Dioxin Contents in Fly Ash of MSW Incinerator in Zhejiang

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Introduction

It has been reported that the combustion of the Municipal solid waste (MSW) is the major source for emitting PCDD/Fs into the atmosphere [1], and almost produced 10%~40% of the total amount of the PCDD/Fs[2]. Now three possible reaction mechanism for PCDD/Fs formation in combustion systems have been proposed: heterogeneous (solid-phase) reactions include (1) Formation from precursors, (2) De novo formation, and Homogeneous (gas-phase) reactions include (3) high temperature synthesis reaction (500-800^{o}C)[3], but (1) and (2) process was more strongly held than the homogeneous reaction. Generally, the Fly ash in the stack with quantity of active solid surface, the elemental carbon, and some heavy metal elements just like copper, acts as a heterogeneous catalyst in the synthesis of PCDD/Fs and plays an important role in (1) and (2) formation mechanism [4-7].

In this study, fly ash samples were collected from four MSW incinerators equipped with different kinds of furnaces and air pollution control devices for the purpose of investigating the level of the PCDD/Fs concentration and the distribution of the PCDD/Fs congeners, the influence of the active carbon to the fly ash was also considered.

Methods and Materials

Sample collection: The fly ash samples were collected from four different MSW incinerators in Zhejiang Province, P. R. China. The characteristics of four incinerators were list in table 1, they are fixed grate furnace (A), step grate furnace (B), Slopping reciprocating grate furnace (C) and fluidized bed furnace (D) individually. Except the fixed grate furnace equipped with a wet scrubber as the air pollution control device, other device were similar, i.e. they are all equipped with a half-dry lime scrubbing device to destroy the SO_2, HCl et al, and a bag house to remove the dust. Active carbon was injected into the flue gas in B and C.

Four fly ash samples (named ash A, ash B, ash C and ash D) were collected from the bottom of the bag-house. And we also collected different fly ash samples and gas samples with/without the active carbon to remove the dioxin (named ash C and ash C', gas C and gas C').

PCDD/Fs Analysis: All the samples were analysis according to the method of EN1948 and German VDI3499-2. Samples were extracted by refluxing with toluene for almost twenty-four

hours and concentrate the solvent and constant the volume. Then took half of the solvent and spiked with known amounts of ^{13}C isotopically labeled internal standard solution, and clean-up the sample with muti-layer silica gel column and alumina column.

The PCDD/Fs analysis was carried out with HRGC/HRMS (high resolution gas chromatography/high resolution mass spectrometer), the type of the HRGC/HRMS was Fisons CE 8000 GC/VG Autospec Ultima system, and the column was DB-5MS (60m×0.32mm×0.1μm).

Table 1 Parameters of the four incinerators

Incinerator	A	B	C	D
Scale(T/d)	3.6	350	350	300
Incinerator	Fixed-grate furnace	Step grate furnace	Slopping reciprocating grate furnace	Fluidized bed furnace
Burning materials	MSW	MSW	MSW	MSW +20% coal
Temperature of furnace	650-850^{0}C	800-1000^{0}C	800-1000^{0}C	800-900^{0}C
Time (s)	<1	>2	>2	>2
Air pollution control device	Wet scrubber	Half-dry lime scrubbing &active carbon&bag-house	Half-dry lime scrubbing & active carbon& bag-house	Half-dry lime scrubbing &bag-house

Results and Discussion

The congener distribution of fly ash: The 2,3,7,8-PCDD/Fs congeners distribution of fly ash of four kinds of MSW incinerators were shown in Figure 1. The distribution of PCDDs and PCDFs congeners are quite similar in fly ash A, C, and D although they have different type of furnace and air pollution control devices, but the fly ash B was different. In ash A, C, and D, the concentration distribution of lower-chlorinated congeners of PCDF are remarkably higher than that of other PCDD/Fs, and the percentage is about 55%~75% for all types of fly ash of three MSW incinerators. The results was quite different with the report of [8] and [9]. In reference [8], the concentration of higher-chlorinated congeners was remarkably higher than that of other lower-chlorinated congeners. It can be explained that high volatile, i.e., lower-chlorinated, congeners were adsorbed comparatively more strongly than low volatile ones [10], that is say, the lower-chlorinated PCDD/Fs in the gas stream was easier absorbed by fly ash relatively to the higher-chlorinated congeners. In fly ash B, high-chlorinated congeners (HpCDD/F+OCDD/F) of PCDDs and PCDFs are higher than that of other lower-chlorinated congeners, the percentage is above 60% for all, the result was almost identical with the report of [8]. An interesting resemble will be found in four kinds of ash samples, the concentration distribution of higher-chlorinated congeners of PCDDs is higher than that of PCDFs, and the concentration distribution of lower-chlorinated congeners of PCDFs is higher than that of PCDDs. These results indicated that the distribution of PCDD/Fs congeners in the combustion of MSW had less relativity to the type of the furnace and the air pollution control device, and the formation of the dioxin in the fly ash maybe contributed to the operation conditions, the gas composition and the characterized of the particle surface.

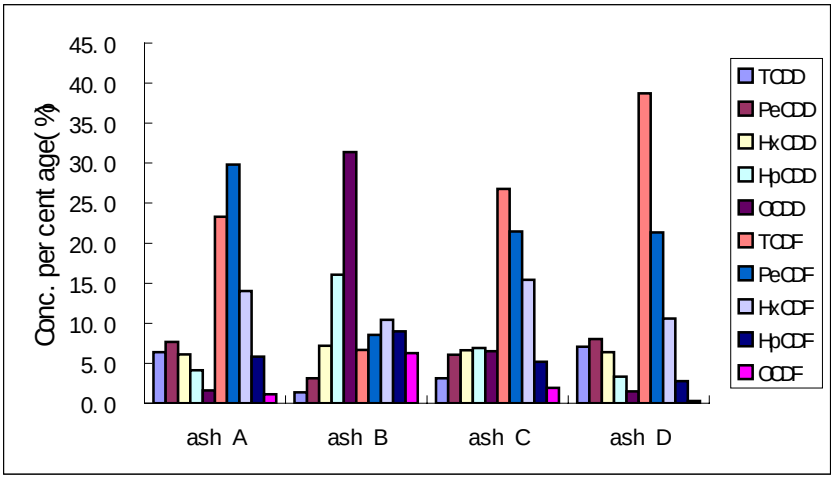

Figure 1 the distribution of the PCDD/Fs of the four fly ash samples

PCDD/Fs concentration and PCDD/PCDF ratio distribution: Figure 2 appears the PCDD/Fs concentration and PCDD/PCDF ratio distribution of four types of fly ash samples. The PCDD/Fs concentration of the ash samples of the grate furnace (ash A, B and C) was much higher than the fluidized bed (ash D), it maybe contributed to the dilution of the coal ash in fluidized bed furnace and the combustion conditions, for the combustion condition in the fluidized bed furnace was much better than the grate furnace in these factories.

Figure 2 also showed the ratio of the PCDFs to the PCDDs. It was reported that the ratio of the PCDF/PCDD in fly ash was 2.0 generally in different MSW incinerator despite this value would be influenced by the air pollution control device, the operation temperature, size distribution of particles, dust concentrations, and so on [8]. For the ash sample A, C and D, the ratio of the PCDFs/PCDDs was similar to the reference, the value of these sample was above than 2.0. To the sample B, the result was contrarily, the ratio of the PCDF/ PCDD was less than 1.0. It indicated that the influence factor of the furnace B was different to the others. It can be explained that the dioxin synthesis of the furnace B was major done by precursors, and the other three one was major done by De novo.

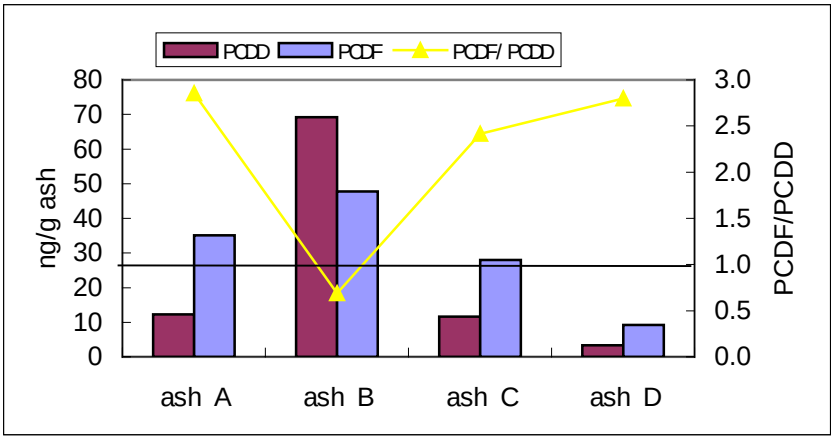

Figure 2. the PCDD/Fs concentration and PCDF/PCDD ratio distribution for four types of fly ash samples.

The influence of the active carbon to dioxin concentration of the fly ash: In incinerator C, a comparable experiment was made by whether or not injecting the active carbon into the stack to investigate the influence of the dioxin concentration in the fly ash, results was shown in Figure 3. Figure 3 (a) shows the distribution of PCDD/Fs patterns in the fly ash and flue gas without injecting the active carbon into the stack, the PCDD/Fs concentration of the fly ash was 36.8ng/g, and the PCDD/Fs in flue gas was 377 ng/m^3, (b) shows the results after injecting the active carbon and changing some combustion conditions, for example, the secondary overfire air, the feeding system and so on, the PCDD/Fs of the fly ash was increase to 39.6 ng/g and down to 1.12 ng/m^3 for glue gas. It was obvious that the absorption of the PCDD/Fs of the flue gas increased the PCDD/Fs concentration in the fly ash after injecting the active carbon powder.

Compared to the PCDD/Fs contribution of the fly ash with/without the active carbon powder, the patterns of the congeners of the dioxin was almost the same. It indicated that the contribution patterns of the PCDD/Fs congeners were not influenced whether or not injecting the active carbon into the flue gas. But the patterns of the flue gas was quite different after adding the active carbon, the contribution of the PCDD/Fs congeners was changed also. The absorption of the fly ash can explain it.

Conclusions

1, similar distribution of PCDD/Fs congeners in various types fly ash A, C and D shows that the formation of the PCDD/Fs was less relativity to the type of incinerator and the air pollution control device.

2, different distribution of PCDD/Fs congeners in fly ash B and C shows the different dioxin synthesis mechanism of the furnace B and C in spite of the similar grate furnace and the same air pollution control devices, furnace B was major done by precursors, and the furnace C was major done by De novo.

3, Injection the active carbon powder into stack was effective to decrease the concentration of the PCDD/Fs in the flue gas and increase the concentration in fly ash, but it couldn't influence the distribution patterns of the PCDD/Fs congeners in the fly ash.

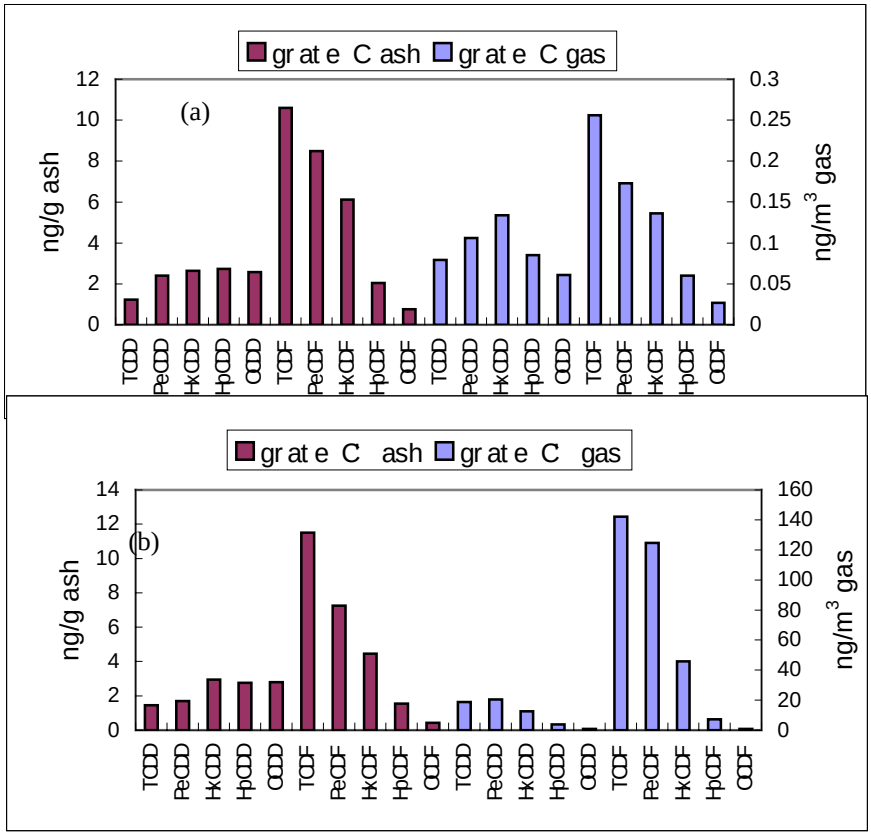

Figure 3 Distribution of PCDD/Fs patterns of fly ash and flue gas with/without active carbon powder in incinerator C

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