Formation of Dioxins(PCDDs/PCDFs) on fly ash as a catalyst and relation of chlorine-sources

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Introduction.

There are many reports on the formation of Dioxins(PCDDs,PCDFs) from incineration processes. Three pathways have been proposed so far to explain the formation of PCDs,PCDFs during incineration : high temperature pyrosynthesis [1)], low temperature *de novo* formation from macromolecular carbon and organic or inorganic chlorine present in the fly ash matrix [2)], and formation from organic precursors [3)] in which fly ash has an important role as a catalyst. Although all these mechanisms have been known for a number of years, few detailed reaction mechanisms can yet be offered due to the extreme complexity of the fly ash matrix.

In this report the result of a simplified model formation experiment using Dioxin-free fly ash as a catalyst and organic or inorganic chlorine sources is shown.

Fly ash can catalyze the reaction between oxygen and hydrogen chloride, giving molecular chlorine and chlorine radicals via the Deacon type reaction. Many copper catalyst and Fe-based catalyst can promote this reaction (a,b).

$$2R\text{-}H + 2[CuCl_2 \text{ or } FeCl_3] + (O) \Rightarrow 2R\text{-}Cl + 2[CuCl \text{ or } FeCl_2] + H_2O \quad (a)$$

$$2[CuCl \text{ or } FeCl_2] + 2HCl + (O) \Rightarrow 2[CuCl_2 \text{ or } FeCl_3] + H_2O \quad (b)$$

Materials and Methods.

Fly ash was collected from the electrostatic precipitator of a stoker-type municipal solid waste incinerator. The Dioxin-free fly ash was produced by heating the original fly ash at 500℃ for 2 hours under a nitrogen stream. The Dioxin-free fly ash produced had negligible level of Dioxins(99.99% of Dioxins were removed) and inorganic compounds were unchanged **(Table1)**.

For the formation experiment of HCl, NaCl was used as an inorganic chlorine source. Heating of 1% NaCl-coated activated clay in quartz tube formed HCl. **Table 2** shows the conversion ratio of HCl from NaCl at several temperature within 15 min. The conversion ratios were 50% at 300 ℃, >80% at >700℃ quantitatively. HCl concentration in the stream was 100-200 ppm. **Figure 1** shows the model experiment. Two heating furnaces were used with on air stream of

2l/min in a quartz tube. The first furnace was used as a combustion zone at 750 or 900℃ and the second furnace was used as a reaction zone at 300℃ filled with 1 g of Dioxin free fly ash. Chlorine sources were PVC, NaCl coated activated clay and HCl stream. Many kinds of combustible samples were selected. Samples were applied to the furnace very carefully with continuous monitoring of CO and O_2. It took several hours to complete each experiment.
HRGC-HRMS was performed on a Micromass Autospec Ultima or Kratos Concept with a Hewlett Packard HP6980 or Shimadzu GC 14A fitted with a SP-2331 (60m, 0.32mm, 0.20μm) and DB-17(30m, 0.32mm, 0.25μm) capillary column. The MS was operated at a resolution >10,000. Two ions were monitored for each congener group. Additionally chlorobenzenes(CBzs), chlorophenols(CPhs), PAHs were analyzed and a GC-MS scanning analysis was performed.

Results and Discussion.

Figure2 and **Table3** show the results of the formation experiments.
The heating of Dioxin-free fly ash alone clearly formed Dioxins. This indicates that Dioxins were formed by inorganic chlorine and unburnt carbon in the Dioxin-free fly ash.
The heating of samples that did not contain a chlorine source in the absence of Dioxin-free fly ash did not form Dioxins or the level of formation was comparable to the blank level.
The heating of samples that contained a chlorine source in the absence of Dioxin-free fly ash formed Dioxins at a low level although HCl was present in the gas stream. These samples were PVC and paraffin with NaCl-coated activated clay.
On the other hand, the heating of samples that did not contain a chlorine source with Dioxin free fly ash increased Dioxins formation to a level around 10 times higher than the heating of Dioxin-free fly ash alone. It was observed clearly that fly ash catalyzed Dioxin formation although there was a limit to Dioxin formation when active chlorine in Dioxin-free fly ash was the only chlorine source. The formation being limited by the available chlorine.
The heating of samples that contained a chlorine source or 100ppm of HCl stream with Dioxin-free fly ash increased Dioxins dramatically to a level around 10 times higher than the heating of samples that did not contain a chlorine source with Dioxin-free fly ash. In these cases the Deacon type reaction could take place on the active point of the fly ash, where HCl in the gas stream could react to produce radical chlorine continuously.
In case of PVC experiment the level of HCl would be expected to be several thousand ppm. On the other hand both the experiments with newspaper and a 100ppm HCl stream, and paraffin with NaCl coated activated clay, the level of HCl would be only several hundred ppm. But the level of Dioxin formed was about the same. These phenomena indicate that the catalytic activity of the Dioxin-free fly ash has a limit and Dioxin formation is not increased although HCl concentration increased. It is necessary that kinetic analysis of fly ash to clarify the effect of the concentration of the chlorine source.

References.

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Table 1. Composition of inorganic component and concentration of PCDDs and PCDFs in fly ash before and after treatment(500℃, 2hr. in N_2).

	Inorganic component (%)									Dioxins (ng/g)	
	Si	Al, Ca	Cl	C (unburnt)	Mg	Fe, S	Na, Ti, Zn	K, Pb	Cu, Mn, Sn	PCDDs +PCDFs	TEQ
Original fly ash	>62	10	9.1	2.2	2.0	1.0	0.5	0.2	0.1	554	5.71
Treated fly ash	>62	10	9.1	2.0	2.0	1.0	0.5	0.2	0.1	0.02	0.00022

Table 2. Conversion ratio of HCl from 1% NaCl coated activated clay.

Temperature (℃)	900	700	500	300
Conversion ratio (%)	87.6	97.2	79.0	50.3

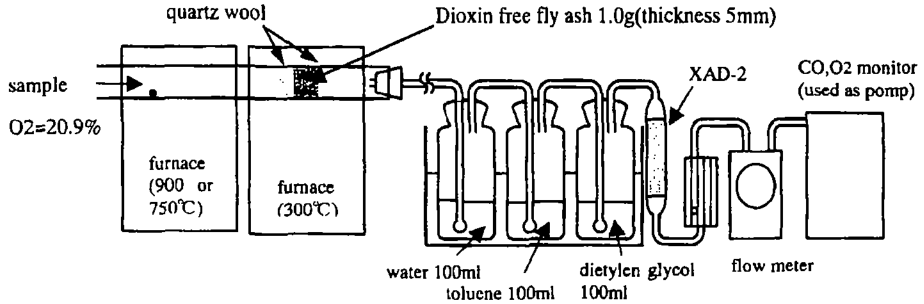

Figure 1. Experimental apparatus.

Table 3. Results of the formation experiment.

Combustion sample	Dioxin free fly ash (1g) In reaction zone	Combustion zone temp. (℃)	PCDDs (ng/g)	PCDFs (ng/g)	TEQ (ng-TEQ/g - sample)	CBz (ug/g)	CPh (ug/g)	CO averaged (ppm)
procedure blank	no	750	0.033	0.084	<0.00(0.0025)	0.66	0.28	2
Paraffin:10% NaCl coated activated clay (90:10) (1g)	no	**900**	1.6	5.4	0.16	N.A.	N.A.	N.A.
PVC (1g)	no	750	53	110	1.7	34	21	44
news paper (1g)	no	750	0.047	0.061	<0.00(0.0014)	0.45	0.087	61
Kerosen (1g)	no	750	0.21	0.19	<0.00(0.0053)	0.52	0.17	606
PP (Poly propylene) (1g)	no	750	0.24	0.31	<0.00(0.0044)	0.56	0.13	415
PE (Poly ethylene) (1g)	no	750	0.21	0.74	<0.00(0.0084)	0.69	0.32	888
nothing	yes	750	11	190	2.4	13	0.58	30
paraffin (1g)	yes	**900**	62	530	10	N.A.	N.A.	
news paper (1g)	yes	750	120	820	14	22	1.6	48
Kerosen (1g)	yes	750	84	1100	15	26	4.3	213
PP (1g)	yes	750	85	1300	16	21	19	512
PE (1g)	yes	750	320	2800	47	21	8.6	574
Paraffin:10% NaCl coated activated clay (90:10) (1g)	yes	**900**	1600	7300	160	N.A.	N.A.	N.A.
news paper (1g) *	yes	750	8500	10000	204	79	75	36
PVC (1g)	yes	750	6100	7400	125	77	59	383

*:HCl 100ppm stream, N.A.:not analysed

Supplied gas were technical air or indoor air at 2 l/min

Second furnace was used as a reaction zone at 300℃ with or without 1 g of Dioxin-free fly ash.

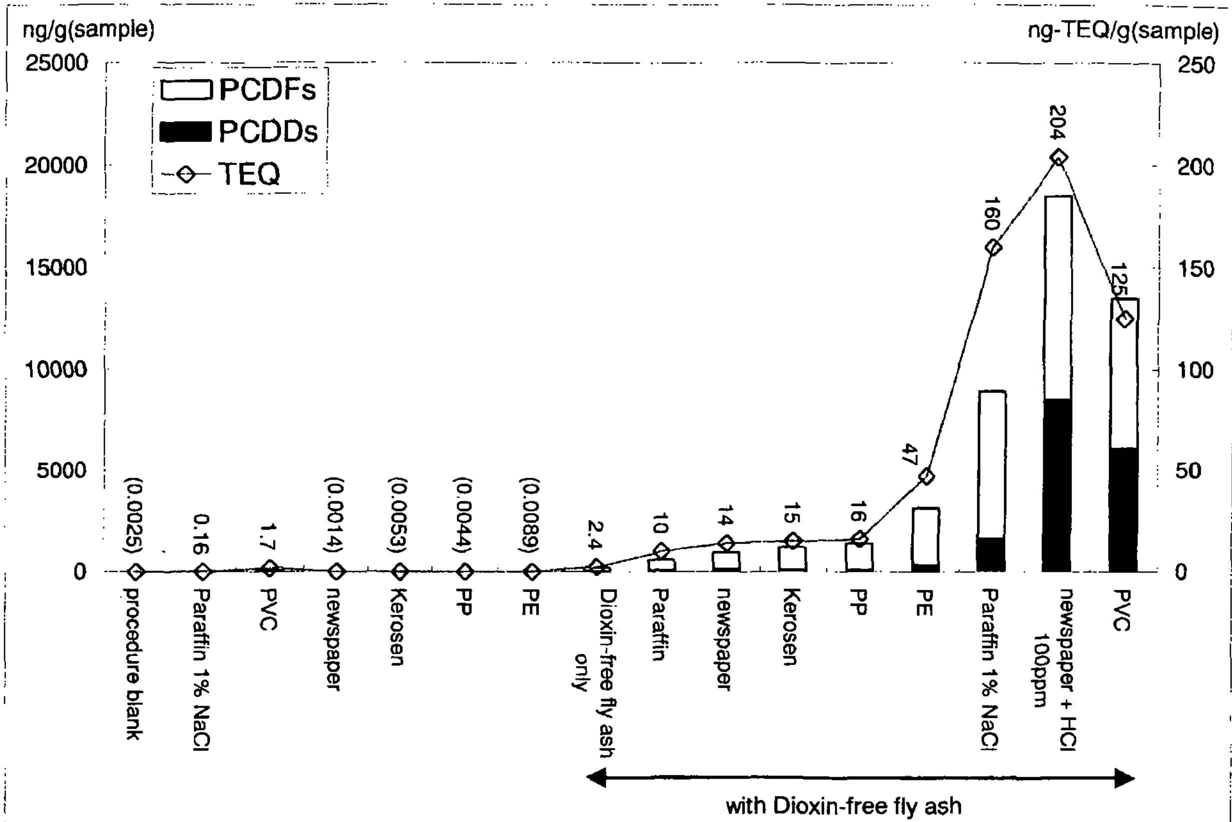

Figure 2. Results of the formation experiment.