PCDD/Fs INHIBITION ON MODEL FLY ASH BY SLUDGE DRYING GASES

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Introduction

The amount of municipal solid waste (MSW) generated in China has increased to 170.8 million ton in 2012 and over 25 % of the MSW was disposed of by incineration. However, incineration is still controversial for it might cause secondary pollution, in particular by the emission and eventual deposition of PCDD/Fs[1]. Numerous studies have been performed on the inhibition of PCDD/Fs by chemical suppressants, especially N- or S-containing compounds, such as NH_3, $(NH_4)_2SO_4$, urea and SO_2[2, 3]. The suppressants are added to the raw MSW or injected into incinerator flue gases. However, the cost of supplying such substances is tangible, so finding cheap and effective suppressants has been a topical subject for R&D initiatives.
Sludge drying gases (SDG), evolving from drying and from mild thermal decomposition of sewage sludge, contain NH_3 and SO_2 as well as other, unidentified N- and S-compounds[4, 5]. This study examines the suppression effects of the *de novo* sythesis of PCDD/Fs in tests related to the temperature and oxygen content during sludge drying. Most importantly, these experiments also established the appropriate conditions to inhibit the formation of PCDD/Fs in 650 °C efficiently. In addition, the effects of injecting NH_3 together with SO_2 into the flue gas on the concentration of PCDD/F congeners have been considered. The results could confirm the important role of both NH_3 and SO_2 in the suppression of PCDD/Fs by SDG.

Materials and methods

Experimental materials
In this study a synthetic model fly ash was used to simulate PCDD/Fs formation. This model fly ash is composed of (in wt. %) 91.8 % of SiO_2, 3 % of activated carbon, 5 % of NaCl and 0.2 % of $CuCl_2$. The sludge samples were collected from a municipal wastewater treatment plant in Shanghai. The raw sludge samples were dried for 24 h in an oven at 105 °C, and the moisture content decreased to 7.09 %. The dried sludge (DS) have a high N content (4.87 wt. %) and a low S content (0.79 wt. %).

Experimental set-up and design
Thermal drying and decomposition of the DS samples were accomplished using the experimental set-up described in Figure 1. It comprises a tubular furnace consisting of three sections a, b, and c wiht independent temperature controllers. The simulated flue gas (300 ml/min; 12 % O_2 in N_2) was divided into two parts (Gas A and Gas B). Gas A consisted of N_2 (264 ml/min) yet it featured different contents of oxygen when it was used to prepare the sludge drying gases (SDG) used as suppressant. Gas B contained the oxygen necessary to conduct a PCDD/F generation test at a fixed concentration of 12 vol. %. The experimental test conditions are listed in Table 1. Test A is considered to be a blank test; Then, in the series B, sludge samples were tested as suppressants; whereas series C tests the effect of specific mixes of NH_3 and SO_2 in suppressing PCDD/F formation.

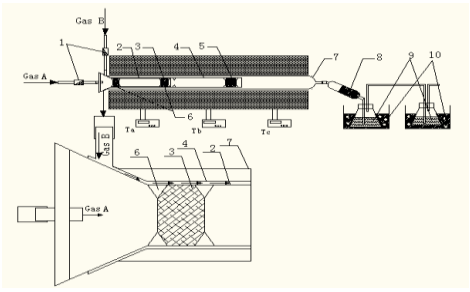

Fig.1 Experimental system for conducting the PCDD/Fs suppression experiments (1: Mass flow meter, 2: Short quartz tube, 3: Dry sludge, 4: Internal quartz tube, 5: Model fly ash, 6: Quartz rod, 7: External quartz tube, 8: XAD-Ⅱ resin, 9: Toluene, 10: Ice bath)

Table 1 Experimental design conditions

No.	Inhibitor	Ta	Tc	O_2	No.	Inhibitor	Ta	Tc	O_2
A-1	none	-	350 °C	12%	A-2	none	-	650 °C	12%
B-1	1 g DS	300 °C	350 °C	12%	B-2	1 g DS	300 °C	350 °C	6%
B-3	1 g DS	300 °C	350 °C	0%	B-4	1 g DS	250 °C	350 °C	12%
B-5	2 g DS	300 °C	650 °C	0%	C-1	900 ppm NH_3 + 100 ppm SO_2	-	350 °C	12%
C-2	100 ppm NH_3 + 900 ppm SO_2	-	350 °C	12%	C-3	500 ppm NH_3 + 500 ppm SO_2	-	350 °C	12%

PCDD/Fs analysis

The cleanup procedure of PCDD/Fs samples was conducted according to the USEPA 1613 method. A DB-5ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column was used for separation of the different PCDD/Fs congeners. All tests were conducted in duplicate, except for the tests A, which were repeated four times; the arithmetic average of the results was further used in our analysis of suppression. Target compounds were the 17 toxic 2,3,7,8-substituted PCDD/Fs congeners.

Results and discussion

PCDD/F synthesis

Experiment A-1 was conducted five times to confirm the total PCDD/Fs produced from the model fly ash. The average concentration of total PCDD/Fs was 2534 +/- 222 ng/g (or 77.7 +/- 32.9 ng I-TEQ/g). The PCDD/F congener distribution is dominated by the PCDF, with 70.0 +/- 2.9 % of the total PCDD/F, and also by OCDF (41.3 +/- 4.1 %) and OCDD (25.2 +/- 1.65 %). The best defined congeners are OCDD (+/- 9 %) and 1,2,3,4,6,7,8-HpCDF (+/- 10 %). The blank experiment showed an unusually high weight average degree of chlorination, with values of 7.81 for Cl-PCDD and 7.31 for Cl-PCDF.

Experiment A-2 was conducted twice and the average concentration of total PCDD/Fs was 1211 +/- 138 pg/g (or 34.1 +/- 10.7 pg I-TEQ/g). The PCDD/F congener distribution is dominated by OCDF (37.0 +/- 1.0 %) and OCDD (32.7 +/- 0.4 %). The weight average degrees of chlorination are 7.69 for PCDD and 7.45 for PCDF. Remarkably, the I-TEQ contributions of 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD are 25.3 % and 25.9 % respectively.

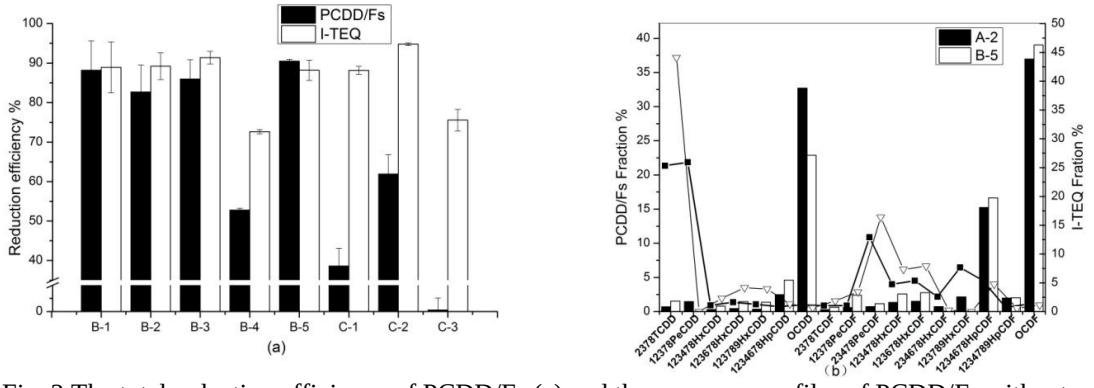

Fig. 2 The total reduction efficiency of PCDD/Fs (a) and the congener profiles of PCDD/Fs without and with SDG in 650 °C (b)

PCDD/F inhibition by SDG

The emission characteristics of these compounds liberated during DS drying could be affected by the oxygen content and thus the suppression efficiencies would be varied. As described in figure 2a, no significant and systematic changes were observed in the PCDD/F suppression efficiencies when the oxygen content of the sludge drying atmosphere was varied (0 %, 6 % and 12 %). Comparison between B-1, B-2 and B-3 showed that B-1 and B-3 had a stronger suppression effect on PCDD/Fs than B-2, revealing that DS heated in 6 % O_2 of carrier gas may release much less N- and S-compounds. The result for the PCDD/F congeners was very different, yet without any clear trends in the reduction of their concentration in the presence of SDG. Interestingly, the

chlorination level of PCDD/Fs when DS heated in 6 % of drying atmosphere was higher than that of 0 % and 12 %. As for I-TEQ value, no obvious differences were observed, and the suppression efficiencies of them were ca. 90 %.

The effects of DS drying temperature on PCDD/Fs inhibition were studied by a comparison between the experiments B-1 (250 °C) and B-2 (300 °C). Comparison shows an increase in chlorination levels of both PCDD and PCDF when the sludge drying temperature (300 °C) was changed: the fraction of OCDD and OCDF increased (see Figure 3). The results in this study revealed that the reduction of low substituted congeners with high toxic equivalency value were more favorable at 250 °C than that of 300 °C. Comparison also shows an increase in chlorination levels of both PCDD and PCDF when the sludge drying temperature was varied: the fraction of OCDD and OCDF increased (see Figure 3). The results in this study revealed that the reduction of low substituted congeners with high toxic equivalency value were more favorable at 250 °C than at the standard sludge drying temperature of 300 °C.

SDG were able to inhibit the formation of PCDD/Fs on model fly ash in 650 °C efficiently. The suppression efficiencies were up to 90.5 % for PCDD/Fs and 88.2 % for I-TEQ. The PCDFs:PCDDs ratio increased from 1.60 to 2.06 with the addition of SDG. Moreover, OCDD were reduced by 9.8 %, whereas 1,2,3,4,6,7,8-HpCDF and OCDF slightly increased by 1.4 % and 2.0 % respectively. As for I-TEQ value, the concentration of 2,3,7,8-TeCDD increased to 44.1, whereas almost no 1,2,3,7,8-PeCDD obtained with the SDG injection (see Figure 2b).

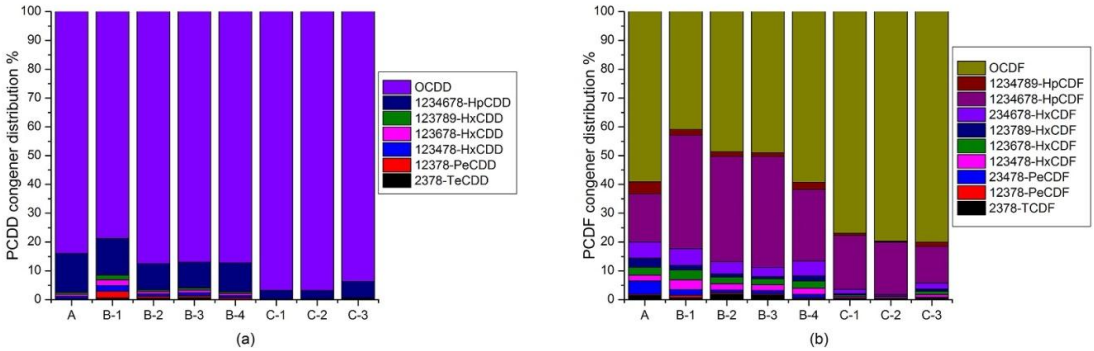

Fig. 3 Congener profiles of the PCDD (a) and PCDF (b) without and with various inhibitors in 350 °C

Table 2 Results regarding the suppression of PCDD and PCDF

item	A-1	A-2	B-1	B-2	B-3	B-4	B-5	D-1	D-2	D-3	unit
PCDD	761	0.466	61.2	102	77.5	0.656	0.038	343	259	679	ng PCDD/g MFA
PCDF	1773	0.745	235	337	278	1.79	0.077	1212	706	1847	ng PCDF/g MFA
PCDD/ PCDF	42.9	62.6	26.0	30.3	27.9	36.6	49.4	28.3	36.7	36.7	%, PCDD/Fs
ΣPCDD/Fs	2534	1.21	296	439	357	2.44	0.115	1555	965	2526	ng PCDD-F/g MFA
PCDD/Fs reduction, %	0	0	88.2	82.7	86.0	99.9	90.5	38.7	61.9	0.284	%, PCDD/Fs
I-TEQ	77.7	0.034	8.61	8.37	6.69	0.643	0.004	9.20	4.05	19.0	ng I-TEQ/g MFA
I-TEQ reduction, %	0	0	88.9	89.2	91.4	99.2	88.2	88.2	94.8	75.6	%, I-TEQ
Cl-PCDD	7.81	7.69	7.67	7.82	7.81	7.82	7.45	7.96	7.96	7.93	Weight average level of chlorination.
Cl-PCDF	7.31	7.45	7.19	7.30	7.33	7.25	7.36	7.73	7.77	7.73	

PCDD/F inhibition by gaseous NH_3 and SO_2

The results obtained with (mainly) NH_3 injection (experiment C-1) are presented in Table 2. The suppression efficiency recorded on PCDD/Fs was 38.7 %, which was well within the range (34-75 % for the solid phase and 21-40 % for the gas phase) reported by Hajizadeh et al.[6]. Interestingly, suppression was much stronger for PCDD than PCDF: 54.9 % and 31.6 %, respectively. Moreover, when compared with the base case both chlorination levels increased, with a significant decrease in I-TEQ value as a consequence. The reduction of lower chlorinated congeners was greater than that for high chlorinated ones, for both PCDD and PCDF congeners (see Figure 3). For example, 1,2,3,7,8-PeCDD and 1,2,3,7,8-PeCDF were reduced by 92.9 % and 93.8 % respectively, whereas OCDD and OCDF reduced by 48.1 % and 11.0 % respectively. In contrast with the addition of SDG,

2,3,4,7,8-PeCDF is not the major contributor to I-TEQ, since it accounts for only 13.8 %, whereas the percentage of 2,3,4,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF are 19.5 % and 24.6 % respectively. In addition, PCDF is still the major contributor to I-TEQ, which accounts for 93.8 % of total I-TEQ. This could be mainly attributed to the exceptionally high levels of PCDF in terms of I-TEQ.

The suppression efficiency obtained with (mainly) SO_2 injection on PCDD/Fs was 61.9 %. In contrast with the addition of 900 ppm NH_3, the suppression effects on PCDD and PCDF were quite close, 66.0 % and 60.2 %, respectively. Moreover, the reduction efficiencies of OCDD and OCDF were only 60.7 % and 46.4 %, whereas the average values of suppression efficiencies of the lower chlorinated exceed 90 %. Therefore, the I-TEQ value decreased by 94.8 %, even more than with the SDG produced from 1 g DS. In addition, 1,2,3,4,6,7,8-HpCDF was also the major contributor to I-TEQ, which accounted for ca. 31.7 %.

Remarkably, during the two tests with a joint injection of 500 ppm NH_3 and 500 ppm SO_2 a negative reduction for the sum PCDD/Fs was observed. Although a clear decrease in the concentrations of PCDD/Fs occurred when either 500 ppm NH_3 or 500 ppm SO_2 was injected, only 0.3 % of PCDD/Fs reduction was achieved in these experiments when they were injected together. The experiments were conducted in duplicate and the results were well reproducible, with values for the standard variation of 11 % for PCDD, 8 % % for PCDF and 16 % for I-TEQ. Strangely enough, a strong reduction was observed on all lower chlorinated PCDD, ranging from 83.9 % for 2378-TeCDD to 62.3 % for 1,2,3,4,6,7,8-HpCDD, yet only 0.4 % for OCDD. The situation was fairly similar for PCDF, with strong reductions for lower chlorinated PCDF, culminating in a 92.5 % reduction for 2,3,4,7,8-PeCDF and lowest for the two main PCDF congeners: only 20.8 % for 1,2,3,4,6,7,8-HpCDF and a negative reduction of -41.1 % for OCDF.

Acknowledgements

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