Characterization of Polychlorinated dibenzo-p-dioxins and Dibenzofurans in Fly ash Produced from Typical Municipal Solid Waste Incinerators in China

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Introduction

Fly ash could promote the formation of Polychlorinated dibenzo-p-dioxins and dibenzofurans(PCDD/Fs) in the combustion process of Municipal Solid Waste□MSW□.

In this paper, we collected two fly ash samples produced from bag filters of different type of incinerator. Fly ash samples were classified by sieves and PCDD/Fs in fly ash of different fractions were measured. The homologue profiles of PCDD/Fs and the effect factors of PCDD/Fs levels were also studied.

Materials and Methods

The source of fly ash samples is listed in Table 1. Fly ash samples were classified by sieves into six different fractions (i.e. <43μm□43-74μm,74-105μm,105-175μm,175-295μm, and >295μm). Fly ash samples clean up and analysis for PCDD/Fs have been described elsewhere.[1]

Table 1 Source of fly ashes

NO	Furnace type	Capacity(ton/d)	Fuel type
S1	Inclined to-and-fro ladder mechanical grate	350	MSW
S2	Circulated fluidized bed	300	Coal/MSW=20/80

Results and Discussion

Figure 1 shows the mass percents of different sized fly ash samples. There were not found for larger than 295μm particles in S1 sample. Size distributions of two fly ash samples were not quite

similar. The reason might be the different combustion technology. For S1 sample, the mass percent of particles which size are smaller than 175μm was more than 75□, which similar with the three fly ash samples characteristics in Taiwan.[2]

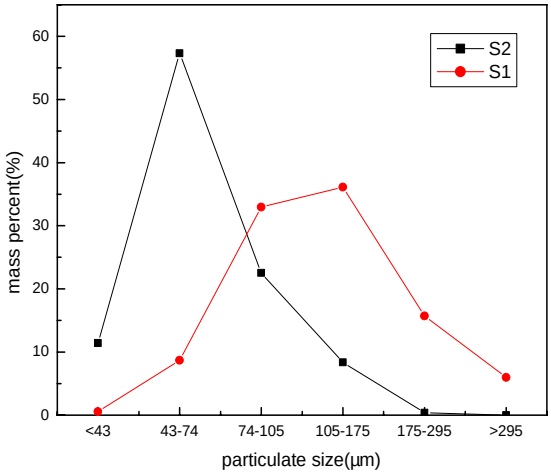

Figure 1 Size distribution of fly ash

The PCDD/Fs levels of fly ashes with different fractions are shown in Table 2. In general, the levels of PCDD/Fs were increased with decreasing particle size. Kaupp et al reported about 90% PCDD/Fs were adsorbed into the particles which size were smaller than 1.35μm.[3] PCDD/Fs in different fractions of S1 were observed in significantly higher levels compared to S2, which could be due to either of the following reasons.

(1) S1 was fly ash collected from an incinerator using MSW which contain higher chlorine content compared to S2 from a MSW and coal co-firing incinerator.

(2) Inclined to-and-fro ladder mechanical grate incinerator adopts active carbon adsorbing unit, which could adsorb the pollutants (such as PCDD/Fs, heavy metals), then the pollutants would be intercepted into fly ash by bag filter.

Table 2 shows the PCDDs□PCDFs levels and the ratio of PCDDs/PCDFs in different fractions. PCDDs in S1 were predominant compared to PCDFs. The ratio of PCDDs/PCDFs was higher than 1. For S2, the concentrations of PCDDs in particles with 105-175μm and 175-295μm range were also higher than PCDFs. However the mass percent of the above particles were only 30% of the total particles .Experiments focusing on de novo formation of PCDD/Fs results showed the ratios of PCDD/Fs were mostly less than 1. The de novo mechanism of PCDD/Fs leads preferentially to the formation of PCDFs in addition to PCDD, in contrast to most of the known precursor routes that generate PCDDs.

Table 2 PCDD/Fs levels and the ratio of PCDDs/PCDFs in fly ashes of different size

NO.	PCDD/Fs concentrations□ng/g□	Particle size interval □μm□					
		<43	43-74	74-105	105-175	175-295	>295
S1	PCDDs	153.06	64.58	41.29	44.69	9.55	5.88
	PCDFs	79.47	51.31	27.18	27.90	4.07	2.57
	PCDDs/PCDFs	1.93	1.26	1.52	1.60	2.34	2.29
S2	PCDDs	6.15	2.1	4.87	1.91	2.58	n.d
	PCDFs	13.06	2.87	13.06	1.37	1.32	n.d.
	PCDDs/PCDFs	0.47	0.73	0.37	1.40	1.96	n.d.

Note□"n.d." =not detectable.

The levels of 2,3,7,8-subsituted PCDD/Fs and the I-TEQ values of size fractionated fly ashes are listed in table 3.The I-TEQ values were in the range of 0.002ng TEQ/g (S1,175-295μm) to 1.35ng TEQ/g (S2,43μm).□1,2,3,7,8,9-HxCDF contributed most of the toxic equivalent quantity, though major species homologue were 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDD for S1. However, 2,3,4,7,8-PeCDF contributed most of the TEQ for S2.

Table 3 Total levels of 2,3,7,8-PCDD/Fs and the I-TEQ values of fly ash samples with different size

No	PCDD/Fs concentrations□ng/g□	Particle size interval (μm)					
		43	43-74	74-105	105-175	175-295	>295
S1	∑2,3,7,8-PCDD/Fs	78.44	25.22	20.53	22.20	5.20	3.44
	I-TEQ	1.35	0.7	0.56	0.57	0.08	0.06
S2	∑2,3,7,8-PCDD/Fs	4.65	1.14	3.67	1.43	0.45	n.d.
	I-TEQ	0.43	0.05	0.42	0.01	0.002	n.d.

Figure 2 shows the homologue profile of PCDD/Fs in two fly ash samples. The total amounts of PCDD/Fs in S1 were higher than that in S2. The PCDD/Fs distribution of two fly ash samples showed similar homologue profiles, which also alike to that of another study.[2] Major species were hexachloro homologues for PCDDs. The levels of PCDFs would be decrease with increasing the amounts of chlorine. The ratios of PCDDs/PCDFs were different between two samples. The ratio of PCDDs/PCDFs for S1 was lager than 1, however the ratio of PCDDs/PCDFs for S2 was less than 1.

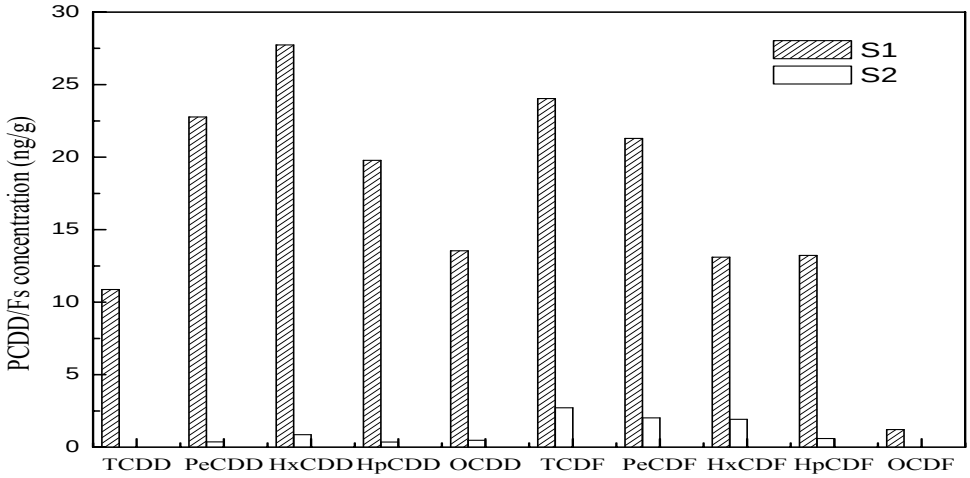

Figure 2 Homologue profiles of PCDD/Fs in fly ashes

Figure 3 shows the distribution of 2,3,7,8-subsituted PCDD/Fs in two fly ash samples. The concentration of S1 and S2 was 5.16ng TEQ /g, 0.24ng TEQ/g respectively. Their homologue profiles were different from each other. The major species of homologue profiles in S1 were 1,2,3,4,6,7,8-HpCDF□1,2,3,4,6,7,8-HpCDD and OCDD. For S2 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF and OCDD were dominant components. The major homologues were both higher chlorinated homologues. The results might be due to lower chlorinated homologues which have higher vapor pressure would be gasified and emitted to flue gas. Instead, homologues with higher chlorinated and lower vapor pressure would stay in the fly ash [4].

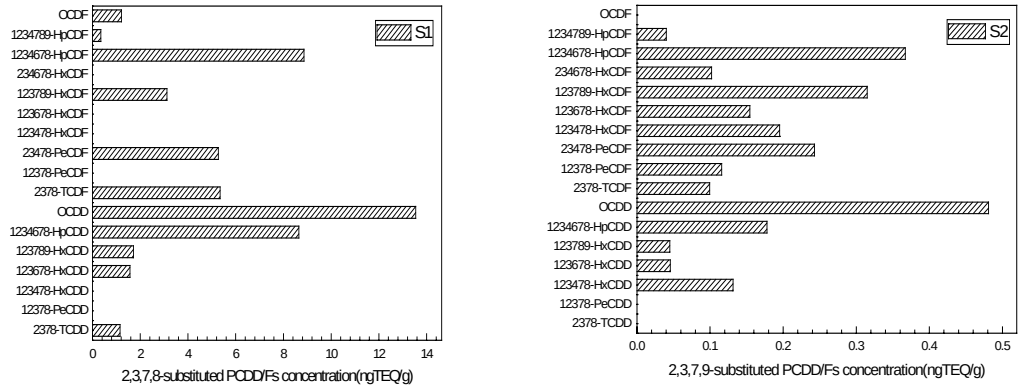

Figure 3 Homologue profiles of 2,3,7,8-subsituted PCDD/Fs in fly ashes(S1-S2)

Conclusion
Preliminary experiments lead to the following conclusions:
1. The levels of PCDD/Fs in size fractionated fly ash samples were increased with decreasing particle size. The levels of 2,3,7,8-subsituted PCDD/Fs and the I-TEQ values of that showed the same property.
2. The homologue profile of PCDD/Fs in fly ash samples produced from different furnace type were similar. However, the ratio of PCDDs/PCDFs was different. PCDDs were predominant than PCDFs for grate incinerator. It was contrary for circulated fluidized bed.

Acknowledgement

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Reference

1. Xu, X., Li,X.D., Yan, J.H., Gu, Y.L., Chi, Y., Cen, K.F. (2001) Journal of Zhejiang University Science. 2,278.
2. Chang M.B., Chung Y.T. (1998) Chemosphere 36,1959.
3. Kaupp H., Towara,J., Mclachlan,M.S. (1994) Atomspheric Environment 28,585.
4. Shin, K.J. and Chang Y. S. (1999) Chemosphere 38, 2655.