THE INFLUENCE OF PCDD/F MEMORY EFFECT FROM SCRUBBING SYSTEM IN FULL-SCALE MUNICIPAL SOLID WASTE INCINERATION

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1. Introduction

Municipal solid waste incineration (MSWI), an effective waste disposal method, gets increasingly popular for the advantages of volume reduction, safe disposal, and energy recovery[1-3]. However, polychlorinated-ρ-dibenzodioxins and dibenzofurans (PCDD/Fs) have received the global attention because of their extreme toxicity and high risk to human health[4-6].

For some waste-to-energy plants, especially the newly-built ones, usually a wet scrubber as the final step to be set for achieving ultra-low emission of acid pollutant and dust. Wevers et al. and Lehner et al. reported the positive effect of PCDD/Fs removal efficiency by WSS[7-8]. Other researchers found the converse results that wet scrubbing system (WSS)ncreased the emission concentrations of PCDD/Fs in flue gas by ten-folds, even though the inlet concentrations were very low[9]. Previous studies explain the obvious rise of PCDD/Fs from inlet to outlet of WSS as "memory effect"[10-11]. Some researches were carried out[9-10, 12], summarizing two mechanisms of memory effect including (i) surface adsorption/desorption of PCDD/Fs; (ii) entraining of scrubbing solution and fine particles[10] have been proposed, and the former is usually considered as the major one.

Few studies concerning "memory effect" have been conducted in China for the less utilization of WSS before. In addition, almost no study focuses on the gas- and solid-phase distribution and the mass balance of PCDD/Fs around the inlet/outlet flue gases, sludges, fillings and solutions of WSS. The present study is mainly carried out in three full-scale municipal solid waste (MSW) incinerators subordinated with WSS, two mechanical grate (MG) (30 t h^{-1}) incinerators and one circulating fludized bed (CFB) (23 t h^{-1}) incinerator. The PCDD/F characteristics in flue gas at the inlet and outlet, in sludges, fillings, and solutions are systematically analyzed to reveal the influencing mechanisms of memory effect on PCDD/F emissions in a WSS of MG MSW incinerator. A comprehensive mass balance model for PCDD/Fs of 1# WSS is also built.

2. Materials and methods

2.1 MSWI system

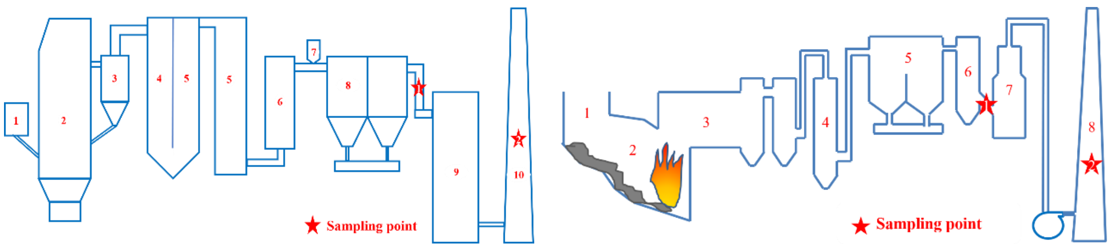
2.1.1 CFB incinerator

The CFB incinerator co-combusts MSW of high moisture content and with coal. The weight ratio of coal/MSW is 0.2.

This MSWI system (Figure 1a) mainly includes a feeder (1), a furnace (2), a cyclone separator (3), a secondary combustion chamber (4), a boiler (5), a semi-dry scrubber (SDS) (6), a fabric filter (FF) (7-8), a WSS, (9) and a stack (10).

2.1.2 MG

As shown in Figure 1b, the two similar incinerators with the same technological process are mainly composed of a feeder (1), a furnace (2), a superheater (3), a SDS (4), a FF (5), a selective catalytic reduction (SCR) (6), a WSS (7), and a stack (8).



(a) (b)

Figure 1. Systemic diagram of the MSWI

2.2 Experimental design

This study focuses on the emission signatures and changes between the inlet and outlet of WSS, and further analyzes the potential mechanisms and influencing factors of memory effect. All three MSW incinerators were operating normally during sampling period.

Two sampling positions of flue gas are set for each WSS, which are inlet (sampling position 1#) and outlet (sampling position 2#), in order to observe the influence of memory effect on PCDD/F emissions. The WSS was cleaned (renewing the scrubber solution and cleaning the sludge) after the first round of sampling (A). Then the second round of sampling (B) started after 12 hours. Further sampling about the sludges, the fillings and the scrubbing solutions were conducted only in the WSS of 2# MSWI. Memory effect is investigated through comparing the PCDD/F concentrations and signatures from inlet to outlet of the WSS at each condition, combining with building the mass balance in 2# WSS. Sampling PCDD/Fs in the flue gas of MSWI was conducted under stable operation and lasts for 6 h (2 h for each one Sample), Thus three parallel samples at each sampling position were obtained. As for the sludge, filling and scrubbing solution, only one sample for each of them is collected for analysis.

2.3 Sampling and analysis

PCDD/Fs in flue gases were collected by an isokinetic sampler (Model KNJ23, KNJ, Korea) followed the US EPA method 23a. The pretreatment procedures of PCDD/F samples follow the US EPA method 1613. The purified samples are analyzed through a high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (JMS-800D, JEOL, Japan). The toxic equivalents (TEQ) are calculated using NATO/CCMS factors[13]. The concentration of PCDD/Fs in gaseous samples is normalized to dry air of 11% O_2 at 101.3 kPa and 0 ℃.

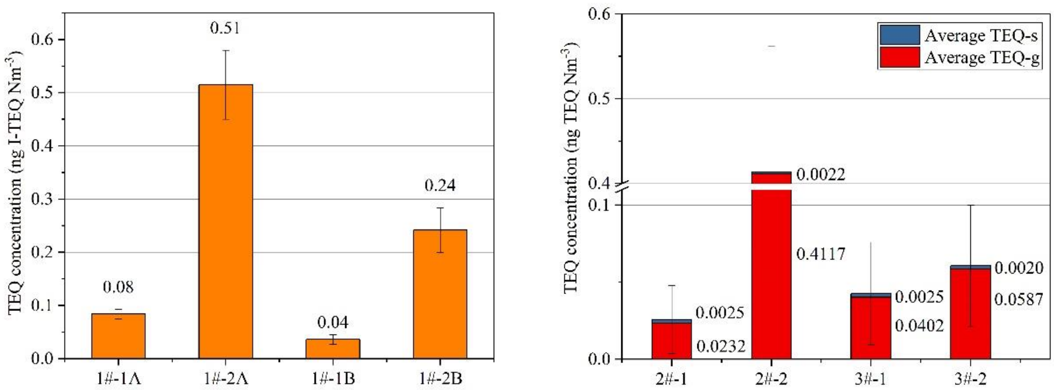
For observing the distribution of PCDD/F congeners from the MG samples detailly, the gas-phase part (adsorbed by XAD-2 resin) and solid-phase part (fine particulars on filter membrane) of all flue gas samples were separated for pretreatment and analysis. In laboratory, the concentration of PCDD/Fs in filling is analyzed by cleaning the surface ash and resining the surface by acetone and toluene, respectively, then the concentration is calculated through dividing the total amount by the weight of surface ash, whose average value is about 0.37 g in each PP filling.

3. Results and discussion:

3.1 Influence of memory effect

3.1.1 Influence on PCDD/F concentration

The TEQ concentration of PCDD/Fs in flue gas is elevated by 6.2, 6.7, 13.6 and 3.0 times, respectively, for 1# (A and B) and 2#, 3# WSS (Figure 2 and Table 1). The TEQ concentrations in inlet flue gas are 0.08, 0.04, 0.03 and 0.02 ng I-TEQ Nm-3 (Fig.2), which all meet the national standard for PCDD/F emissions from MSW incineration in China (0.1 ng I-TEQ Nm^{-3}). The WSS raises the PCDD/F emission concentrations of 1# and 2# WSS to beyond the national standard. As shown in Figure 2 and Table 1, the PCDDs/PCDFs-ratios in flue gas are decreased by the WSS. The PCDD/F concentrations of sludge, filling and solution are 220.32 ng g^{-1}, 77.15 ng g^{-1}, and 4.66 ng L^{-1} (7.28 ng I-TEQ g^{-1}, 1.80 ng I-TEQ g^{-1}, and 0.23 ng I-TEQ L^{-1}), respectively, as in Table 1. The PCDDs/PCDFs-ratios in sludge and filling are 2.69 and 2.99, respectively, showing a dominative position of PCDDs. Conversely, the ratio in scrubbing solution is 0.87, closer to that in outlet flue gas (0.71). Considering the better desorption capacity of PCDFs than PCDDs, the decline of PCDDs/PCDFs-ratios from inlet to outlet flue gases (i.e., from 2.76 to 0.71) is attribute to the PCDD/F desorption from solution, more accurately, from suspended solid (SS).



(a) (b)

Figure 2. TEQ concentration of PCDD/Fs

3.1.2 Influence on gas-solid distributions

As shown in Figure 2b and Table 1, The memory effect mainly affects the gas-phase PCDD/Fs, and the solid-phase PCDD/Fs barely change between the inlet and outlet flue gas. The concentrations of solid-phase PCDD/Fs slightly increase (Table 1), although the proportions of solid-phase PCDD/Fs in outlet flue gas decrease compared with that of inlet, directly indicating the solid-phase PCDD/Fs discharging from WSS.

Specifically, a part of particles existing as SS in solution and the surface ash of filling, which adsorb PCDD/Fs, discharge from solution and filling to the flue gas flow.

Table 1. Concentrations of PCDD/Fs in different wet scrubbing systems

	1#				2#					3#		Unit
	Inlet Flue A	Outlet Flue A	Inlet Flue B	Outlet Flue B	Inlet Flue	Outlet Flue	Sludge	Filling	Water	Inlet Flue	Outlet Flue	
∑PCDDs	0.71	0.58	0.22	0.36	0.58	1.98	160.61	57.80	2.17	0.29	0.46	
∑PCDFs	0.78	2.84	0.3	1.63	0.21	2.81	59.71	19.34	2.49	0.21	0.52	ng Nm^{-3}
∑PCDD/Fs	1.49	3.42	0.52	1.99	0.80	4.79	220.32	77.15	4.66	0.50	0.98	
∑TEQ	0.08	0.51	0.04	0.24	0.03	0.41	7.28	1.80	0.23	0.02	0.06	ng I-TEQ Nm^{-3}
∑PCDD/Fs-gas	\	\	\	\	0.73	4.72	\	\	\	0.47	0.92	
∑PCDD/Fs-solid	\	\	\	\	0.07	0.07	\	\	\	0.04	0.06	
∑PCDD/Fs-gas/∑PCDD/Fs	\	\	\	\	0.91	0.98	\	\	\	0.93	0.94	
∑PCDDs/∑PCDFs	0.92	0.20	0.75	0.22	2.76	0.71	2.69	2.99	0.87	1.36	0.87	
∑PCDFs/(∑PCDD/Fs)	0.52	0.76	0.57	0.82	0.27	0.59	0.27	0.25	0.54	0.42	0.53	
Stand. Dev. PCDD/Fs	0.49	0.57	0.13	0.34	0.35	2.71	\	\	\	0.04	0.39	Duplicate experiments
Stand. Dev. TEQ	0.009	0.065	0.0091	0.042	5.36	0.28	\	\	\	0.00	0.04	

3.1.3 Influence on the distribution of PCDD/F homologues

The profiles of seventeen 2,3,7,8-substituted PCDD/F-congeners in flue gas are shown in Figure 3. Both the gas-phase and solid-phase PCDD/Fs are dominated by the high-chlorinated homologues of PCDDs (HxCDDs to OCDD). Comparing the samples of inlet and outlet, the distribution of gas-phase PCDD/Fs changes apparently, however, the congener distribution of 2# and 3# WSS almost keep similarly changing trends (Figure 3c, d). In particular, the proportions of high-chlorinated homologues of PCDD/Fs (e.g., OCDD/F) in gas-phase and solid-phase both decrease. The congener distribution of solid-phase PCDD/Fs slightly changes, reflecting a slight or even ignorable influence of WSS. It is concluded that memory effect mainly increases the lower-chlorinated homologues in gas-phase, but barely affects the PCDD/Fs in solid-phase. Usually, higher chlorinated homologues are easily adsorbed onto particles due to their lower saturated vapor pressure, i.e., higher chlorinated homologues are harder release from particles, thus influence the distribution of PCDD/Fs.

In summary, the memory effect works on the following three aspects: (i) increasing the total mass concentration of PCDD/Fs, (ii) enhancing the occupations of low-chlorinated PCDD/Fs, and (iii) rising the proportions of PCDFs in PCDD/Fs.

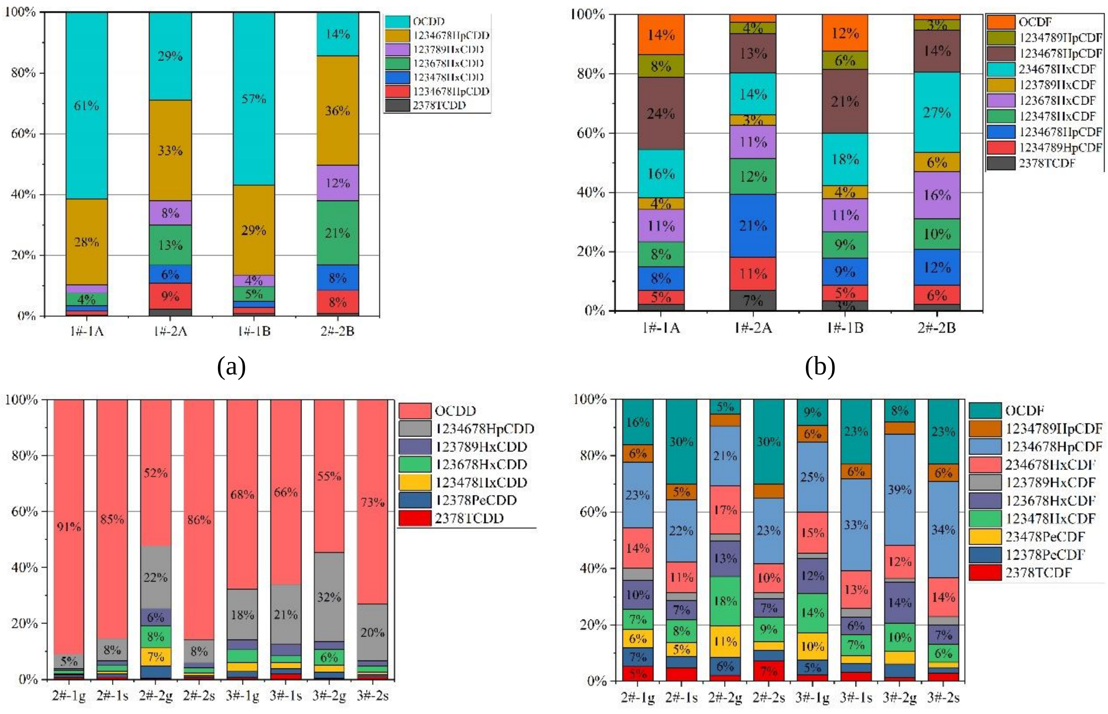


Figure 3. Distribution of the 2,3,7,8-substituted PCDD/Fs: (a, c) PCDD fingerprints; (b, d) PCDF fingerprints.

3.2 Mass balance in 2# WSS

For 2# WSS, the mass balance of PCDD/Fs in WSS mainly has two stages since the first operating day of WSS: (i) dominated by accumulating; (ii) dominated by discharging. And the former is the preparation for the second stage or the memory effect. And the latter is the reflection of memory effect. In other words, a similar model can be established as following equation:

Input = (Adsorption - Desorption) + Output

Considering that the samples stand for few hours, the mass balance of PCDD/Fs in WSS 2# is calculated throughout 1 h as a period based on the operation parameters and Table 1. The results are shown in Figure 4.

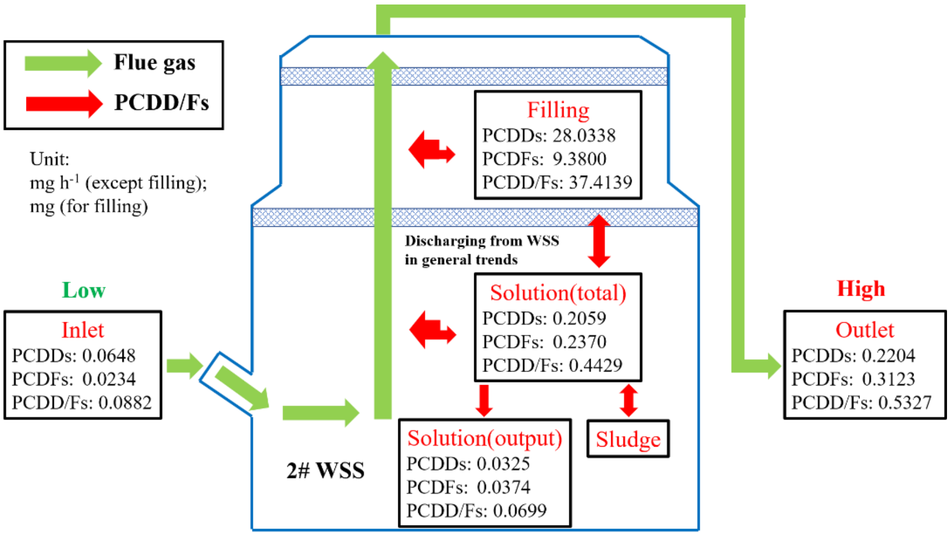


Figure 4. The mass balance of PCDD/Fs in 2# WSS.

The PCDD/Fs in solution and filling are 1-3 orders of magnitude higher than that in the inlet flue gas. The solution/inlet ratio for PCDD and PCDF (3.18 and 10.11) is similar to that of outlet/inlet ratio for PCDD and PCDF (3.40 and 13.32), however, both are smaller, indicating the discharge of PCDD/F from scrubbing solution to flue gas. Considering the obviously higher ratio of filling/inlet and outlet/inlet for PCDDs and PCDFs, the filling is supposed to be the largest potential discharging source of PCDD/F. Such high amount of PCDD/Fs is closely related with the long operation period without changes of filling since the WSS was put into operation.

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