

Formation and Removal of Dioxins in a MSWI during Different Operating Periods

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Introduction

There was little literature to report the dioxin emission concentrations and characteristics during start-up and burndown periods. This research aims to establish the databases of dioxin concentrations in the flue gas and evaluate the dioxin removal efficiencies by air pollution control devices (APCDs) at different operating periods (during start-up, normal operating and burn down periods).

Methods and Materials

The incinerator investigated in this study consists of four parallel lines, each with its own mechanical type grate (capacity 375 ton/day-incinerator), secondary combustion chamber and steam boiler for energy recovery. The flue gas cleaning equipment included an electrostatic precipitators (ESP) for dust removal, a two-stage wet scrubber (WS) for acid gas removal and a selective catalyst reactor (SCR) as a retrofit technology for reducing dioxin emission to meet the standards (0.1 ng-TEQ/Nm³). A measurement program was conducted at several sampling positions (ESP inlet, ESP outlet, SCR inlet, and stack) during the different operating conditions (during start-up, normal operating and burn down periods). Table 1 summarizes the operational conditions in samplings during the different operating periods. Dioxin sampling procedure is referred to U. S. EPA Method 23A¹. Dioxins were collected in the sorbent trap filled with XAD-2 resin, glass fiber filters, and related sampling rinsing solvents. Before sampling, XAD-2 resin was spiked with isotope labeled PCDD/F (surrogate standards. After pretreatment, i.e., extraction, concentration, clean-up procedures and so forth, these samples were injected into GC/HRMS with ¹³C-Isotope Dilution Method to determine the concentrations (ng-TEQ/Nm³) of 17 polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The analytical procedure is referred to U. S. EPA Method 23A¹. Dioxins were analyzed with high resolution gas chromatography / high resolution mass spectrometer (HRGC/HRMS) (JEOL JMS 700D) equipped with a DB5-MS capillary column (60m × 0.25mm × 0.25 μm film thickness).

Results and Discussion

The furnace operating procedure includes start-up, normal operating and burn down periods. There were two models of increasing temperature under start-up status (19 hours and 12 hours increasing temperature curve in Figs. 1) (e.g., it takes 19 hours from ignition to stable burning when the operating temperature reaches 850 °C). The analyzed results are shown in Table 2 and Table 3. At the boiler outlet or the inlet of the air pollution control device, dioxin emission concentrations during start-up periods were much higher than that of normal operating and burn down periods. The dioxin concentrations at the boiler outlet during start-up were 15 times higher than normal operating period. CO concentration was between 400 and 1000 ppm during start-up periods, which was about 50 times higher than normal combustion. Combustion condition has a great influence on PCDD/Fs. Under good and stable combustion conditions (e.g. during normal operating period), the PCDD/Fs were completely destroyed inside the combustion chamber and emission concentrations were lower. However, bad and unsteady state of combustion conditions resulted in high concentrations of products of incomplete combustion (PICs) like CO, soot, hydrocarbons and dioxins². It was attributed to the fact that the combustion temperature (300-800 °C) was not high enough to burn completely during start-up period. Those PICs in the high temperature flue gas will be brought to the steam boiler. The operating temperature of the boiler was between 220 °C and 650 °C and which was in the dioxin de novo synthesis temperature windows of 200 °C-450 °C³. Excess air (O₂: 13-16%) and unburned carbon (soot) in the fly ash at temperature above 200 °C will cause significant amounts of dioxins to generate at the boiler during start-up period. Although the dioxin concentrations in the flue gas downstream of the boiler were different at three operating periods, the PCDF/PCDD ratio at the boiler outlet approximated to 1.0 at all operating periods (Table 4). It indicates that de novo synthesis might be the major mechanism in the boiler at three operating periods. The congener profiles of PCDD/Fs at the outlet of the boiler during three periods were shown in Figs. 2 - Figs. 3. It was observed that the emission concentration of PCDD/F during burn down period was lower than normal operating. It might be due to the combustion condition in furnace was similar (e.g. operating temperature 960 °C), and the wastes stop to be fed during burn down period. The concentration of PCDF was higher than that of PCDD. Figs. 3 compares the concentration profiles of PCDD/Fs during two start-up models. PCDD/F concentration of 19 hours model was higher than 12 hours on total concentration, but 19 hours model was lower than 12 hours on the TEQ basis. It indicates that PCDD congener formation concentration was almost the same, but a significant amount of PCDF with high TEF (toxicity equivalency factor) formed during the 12 hours model. Although dioxin emission concentrations were different, the congener contributions were similar. 2,3,4,7,8-PeCDF is the dominated congener on the TEQ basis at all periods (Figs. 4).

Removal efficiencies of PCDD/Fs by APCDs at different operating periods were evaluated. As shown in Figs. 5 and 6, it was observed that the dioxin concentration decreased after passing ESP during start-up period, but increased during normal operating and burn down period. It may be attributed to the fact that ESP temperature during normal operating was between 210 °C and 240 °C and which was in the de novo synthesis temperature windows. Although ESP can also capture the solid phases, the re-synthesis dioxin in the fly ash partly desorbed to the gas phase and increased the outlet concentration. Figs. 7 compares the removal efficiencies of PCDD/F congeners by ESP at different operating periods. At normal operating and burn down periods, they were similar to each other. The medium-chlorinated PCDD and PCDF congeners have higher increasing

rate. Although the real reason is still unknown, it was the composite result of gas phase increase and solid phases decrease. The measurement for long time period is needed. The operating temperature of ESP during start-up was lower (180-205 °C) and it could decrease the possibility of dioxin re-synthesis in the fly ash. ESP could capture particulate matter with a very high collection efficiency (over 99%). The PCDD/Fs adsorbed on the particulate matter could be removed simultaneously and caused the concentration at the outlet of ESP to decrease. The removal efficiency of dioxin during start-up increased with the increasing chlorination. It is partly attributed to the fact that the vapor pressures of higher-chlorinated dioxin was lower than that of lower-chlorinated congener and has a higher tendency to condense on particles as the solid phases and which could be removed by ESP.

The dioxin emission concentrations after WS decreased during start-up period. The removal efficiency of PCDD/Fs by WS was between 77% and 84% on total PCDD/Fs (between 69% and 79% in terms of TEQ). The removal efficiency of dioxin increased with the increasing chlorination during start-up (Figs. 8). This maybe be attributed to the phenomenon that the operating temperature of WS was only 55 -64 °C, most gas-phase PCDD/Fs condensed on the particles as the solid phases. The vapor pressures of higher-chlorinated dioxins were lower than that of lower-chlorinated dioxins and their partitions in particle-bound phase were high. Some dusts were removed in the wet scrubber. The second reason is that gaseous dioxin in flue gas dissolved partly into scrubbing water and moved to the surface of suspended solid particles and which were removed partly by WS⁴. However, the removal efficiency was low at the normal operating and burn down periods (17% and 2.3% on TEQ basis, respectively). This may be attributed to the fact that removal efficiencies of the lower chlorinated congeners were negative at the normal operating and burn down periods. The increase of lower chlorinated congeners may be attributed to the dechlorination of higher-chlorinated dioxin and memory effect in WS⁵. Dioxins in the flue gas will be transferred to the surface of wall or packing materials, but some PCDD/Fs were desorbed and transferred to outlet gas again. The vapor pressure of dioxin congener decreases with increasing chlorination. The lower chlorinated congeners were more volatile and easy to desorb and transfer to outlet gas. The removal efficiency of the other congeners increased with the increasing chlorination. This may be attributed to the fact that higher-chlorinated congeners partitions in particle-bound phase were high and easy to be removed by WS. "Memory effect" was especially evident when the dioxin concentration in the flue gas was low (e.g. during the normal operating and burn down periods), but was unapparent when the concentration of dioxin in flue gas was high and desorption seldom happened. (e.g. during the start-up period).

Removal efficiency of dioxin by SCR depends on operation temperature and the inlet concentration of particle. The removal efficiencies of dioxins by SCR system during normal operating and burn down periods were as high as 99% when operation temperature is over 210 °C and particulate matter is less than 20 mg/Nm³. The SCR system seems to decompose all congeners of tetra- to octa-dioxins (Figs. 9). During 19 hours start-up period, removal efficiency of dioxin was only 42% and removal efficiency of dioxin decreased with the increasing chlorination. Lower chlorinated congeners were decomposed easily by SCR. It was attributed to the fact that temperature (only 199 °C) was not enough to decompose higher-chlorinated dioxins which were easy to condense on the particles.

Although the total removal efficiencies of dioxins by APCDs at different periods were between 97% and 99% (Figs. 10), the emission concentrations at the stack were sometimes higher than the

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limit of 0.1 ng-TEQ/Nm³ during the start-up. This was attributed to the high concentration of PCDD/Fs entering the SCR. For reducing the dioxin emission concentrations, waste had to be processed prior to combustion (drying, shredding, or separation) and the initial temperatures of the feeding wastes during the start-up periods should be raised if possible.

Acknowledgements

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Table 1 Operational conditions at different operating periods

Parameter	Start-up (19 hours)	Start-up (12 hours)	Normal operating	Burn down
Secondary chamber temp. ()	320-800	330-800	900-1040	960-560
Boiler temp. ()	220-570	220-650	260-670	250-650
ESP temp. ()	180-205	180-200	215-240	205-230
WS temp. ()	55-64	55-63	68	66
SCR temp. ()	199-200	203-215	208-212	208-220

Table 2 PCDD/Fs concentrations during four different operating periods (all values in normal conditions, dry gas at 11%O₂)

Stages Position	PCDD/Fs (ng/Nm ³)				PCDD/Fs (ng-TEQ/Nm ³)			
	Start-up		Normal	Burn down	Start-up		Normal	Burn down
	19 hours	12 hours	operating		19 hours	12 hours	operating	
Boiler outlet	4919.1	4525.6	314.9	188.8	304.386	346.341	19.146	11.595
ESP outlet	1172	1238.5	422.4	219.3	77.013	122.404	28.460	13.734
SCR inlet	191.2	281.3	262.4	157.6	24.077	25.909	23.595	13.412
Stack	109.1	18.5	3.5	1.4	7.001	1.106	0.100	0.088

Table 3 Removal efficiencies of PCDD/Fs by APCDs at different periods

Stages Position	Removal efficiency (%)				Removal efficiency for TEQ (%)			
	Start-up		Normal	Burn down	Start-up		Normal	Burn down
	19 hours	12 hours	operating		19 hours	12 hours	operating	
ESP	76.2	72.6	-34.1	-16.2	74.7	64.7	-48.6	-18.4
WS	83.7	77.3	37.9	28.1	68.7	78.8	17.1	2.3
SCR	42.9	93.4	98.6	99.1	70.9	95.7	99.6	99.3
APCDs	97.8	99.6	98.9	99.3	97.7	99.7	99.5	99.2

“-” dioxin concentration increase

Table 4 PCDF/PCDD ratio

PCDF/PCDD ratio for total concentration				
Stages Position	Start-up		Normal	Burn down
	19 hours	12 hours	operating	
Boiler outlet	1.0	1.4	1.2	1.4
ESP outlet	0.9	1.4	1.2	1.2
SCR inlet	2.0	1.8	1.5	1.6
Stack	1.0	1.1	0.9	1.2

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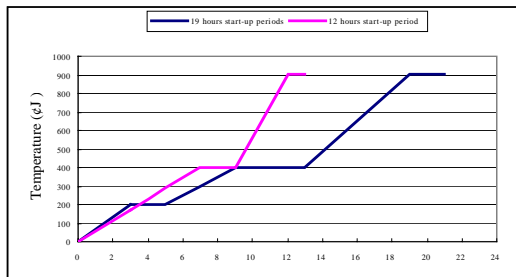


Fig. 1. The operating temperatures during start-up periods

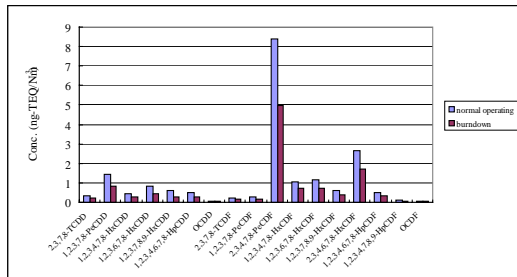


Fig. 2. Concentration of 2,3,7,8-substituted PCDD/F congeners at the boiler outlet during normal operating and burndown periods

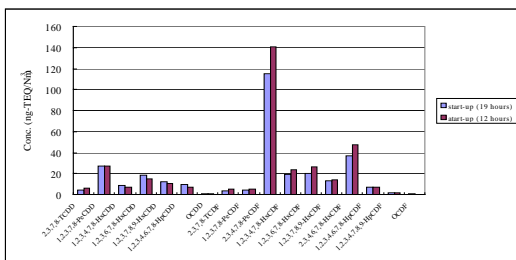


Fig. 3. Concentration of 2,3,7,8-substituted PCDD/F congener at the boiler outlet during start-up

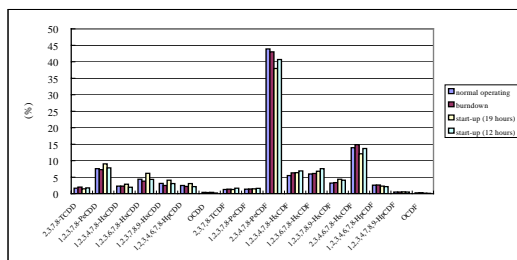


Fig. 4. The dioxin congener contribution at the boiler outlet during different operating periods

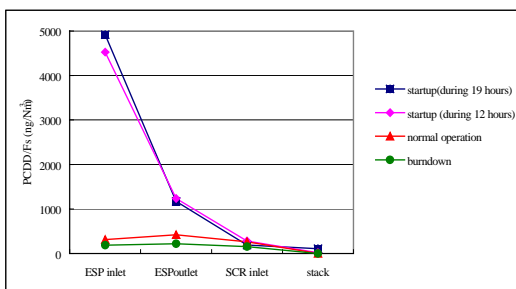


Fig. 5. The dioxin concentration at different positions (total concentration)

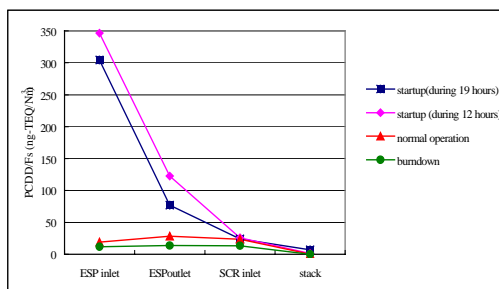


Fig. 6. The dioxin concentration at different positions (TEQ basis)

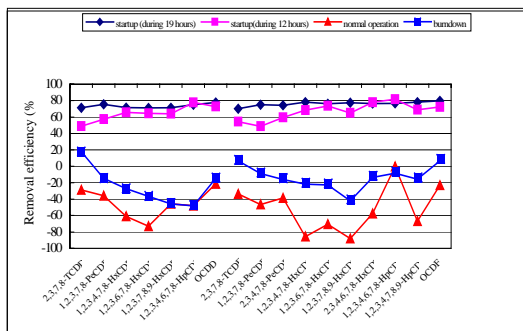


Fig. 7. The dioxin removal efficiencies by ESP

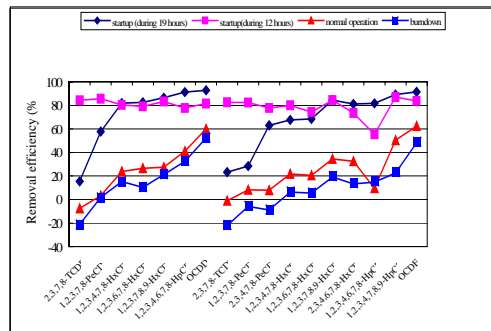


Fig. 8. The dioxin removal efficiencies by WS

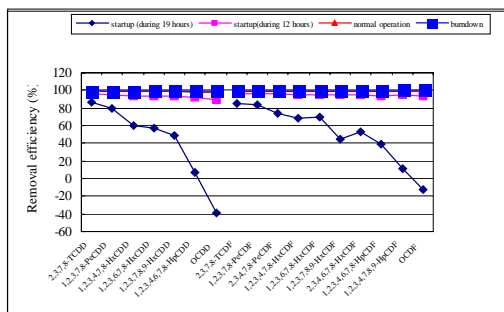


Fig. 9. The dioxin removal efficiencies by SCR

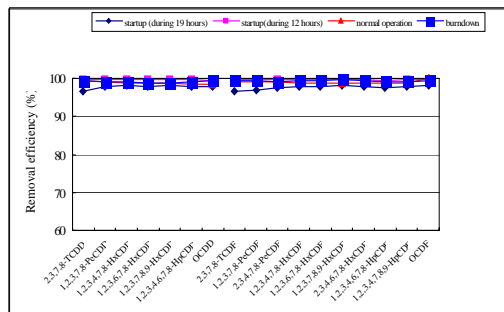


Fig. 10. The dioxin removal efficiencies by APCDs

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