FORMATION AND SOURCES

INVESTIGATION OF CATALYTIC ACTIVITY OF SEWAGE SLUDGE COMBUSTION ASH FOR PCDD/F FORMATION

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Introduction

Municipal waste incinerators and sintering processes have been recognized as an important source of emissions of polychlorinated dibenzodioxins (PCDD), furans (PCDF) and other chlorinated compounds. Johnke and Stelzner measured the concentration of PCDD/Fs in different zones of incineration systems, and found that more than 96% of these compounds are generated in the post-combustion zone [1]. Combustor fly ash is suspected to play a dominant role in formation PCDD/F in the combustor post-combustion zone. The fly ash acts as an active surface and the pollutant formation reactions are catalyzed by many transition metal ions present in fly ash over a temperatures ranging from 250 to 500 ºC. Sewage sludge combustion is known to generate large amounts of ash, which is rich in transition metals such as Cu, Fe and Cr. In this work, the catalytic activity of sewage sludge combustion ash is investigated in relation to PCDD/F formation.

Methods and Materials

All experiments in this study were conducted in a horizontal furnace shown in Figure 1. The nominal temperature of the runs was 850 ºC. Figure 1 also shows a typical temperature profile of a combustion experiment. In each experiment, 2.5 g of the material whose catalytic activity was being investigated was distributed along 50 mm of the quartz tube in the post-combustion zone. In the post-combustion zone the temperature ranged from 300 to 500 ºC (see Figure 1). The residence time of the gases in the post-combustion zone was approximately 0.1 sec. For each experiment, 0.1 g of sludge was placed in the sample holder and combusted by introducing the sample holder inside the furnace at a specific velocity (0.5 mm/s). The chemical composition of sludge used in this study is shown in Table 1. After passing through the catalytic bed, the reactor gas was collected in an adsorptive trap. After each experiment, the adsorptive trap was extracted and the extract was analyzed using different GC-MS techniques, as this study involves analysis of several different classes of compounds. More than 100 semivolatiles were analyzed by low resolution mass spectrometry (LRMS) in Scan mode, as described previously [2]. PCDD/Fs from tetra to octa were analyzed by high resolution mass spectrometry (HRGC-HRMS). The HRGC-HRMS analyses were performed on a Finnigan MAT 95 apparatus, equipped with a Hewlett-Packard GC. The spectrometer was operated in the electron impact ionization mode at 10,000 resolving power. For PCDD/F analysis, ^{13}C-labeled PCDD/F standards (Wellington Labs, Canada) were used. Quantitative determination was performed by the isotope dilution method based on the relative response factors previously obtained from three standard solutions (EPA1613-CS1, CS2 and CS3).

In this study, four different sets of experiments (A, B, C and D) were performed. The first set experiments (A) were the baseline experiments with no catalyst bed in the post-combustion zone. In the second set of experiments (B), a catalyst bed was made from sludge ash generated by combusting the sludge sample at 750 ºC for 24 hours. In the third set (C), the second set experiments was repeated in the presence of 35 ppm of HCl in the air. In the fourth set (D), $CuCl_2$ impregnated quartz wool was used as a catalytic bed.

FORMATION AND SOURCES

Table 1. Chemical composition of sewage sludge on dry basis(weight percent)

PCI	H	C	N	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Se	Sr	Sn	Ba	La	Pb
15530 kJ/kg	5.3	32.2	0.85	0.2	0.7	4.9	4.8	<1	0.18	0.1	7.1	0.22	0.01	0.3	0.03	4.7	0.44	1.3	0.8	0.02	0.28	0.05	0.04	0.08	0.11
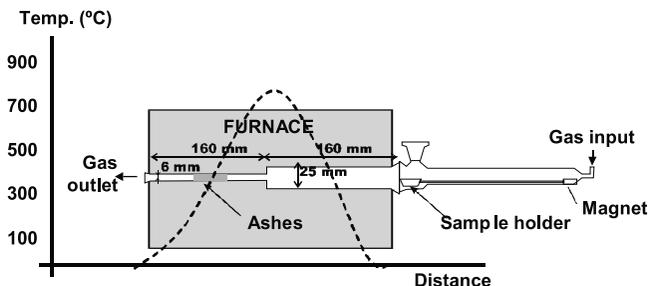
Figure 1. Schematic of the flow reactor system with temperature profile.

Results and Discussion

Yields of chlorinated non-PCDD/F pollutants of interest and PCDD/Fs are listed in Tables 2 and 3, respectively. Table 2 only lists results from experimental sets A, C, and D because the results of experimental set B were very similar to experimental set A with very small yields of chlorinated non-PCDD/F pollutants (not detectable in the 10 mg/kg range). The absence of this kind of compound in these runs is surprising, since the literature describes the chlorination of combustion products as a consequence of ash-catalyzed reactions, and also because the sludge ash used in this study is rich in transition metals (see Table 1). The only plausible explanation is that the chlorine present in the sludge was already tied up and no free chlorine was available for transition metal catalyzed chlorination reactions of organics. Initial chlorine (0.18 %, see Table 1) was possibly tied up as HCl or as high molecular weight chlorinated organics like PCDD/Fs because PCDD/Fs were observed in both experimental sets A and B (see Table 3). In experimental set A, PCDF/PCDD ratio was 8.2, which is similar to PCDF/PCDD ratios (~10-30) observed by Samaras, et al. in their sewage sludge combustion experiments [3]. This similarity in results between experimental set A and the Samaras, et al. experiments is not surprising, since both studies were conducted without the use of a catalytic bed in the post-combustion zone. Table 3 also shows that experimental set A has a higher yield of PCDD/Fs than experimental set B (conducted using a sludge ash catalytic bed in the post-combustion zone). This difference in PCDD/F yields between experimental sets A and B could perhaps be due to destructive (due to the presence of transition metal oxides in ash in the absence of chlorine source) or nondestructive adsorption of PCDD/Fs on ash surface in the post-combustion zone. Neither of these hypotheses can be verified since catalytic beds were not extracted or analyzed for PCDD/Fs.

Based on the results of our previous sludge combustion study, we are certain of the validity of both these hypotheses [4]. In our previous sludge combustion study, we conducted an extensive investigation of catalytic effect of sludge ash on the chlorination of phenol, benzene, naphthalene and biphenyl (possible precursors of PCDD/Fs) [4]. Our conclusions from this study are listed below:

1. Oxidation of chlorophenols and chlorobenzenes is catalyzed by ashes in the absence of HCl;

2. Chlorination of benzene and phenol at 300ºC is catalyzed by Cu, but at higher temperatures Cu catalyzes oxidation reactions leading to destruction of these compounds;

3. In the presence of HCl, the yields of chlorophenols, chlorobenzenes, chloronaphthalenes, and chlorobiphenyls increases almost tenfold, and the effect is greater at the higher temperatures;

4. Chlorophenol produced in major yield is 2,4,6-trichlorophenol. Based on these results it is plausible to say that in experimental set B, ash catalyzed the decomposition of chlorinated compounds, yielding a low amount of PCDD/Fs.

Table 2. Yield of chlorinated non-PCDD/F pollutants analyzed by LRMS (mg/kg sludge).

	A) No Catalyst	C) Ash + HCl	D) CuCl$_2$
Chlorobenzens	$\cong 0$	44	97
Chloronaphtalenes	$\cong 0$	410	890
Chlorobiphenyls	$\cong 0$	160	77
Chlorophenols	$\cong 0$	86	$\cong 0$
Total semivolatiles	12000	3900	1700

Experimental set C was conducted based on the results of our previous sludge combustion study and to investigate the significance of HCl in PCDD/F formation. In experimental set C, sludge ash catalytic activity was investigated in the presence of HCl (35 mg/L of air). It should be noted that the total yield of semivolatiles in experimental set C is significantly lower than the yield obtained in runs A and B (see Table 2). This decrease in total semivolatile is completely unexpected because the addition of a chlorine source is known to increase soot yields [5, 6]. The increase in soot yield is attributed to the fact that added HCl can react with H atom (Rxn 1), thus competing with the main oxidation branching

Table 3. PCDD/F yields(ng/kg sludge) for all four experimental sets

	A) No Catalyst	B) Ash	C) Ash +HCl	D) CuCl2
2,3,7,8-TCDF	1297	nd	1300	246000
Total TCDFs	1300	142	58000	710000
1,2,3,7,8-PeCDF	656	181	75	550000
1,3,4,7,8-PeCDF	574	nd	290	175000
Total PeCDFs	1250	213	1500	1300000
1,2,3,4,7,8-HxCDF	712	80	890	64000
1,2,3,6,7,8-HxCDF	nd	nd	200	740000
2,3,4,6,7,8-HxCDF	nd	44	370	22000
1,2,3,7,8,9-HxCDF	nd	44	2210	120000
Total HxCDFs	1900	168	4500	1600000
1,2,3,4,6,7,8-HpCDF	1634	64	5300	310000
1,2,3,4,7,8,9-HpCDF	nd	60	1040	280000
Total HpCDFs	1730	124	8400	950000
OCDF	10650	136	11000	1400000
Total furans	*21703*	*1256*	*95075*	*8467000*
2,3,7,8-TCDD	nd	nd	3300	3200
Total TCDDs	nd	1	3300000	3600
1,2,3,7,8-PeCDD	139	65	28	2400
Total PeCDDs	145	105	2100	6000
1,2,3,4,7,8-HxCDD	64	64	nd	1800
1,2,3,6,7,8-HxCDD	nd	32	nd	5700
1,2,3,7,8,9-HxCDD	nd	nd	nd	2700
Total HxCDDs	75	100	1100	17000
1,2,3,4,6,7,8-HpCDD	888	524	260	11200
Total HpCDDs	890	525	260	55000
OCDD	447	110	500	30000
Total dioxins	*2648*	*1526*	*3307548*	*138600*
Furans/Dioxins	8.20	0.82	0.03	61.09

Figure 2. Total yields of dioxins and furans.
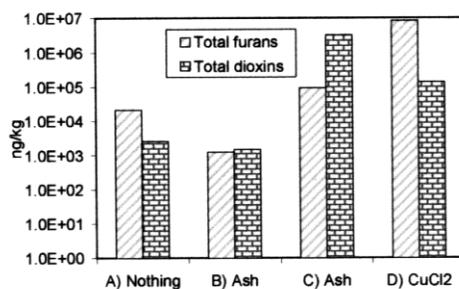
reaction (Rxn 2) and thereby inhibiting oxidation of organics, resulting in an increase in PAHs. At 1000K, Rxn 1 is 50 times faster than Rxn 2.

$$H + HCl = H_2 + Cl \qquad \text{(Rxn 1)}$$
$$H + O_2 = OH + O \qquad \text{(Rxn 2)}$$

However, the chlorine radical generated in Rxn 1 can do two things: chlorinate organics and abstract H-atoms from high molecular mass aromatics [7,8]. The abstraction of H-atom from high molecular weight aromatics accelerates their conversion to soot, thus increasing soot yields and decreasing semivolatile yields. Both these effects resulting from the addition of HCl are exhibited in the results of experimental set C (see Table 2 and 3). Experimental set C had higher yields of PCDD/Fs and chlorinated semivolatiles (chlorination by Cl radical) than experimental sets A and B, but a much lower yield of non-chlorinated semivolatiles (H-atom abstraction by Cl radical).

It is also interesting to note that the highest yield (86 ppm) of chlorophenols (precursor of PCDD/Fs) is obtained in experimental set C but trichlorophenol (a major species in the chlorination of phenol) is not observed. Table 3 shows that the amount of TCDD from experimental set C is much higher than

FORMATION AND SOURCES

the amount of any other PCDD/Fs. Furthermore, the detailed analysis of the chromatograms reveals that the major contribution to the TCDD amount is from the two isomers 1,3,6,8- and 1,3,7,9-TCDD. It has been shown by Sidhu, et al. that during slow oxidation 2,4,6-trichlorophenol yields 1,3,6,8- and 1,3,7,9-TCDD via the Smiles rearrangement [9]. The high yield of TCDD isomers explains the absence of trichlorophenol in experimental set C.

Experimental set D was conducted because the formation of PCDD/Fs in the post-combustion zone are generally attributed to the catalytic effect of $CuCl_2$ present in the fly ash. This compound has been described as one of the most important chlorination agents because of its ability to decompose to CuCl and Cl_2 at temperatures between 250 and 400ºC. Table 2 shows that presence of $CuCl_2$ in the post-combustion zone reduces the total yield of all the semivolatile compounds. The total yield of semivolatile compounds identified is almost ten times lower than in experimental set A. This reduction in the total semivolatile yield could be due to a catalytic effect of the Cu on the oxidation of these compounds. High yields of chlorinated compounds, primarily chlorobenzene, chloronaphthalenes, and chlorobiphenyls was also observed in experimental set D. The total PCDD/F yield in experimental set D is about 300 times higher than that observed in experimental sets A and B. The increase in the PCDD/F yields is probably due to the presence of Cl_2 (as a consequence of the decomposition of $CuCl_2$).

Figure 2 shows the total yields of PCDD and PCDF from all four experimental sets. From Figure 2, it is evident that the $CuCl_2$ catalyst is more efficient in forming furans than dioxins under the conditions investigated in this study. Exactly the opposite is true for experimental set C, where dioxin yields are much higher than furan yields. Under the conditions of this study, for the same organic feed, both of these catalytic systems will produce different degrees of chlorination (e.g., mono-, tetra-, hexa-, etc.), extent of chlorination (percentage organics chlorinated) and pattern of chlorination (e.g., 1,2,3 or 2,4,6) which could lead to the observed difference in PCDD and PCDF yields. Similarly, comparing experimental set B with set A, it is interesting to note that the ash catalytic bed (B) in the post-combustion zone reduced the yield of total furans more effectively than the yield of dioxins. Is this difference in PCDD and PCDF yield an indication that perhaps PCDD and PCDF have a different destruction mechanism or is it due to the fact that dioxins yields were too close to detection limits to observe any significant decrease in yield? It is not possible to answer this question based on the data collected in this study. The difference in PCDD and PCDF yields observed in this study should not be taken out of context and should certainly not be used to draw any mechanistic conclusions because the data collected in this study is limited with too many variables.

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