Formation and Destruction of PCDD/PCDF During Heat Treatment of Fly Ash from Fluidized Bed Incinerators

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INTRODUCTION

Heating fly ash from municipal waste incinerators (MWI) in a stream of air at 300°C results in an increase of PCDD/PCDF by *de novo* synthesis, catalyzed by the fly ash [1-3]. In contrast, under oxygen deficiency conditions the fly ash catalyzes the decomposition of PCDD/PCDF by dechlorination/hydrogenation [3]. In these and subsequent studies verifying these phenomena fly ash from grate fired incinerators was always used [4-6].

When we observed that the PCDD/PCDF isomer distribution pattern of fluidized bed incinerators (FBI) was distinctly different from those of grate fired incinerators [7] it seemed of interest to study the PCDD/PCDF formation potential of FBI fly ash in comparison to fly ash from grate fired incinerators.

MATERIALS AND METHODS

Fly ash samples were obtained from 10 different MWI in Japan. Eight from FBIs (A-H) and two from grate fired incinerators (J1, J2). Prior to experiments, the materials were homogenized.

In the experiments with the addition of activated carbon (WAKO Pure Chemical Industries, Ltd., Japan) or KCl (*dito*), the fly ash samples or the silica gel (in the case of model fly ash) were mixed with the respective material and suspended in water. After thorough mixing, the slurries were treated for 15 minutes in an ultrasonic bath and finally the samples were dried.

The samples (0,5-2g) where heated in a horizontal quartz tube in a stream of oxygen/nitrogen (10/90) or argon with a flow rate of 50 ml/min. The temperature varied between 290 and 400°C, the reaction time from 1 to 8 hours. The gas stream was passed through a washing bottle with toluene. After the experiment the glass tubes were rinsed with toluene. These rinses were combined with the toluene in the washing bottle.

Extraction, clean up procedure and quantification is described elsewhere [8,9].

RESULTS

The maximum of PCDD/PCDF formation during heat treatment in the presence of oxygen for fly ash samples from grate fired incinerators is around 300°C [1-3] or somewhat higher [5,10]. The same is true for model fly ash samples [11]. The PCDD/PCDF formation potential for all ten ash samples was therefore studied at 310°C. Additionally, the temperature dependency of PCDD/PCDF formation was studied with two ash samples from FBIs in the range of 290 to 400°C.

The two ash samples from Japanese grate fired incinerators (J1, J2) did show a five/twelve-fold increase of PCDD/PCDF concentration during the heat treatment (Figure 1A), as previously described for fly ash samples from grate fired incinerators in Germany [1-3].
However, the 8 fly ash samples from the fluidized bed incinerators (A-H) showed a totally different behavior in the thermal treatment (Figure 1B). The highest increase of total PCDD/F concentration was by a factor of 1.4 for fly ash samples B and F. The ash samples from three facilities (A,E,G) showed an increase by a factors 1.1 to 1.3. Even a decrease in total PCDD/F concentration was found for three fly ash samples (C, D, H).

With ash A the time dependency of the *de novo* synthesis was investigated at 310°C (Figures 2A, 2B). Extending the temperature treatment for a few hours with fly ash A, which showed an 1.15 fold increase during the first 1.5 hours, resulted in a final decrease of the PCDD/F concentration (Figures 2A, 2B). Therefore the low *de novo* synthesis potential seems to be consumed after a few hours. A difference in the formation/destruction behavior is observed for PCDD and PCDF. PCDD increased only slightly during the first hour resulting after 8 hour treatment in a net decrease of 50% (Figure 2A), while PCDF showed a 30% increase during the first hour which slowly decreased after 4 hours to yield after 8 hours about the starting concentration (Figure 2B).

During this heat treatment the PCDD/PCDF homologue pattern shifts towards the lower chlorinated congeners (Figures 2A and 2B). This is more pronounced for the PCDF for which after 8 hours heat treatment, only 16% of the O_8CDF remains while the T_4CDF and P_5CDF show a four- and three-fold increase respectively. Therefore a considerable part of the destruction of PCDD/PCDF is due to a hydrogenation/dechlorination process. This hydrogenation/dechlorination reaction is seen with ash samples from grate fired incinerators only under oxygen deficiency conditions (3,12).
As a consequence of the dechlorination of the PCDD/PCDF congeners, the I-TEQ value increases about 40% although the total PCDD/PCDF concentration decreases. This shift of PCDD/PCDF homologue pattern towards the lower chlorinated congeners is also observed with the other 7 FBI fly ash samples resulting in an increase of total I-TEQ, including the three ashes were already after 1 hour a net decrease in PCDD/PCDF concentration was observed.

The temperature dependency of the PCDD/PCDF formation in the FBI ash samples A and F is shown in Figures 3A and 3B (1.5hr treatment). The PCDD/PCDF formation potential reaches its optimum between 290 and 330°C. At 350°C already a net decrease in PCDD/PCDF conc. is observed for both samples, starting for sample A at 330°C. After 1.5 h of heat treatment at 400°C the PCDD/PCDF concentration has decreased for sample A by 86% and for sample F by 82%. PCDF are generally formed faster/decomposed slower than PCDD here (Figures 3A, 3B).

Explanation of the observed formation/destruction behavior
Fly ash catalyzes two processes: PCDD/PCDF formation and PCDD/PCDF destruction [3]. The temperature dependency of these two processes in the presence of oxygen is schematically shown in Figure 4. While the formation reaches a plateau at about 300°C to 350°C the PCDD/PCDF destruction increases exponentially with increasing temperature. The net formation/destruction observed in the presence of oxygen at any temperature is dependent on the catalytic properties of the individual fly ash. Obviously for the ash samples from grate fired incinerators at 300°C the formation outweighs the destruction considerably. Only at temperatures above 450°C the destruction rate is higher than the formation rate and a decrease in PCDD/PCDF formation is observed. For the eight fly ash samples from fluidized bed incinerators the curves of

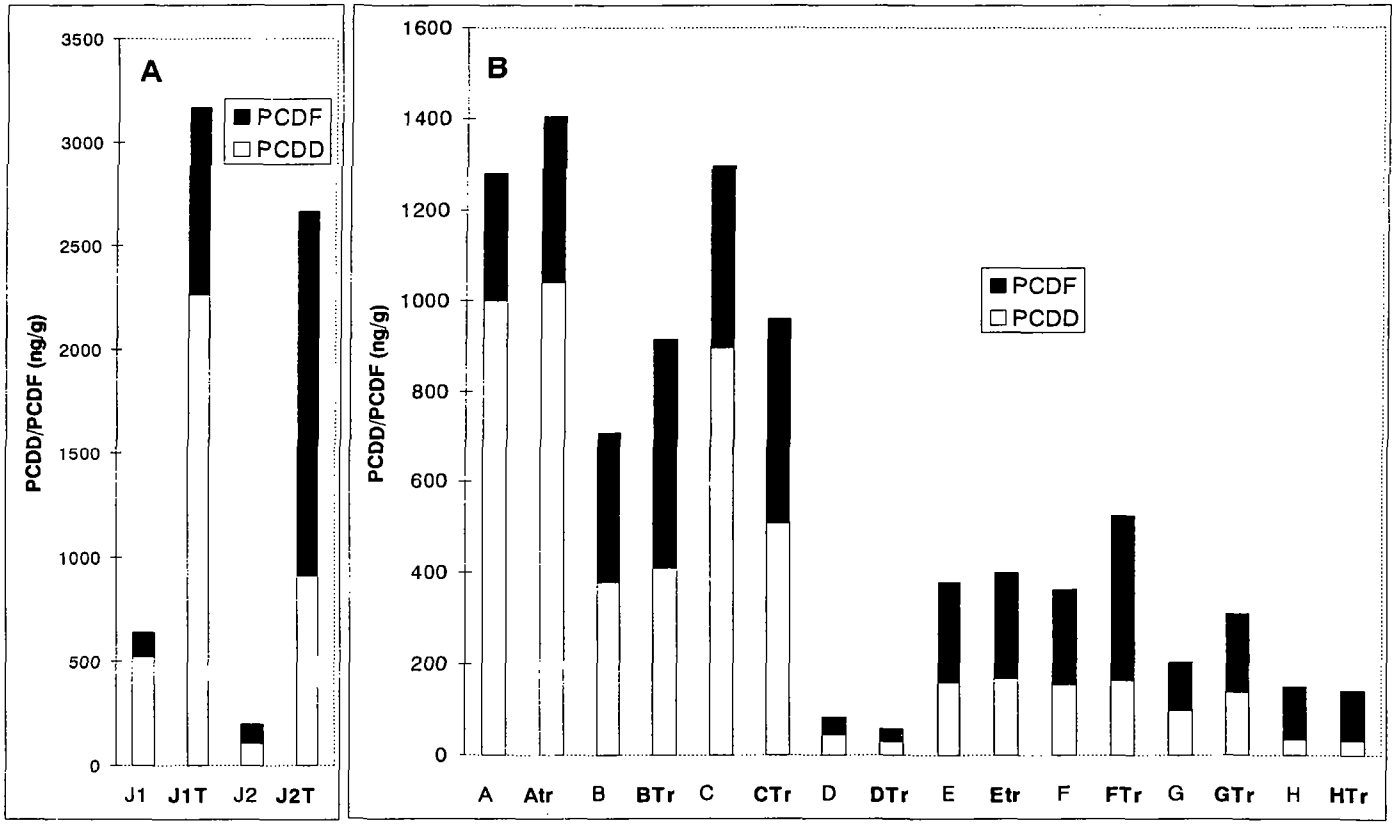

Figure 1A: PCDD/PCDF conc. in fly ash from "stoker" facilities before (X) and after (**XTr**) heat treatment (310°C, 1.5 hr)
Figure 1B: PCDD/PCDF conc. in fly ash from FBIs before (X) and after (**XTr**) heat treatment (310°C, 1.5 hr)

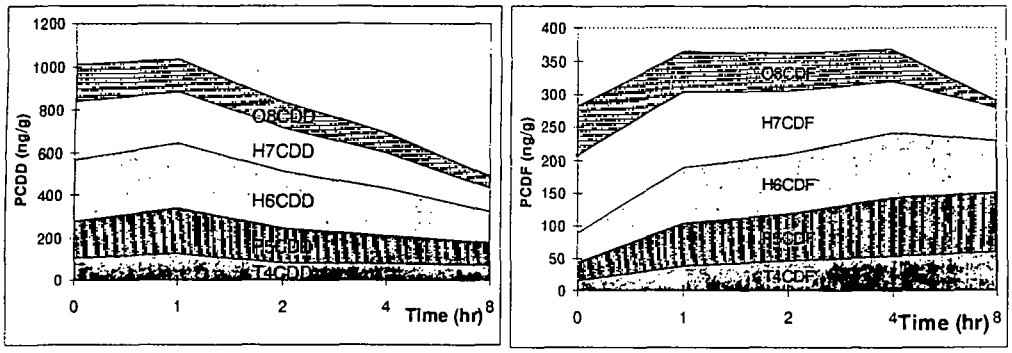

Figure 2A: Time dependence of PCDD conc. in fly ash A during heat treatm. (310°C, 10% O_2)
Figure 2B: Time dependence of PCDF conc. in fly ash A during heat treatm. (310°C, 10% O_2)

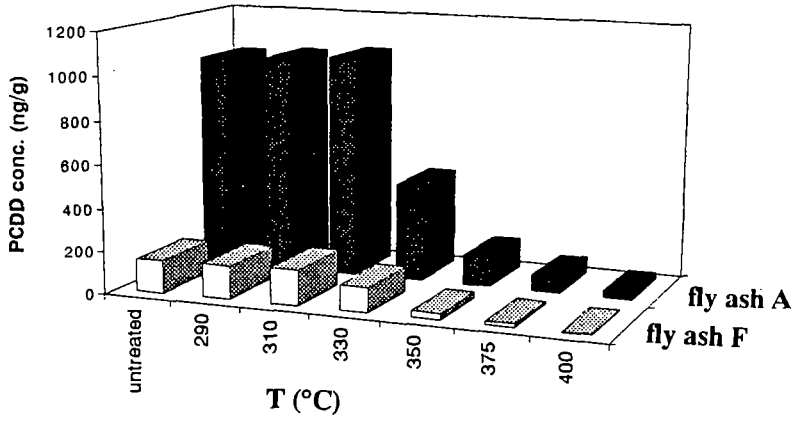

Figure 3A: Temperature dependence of PCDD conc. in fly ash A and F (10% O_2, 1.5hr)

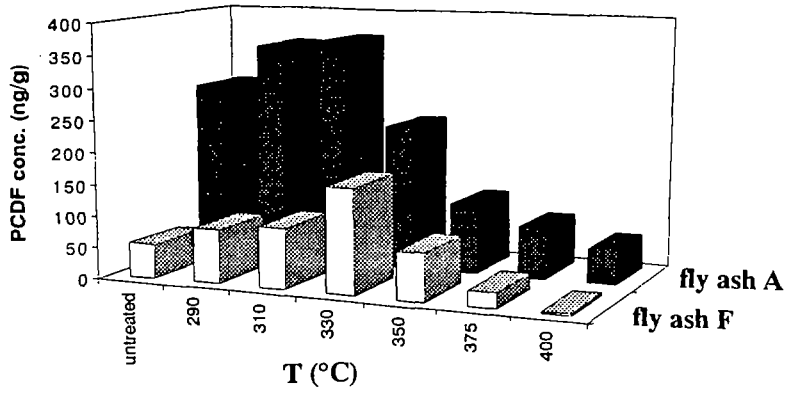

Figure 3B: Temperature dependence of PCDF conc. in fly ash A and F (10% O_2, 1.5hr)

PCDD/PCDF formation and destruction in Figure 4 appear to be shifted. Whether these ashes have a lower formation potential or a higher destruction potential cannot be decided a priori.

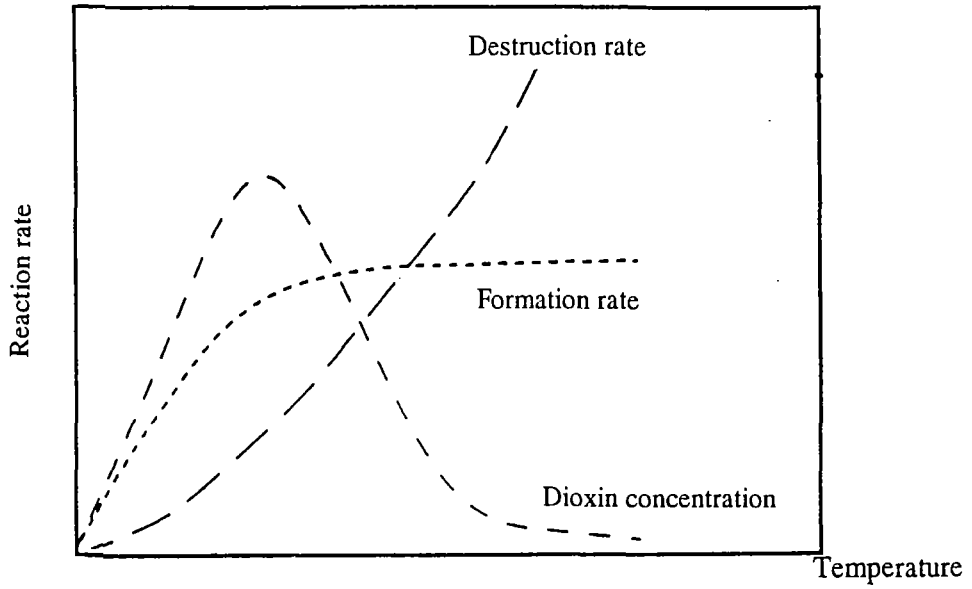

Figure 4: "Dualistic principle" of formation and destruction of PCDD/PCDF in fly ash

Destruction potential

For two FBI fly ash samples (A, F), the destruction potential was investigated under oxygen deficiency conditions (argon atmosphere). A 30 minute heat treatment at 400°C resulted in a destruction efficiency of 98 to 99% which is comparable to fly ash from grate fired incinerators.

Formation potential

It was recognized that the presence of organic carbon, a chlorine source and the catalytic influence of metals (matrix) are the prerequisites for PCDD/PCDF formation in thermal reactions. The question is which parameter (if not all three) differs in the fly ash from FBI compared to fly ash from grate fired incinerators and whether it can be identified as the limiting factor for the PCDD/PCDF formation.

A) Chlorine source

The chlorine content of the fly ash samples investigated is 3.7 - 10.9 % and therefore comparable to the chlorine content of fly ash from grate fired incinerators. Addition of 4% chloride to the ash samples D and F (with the lowest chlorine content) did not change the PCDD/PCDF formation potential of these ash samples. The homologue profile was not influenced either.

B) Carbon content

The carbon content of the 10 fly ash samples from FBIs lies between 0.4 and 1.1%. This is much lower[1] than the carbon content reported for fly ash samples from grate fired incinerators with

[1] the low carbon content is due to a five times higher amount of fly ash compared to grate fired incinerators

about 1 to 5%. By adding activated carbon to carbon free fly ash Stieglitz *et al.* has demonstrated that the amount of PCDD/PCDF formed correlates with the carbon content [2].

In our experiments an addition of 2% activated carbon to fly ash sample D (lowest PCDD/PCDF formation potential, lowest PCDD/PCDF concentration) resulted in additional formation of 60 ng PCDD/PCDF compared to the heat treatment without addition of activated carbon. This is equivalent to a 50% increase in PCDD/PCDF concentration.

Therefore, with the FBI fly ash samples, the low carbon content appears to be one of the limiting factors in PCDD/PCDF formation under heat treatment.

C) Matrix

However, with a model fly ash on silica gel basis using the same activated carbon, we observed a formation of 5723 ng PCDF and 2135 ng PCDD during the identical heat treatment. This is 50 times the amount obtained with the FBI ash D with activated carbon addition.

The other two important parameters for *de novo* synthesis, the copper content (0,4%) and chloride concentration (4%), were practically identical in the model fly ash and the fly ash sample D. Therefore, the matrix has a decisive influence on the resulting PCDD/PCDF concentration during *de novo* synthesis.

The elementary analyses of these fly ash samples from fluidized bed incinerators shows a comparatively high content in calcium (16-25%) and iron (4-11%). The high calcium content is due to the injection of either $Ca(OH)_2$ or $CaCO_3$ for removal of HCl and SOx. This addition of Ca results in rather high pH of 10.5-12.5 for the fly ash samples.

Whether the pH is a dominating factor in the *de novo* synthesis or whether the concentration of heavy metals have a significant impact on the formation rate is currently under investigation.

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