PCDD/F EMISSION FROM A LOW-LEVEL RADIOACTIVE WASTE INCINERATOR TREATED WITH CATALYTIC FILTER SYSTEM

Wang HC [1] , Hwang JF [1] , Chen W [1] , Chang MB [2]

[1] Industrial Energy Conservation Technology Division, Energy and Environmental Research Laboratories, Industrial Technology Research Institute, Hsin-Chu 310, Taiwan; [2] Graduate Institute of Environmental Engineering, National Central University, Chungli 320, Taiwan.

Introduction

The incinerator investigated was designed to treat low-level radioactive wastes. Major compositions of waste include plastic, rubber, and paper (Table 1). The incineration system consists of a fix-bed type furnace with a capacity of 100 kg per hour and a cooling tower for reducing the temperature of the flue gas. Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/Fs) emissions at the stack measured were between 6 and 7 ng-TEQ/Nm^3 when the original air pollution control devices (APCDs) consisting of baghouse (Baghouse-1) with fiberglass fabric filter, high efficiency particulate air filter (HEPA) and wet scrubber (WS) were applied. To meet the stringent PCDD/F emission standards of small-scale incinerator (0.5 ng-TEQ/Nm^3), the incinerator retrofitted with catalytic filter in the baghouse-1. Additionally, injection of activated carbon and a new baghouse (Baghouse-2) with fiberglass fabric filter installed after the HEPA were applied (Fig. 1). This paper presents the results on PCDD/F reduction after improvement.

Materials and Methods

Catalytic filter system

REMEDIA D/F catalytic filter system (W. L. Gore & Associates, Inc.) is a novel approach that combines particulate removal with catalytic destruction of dioxins. Particulates can be captured on the membrane and the gas-phase dioxins passing through the membrane will be destroyed to form CO_2, H_2O, and HCl within the felt[1,2]. The incinerator investigated applies catalytic filters in the existing baghouse (Baghouse-1) as a retrofit technology for reducing dioxin emission.

PCDD/F sampling

The sampling campaign was performed during normal operating period. Table 2 summarizes the operating conditions of the incinerator in samplings. The flue gas sampling was conducted with Graseby Anderson Stack Sampling System complying with the USEPA Method 23. The gas-phase sample was collected by XAD-2 resin whereas the particle-bound portion was collected by the fiber glass filter and by rinsing of the sampling probe thereafter. The samples collected were analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners with a 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

Fig. 2 shows the PCDD/F concentrations measured at the stack during different stages. Before dioxin improvement engineering was adopted, existing APCDs including baghouse and HEPA had a high collection efficiency of particulate matter (over 99%), the PCDD/Fs adsorbed on the particulate matter could be removed simultaneously and the solid-phase dioxins should have been mostly removed. However, the concentrations of PCDD/Fs at the stack were still high (between 6 and 7 ng-TEQ/Nm^3). This was attributed to the fact that the concentration of gaseous PCDD/Fs in the flue gas was high. For the decomposition of gaseous PCDD/Fs, catalytic filter was applied in the existing baghouse. Unfortunately, the level of PCDD/Fs measured at the stack was 2.77 ng-TEQ/Nm^3, which was still higher than the PCDD/Fs emission standard for small -scale incinerators in Taiwan. The removal efficiency of PCDD/Fs was only 58.4%. It might be attributed to some reasons. As the existing baghouse was old, the operating temperature was controlled between 165 to 180℃, which was lower than that of the typical catalytic filter system (180℃ to 250℃). It was not high enough to decompose dioxins within the felt. The second one is the original filter may be broken and the dioxins in the flue gas may just

penetrate through the filter. Additionally, memory effect in the WS might be another reason for the high PCDD/F emission.

In order to examine the real causes, flue gases were sampled and analyzed at different points including HEPA outlet, WS outlet and the stack. Due to the limitation of the space, flue gas sampling at baghouse-1 outlet could not be conducted. Fig. 3 shows the variation of PCDD/F concentrations at different sampling points in the incinerator investigated. When the operating temperature of the baghouse-1 was increased to ＞190℃, the PCDD/F concentrations were 0.10 ng-TEQ/Nm^3 at HEPA outlet, 1.64 ng-TEQ/Nm^3 at WS outlet, and 1.18 ng-TEQ/Nm^3 at stack, respectively. It indicates that PCDD/F concentration at the HEPA outlet was low. Fig 4 shows the characteristics of PCDD/F congener distribution at the outlet of HEPA. It indicated that PCDF/PCDD ratio was close to 1.0 and highly-chlorinated congeners (1,2,3,4,6,7,8-HpCDD/F and OCDD/F) were the dominated congeners based on the total concentration. It was attributed to the fact that lowly-chlorinated congeners may be destroyed easily by the catalytic filter system and highly-chlorinated congeners are of lower vapor pressure compared with lowly-chlorinated congeners and have a higher tendency to condense on fine particles. Therefore, highly-chlorinated congeners adsorbed on the surface of fine particles were not easily decomposed by catalyst. Although low PCDD/F concentration at the HEPA outlet was observed, PCDD/F concentrations in the flue gas increased again after passing through WS, resulting in negative dioxin removal efficiencies (-94%). Fig 5 shows the increase rate of congeners across the WS. It indicates that all congeners increased after passing WS, and the increase rates of lowly-chlorinated congeners were higher than that of highly-chlorinated ones. Besides, PCDD/F congener distribution profile at WS outlet was different from that of the outlet of HEPA (Fig 4). PCDF/PCDD ratio at WS outlet was 2.5. Lowly-chlorinated congeners increased but highly-chlorinated congeners decreased after passing through the WS. It could be attributed to the fact that the memory effect of the wet scrubber[4]. Dioxins were significantly generated during the start-up stage and transferred to the surface of wall or packing materials in WS, but parts of PCDD/Fs adsorbed on the surface of wall or packing materials desorb and transfer to flue gas again when the temperature or the dioxin concentration changed. The desorption rate increased with an increase in temperature from 65℃ to 90℃[5] and the desorption was especially obvious when the PCDD/F concentration in the flue gas was low. Lowly-chlorinated congeners with higher vapor pressure compared to highly-chlorinated congeners were easy to desorb. It indicates that WS might be another potential PCDD/F source. Memory effects in this study were minimized by renewing the packing materials and removing the fly ash which was deposited on the surface of wall. After these clean-up procedures, a significant decline in PCDD/Fs emission at the stack was observed and emission levels were around 0.1 ng-TEQ/Nm^3. The results indicate that it is not necessary to inject activated carbon. Fig 6 shows the PCDD/F congener profiles at the stack after dioxin improvement engineering. It was observed that PCDF was dominant (PCDF/PCDD=3.0) and 1,2,3,4,6,7,8-PCDD/F was the major congener at the stack for total concentration, while the dominating toxic congener is 2,3,4,7,8-PeCDF on the TEQ basis.

This study indicates that a significant decline in PCDD/Fs emission at the stack was observed and levels were controlled around 0.1 ng-TEQ/Nm^3 when the inlet temperature of the baghouse-1 is maintained ＞190℃, renewing the packing materials and removing the fly ash deposited on the surface of wall decrease the memory effect. However, the installation position of the catalytic system should be noticed. As the clean flue gas entered the old WS, the PCDD/F concentration may increase again possibly due to the memory effects taking place in WS.

Acknowledgements

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Table 1 The compositions of the wastes

Plastic & rubber	45~55 % wt.
PVC	≦1 % wt.
water	3~5 % wt.
paper, cloth, etc.	40~50% wt.

Table 2 Operating conditions in samplings

Parameter	Range
Temperature in primary chamber (℃)	856-900
Temperature in secondary chamber (℃)	1,040-1,080
Temperature at baghouse-1 inlet (with catalytic filter) (℃)	180-200
Temperature at baghouse-1 outlet (℃)	166-168
Temperature at HEPA outlet (℃)	165
Temperature at baghouse-2 outlet (℃) (with fiberglass fabric filter)	150
Temperature at WS inlet (℃)	130
Temperature at WS outlet (℃)	45-47
CO (ppm)	15-33
HCl (ppm)	0.1
Gas flow rate (Nm^3/min)	20-22

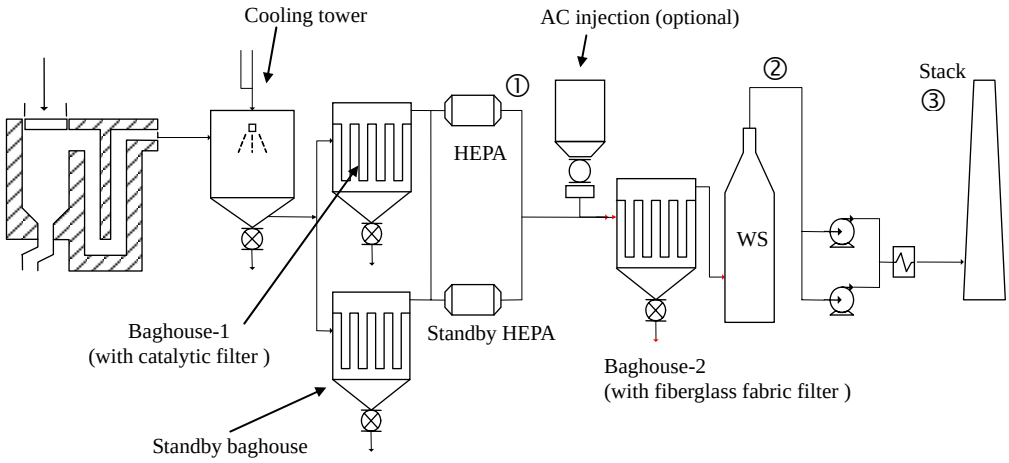

Fig. 1 Flow diagram and sampling points of the incinerator investigated.
① HEPA outlet, ② WS outlet, ③stack

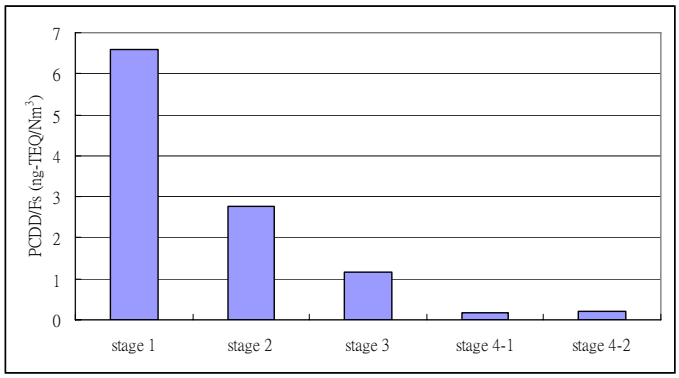

Fig. 2 PCDD/F concentrations at the stack measured at different operating modes.

Stage1: Baghouse-1 (with fiberglass fabric filter)+HEPA+WS (old)
Stage2: Baghouse-1 (with catalytic filter)+HEPA +WS (old)
Stage3: Baghouse-1 (with catalytic filter)+HEPA+AC (0.3 kg/hr) / Baghouse-2 (with fiberglass)+WS (old)
Stage4-1: Baghouse-1 (with catalytic filter)+HEPA+ Baghouse-2 (with fiberglass)+WS (new)
Stage4-2: Baghouse-1 (with catalytic filter)+HEPA+AC (0.3 kg/hr) / Baghouse-2 (with fiberglass)+WS (new)

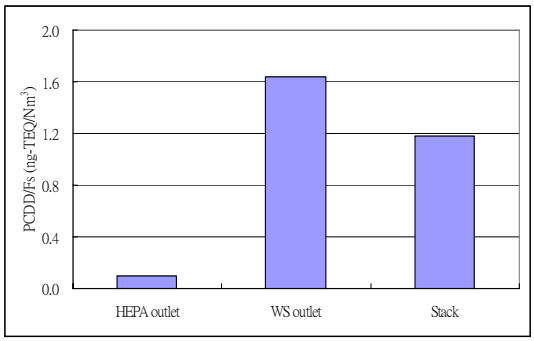

Fig. 3 PCDD/F concentrations at different sampling points.

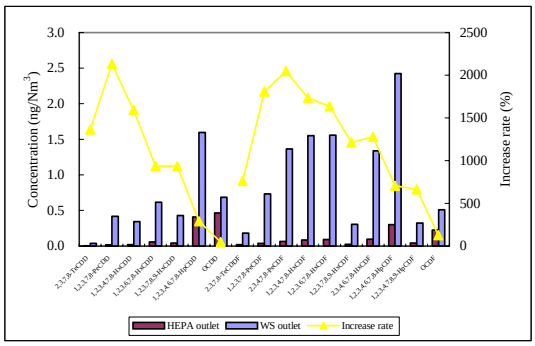

Fig. 4 Concentrations of PCDD/F congeners at WS outlet and the increase rate across the WS.

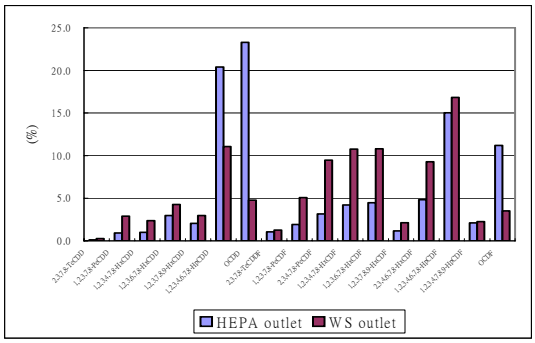

Fig. 5 PCDD/F congener distribution at HEPA outlet and WS outlet.

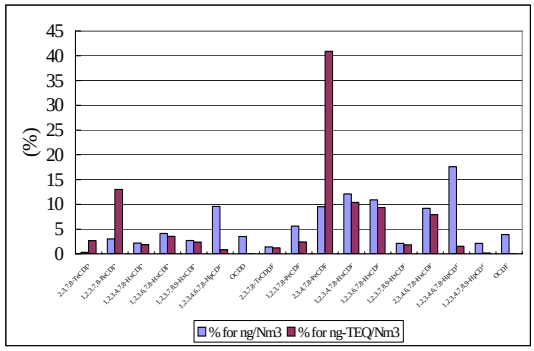

Fig. 6 The congener profiles of PCDD/F at the stack.