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PCDD/FS EMISSION IN A 150T/D MSW AND COAL CO-FIRING FLUIDIZED BED INCINERATOR*

XU Xu (徐　旭), LI Xiao-dong(李晓东), YAN Jian-hua(严建华), LU Sheng-yong(陆胜勇), GU Yue-ling(谷月玲), CHI Yong(池涌), CEN Ke-fa(岑可法)

(*Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China*)

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Abstract: Incineration as a method of reducing Municipal Solid Waste (MSW) volume and recovery of energy has been developed gradually in China. More attention is paid on polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) formed in MSW incineration process. This paper presents results of the analysis of PCDD/Fs in the residues of a fluidized bed incinerator co-firing MSW and coal in the Yuhang Thermal Power Plant. The effects of operation conditions and the wet scrubber system on PCDD/Fs formation were also analyzed. PCDD/Fs emitting from the smoke stack was 0.92 I-TEQ ng/Nm^3. After the wet scrubber emission of dioxins increased and the shifting of homologue profiles in flue gas was also observed, PCDFs were not detected in the incinerator residues. From this, we can see that in the MSW incineration process, the formation mechanism of PCDFs was different from that of PCDDs. The results will benefit further research on the optimal operation of incinerator and control of PCDD/Fs emission from the MSW incinerator.

Key words: municipal solid waste, incineration, PCDD/Fs
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INTRODUCTION

The improving of science and technology in the world not only increases economic development and living conditions but also generates a huge quantity of MSW, whose output in China was about a hundred million tons in 1993, and accelerating at 8% - 10% per year (Tian et al., 1998).

Disposal by incineration was rapidly increased in recent years in China because of a lack of suitable sites near large cities and the growing concern for ground water contamination, which limit the development of landfill. This trend has led to an increase in the number of MSW incinerators being constructed. The first modern MSW incinerator (150t/d, Martin Stoke Type licensed Via Mitsubishi) in China was built in Shenzhen city of Guanzhou Province in 1988. And new incinerators will be constructed in Zhuhai, Beijing, Shanghai, Tianjin, Guanzhou, Chengdu and so on.

This trend may raise an environmental problem of pollution by polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) which are formed in MSW incineration (MSWI). In order to solve the problem of PCDD/Fs emitting from MSWI, many scientists and engineers paid great deal of attention to the formation mechanism of PCDD/Fs and controlling measures (Olie et al., 1977; Manscher et al. 1990; Brown et al., 1990; Kari Tuppurainen et al., 1998). The formation mechanisms of PCDD/Fs in the MSWI are "de novo synthesis" and precursor reaction considered as very complicated processes mainly occurring in the low temperature post-combustion zone (Kari Tuppurainen et al., 1998). The technique to control PCDD/Fs emission focuses on the optimal design and operation of incinerator and adoption of advanced flue gas cleaning system (Hajime Tejima et al., 1998).

Using results of studies on the properties of waste, the secondary pollution performances and

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some related technologies, the Institute of Thermal Power Engineering (ITPE) of Zhejiang University developed a new waste incineration technology-differential density fluidized bed (DDFB). Many experiments were carried out to evaluate this technology. In this work, the PCDD/Fs in MSW residues such as flue gas, bottom ash and wet scrubber waste cooling water were analyzed. The effects of operation condition and flue gas cleaning system on PCDD/Fs' emission were also studied. The analysis results will benefit further research on the optimal operation of incinerator and control of PCDD/Fs emission from the MSWI.

EXPERIMENTAL DETAILS

Incinerator: DDFB technology was applied to Hangzhou City's 150 t/d incinerator built in the Yuhang Cogeneration Power Plant. The incinerator has been in commercial operation since 1998. Fig. 1 shows the scheme of the incinerator system. This incinerator was retrofitted from an original coal-fired 35t/h Stoke boiler (steam temperature: 450℃, steam pressure: 3.85 MPa) to a coal and MSW co-firing incinerator. The flue gas cleaning system was modified from a former water dust tower, and cooling water was injected (pH ≥ 12) from the top of the scrubber, which was a modified wet scrubber. Flue gases from the chamber pass through the steam superheater, economizer, air pre-heater, louver inertial separator, and boiling surface, then emit to the atmosphere.

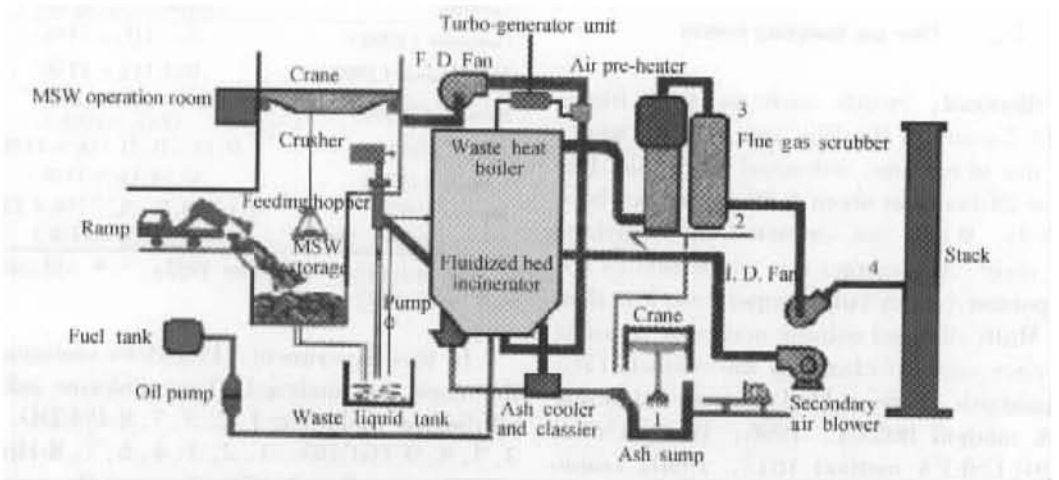

Fig.1 Scheme of 150t/d co-firing MSW and coal fluidized bed incinerator system
1. bottom slag; 2. waste cooling water; 3. flue gas before wet scrubber; 4. flue gas after wet scrubber

Experiment conditions: The experiments were carried on under two combustion conditions: 1. Operation under designed condition (MSW: coal = 66.54: 33.46, experiment time: January 24th 15:00 - 22:00, 1999); 2. Un-designed incineration situation, MSW about 200t/d (MSW: coal = 74.34: 25.66, experiment time: January 24th 22: 00 to January 25th 2: 00, 1999). Table 1 lists the mixing fuel proportions and corresponding heat values.

Table 1 Mixing fuel proportions and corresponding heat values

No	MSW: coal	C_{ar}(%)	H_{ar}(%)	O_{ar}(%)	S_{ar}(%)	N_{ar}(%)	A_{ar}(%)	W_{ar}(%)	Q_{ardw}(kJ/kg)
1	66.54:33.46	28.69	2.57	9.09	0.17	0.52	19.43	39.41	11591.4
2	74.34:25.66	25.07	2.42	9.40	0.15	0.59	19.32	43.02	10143.4

Sampling: Fig. 1 shows the sampling sites of bottom ash, flue gas and waste water. The bottom slag and recycling cooling water were collected every half hour, then mixed together into a unique sample. The flue gas samples were collected by a modified SYC-III dust collector unit.

The system of flue gas sampling was given in Fig. 2 (Brown et al., 1990; USEPA method 0023A, 1990; Horaguchi et al., 1989; Yoshio Akimoto et al., 1994). PCDD/Fs in flue gas were condensed in the first and second impingers with 200 ml water, passed through XAD-2 resin tube, then absorbed in the impinger with 200 ml diethylene glycol (DEG) in an ice bath.

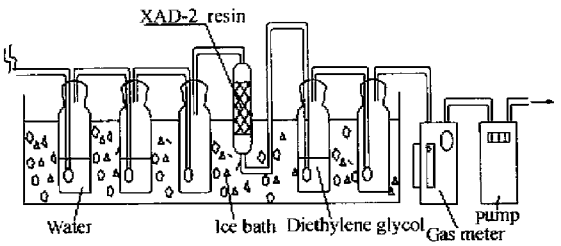

Fig. 2 Flue gas sampling system

Pre-disposal: Solids such as ash, filter, and XAD-2 resin in the flue gas samples were, with the use of toluene, extracted by Soxhlet Extractor for 24 hours at about 5-10 cycles per hour respectively. Water was extracted by methylene chloride resin. The extract was condensed by rotary evaporator (water bath temperature less than 45℃). Multi silicagel column and basic alumina column were used to clean up the extract. 13C-lable standards were added before extraction (USEPA method 0023A, 1996; Horaguchi et al., 1989; USEPA method 1613, 1990; Yoshio Akimoto et al., 1989; Jiang, 1996).

Analysis: All analyses were performed on a low resolution Finngan Voyager mass spectrometer (LRMS) with a trace 2000 high resolution gas chromatograph (HRGC). Chromatographic separations were carried out on a 30 m DB-5 column with internal diameter of 0.25 mm and a stationary phase film thickness of 0.25 μm. Ultrahigh purity helium was used as the carrier gas. The GC oven temperature program was: Initial temperature 70℃, held for 1 minute, 1st temperature ramp of 40℃/min until 200℃, 2nd temperature ramp of 6℃/min until 280℃, held for 20 minutes. Electron impact ionization was done at 70 ev. In GC/MS analysis the selected ion monitoring mode was set to monitor two characteristic ions for each of the congener groups from Tetra-CDD to Octa-CDD and corresponding PCDFs.

RESULTS AND ANALYSIS

1. PCDD/Fs emission from stack

MSWI is considered as an important source of PCDD/Fs. The extremely high toxicity of PCDD/Fs has led to strict limits in some countries on the emission of PCDD/Fs from incinerators. Table 2 shows the emission limit of PCDD/Fs from incinerator in some countries. In China, the controlling limit was officially set at 1.0 TEQ ng/Nm^3 (11% O_2) on June 1, 2000 in four large cities.

Table 2 Emission limit of PCDD/Fs in some countries

Country	Limit(TEQ ng/Nm^3)
Germany (1993)	0.1 (O_2 = 11%)
Netherlands (1993)	0.1 (O_2 = 11%)
Sweden (1991)	0.1*, 0.1 – 2.0** (CO_2 = 10%)
USA (1993)	0.14 – 0.21 (O_2 = 11%)
Canada (1992)	0.14(O_2 = 11%)
Japan (1993)	0.1*, 0.5 – 5** (O_2 = 12%)
China (June 1, 2000)	1.0(O_2 = 11%)

* new incinerator built after 1995; * * old incinerator built before 1995

In this experiment, PCDD/Fs emission from the stack was analyzed. Toxic chlorine substituted dioxins including 1, 2, 3, 7, 8-PeCDD, 1, 2, 3, 7, 8, 9-HxCDD, 1, 2, 3, 4, 6, 7, 8-HpCDD, OCDD were found. Fig. 3 gives the profile of dioxins in the flue gas. The concentration of PCDFs was below detection limit. The total emission of PCDD/Fs in the flue gas before the stack was 343.78ng/Nm^3 (O_2 = 11%) in the designed condition, and the TEQ value of PCDD/Fs in the flue gas was 0.92 I-TEQ ng/Nm^3 (O_2 = 11%).

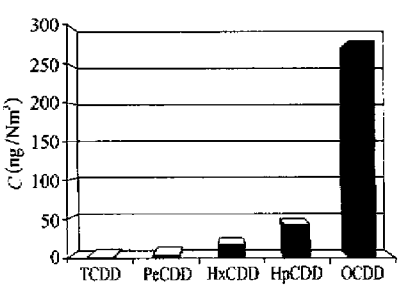

Fig. 3 PCDD/Fs emission from stack

2. PCDD/Fs in the residues of MSW incinerator

Table 3 gives the analysis results for dioxins in the residues of MSW incinerator operated under designed condition, and Fig.4 gives the distribution profile of dioxins in the bottom ash produced under un-designed operating condition. From Table 3 and Fig.4, we can see that dioxins were not detected in the bottom ash under designed operating condition, so a large quantity of bottom ash can be safely disposed by landfill. However operated under un-designed operating condition, dioxins were found in the bottom ash. When the incinerator was operated under un-designed operating condition, not only was the incinerator's thermal efficiency decreased from 82.06%(designed condition) to 79.24%, but, the output of micro-pollutants (such as HCl, SO_2, NO_2, heavy metals and dioxins) was enhanced. When Zhejiang University adopted DDFB technology to design the incinerator built in the Yuhang Thermal Power Plant, "3-T's" rules (Time, Temperature and Turbulence) were considered adequately. Many measures were introduced to realize "3-T's" rules, for example, keeping the bed temperature at 850℃ – 1000℃, more than 3 second flue gas residence time in the incinerator, and boosting a second burst of air from the freeboard of the fluidized bed incinerator to strengthen the gas turbulence for a second combustion.

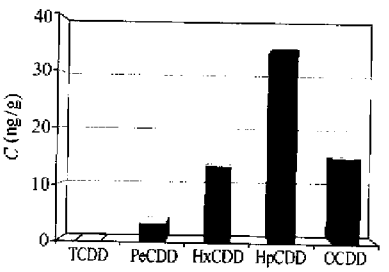

Fig.4 Distribution of dioxins in bottom slag of incinerator operating under un-designed condition

Table 3 PCDD/Fs in the residues of MSW incinerator under designed operating condition

Samples	Unit	TCDD	P_eCDD	H_xCDD	H_pCDD	OCDD
Bottom slag	ng/g	nd *	nd	nd	nd	nd
Waste cooling water	ng/L	nd	nd	nd	4.9708	2.34232
Flue gas in stack	ng/Nm^3	1.5400	4.5262	16.9851	42.9224	277.81

* nd-no detected

In the waste cooling water of the wet scrubber, dioxins were found (TEQ value = 0.024 I-TEQ ng/L). When the flue gas passed through the flue gas cleaning system, large quantity of dusts was captured by the scrubber system, reducing dusts in the flue gas from 1.82×10^4 mg/Nm^3 before scrubber to 248 mg/Nm^3. The cooling water must be made harmless for disposal before it is recycled in the incineration system, and attention should be paid to the proper disposal of ash in the sedimentation pool.

3. Distributing of dioxins before and after the wet scrubber

Many researchers found that dioxins can be generated in the incinerator low temperature zone, especially in ESP. But as to the wet scrubber, there were some different opinions. H. Hunsinger et al. (1993) found that no dioxins were formed in the wet scrubber after a mass balance experiment on dioxins by using a glass wet scrubber. Stellan Markunel et al. (1993) analyzed dioxins in flue gas before and after the scrubber, and found that dioxins in the flue gas were increased five times after the scrubber.

The wet scrubber in the YuHang Thermal Power Plant had some efficiency in decreasing common pollutants: the efficiency for SO_2 was about 75.1%, for NO_x about 20.5%, for Hg about 37.9%, for Pb about 94.2%, and for Cd about 89.7%. Table 4 gives the operating parameters of the wet scrubber under two experimental conditions and concentration of CO in the flue gas.

Table 4 Operating parameters of wet scrubber under two experimental conditions

No	Temperature of flue gas Ts(℃)		Velocity of flue gas Qs (N.d.m^3/h)		Oxygen O_2(%)		C_{co} mg/Nm^3	
	In	Out	In	Out	In	Out	In	Out
1	105	47	6.09×104	6.34×104	9.0	10.7	90.6	81.5
2	104	52	5.97×104	6.20×104	8.6	10.2	107	96.2

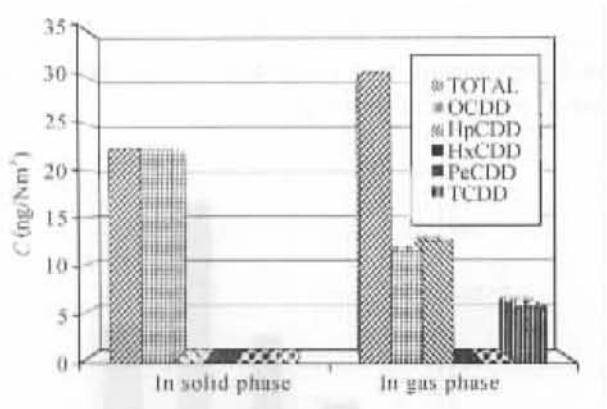

Fig.5 Distribution of PCDDs in solid phase and gas phase of flue gas before scrubber

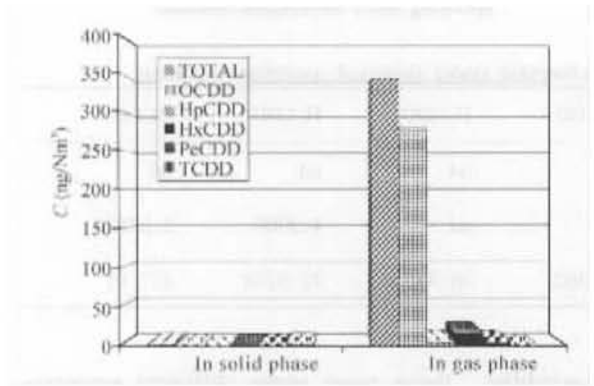

Fig.6 Distribution of PCDDs in solid phase and gas phase of flue gas after scrubber

Fig.5 and 6 give the distributing profile of dioxins in the solid phase and gas phase of the flue gas before and after the wet scrubber system. In the input flue gas before the scrubber, dioxins were distributed in gas phase and solid phase relatively evenly; about 57.53% in gas phase. Nevertheless in the output flue gas after the scrubber, most flue gas dioxins were concentrated in the solid phase, comprising nearly 99.5%, which means that when flue gas passed through the wet scrubber, the temperature of flue gas was cut down from 165℃ to 45℃, dioxins in flue gas were condensed and agglomerated to fine particles.

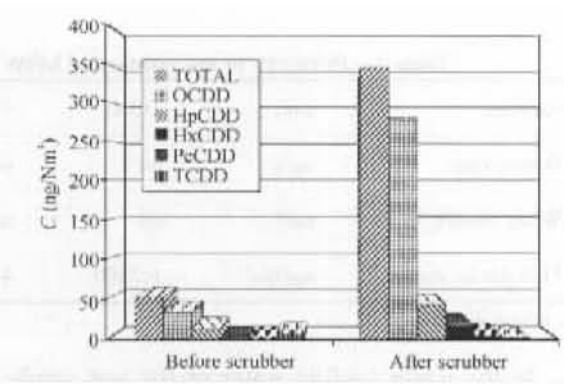

Fig.7 Distribution of dioxins in flue gas before and after wet scrubber

Fig.7 shows the distribution of dioxins in the flue gas before and after the wet scrubber system. The dioxins in the flue gas before the scrubber were TCDD, HpCDDs and OCDD, mostly mass concentrated in the higher chloride portion. In the flue gas after the scrubber, TCDD, PeCDDs, HxCDDs, HpCDDs andOCDD were detected, and OCDD was the uppermost isomer. Fig.7 shows that the value and the concentration and category of dioxins in the flue gas varied after passage through the wet scrubber. The reasons may be that dioxins were formed in the wet scrubber as stellan Markunel et al. described and increased dioxins were contributed **by fly ash adhered on the scrubber wall and washed by flue gas.**

CONCLUSIONS

1. The emission of PCDD/Fs in the stack of the incinerator when operated under designed condition was 0.92 I-TEQ ng/Nm_3, less than the limit set for Chinese MSWI

2. When the incinerator was run under properly designed condition, no dioxins were found in the bottom ash, whereas under un-designed condition, dioxins were detected in the bottom

ash, produced by the incomplete combustion of MSW. Therefore steady operation prevents formation of dioxins from incomplete combustion. Dioxins were also found in the waste cooling water of the wet scrubber. Therefore more attention should be paid to dealing with the cooling water and its recycling.

3. The distribution of solid phase and gas phase dioxins in flue gas varied after passing through the wet scrubber. In the flue gas before the wet scrubber, dioxins were distributed evenly in solid phase and gas phase; but after the scrubber, most dioxins were concentrated in the solid phase.

4. Dioxins in flue gas were increased after passing through the scrubber. The reason may be the formation of dioxins in the wet scrubber or the contribution of fly ash adhered its wall and washed down by flue gas.

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