (Fig.1) of PCDD/F in this experiment shows that the chlorinating activity of the catalyst was only partly recovered with the combustion off gas of paraffin.

When the paraffin combustion gas was passed through the FA-3(N₂) bed in the presence of 1000 ppm HCl, 12500 ng PCDD/PCDF/g ash (200ng I-TEQ/g) was formed. And the homologue pattern (chlorination degree) shifted towards higher chlorinated PCDD/PCDF typical for incineration (Fig.1).

Table 3: PCDD/PCDF concentration resulting from *de novo* synthesis when passing air through FA-3 (nitrogen treated) containing whether HCl (1000ppm) or off gas of paraffin combustion or HCl (1000ppm) and the off gas of paraffin combustion

Sample	before heat treatment		after 1h heat treatment			
	FA-3 crude	FA-3(N ₂) after N ₂ treatm.	FA-3(N ₂) air	FA-3(N ₂) air+HCl	FA-3(N ₂) Paraffin	FA-3(N ₂) Paraffin+HCl
ΣPCDD	16	0	0.9	11	205	2580
ΣPCDF	31	0	8.6	54	3280	12500
I-TEQ	0.55	0	0.23	1.4	29	200

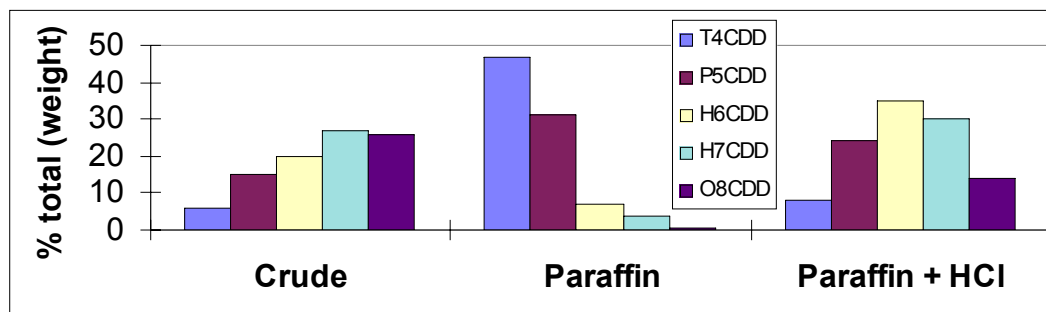


Figure 1: Homologue pattern (chlorination degree) of PCDD in crude FA-3 compared to the heat treatment of FA-3(N₂) in a stream of paraffin combustion of gas or paraffin combustion off gas + HCl (1000ppm)

Conclusion

Basic oxides inhibit the *de novo* synthesis of PCDD/F in heat treatment in air. Acidification the gas phase by HCl can annul the inhibitory effect of the basic oxides on the *de novo* synthesis without neutralizing the ash itself. The off gas of paraffin combustion increases the *de novo* synthesis of PCDD/F on basic fly ash. However a lower degree of chlorination is found. Addition of HCl resulted in a further increase of PCDD/PCDF formation and a the homologue pattern shifted towards that typical of incineration. This interaction of combustion off gas and basic ash in the presence of HCl elucidate why basic ashes showing no *de novo* formation in the heat treatment in the presence of air are potent catalysts for dioxin formation in actual plants. Additionally it explains why Ca(OH)₂/CaCO₃ does not substantially change the PCDD/F formation in the investigated incinerators.

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