EVALUATION OF PCDD/F CONGENER DISTRIBUTION IN AMBIENT AIR IN THE VICINITY AREA OF A WAELZ PLANT

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Introduction

The Waelz process is widely used for recovering zinc from electric arc furnace (EAF) dusts containing relatively high concentrations of PCDD/Fs (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) as well as heavy metals, such as Zn, Pb, and Cu, and chlorine. Previous study[1] indicates the PCDD/F concentration measured in stack gas of the Waelz plant reaches 145 ng-TEQ/Nm^3 in Taiwan due to its lower PCDD/F removal efficiency (<70%) achieved with bag filter (BF). Since the Waelz plant becomes the most important anthropogenic source of PCDD/Fs in Taiwan[2], PCDD/Fs emitted from existing Waelz plant has caused much public concerns. In October 2005, Taiwan government set 9.0 ng-TEQ/Nm^3 as the PCDD/F emission limits for existing Waelz plants and then 1.0 ng-TEQ/Nm^3 will be in effect starting from September 2006. Taiwan government also promulgated the dioxin emission limit for newly built Waelz plants (0.4 ng-TEQ/Nm^3) starting from October 2005. The retrofit technology for reducing PCDD/F emissions from existing Waelz plant had been evaluated at the same time. The activated carbon injection (ACI) technology typically has two advantages: (1) it can be added to almost all kinds of air pollution control devices (APCDs) and (2) it is cheaper and simpler to install than other retrofit technologies[3]. For better controlling the PCDD/F emissions from the Waelz plant investigated, the ACI technology has been applied in this Waelz plant for reducing PCDD/F emissions to meet the standard in 2006. In this study we monitored the concentrations of vapor/solid-phase PCDD/F compounds in the vicinity area of a Waelz plant using PS-1 samplers at four sampling sites. The objective of this study was to evaluate the variation of ambient PCDD/F concentration during the shutdown and operation stages of Waelz plant.

Materials and Methods

Sampling sites

The Waelz plant investigated in this study started to operate in 1999. It is a rotary type kiln and has a capacity of 12 tons EAF dusts per hour. Over 70,000 tons EAF dusts can be processed and over 12,000 tons zinc can be recovered annually by this Waelz plant. To reduce the emission of particulate matter, the Waelz plant investigated is equipped with a dust settling chamber (DSC), a venturi cooling tower, a cyclone (CY) and BF. Since January 2006, the ACI technology was applied in the Waelz plant investigated for reducing PCDD/F emission to meet the stringent standards. The flue gas PCDD/F samples were collected at stack to obtain the partitioning and concentration of vapor/ solid-phase PCDD/Fs. For ambient PCDD/F concentration measurement, four sampling sites (A, B, C, and D) were set up based on the meteorological records and relative locations to the Waelz plant investigated. Due to the topographical features, north wind predominates in this area all year around except for summer season. All air samples were taken from August 2005 through March 2006 at four sampling sites. Description and location of those four sampling sites are given at Table1 and Fig. 1.

Sample collection and analysis

The flue gas sampling was conducted with the Graseby Anderson Stack Sampling System complying with the USEPA Method 23A. The vapor-phase sample was collected by XAD-2, while the particle-bound portion was collected by the fiber glass filter and by rinsing of the sampling probe thereafter. The ambient air samples were collected with PS-1 air samplers (Tisch PS-1) complying with USEPA TO-9A. The PS-1 samplers are equipped with Whatman fiber glass filters for collecting particle-bound PCDD/Fs and polyurethane (PU) foam plugs retaining PCDD/F compounds in the gaseous phase. The total volume of the air sampled was more than 1,500 m^3 for a typical sampling duration of 4-5 days. Once the sampling was completed, the samples were brought back to the laboratory under refrigeration. They were then spiked with known amounts of USEPA Method 23 internal standard solution. Thereafter, the PU foam and filter sample were Soxhlet extracted with toluene for twenty four hours. The toluene extract was then concentrated to about 1ml by rotary evaporation

and was replaced by 5ml hexane for pretreatment process. Having been treated with conc. sulfuric acid, the sample was then subjected to a series of clean-up columns including sulfuric acid silica gel column, acidic aluminum oxide column and Celite/Carbon column. Finally, the cleaned up solution was spiked with known amounts of M23 recovery standard solution, and then analyzed with high resolution gas chromatography (HRGC) (Hewlett Packard 6890 plus)/high resolution mass spectrometer (HRMS) (JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS (60m x 0.25 mm x 0.25μm, J&W).

Results and Discussion

Fig. 2 shows the PCDD/F concentrations measured in stack gas with and without AC injection, respectively. Without AC injection, the PCDD/F concentration measured in the stack gas was 139 ng-TEQ/Nm^3. The results also indicate that over 75% PCDD/Fs are existed in vapor phase in the stack gas achieved with BF. That is attributed to the fact that only particulate matter and solid-phase PCDD/Fs can be effectively removed by BF but vapor-phase PCDD/Fs can not. In December 2006, the ACI system has been applied in this Waelz plant, the PCDD/F concentration measured in stack gas decrease to 4.86 ng-TEQ/Nm^3 with ACI at a rate of 300 mg/Nm^3. The results also indicate that the ACI technology can effectively remove 96.5% vapor-phase PCDD/Fs in the flue gas. Table 2 indicates that the PCDD/F TEQ concentrations in ambient air sampled in the vicinity areas during different operating stages of the Waelz plant investigated. When, the Waelz plant was shutdown for retrofit, the ambient PCDD/F concentrations measured at four sampling sites were considerably lower than the concentrations measured in Korea and Japan[4] and the ambient air quality standard proposed in Japan (600 fg-I-TEQ/m^3). When the Waelz plant investigated was in operation without the ACI technology, the ambient PCDD/F concentration measured at site C (directly downwind of the Waelz plant) was 4 to 20 times higher as that measured during the shutdown-stage of the Waelz plant and close to the air quality standard proposed in Japan. In the meantime, significant increase of ambient PCDD/F concentrations was not observed at sites A (upwind of the Waelz plant) and B (slightly downwind of the Waelz plant). After the ACI system has been applied in this Waelz plant, significant decrease of the ambient PCDD/F concentration measured at site C is observed. However, the ambient PCDD/F concentrations measured at site D (179~1,465 fg-TEQ/m^3) are significantly higher than other sampling sites during all operating stages of the Waelz plant. We speculate that is affected by the re-suspension of the slag and fly ash containing PCDD/Fs from the storage area of the Waelz plant investigated (Fig. 1).

Fig. 3 shows the PCDD/F congener distributions measured in ambient air during different operating stages of the Waelz plant investigated. When the Waelz plant was shutdown, the PCDD/F congener distributions observed at four sampling sites are quite close. In addition, PCDFs account for 80% of the total TEQ concentrations, 2,3,4,7,8-PeCDF at all sampling sites accounted for more than 45%. It is caused by the fact that the TEF value of 2,3,4,7,8-PeCDF (TEF=0.5) is significantly higher than other congeners. During the operating without ACI stage, the distribution of PCDD/F congener observed in ambient air at sites A and B did not change significantly, but that observed at site C did. The distribution of PCDD congeners observed at site C increases from 17% to 25%, especially of 1,2,3,7,8-PeCDD. Previous study[1,5] indicates that distribution of 1,2,3,7,8-PeCDD (based on TEQ) measured in the stack gases of municipal waste incinerator and EAF is generally about 5~10%, but that observed in the stack gases of the Waelz plant is greater than 20%. Hence, that congener can serve as the indicator for the ambient air affected by Waelz plant. Fig 4 shows the variation of vapor/solid-phase PCDD/F concentrations measured at four sampling sites during different operating stages of the Waelz plant investigated. At sampling sites A, B and C, over 50% PCDD/Fs existed in vapor phase in the ambient air as the Waelz plant was shutdown. When the Waelz plant started to operate, the ambient PCDD/Fs become to distribute in solid phase at those three sampling sites. The significant decrease of solid-phase PCDD/Fs measured at sampling site C is observed as the ACI system has been applied, but the variation of vapor-phase PCDD/Fs is not obvious. Furthermore, the ambient PCDD/Fs measured at site D are distributed in solid phase during all operating stages of the Waelz plant. That result confirms the re-suspension of slag and fly ash from the storage area.

Acknowledgements

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References

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Table 1 Description of ambient air sampling sites in the vicinity area of Waelz plant investigated..

Sampling site	Description
A	A primary school about 5 km from the Waelz plant (upwind of the Waelz plant).
B	A junior high school about 3.5 km from the Waelz plant (slightly downwind of the Waelz plant).
C	A duck farm about 2.5 km from the Waelz plant (directly downwind of the Waelz plant).
D	Roof of the office building in the Waelz plant (about 300 m from the stack).

Table 2 PCDD/F TEQ concentrations measured in ambient air at four sampling sites during different operating stages of the Waelz plant investigated.

PCDD/F concentration (fg-TEQ/m^3)	**Shutdown**		**Operating without ACI**	**Operating with ACI**	
	August 2005	November 2005	December 2005	January 2006	March 2006
Site A	***174***	***76***	***72***	***279***	***148***
Site B	***137***	***32***	***94***	***299***	***192***
Site C	***140***	***24***	***568***	***337***	***206***
Site D	***179***	***262***	***1,465***	***641***	***379***

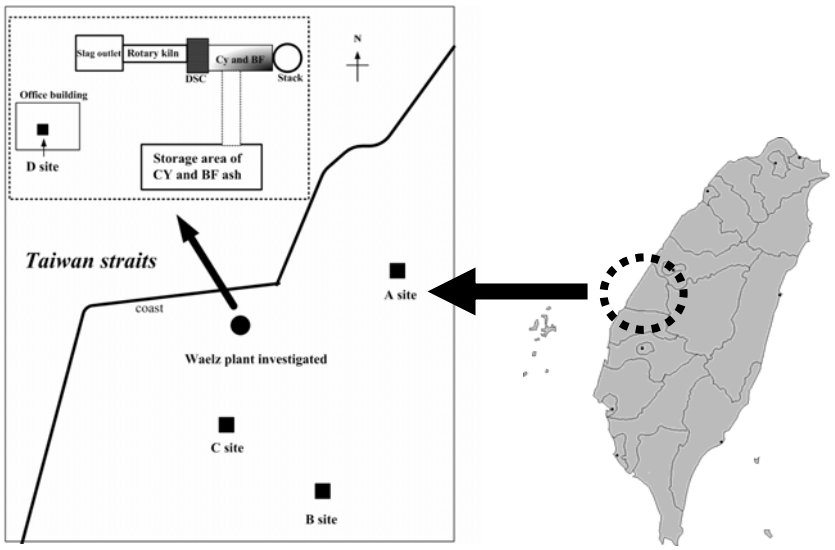

Fig. 1 Location of sampling sites in the vicinity area of the Waelz plant investigated.

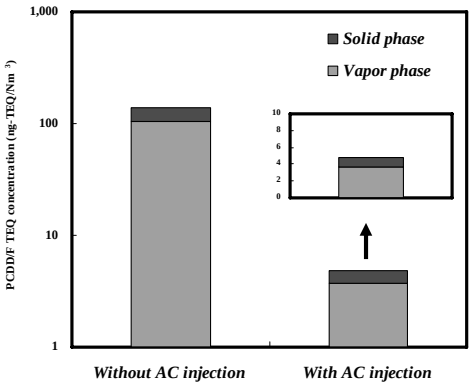

Fig. 2 PCDD/F emissions with/without AC injection in the Waelz plant investigated.

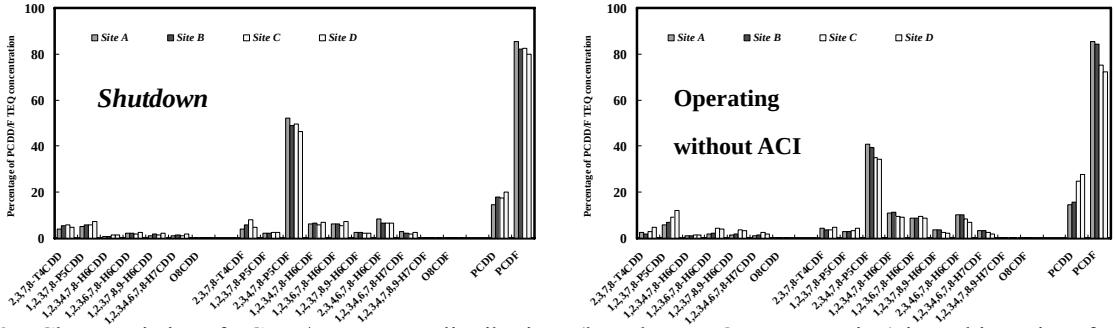

Fig. 3 Characteristics of PCDD/F congener distributions (based on TEQ concentration) in ambient air at four sampling sites during different operating stages of the Waelz plant investigated.

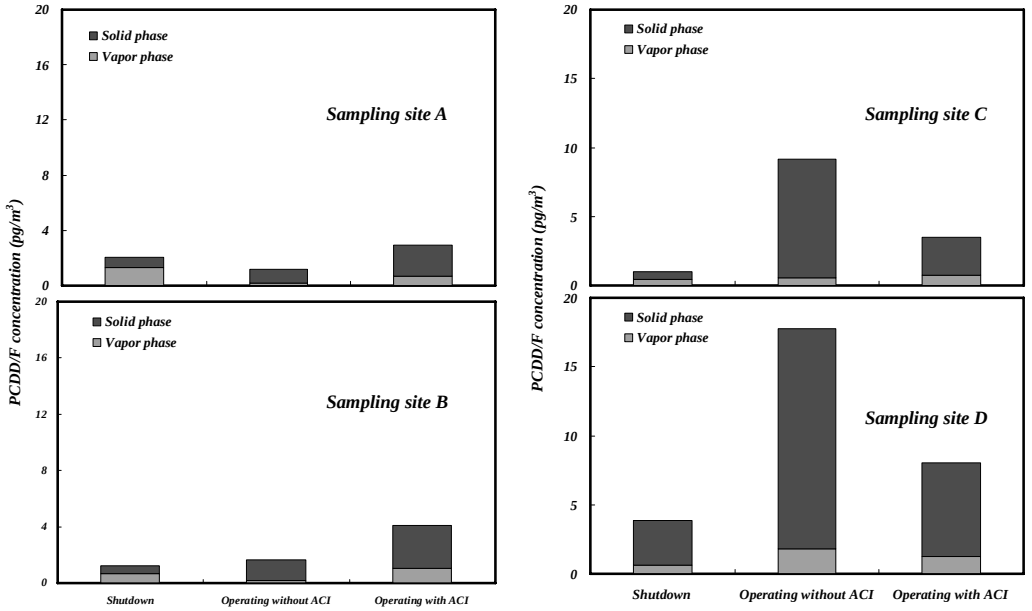

Fig. 4 Variation of PCDD/F concentrations in vapor/solid phases at four sampling sites during different operating stages of the Waelz plant investigated.