REDUCTION OF DIOXIN EMISSIONS FROM WAELZ PROCESS OPERATED IN ACIDIC OR BASIC MODE

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

Abstract
Polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) concentration measured in stack gas of the Waelz plant investigated was as high as 150 ng-TEQ/Nm^3 in 2005 due to its relatively high dioxin formation potential and low PCDD/F removal efficiency (<70%) achieved with the bag filter (BF). In 2006, activated carbon injection (ACI) technology was adopted in the Waelz plant investigated 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 + BF, the PCDD/F concentrations of stack gas was dramatically decreased to 3.38 ng-TEQ/Nm^3 as the activated carbon injection rate was controlled at 40 kg/h. With adsorbent injection + dual baghouse filter (DBF) system being adopted in 2007, the PCDD/F concentration in stack gas was significantly reduced to 0.235 ng-I-TEQ/Nm^3 with the adsorbent injection rate at 16 kg/h**.** In practice, the carbon-type adsorbent is mixed with part of the fly ash collected by cyclone and then injected into the flue gas. In 2008, $Ca(OH)_2$ was applied to replace SiO_2 as part of the input material of this facility and its operation was converted from acidic mode to basic mode. In the meantime, the PCDD/F concentration measured at stack gas was further reduced to 0.123 ng-TEQ/Nm^3. With this operation mode, the total PCDD/F emission flow on the basis of treating one kg of EAF dust in this facility was dramatically decreased from 1,925 to 269 ng-I-TEQ/kg EAF-dust treated.

Introduction

Relevant study[1] indicated that about half of the total PCDD/F mass flow in electric arc furnace (EAF) was discharged via EAF dusts. Over 150,000 tons of EAF dusts containing relatively high concentrations of heavy metals and PCDD/Fs are generated each year in Taiwan. The Waelz process has long been applied for treating and decontaminating zinc-containing EAF dusts which are regarded as hazardous wastes. Depending upon the characteristics of the input materials of the Waelz process , the slag may be acidic or basic[2]. SiO_2 is added with the input material in the acidic process while lime, limestone or burnt lime is added in the basic process. As a result of the thermal treatment of the residues [3], PCDD/Fs are formed and liberated in the flue gas, requiring the installation of additional air pollution control device (APCD) to reduce PCDD/F emissions and this has posed a serious challenge for secondary metallurgical smelting facilities. Previous study[4] indicates the PCDD/F concentration measured in stack gas of the Waelz plant investigated reached 148 ng-I-TEQ/Nm^3 due to the significant PCDD/F formation of the process and 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. Researchers attempted to correlate the formation and concentration of PCDD/F with operating parameters of the Waelz kiln plant such as the acidic/basic mode of operation. Previous study[2] indicated that the PCDD/F contents of 140-1000 ng-I-TEQ/kg in the BF ash in acidic mode are distinctly higher than the values determined in the basic mode (0.5-38 ng-I-TEQ/kg). The highest chlorine concentrations in BF ash were found in the case of the acidic operating mode. For this reason, the changeover to the basic operating mode is of particular significance for the suppression of PCDD/F formation. 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 processes (acidic and basic modes) to further investigate its effect on PCDD/F formation.

Materials and Methods

The Waelz plant investigated is basically a rotary kiln plant with the capacity of treating 12 tons of EAF dusts per hour. Over 70,000 tons EAF dusts can be processed and over 20,000 tons zinc are recovered annually by this Waelz plant. Typical feed composition is sand (SiO_2), coke and EAF dust during the acidic kiln process.

By changing over to basic operation, the feed composition is sand mixed with $Ca(OH)_2$, coke and EAF dust. 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). In 2007, the adsorbent injection + dual bag filter (DBF) technology was applied at the Waelz plant investigated to meet the new standard of 1.0 ng-I-TEQ/Nm^3. The mixing ratio of adsorbent and CY ash is regulated according to the flue gas conditions such as particulate matter concentration, temperature, filter loading and pressure drop observed in the filter bag. In this study, vapor and solid-phase PCDD/Fs in the flue gases were separately yet simultaneously collected at different sampling points including: the CY outlet, primary BF outlet and the stack in the Waelz plant (Fig. 1). Samplings were conducted during the stages of the plant operating with the acidic and basic kiln processes, respectively. In addition, the ash samples at various sampling points were also collected for characterizing the PCDD/F formation. 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 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) (Thermo Trace GC) /high resolution mass spectrometer (HRMS) (Thermo DFS) 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 each APCD for evaluating the effectiveness to reduce PCDD/F emissions from the Waelz plant operating with either acidic or basic kiln mode (Table 1). As the Waelz plant was operated in acidic kiln mode, the PCDD/F concentration was measured as 164 ng-I-TEQ/Nm^3 at the CY outlet. By changing over to basic operation, the PCDD/F concentration in flue gases was significantly reduced to 17.8 ng-I-TEQ/Nm^3 at the CY outlet. Table 2 also shows the PCDD/F concentration measured in feeding material and ash samples of the Waelz plant investigated at different operating conditions. Significantly higher PCDD/F concentration (104 ng-I-TEQ/g) measured in 2nd BF ash is mainly attributed to the fact that the adsorbent injection + DBF system effectively transfers vapor-phase PCDD/Fs from flue gas to solid phase (BF ash) at the Waelz plant investigated. As $Ca(OH)_2$ was applied to replace SiO_2 as part of the input material, the PCDD/F concentration measured in DSC ash was significantly reduced from 3.44 to 0.964 ng-I-TEQ/g. Previous studies[4, 5] indicated that with the environment (temperature window, sufficient retention time, chlorine and catalysts available) conducive to PCDD/F formation in DSC, relatively high PCDD/F concentration (394 to 1,223 ng-TEQ/Nm^3) was measured in flue gas downstream the DSC of the Waelz plant investigated. The significant decrease of PCDD/F concentrations measured in flue gases and ash samples of the Waelz process is attributed to the lower PCDD/F formation during the basic kiln mode. The basic substances such as $Ca(OH)_2$ will prevent the formation of PCDD/F on particulate matter in flue gas. It is assumed that the basic substances react with HCl in the flue gas and thus reduce the chlorine supply needed for PCDD/F formation. As the flue gas passed through the adsorbent injection + DBF system, PCDD/F concentration measured at the primary BF outlet are 46.5 and 2.98 ng-I-TEQ/Nm^3 during the acidic and basic kiln mode operation, respectively. Fig. 2 shows that PCDD/Fs are predominantly distributed in solid phase in the flue gases upstream of the adsorbent injection + DBF system. As the flue gas passes through the 1st BF, around 72~83% PCDD/Fs are removed by the primary BF with adsorbent injection. During the basic kiln mode operation of this facility, the lower PCDD/F formation in flue gas results in the higher PCDD/F removal efficiency by primary BF with adsorbent injection. As the flue gas passes through the secondary BF, the PCDD/F concentrations measured in flue gases are 0.235 and 0.123 ng-I-TEQ/Nm^3 during the acidic and basic kiln mode operation, respectively. Over 99.5% PCDD/Fs in the flue gases are removed by the secondary BF with adsorbent injection. The results also demonstrate that, as the adsorbent injection + DBF system is adopted in this facility, the PCDD/F concentration emitted from this facility is lower than the dioxin emission limit set for existing Waelz plants (1.0 ng-I-TEQ/Nm^3). Significantly higher removal efficiencies of PCDD/Fs observed in Waelz plant can be attributed to two causes. First, the adsorbent injection rates in the Waelz plant investigated was controlled at 16 kg/h (215 mg/Nm^3). Previous study[6] indicated that excessive adsorbent injection rate in flue gas prior to the BF might actually increase the potential of PCDD/F formation on the filter cake accumulated on the filter bag operating at 200°C. The second possible cause is that the presence of the particulate matters, heavy metal and other organic compounds in the flue gas, may inhibit the PCDD/F adsorption with adsorbent, due to their competition with PCDD/F molecules for adsorption on the pore sites of adsorbent. As the particulate matters, heavy metal and other organic compounds in flue gas are previously removed by the primary BF with adsorbent injection, PCDD/Fs are more effectively removed by the secondary BF. Based on the operating data and the sampling results of flue gas and fly ash, Fig. 3 shows the PCDD/F mass flows on the basis of treating one kg of EAF dust at the Waelz plant investigated with acidic/basic kiln operation, respectively. During the acidic kiln operation, PCDD/Fs discharged via stack gas are around 1.45 ng-I-TEQ/kg EAF-dust. The total PCDD/F emission flow (including stack gas and ash) is 1,925 ng-I-TEQ/kg EAF-dust treated, which is slightly lower than the input flow (2,170 ng-I-TEQ/kg EAF-dust treated) of this facility. By changing over to basic operation, the PCDD/Fs (0.760 ng-I-TEQ/kg EAF-dust treated) emitted via the stack gas at this facility are significantly lower than that measured at acidic kiln mode. It is interesting to note that the total PCDD/F emission flow (269 ng-I-TEQ/kg EAF-dust treated) is significantly lower than the PCDD/F input mass flow (920 ng-I-TEQ/kg EAF-dust) due to lower PCDD/F formation operated in the basic kiln mode. .

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

Sampling location		***CY outlet***	***Primary BF outlet***	***Stack (Secondary BF outlet)***
Acidic kiln mode	O_2 (%)	17.5	18.3	18.2
	PM concentration (mg/Nm^3)	2,080	843	4.4
	PCDD/F concentration (ng-I-TEQ/Nm^3)	**164**	**46.5**	**0.235**
Basic kiln mode	O_2 (%)	18.0	18.7	18.6
	PM concentration (mg/Nm^3)	654	4.32	7.58
	PCDD/F concentration (ng-I-TEQ/Nm^3)	**17.8**	**2.98**	**0.123**

Table 2   PCDD/F concentration in feeding material and ash samples of the Waelz plant investigated at different operating conditions.

Ash samples	*Acidic kiln mode*	*Basic kiln mode*
	PCDD/Fs (ng-I-TEQ/g)	**PCDD/Fs (ng-I-TEQ/g)**
Input material	2.17	0.919
Slag	0.017	0.002
DSC ash	3.44	0.964
CY ash	0.514	0.304
1st BF ash	13.2	2.92
2nd BF ash	103	12.3

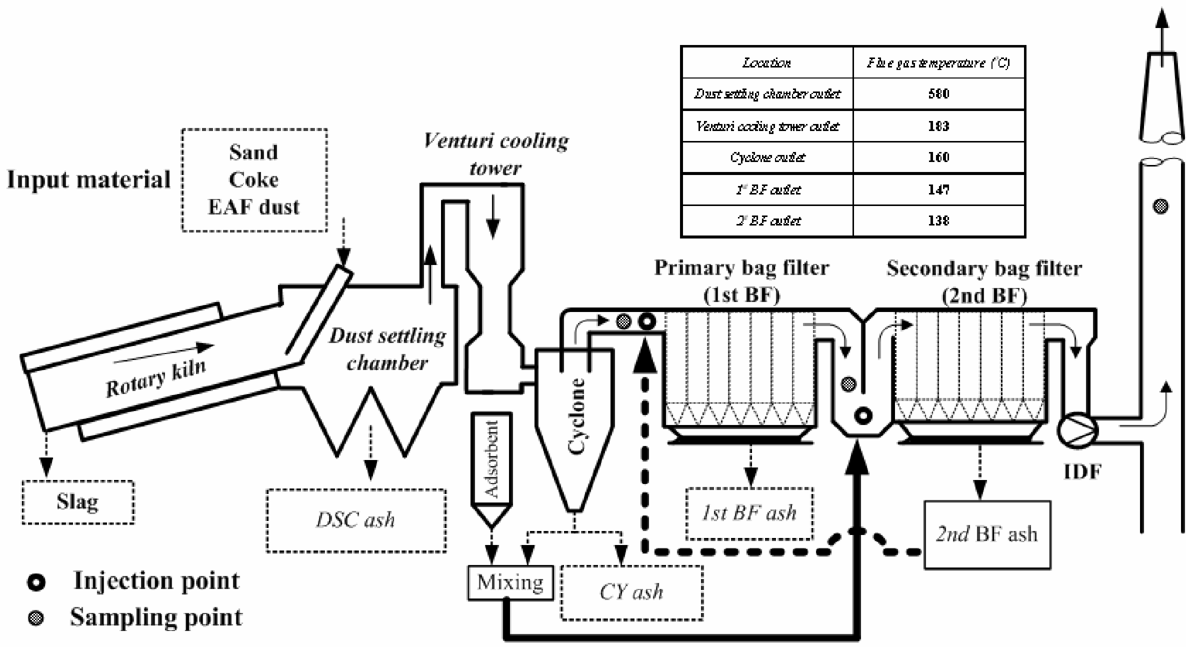

Figure 1.   Flow diagram and sampling points of the Waelz plant investigated.

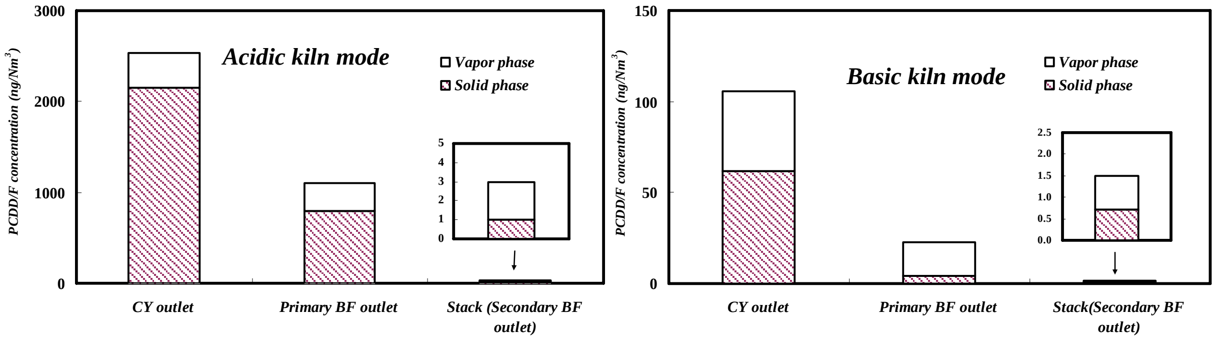

Figure 2 Variation of vapor/solid-phase PCDD/F concentrations in flue gases at different sampling points in the Waelz plant investigated.

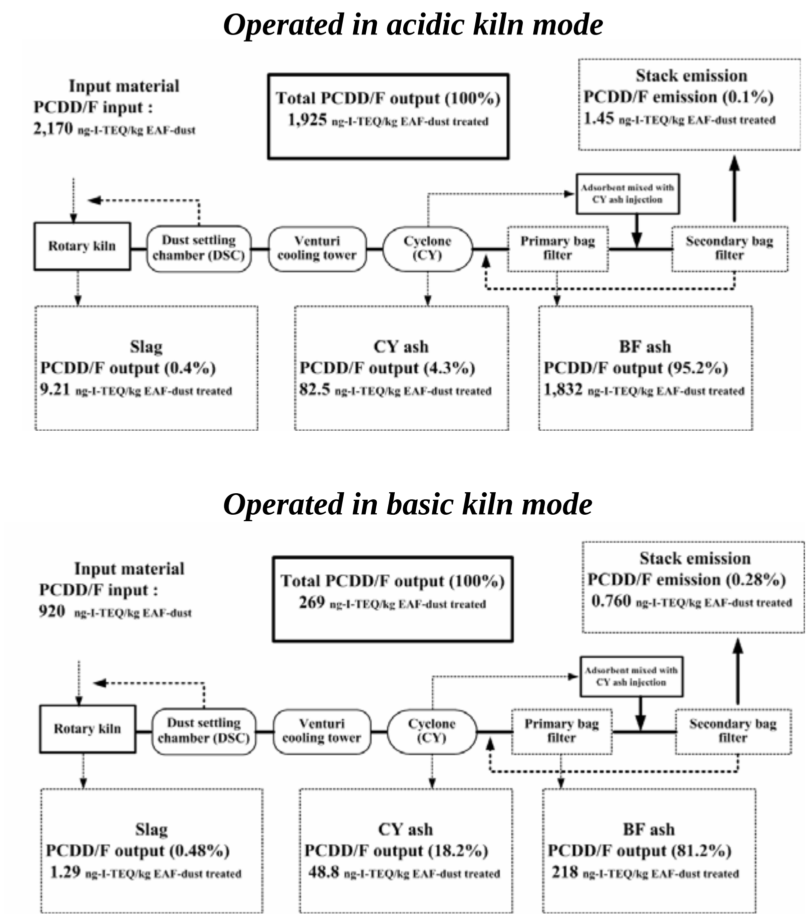

Figure 3 PCDD/F TEQ flows in the Waelz process operated in acidic and basic kiln mode.