Characterization of PCDD/Fs and dl-PCBs emission from combustion of PCB-containing oil in a fluidized bed incinerator

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) have caused much public concern due to high toxicity and persistence in environment and are listed as persistent organic pollutants (POPs) by the Stockholm Convention. Although municipal waste incinerators (MWIs) are important source of PCDD/Fs and dl-PCB in ambient air, Dopico and Gomez [1] report that the emission factor of PCDD/Fs from hazardous waste incinerators (HWIs) is significantly higher than those from MWIs. Therefore, it is important to control the PCDD/Fs and dl-PCBs emission from HWIs. On the other hand, PCB-containing oil is commonly used in transformers, lubricants, capacitors as they have excellent electric insulation and chemical stability. Although the usage of PCB-containing oil has been banned in many countries since 1970s, PCBs still exist at a high concentration in the environment due to the leakage of PCBs-containing material. Therefore, proper treatment of the PCB-containing oil has become an important issue and high-temperature combustion is considered as an effective approach.

Methodology

In this study, a fluidized bed incinerator treating 135 liters of PCB-containing oils per hour in northern Taiwan is investigated. The air pollution control devices (APCDs) equipped include ultrasonic wet scrubber, activated carbon injection (ACI) and baghouse (BF). As flue gas passes through the first combustion chamber, calcium carbonate (CaCO₃) is injected to remove acid gases. Furthermore, calcium hydroxide (Ca(OH)₂) and powder activated carbon (PAC) are injected to remove acid gases and dioxin prior to the baghouse. The operating parameters of the HWI investigated are shown in Table 1.

As presented in Figure 1, flue gas samples are taken simultaneously at three locations, i.e., outlet of ultrasonic wet scrubber (location A), outlet of heat exchanger (location B) and stack (location C). In addition, solid matter samples are also collected from the furnace (bottom ash, BTA), ultrasonic wet scrubber (sludge, SLD), heat exchanger (heat exchanger ash, HEA) and baghouse (baghouse ash, BHA). Glass fiber filter is used to collect solid phase samples while XAD-2 spiked with known surrogate standard solution is applied to adsorb gas-phase sample. Thereafter, the XAD-2, fiber glass filters and solid matter samples are extracted for 24 h by Soxhlet extraction with toluene before being treated with series of clean-up columns. Finally, samples are analyzed for the seventeen 2,3,7,8-substituted PCDD/F congeners and twelve dl-PCB congeners with HRGC/MS using a fused silica capillary column DB-5 MS.



Figure 1. Flow diagram and sampling points of the HWI investigated

Results and discussion

The PM concentrations measured are 151, 94.9 and 2.50 mg/Nm³ at outlet of ultrasonic wet scrubber, the outlet of heat exchanger and stack, respectively. For solid samples, PCDD/Fs concentration measured are 2.76, 9.02, 10.1, and 18.6 ng/g while dl-PCBs concentration measured are 1.25, 4.35, 2.74, and 4.89 ng/g in BTA, SLD, HEA and BHA samples, respectively (Table 2). In addition, PCDD/Fs concentrations in flue gas stream measured are

16.3, 19.6 and 8.07 ng/Nm³ while dl-PCBs concentrations measured are 7.75, 10.1 and 3.81 ng/Nm³ at outlet of ultrasonic wet scrubber, the outlet of heat exchanger and stack, respectively. PCDD/Fs and dl-PCBs measured at the baghouse inlet are the highest due to significant de novo synthesis which occurs during heat exchanging process at 215-240°C.

Table 1. Operating parameters of the hazardous waste

incinerator		
Waste incinerated	Operating parameter	
Capacity	135 L/h	
Vortex fluidized bed combustion temperature (°C)	500~600	
Temperature of primary combustion chamber (°C)	774~906	
Temperature of secondary combustion chamber (°C)	910~954	
Temperature of ultrasonic wet scrubber (°C)	215~229	
Temperature of baghouse (°C)	129~148	
CaCO ₃ injection rate (kg/h)	3.5	
AC injection rate (kg/h)	0.2	
Ca(OH) ₂ injection rate (kg/h)	4	

Table 2. Concentration of PCDD/Fs and dl-PCBs in

flue gas and solid samples

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Concentration	PCDD/Fs	dl-PCBs
Point A (ng/ Nm ³)	16.3	7.75
Point B(ng/ Nm ³)	19.6	10.1
Point C(ng/ Nm ³)	8.07	3.81
BTA (ng/g)	3.83	1.98
SLD (ng/g)	13.3	6.67
HEA (ng/g)	7.18	7.60
BHA (ng/g)	9.63	12.9

Distributions of solid-phase PCDD/Fs and dl-PCBs congeners decrease from ultrasonic wet scrubber outlet to stack due to significantly decrease of PM concentration in the flue gas (Figure 2). The dominant PCDD/Fs congeners in flue gas are 1,2,3,4,6,7,8-HpCDD and OCDD while TeCB-77, PeCB-126 and PeCB-105 predominate dl-PCBs congeners profile. The distribution of PCDD/Fs and dl-PCBs congeners in flue gas are similar to those in solid samples with the dominance of highly chlorinated congeners for PCDD/Fs profile and low chlorinated congeners for dl-PCBs profile. Thus, it confirms that de novo synthesis of dl-PCBs during combustion process is more likely to form low chlorinated congener while the evaporation from PCBs-containing oil are more likely to form highly chlorinated dl-PCBs. The total emission factor of PCDD/Fs and dl-PCBs from incinerating PCB-containing oil is calculated as 1.05 ng WHO-TEQ/L.

Although the removal efficiencies (PCDD/Fs + dl-PCBs) in gas stream achieved with BF + ACI is 65.0 %, the total removal efficiencies of PCDD/Fs and dl-PCBs during incineration of PCB-containing oil in the fluidized bed incinerator are 99.93% and 99.9999% for PCDD/Fs and dl-PCBs, respectively (Figure 3).



Figure 2. Gas/particle partitioning of PCDD/Fs and dl-PCBs in gas stream.



Figure 3. Flow diagram, sampling points (A, B and C) and flows of PCBs and PCDD/Fs in the HWI investigated with PCBs-containing oil as feeding material.

Reference:

[1] Dopico, M. and Gomez, A. (2015). "Review of the current state and main sources of dioxins around the world." J Air Waste Manage 65(9): 1033-1049