

CHARACTERISTICS OF DIOXIN EMISSION IN A FULL SCALE MSW INCINERATOR AFTER DIOXIN IMPROVEMENT ENGINEERING

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Introduction

In the past few years, polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/Fs) emissions at the stack of the municipal solid waste (MSW) incinerator investigated were between 5 and 13 ng-TEQ/Nm³ when the original air pollution control devices (APCDs) consisting of electrostatic precipitator (ESP) and wet scrubber (WS) were applied. It began to implement dioxin abatement engineering to comply with the limit of 0.1 ng-TEQ/Nm³ in 2002. The best solution they chose to expand the existing installation was selective catalyst reactor (SCR). An extensive sampling project was conducted. The results were used to establish the databases of dioxin concentrations and homologue profiles at different positions, to evaluate the possible dioxin formation mechanisms in the incineration process and to evaluate the removal efficiencies of PCDD/Fs by APCDs.

Materials and Methods

The large-scale municipal solid waste incinerator (MWI) investigated in this study has four parallel lines, each with its own mechanical type grate (capacity: 375 ton/day-incinerator), secondary combustion chamber and steam boiler for energy recovery. Flue gas was sampled in four different points, located across every single process unit of the flue gas cleaning system (ESP, WS, and SCR). Dioxin sampling and analytical procedure are referred to U. S. EPA Method 23A¹.

Results and Discussion

The sampling campaign was performed during a week of normal operation of the plant. The gas/particle partitioning and homologue profiles of PCDD/Fs through APCDs were discussed. The analyzed results are shown in Table 1 and 2. The operating temperature of the secondary chamber was higher than 900°C, and CO was between 2-20 ppm during the sampling. It indicates the combustion system was maintained in stable condition. However, PCDD/Fs concentration in the flue gas at the outlet of the boiler was 357.9 ng/Nm³ (7.024 ng-TEQ/Nm³). It may be attributed to the de novo synthesis since the operating temperature of the boiler was between 270°C and 670°C, and which was in the de novo synthesis temperature windows of 200 °C-400°C². Since the PCDF/PCDD ratio was 1.1, de novo synthesis might be the major mechanism in the boiler³. At the outlet of the boiler, gas phases were 4.6 times higher than solid phases. Along the flue gas pathway, gas phase concentration levels measured show a slight increase after the ESP, however, a highly removal efficiency for solid phases was observed (around 95.9%). The increase of gas phases across ESP could be attributed to the de novo synthesis since the operating temperature of ESP was between 215°C and 230°C. The re-synthesis dioxins in fly ash were partly desorbed and transferred to outlet gas as the gas phase. Nevertheless, ESP may capture a very high collection efficiency of particulate matter (over 99%). The PCDD/Fs adsorbed on the particulate matter could be removed simultaneously. The removal efficiency of each solid phase dioxin congener was higher than 90% (Figs. 1). The total removal efficiency of PCDD/Fs by ESP was only 8.3% on total PCDD/F, but negative removal efficiency of -13.0% on the TEQ basis. This could be attributed to the fact that lower -chlorinated congeners with higher TEF (toxicity equivalency factor) increased across ESP and increase the TEQ level (Figs. 2). Since the PCDF/PCDD ratio at ESP outlet is 1.0, de novo synthesis might be the major mechanism. ESP seemed to be an important precursor of dioxin formation when the operating temperature was high. For the inhibition of re-synthesis of dioxin, the inlet temperature of flue gas into ESP should be reduced to less than 200°C. The congener profiles of PCDD/Fs at the outlet of ESP were shown in Figs. 3. It was observed that OCDD was the major contributor to total value, but 2,3,4,7,8 -PeCDF is the dominated toxic congener on the TEQ basis.

Gas and solid phase dioxin concentrations in flue gas increased after passing through the WS, resulting in negative removal efficiencies of -27% and -200%, respectively. The increasing rates of solid phase PCDD and PCDF congeners increase as the chlorinated level increases (Figs. 4). Since the operating temperature of WS was only 68°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. It caused the concentration of solid phase dioxins increase and higher-chlorinated dioxins were the dominant at WS outlet. However, gas phase dioxins also show a slight increase after passing the WS. It could be attributed to the "memory effects"⁴. The desorption rate increased with an increase in temperature from 65 °C to 90°C⁵. The total removal efficiency of PCDD/Fs by WS was -28.5% on total PCDD/Fs. It indicates that WS might be another potential PCDD/F source. The methods for decreasing memory effects were by using high volume of fresh water in circulated water or a new packing material, which is well suited for selective absorption of dioxins in wet scrubber⁶.

At the inlet of SCR, gas phase dioxins were the dominant phase. As the major function of the SCR system was for dioxin reduction, the operating temperature of 200 °C is needed. Removal efficiencies of dioxins by SCR system depended on catalyst, operation temperatures, moisture, and inlet concentrations of particulate matter. The SCR system consisted of four layers. The catalyst is a honeycomb type of $\text{TiO}_2/\text{V}_2\text{O}_5/\text{WO}_3$. At the outlet of WS, the flue gas only has a temperature of 68°C and needs to be reheated to above 210°C. To avoid the high moisture content in flue gas entering the SCR, at the outlet of WS was installed of mist eliminator (demisters). Due to the very high collection efficiency of particulate matter (over 99%) achieved with ESP, the inlet concentration of particulate was only between 4 and 20 mg/Nm³. When the inlet temperature of SCR was above 210 °C and the concentration of particulate was less than 20 mg/Nm³, gas phase and solid phase dioxin concentrations in flue gas decreased after passing through the SCR with removal efficiencies of 98% and 73%, respectively. Gas phase dioxins were mostly decomposed by SCR and the removal efficiencies of all the gas phase congeners by SCR were between 98.0% and 99.1% (Figs. 5). However, solid phase dioxins show a lower removal efficiency and which decreased with increasing degree of chlorination (Figs. 6). It may be attributed to the fact that a higher -chlorinated congener is of a lower vapor pressure compared to lower -chlorinated congener and has a higher tendency to condense on particles. Therefore, higher-chlorinated congeners adsorbed on the surface of particles were not easily decomposed by SCR. The congener profiles of PCDD/Fs at the stack were shown in Figs.7. It was observed that higher -chlorinated congener (OCDD) was the major congener at the stack for total concentration, but the dominating toxic congener is 2,3,4,7,8-PeCDF on the TEQ basis. The total removal efficiencies of dioxins by APCDs (ESP/WS/SCR) were 97.5%. The probability to meet the regulatory levels will be increased if ESP operating temperature is controlled preferably between 180 °C and 200 °C, high volume of fresh water in scrubber circulated water for decreasing the memory effect of dioxin, SCR operation temperature of over 210 °C and the inlet concentration of particulate matter was reduced to less than 10 mg/Nm³.

Acknowledgements

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References

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EMV - General – Dioxins and Dioxin-Like Compounds

Table 1 PCDD/F concentrations in flue gas at different sampling points

Sampling point	Inlet Temp. (°C)	PCDD/Fs (ng/Nm ³)			PCDD/Fs (ng-TEQ/Nm ³)	
		Gas	Solid	Total	G/S**	Total
ESP inlet	230	294.3	63.6	357.9	4.6	7.034
ESP outlet	220	325.7	2.6	328.3	125	7.939
SCR inlet	212	414.1	7.8	421.9	53	10.287
stack	179	7.2	1.9	9.1	3.8	0.172

* G/S : the ratio of gas phase to solid phase

Table 2 Removal efficiency (RE) of PCDD/F by APCDs

Unit	RE(%) for total concentration			RE(%) for TEQ		
	Gas	Solid	Total	Gas	Solid	Total
ESP	-10.7	95.9	8.3	-24.8	92.8	-13.0
WS	-27.1	-200.0	-28.5	-28.7	-158.8	-29.6
SCR	98.3	75.6	97.8	98.6	75.0	98.3
APCDs†	97.6	97.0	97.5	97.8	95.3	97.6

† APCDs (%) = [(ESP inlet) - (Stack)] / (ESP inlet) × 100%

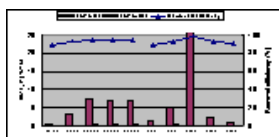


Fig. 1 Solid phase PCDD/F homologue gas and removal efficiency across ESP

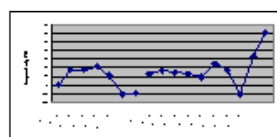


Fig. 2 Total increasing rate of 2,3,7,8-substituted PCDD/F by ESP

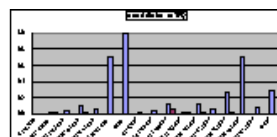


Fig. 3 The compare profiles of PCDD/F at the outlet of ESP

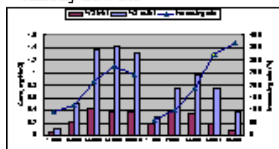


Fig. 4 Solid phase PCDD/F homologue gas and increasing rate across WS

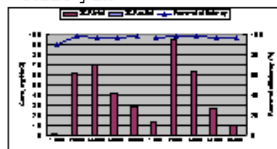


Fig. 5 Gas phase PCDD/F homologue gas and removal efficiency across SCR

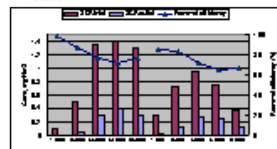


Fig. 6 Solid phase PCDD/F homologue gas and removal efficiency across SCR

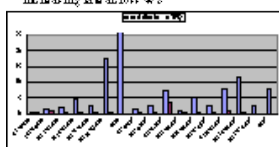


Fig. 7 The compare profiles of PCDD/F at the stack