# REDUCTION OF DIOXIN EMISSIONS FROM WAELZ PROCESS WITH ACTIVATED CARBON INJECTION AND DUAL BAG FILTER SYSTEM

Chang MB[1] Chi KH[2], Chang SH[1] Hong BZ [1]
[1] Graduate Institute of Environmental Engineering, National Central University, Chungli 320, Taiwan; [2] Research Center for Environmental Changes, Academia Sinica, Taipei 115, Taiwan

**Abstract**
In 2005, PCDD/F concentration measured in stack gas of the Waelz plant investigated reached 148 ng-TEQ/Nm$^3$ due to its relatively low PCDD/F removal efficiency (<70%) achieved with bag filter (BF). Besides, the acidic substances such as $SiO_2$ added into the Waelz plant cannot reduce PCDD/F formation. 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$^3$ was in effect starting from September 2006. The retrofit technology for reducing PCDD/F emissions from existing Waelz plant had been evaluated at the same time. Activated carbon injection (ACI) technology is adopted in the Waelz plant investigated in early 2006 to reduce PCDD/F emission. Flue gases samplings were conducted at different sampling points to evaluate the removal efficiency and the partitioning of PCDD/Fs between vapor/solid phases in this facility. By applying ACI, the PCDD/F concentrations of stack gas decreased to 3.38 ng-TEQ/Nm$^3$ at single bag filter (SBF) outlet as the activated carbon injection rate was controlled at 40 kg/h. The ACI + dual bag filter (DBF) system is adopted in this facility for the second stage of improvement. The PCDD/F concentration measured at stack gas was further reduced to 0.203 ng-TEQ/Nm$^3$.

## Introduction

Relevant study[1] indicates that about half of the total PCDD/F mass flow in electric arc furnace (EAF) is discharged via EAF dusts. The Waelz process has long been applied for treating EAF dusts to recover zinc and decontaminate the EAF dust, which is considered as a hazardous waste. Previous study[2] indicates the PCDD/F concentration measured in stack gas of the Waelz plant investigated reached 145 ng-I-TEQ/Nm$^3$ due to the relatively low PCDD/F removal efficiency (<70%) achieved with the BF. In October 2005, the Taiwan government set 9.0 ng-I-TEQ/Nm$^3$ as the PCDD/F emission limits for existing Waelz plants and more stringent emission standard of 1.0 ng-I-TEQ/Nm$^3$ has been effective starting from September 2006. Taiwan government also promulgated a dioxin emission limit for newly built Waelz plants (0.4 ng-I-TEQ/Nm$^3$), starting from October 2005. Activated carbon (AC) has long been used for the removal of vapor-phase organics from industrial flue gas streams. Adsorption of organic compounds on activated carbon is functions of various parameters, including the properties of the adsorbent used and the properties of the pollutants to be removed, the concentrations of other adsorbable gases, operating temperature, and residence time[3]. As a result of the thermal treatment of residues[4], PCDD/Fs are generated during the thermal process, requiring the installation of additional air pollution control devices (APCDs) to reduce PCDD/F emissions; this necessity has created a serious challenge for secondary metallurgical smelting facilities. PCDD/F emission sources use different equipments and procedures, leading to different levels of PCDD/F control. Among the methods being used, applying powdered activated carbon injection (ACI) to adsorb PCDD/Fs in flue gas is considered as the simplest one to meet the stringent PCDD/F emission standards. ACI technology has been applied in this Waelz plant for reducing PCDD/F emissions to meet the standard. In this study the concentrations of both vapor/solid-phase PCDD/F compounds in the flue gases of the Waelz plant investigated were monitored during different operation stages.

## Materials and Methods

The Waelz plant investigated is a rotary kiln plant, operating in countercurrent of feed materials and hot gases from an auxiliary burner, with the capacity of treating 12 tons of EAF dusts per hour. Typical feed composition is sand ($SiO_2$), coke and EAF dust. Over 20,000 tons zinc can be recovered annually by this Waelz plant. To reduce the emissions of particulate matter, the hot off-gas from the kiln is treated with a dust settling chamber (DSC), a venturi cooling tower, a cyclone (CY) and bag filter (BF). Since January 2006, the ACI technology was applied in the Waelz plant for reducing PCDD/F emission to meet the standard of 1.0 ng-I-TEQ/Nm$^3$. In this study, vapor and solid-phase PCDD/Fs in the flue gases were separately yet simultaneously collected at different sampling points including: the DSC outlet, the venturi cooling tower outlet, the CY outlet and the stack in the Waelz plant. Samplings were conducted during the stages of the plant operating with ACI+single bag filter (SBF) and ACI+dual bag filter (DBF) system, respectively, to investigate the effectiveness of the ACI adopted.

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 with XAD-2 while the particle-bound portion was collected by the fiber glass filter and by rinsing of the sampling probe thereafter. To avoid the error and bias caused by sampling of PCDD/Fs bound to the particulate matter, isokinetic sampling has to be conducted in order to collect a representative sample. Once the flue gas samplings were completed, the samples were brought back to the laboratory under refrigeration. Finally, the samples were analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners 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**

The flue gases were sampled simultaneously, before and after APCDs, for evaluating their collection efficiency and effectiveness to reduce PCDD/F emissions from the Waelz plant. Table 1 indicates that the PCDD/F concentrations were 394 ng-I-TEQ/Nm$^3$ at the DSC outlet, 201 ng-I-TEQ/Nm$^3$ at the venturi outlet and 140 ng-I-TEQ/Nm$^3$ at the CY outlet. It is interesting to note the PCDD/F concentration measured at DSC outlet in this study is significantly lower than that measured (1,220 ng-TEQ/Nm$^3$) in 2005[2]. Additionally, PCDD/PCDF ratio in flue gases at DSC outlet increases from 0.43 (measured in 2005) [2] to 0.48 (measured in this study). Previous study[5] indicates that de novo synthesis mostly generates PCDFs. Hence, operating DSC at an appropriate temperature (580$^o$C) effectively reduces the PCDD/F formation via de novo synthesis. With the ACI+ single bag filter (SBF) system, the PCDD/F concentration measured in stack gas was freatly reduced to 3.38 ng-I-TEQ/Nm$^3$ with activated carbon being injected at a rate of 40 kg/h (around 540 mg-AC/Nm$^3$). The results indicate that the ACI system retrofitted in the Waelz plant investigated can effectively reduce PCDD/F emission. As the ACI+DBF system is applied in the Waelz plant investigated, the PCDD/F concentrations measured in stack gas were dramatically reduced to 0.203 ng-I-TEQ/Nm$^3$ with activated carbon being injected at a rate of 16 kg/h (around 215 mg-AC/Nm$^3$). The significant decrease of PCDD/F emission from stack gas is attributed to the fact that the DBF can effectively remove solid-phase PCDD/Fs in the flue gas. In addition, the vapor-phase PCDD/Fs in flue gases are adsorbed by activated carbon in primary BF and secondary BF. Therefore, the PCDD/F concentration measured in stack gas is significantly lower than the PCDD/F emission limit (1.0 ng-I-TEQ/Nm$^3$) promulgated for Waelz plant in Taiwan.

Figure 1 shows the vapor/solid-phase PCDD/F concentrations in flue gases measured at DSC outlet, venturi outlet, CY outlet and stack (ACI+SBF and ACI+DBF outlet) of the Waelz plant. The venturi cooler is used to reduce the flue gas temperature by introducing large quantity of ambient air. The decrease of vapor-phase PCDD/F concentration across venturi cooler is more likely due to the transferring of vapor-phase PCDD/Fs to the solid phase along with the significant decrease of flue gas temperature (573$^o$C→184$^o$C). As the flue gas passes through CY, particulate matter concentration is effectively reduced, and a similar trend is observed for the solid-phase PCDD/F concentration (solid-phase PCDD/F removal efficiency: 32.6%). As the flue gas passes through the CY, vapor-phase PCDD/F concentrations do not change significantly. That is attributed to the fact that no significant vapor-phase pollutant removal mechanism takes place at CY. After the flue gases have been treated with ACI+SBF and ACI+DBF, respectively, significant decreases of vapor and solid-phase PCDD/F concentrations in stack gases are observed. In general, the removal mechanism of solid-phase PCDD/Fs relies on filtration of the bag filter. As expected, the solid-phase PCDD/Fs (99.7%) removal efficiency achieved with DBF is higher than that achieved with SBF (97.3%). In the meantime, over 99% vapor-phase PCDD/Fs are removed by ACI+DBF, and only 94% vapor-phase PCDD/Fs are removed by ACI+SBF. Based on the operating data and the sampling results of flue gas and fly ash, the PCDD/F flows and emission factor of EAF dust recycling processes can be calculated. PCDD/F flow within the Waelz plant with SBF and DBF is designated as mass flow and can be calculated. Figure 2 shows the PCDD/F mass flows on the basis of treating one ton of EAF-dust for the Waelz plant with with SBF and DBF, respectively. After DBF system has been adopted in this Waelz plant, PCDD/Fs discharged via reacted ash and stack gas are dramatically reduced to 1,787 and 1.5 ng-I-TEQ/kg EAF-dust, respectively. The significant PCDD/F reduced is due to the lower AC injection rate (40 kg/h to 16kg/h) and higher PCDD/F removal efficiency. In this study, the ACI+DBF system was adopted in the Waelz plant investigated. Solid-phase PCDD/Fs and fly ash can be removed by the bag filter. Injected activated carbon also transfers the vapor-phase PCDD/Fs into the solid phase by adsorption. Based on the flue gas sampling results, PCDD/F emission via stack gas is dramatically reduced from 3.38 to 0.203 ng-I-TEQ/Nm$^3$. The PCDD/F removal efficiency achieved with ACI+DBF system (99%) is significantly higher than that achieved with ACI + SBF system (95%). However, the activated carbon injection rate in ACI+DBF system (16 kg/hr) is significantly lower than that in ACI+SBF system (40 kg/hr). The ACI+DBF system has been proven effective for the PCDD/F removal in the Waelz plant investigated.

**Acknowledgements**
The authors gratefully acknowledge the financial supports provided by National Science Council (NSC95-2221-E-008-051-MY3) of the Republic of China. Assistance provided by Prof. W. H. Ding of National Central University in analyzing the samples is also acknowledged.

**References**
1. Chang M B, Huang, HC, Tsai S S, Chi K H, Chang-Chien G P. *Chemosphere* **2006**; 62, 1761.
2. Chi K H, Chang S H, Chang M B. *Environmental Science & Technology* **2006;** 40, 1770.
3. Karadenir A, Bakoglu M, Taspinar F, Ayberk S. *Environmental Science & Technology* **2004;** 38, 1201.
4. Mager K, Meurer U, Wirling J. *The Minerals, Metals & Materials Society's Monthly Membership Journal* **2003**; 20.
5. Everaert K, Baeyens J. *Chemosphere* **2002**; 46, 439.

Table 1 PCDD/F concentrations and relevant parameters of the flue gases at different sampling points in the Waelz plant investigated.

| *Sampling location* | *DSC outlet (n=2)* | *Venturi outlet (n=2)* | *Cyclone outlet (n=2)* | *Stack* | |
|---|---|---|---|---|---|
| | | | | **With ACI+SBF** *(n=2)* | **With ACI +DBF** *(n=4)* |
| *$O_2$ (%)* | **8.3** | **17.5** | **18.3** | **18.1** | **18.2** |
| *$H_2O_{(g)}$ (%)* | **4.9** | **5.1** | **4.7** | **4.3** | **4.4** |
| *Temperature ($^0$C)* | **573** | **185** | **157** | **134** | **136** |
| *PM concentration (mg/Nm$^3$)* | **2,160** | **2,080** | **843** | **4.8** | **4.4** |
| *PCDD/F concentration (ng-I-TEQ/Nm$^3$)* | **394** | **201** | **140** | **3.38** | **0.203** |

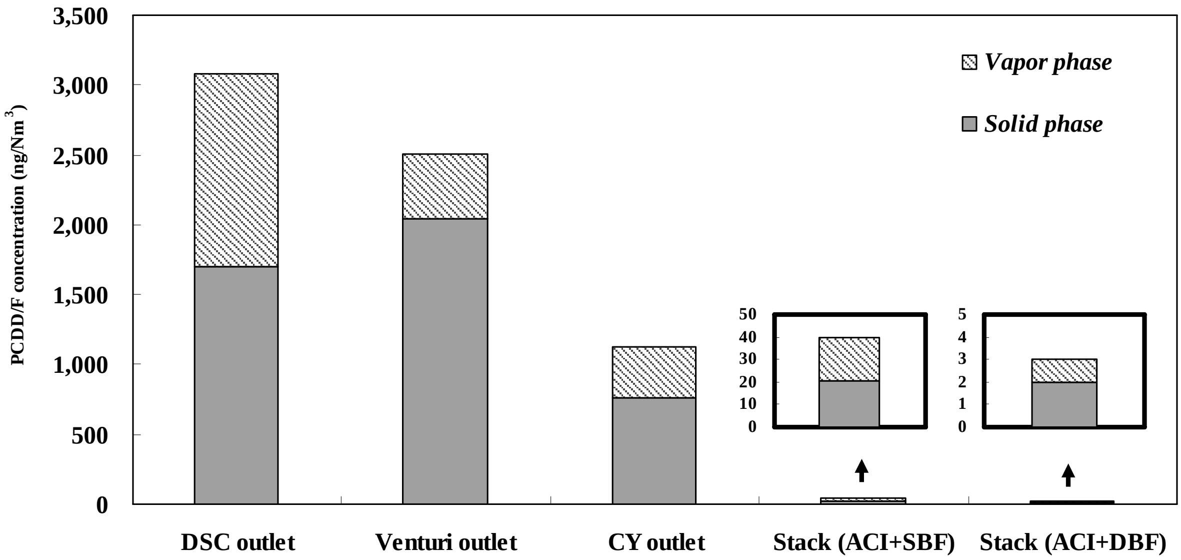


Figure 1 Variation of vapor/solid-phase PCDD/F concentrations in flue gases at different sampling points in the Waelz plant investigated.

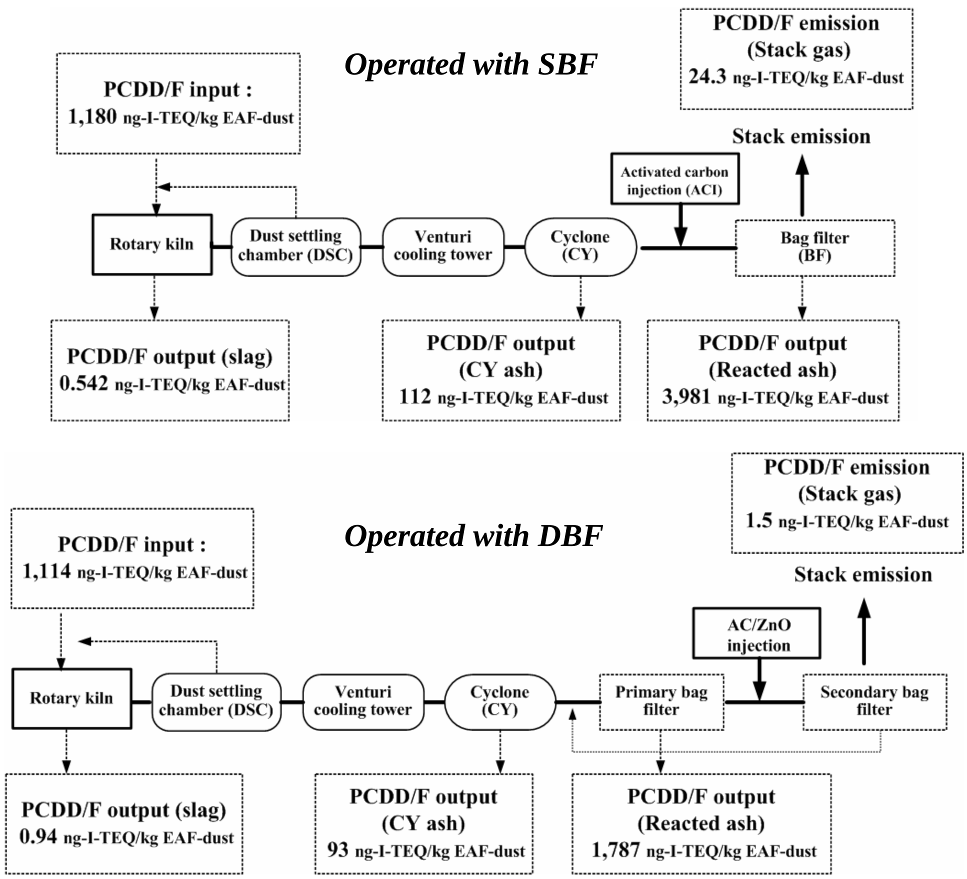


Figure 2 PCDD/F TEQ flows in the Waelz plant investigated with SBF and DBF, respectively.