

Characteristics of dioxin emissions from a Waelz plant with acid and basic kiln mode

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ABSTRACT

The concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were measured in the flue gas of a Waelz plant operated in acid and basic modes, respectively. To abate (PCDD/F) and other pollutants, the plant operates with a post-treatment of flue gases by activated carbon injection and subsequent filtration. Relatively high PCDD/F discharge by fly ashes is found with acid kiln mode of the Waelz process. Therefore, basic kiln mode of the Waelz process is investigated and compared in this plant. With the adsorbent injection rate of 7 kg/h (95 mg/Nm³), the PCDD/F concentration in stack gas was measured as 0.123 ng I-TEQ/Nm³ in the basic operating mode. The added Ca(OH)₂ reacted with metal catalysts and HCl_(g) in the flue gas and thus effectively suppressed the formation of PCDD/Fs. PCDD/F concentrations in fly ashes sampled from the dust settling chamber, cyclone, primary filter and secondary filter in basic kiln mode were significantly lower than that in acid kiln mode. Total PCDD/F emission on the basis of treating one kg of electric arc furnace dust in the basic operation mode was 269 ng I-TEQ/kg EAF-dust treated which was significantly lower than that in acid mode (640 ng I-TEQ/kg EAF-dust treated).

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) can be formed in combustion processes in the presence of a carbon source and chlorine [1,2]. Relevant study indicated that about half of the total PCDD/F mass flow in an electric arc furnace (EAF) is discharged via EAF dusts [3]. The Waelz process has long been used for treating and decontaminating zinc-containing EAF dusts which are regarded as hazardous wastes. However, significant amount of PCDD/Fs may be formed as chlorides, iron and copper coexist in raw materials [4]. Depending on the characteristics of the input materials of the Waelz process, the slag may be acid or basic as SiO₂ or a basic substance is added. The basicity is used to define the properties of slag, particularly in the case of Waelz slag [5]. The index is defined as Basicity = [CaO (%) + MgO (%)]/SiO₂ (%). SiO₂ is added with the input material in the acid process while hydrated lime (Ca(OH)₂), limestone (CaCO₃) or quick lime (CaO) is added in the basic process. The acid process functions at a basicity of 0.2 to 0.5. On the other hand, the basic process to which Ca(OH)₂, CaO, or CaCO₃ is added is operated at a basicity ranging from 1.5 to 4.0 [5]. The basicity of raw EAF dusts was calculated by the contents

of CaO, MgO and SiO₂ as indicated in some literatures to be about 1.2 [6,7]. In Taiwan, the average basicity of the EAF dusts collected from the stainless steel EAF plants is 1.5 [8]. Therefore, the basicity of EAF dusts observed in Taiwan and other countries were within the same level. In addition, as the Waelz plant is operated in basic mode, the capacity of the rotary kiln for treating the EAF dust and zinc oxide (ZnO) produced by the Waelz process is increased because SiO₂ is not added. However, the literature regarding the characteristics of PCDD/F formation in the basic process at the Waelz plant is limited. This may be attributed to the fact that the basic mode is difficult to maintain a stable operation in the Waelz process, and the iron-rich ring is easily formed at the inlet section of the kiln in the basic mode operation.

Oxidation by catalytic process and adsorption by activated carbon are commonly applied to PCDD/F removal. Busca et al. [9] indicate that the TiO₂-based V₂O₅/WO₃ catalysts are effective in the decomposition of gas-phase PCDD/Fs via selective catalytic reduction (SCR). However, removal efficiencies of organic compounds are significantly affected with high concentrations of particulate materials and acid gases (such as SO₂ and HCl) [10]. For keeping high PCDD/F removal efficiencies (>90%) via V₂O₅-WO₃-TiO₂ of catalyst, operating temperature over 200 °C is necessary [11,12]. In the Waelz plant investigated in this study, the flue gas temperature of cyclone outlet is 160 °C which is significantly lower than the temperature needed for catalyst. Hence, the catalytic decomposition

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may be unsuitable to make a post-abatement device of PCDD/Fs in flue gas. "ACI+BF" (activated carbon injection+ bag filter) system can simultaneously remove gas and solid-phase PCDD/Fs, including fly ash which is the main product "primary zinc oxide". Effective reductions of PCDD/F emissions from this plant by retrofitting air pollution control devices including the application of activated carbon injection and dual-BF systems have been reported previously [13–15]. This paper discusses the difference of PCDD/F discharges between acid/basic operating modes of the Waelz process. Mager et al. [5] indicated that HCl concentration in the flue gas in the basic mode was significantly lower than that when operating in the acid mode, resulting in the lower PCDD/F concentration in flue gas.

As a result of thermal treatment of residues with high chlorine contents, PCDD/Fs are formed in the flue gas, requiring the installation of additional air pollution control devices (APCDs) to reduce the emissions and this has posed a serious challenge to the secondary metallurgical smelting facilities [16]. A previous study indicated that the PCDD/F concentration measured in the stack gas of the Waelz plant investigated in the acid process reached 148 ng I-TEQ/Nm³ due to the significant formation of PCDD/F in the process and relatively low PCDD/F removal efficiency (< 70%) achieved with the single bag filter (BF) system [14]. In October 2005, the Taiwan government set a PCDD/F emission limit of 9.0 ng I-TEQ/Nm³ for existing Waelz plants, and a more stringent emission standard of 1.0 ng I-TEQ/Nm³ has been in effect since September 2006. Researchers have attempted to correlate the formation and concentration of PCDD/Fs with operating parameters of the Waelz plant such as the acid/basic mode of operation. A previous study indicated that the PCDD/F content of 140–1000 µg I-TEQ/kg in the BF ash of the Waelz process operating in acid mode was distinctly higher than that measured in basic mode (0.5–38 µg I-TEQ/kg) [5]. In the Waelz plant investigated, a significantly higher PCDD/F concentration (103 µg I-TEQ/kg) was also found in the secondary BF ash of the ACI + Dual BF (DBF) system in acid operating mode [15].

In 2008, over 200,000 ton of EAF dusts containing relatively high concentrations of heavy metals and PCDD/Fs are generated in Taiwan, but the annual capacity of EAF dust in the Waelz process investigated is about 80,000 ton. As the basic kiln mode is applied, the annual capacity can be increased to about 100,000 ton. To decrease PCDD/F content in the fly ash and solve the problems associated with EAF dust in Taiwan, the changeover to basic operating mode is of particular significance for the suppression of PCDD/F formation. In this study, the concentrations of PCDD/Fs in the flue gases of a Waelz plant located in central Taiwan were monitored during different operation processes (acid and basic modes) to further investigate their effects on PCDD/F formation.

2. Materials and methods

2.1. Waelz process investigated in this study

The Waelz plant investigated was basically a rotary kiln plant with the capacity to treat 12 ton of EAF dusts per hour. About 80,000 ton of EAF dusts can be processed and over 25,000 ton of ZnO are recovered annually in this Waelz plant. Based on the operating experience obtained from the Waelz plant investigated, high quality of ZnO can be manufactured as the basicities of the raw mixed material fed are controlled at 0.5 (acid mode) and 2.5 (basic mode), respectively. Therefore, a typical feeding composition is sand (SiO₂, 20%), coke (30%) and EAF dust (50%) in the acid kiln process. By changing to basic operation, the feed composition is mixed with base substance (Ca(OH)₂, 9%), coke (6%) and EAF dust (85%). The treating capacity of EAF dust by the rotary kiln is greatly increased from 12 ton/h in the acid mode to 15 ton/h in the basic mode. 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 a BF in series. For better control of PCDD/F emission, carbon-type adsorbent injection technology has been applied in this Waelz plant. The BET surface area of the carbon-type adsorbent (lignite coke) used in this facility is 300 m²/g. Everaert et al. [17] evaluate PCDD/F removal efficiency by carbon-base adsorbent injection, including coke and activated carbon. The results indicate PCDD/Fs can be removed by AC injection. However, PCDD/Fs may be formed additionally by de novo synthesis on AC surface. To evaluate its efficiency, the flue gases are sampled simultaneously before and after the DBF system equipped to reduce PCDD/F emission in the Waelz plant investigated. The gas flow sheets, flue gas sampling points and temperature profile through the APCDs of the Waelz plant investigated are schematically shown in Fig. 1.

2.2. Sampling points of flue gas and fly ash in the Waelz process investigated

PCDD/F samples in flue gases were simultaneously collected at CY outlet, 2nd BF inlet and stack of the Waelz plant investigated, to evaluate the effectiveness of the DBF system in reducing PCDD/F emission from the Waelz plant operating in either acid or basic kiln mode. The operating parameters and flue gas temperatures of each sampling point are shown in Table 1 and Fig. 1, respectively. The conditions of flue gas were similar for both acid and basic-kiln operation modes except that the basicities of input materials were changed. Flue gas samples collected were analyzed for seventeen 2,3,7,8-substituted PCDD/F congeners with International Toxic Equivalent Factors (I-TEF) values. The flue gas sampling was conducted with the Graseby Anderson Stack Sampling System complying with the USEPA Method 23. Gaseous PCDD/Fs can be effectively collected by XAD-2 resin while the particle-bound portion is collected by the fiberglass filter and by rinsing of the sampling probe. In addition, the ash samples including input materials, slag, DSC ash, CY ash, and reacted ash (1st BF and 2nd BF ash) of the Waelz plant investigated were also collected and analyzed for PCDD/F contents. The ash samples were collected at the same intervals as stack sampling was conducted.

2.3. PCDD/F analysis of samples collected from flue gas and fly ashes

Once the flue gas and ash samples were completed, the samples were transported to the laboratory under refrigeration. For PCDD/F analysis, the samples were then spiked with known amounts of internal standard solution using Method 23 (for flue gas samples) and labeled compound solution using Method 1613 (for ash samples), respectively, following internal quantification standards. After the clean-up procedures, seventeen 2,3,7,8-substituted PCDD/Fs were analyzed with high resolution gas chromatography (HRGC) (Thermo Trace GC)/high resolution mass spectrometry (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 µm, J&W). The mean recoveries of the standards for all ¹³C₁₂-2,3,7,8-substituted PCDD/Fs ranged from 53% to 105%. The recoveries were all within the acceptable 40% to 130% range set by the U.S. EPA in Method 23.

3. Results and discussion

3.1. PCDD/F concentrations measured in flue gases of the Waelz plant operated in acid and basic kiln modes

When the Waelz plant was operated in acid kiln mode, the average PCDD/F concentration ($n=2$, n is the sampling times) in the

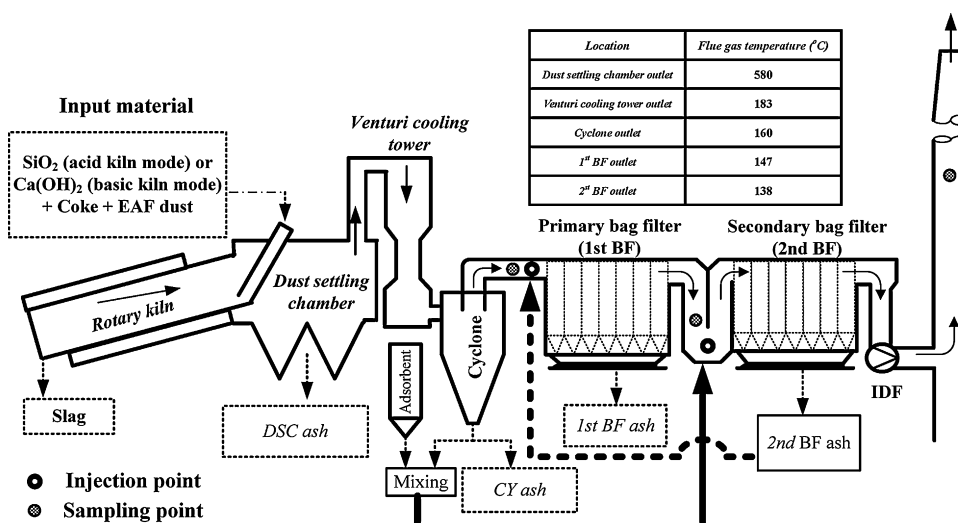


Fig. 1. Flow diagram and sampling points of the Waelz plant investigated with acid and basic kiln modes.

Table 1
Operating parameters of Waelz process with acid and basic modes.

Operating mode	Location	Particulate matter (mg/Nm ³)	O ₂ (%)	CO ₂ (%)	H ₂ O _(g) (%)
Acid mode	Cyclone outlet	2550	18.8	2.2	9.5
	1st BF outlet	5.9	18.8	2.2	10.0
	2nd BF outlet	1.4	18.5	2.5	8.6
Basic mode	Cyclone outlet	4770	18.9	2.1	12.4
	1st BF outlet	0.35	19.0	2.0	12.6
	2nd BF outlet	0.73	19.0	2.0	11.1

flue gas at the CY outlet was measured as 128 ng I-TEQ/Nm³. By changing over to basic operation, the average PCDD/F concentration ($n = 2$) in flue gases was significantly reduced to 17.8 ng I-TEQ/Nm³ at the CY outlet even though the particulate matter concentration measured at cyclone outlet was significantly higher than that with acid kiln mode as presented in Table 1. Table 2 also shows the PCDD/F concentrations measured in feeding material, slag and ash samples of the Waelz plant investigated at different operating conditions. Significantly higher PCDD/F concentration (105 ng I-TEQ/g) measured in 2nd BF ash was mainly attributed to the fact that the adsorbent injection + DBF system effectively transfers gas-phase PCDD/Fs from flue gas to solid phase (BF ash) at the Waelz plant investigated. As Ca(OH)₂ was applied to replace SiO₂ as part of the input material, the PCDD/F concentration measured in relatively ash was significantly reduced from 3.57 to 0.964 ng I-TEQ/g. In the meantime, the average PCDD/F concentration ($n = 3$) measured at stack gas decreased from 0.886 ng I-TEQ/Nm³ with acid operating mode to 0.123 ng I-TEQ/Nm³ with basic operating mode. That was significantly lower than the PCDD/F emission limit (1.0 ng I-TEQ/Nm³) for existing Waelz plant promulgated by the Taiwan

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

Ash samples	Acid kiln mode ($n^a = 2$)		Basic kiln mode ($n^a = 3$)	
	ng/g	ng I-TEQ/g	ng/g	ng I-TEQ/g
Input material	29.4	1.18	12.0	0.917
Slag	0.151	0.017	0.134	0.002
DSC ash	78.8	3.57	13.7	0.964
CY ash	10.6	0.398	2.17	0.304
1st BF ash	176	13.2	24.2	2.92
2nd BF ash	903	105	85.0	12.3

^a n is the sampling times.

EPA. As the Waelz plant was operated in the acid kiln mode, over 90% of PCDD/F compounds were distributed in vapor phase at different sampling points. The solid-phase portion slightly increased from 3% to 10% as the flue gas passes through the adsorbent injection + DBF system. Interestingly, the partitioning of PCDD/F compounds between vapor and solid phases changed significantly across the APCDs of the Waelz plant investigated by changing over to basic kiln mode. The solid-phase portion decreased from 57% to 10% as the flue gas passes through the APCDs.

Previous studies indicate that within the environment favorable to PCDD/F formation in a DSC (temperature window, sufficient retention time, chlorine and catalysts available), relatively high PCDD/F concentration was measured in flue gas downstream the DSC of the Waelz plant investigated [13,15]. Additionally, only particulate matter and solid-phase PCDD/F compounds were effectively removed by existing CY and BF, but vapor-phase compounds were not. The significant decrease of PCDD/F concentrations measured in flue gases and ash samples of the Waelz process was attributed to the lower PCDD/F formation with the operation in basic kiln mode. Previous studies indicate that the alkaline materials such as Ca(OH)₂ and NaOH greatly reduced PCDD/F formation and were commonly applied for controlling acid gas emission in the incineration process [18,19]. However, when inhibitors are applied to reduce PCDD/F formation, they should be introduced into the early stage of incineration facility such as in a furnace or a quench system. Hence, the basic substances (Ca(OH)₂) added with the input material in the Waelz plant operated in the basic kiln mode can react with metal catalysts and HCl and thus effectively suppress the formation of PCDD/Fs and their precursors. Fig. 2 shows PCDD/F congener distributions based on I-TEQ concentrations at different sampling points in flue gases of the Waelz plant operated in acid and basic modes. As the Waelz plant was operated in the acid kiln mode, PCDFs account for 56–63% of total PCDD/Fs at all

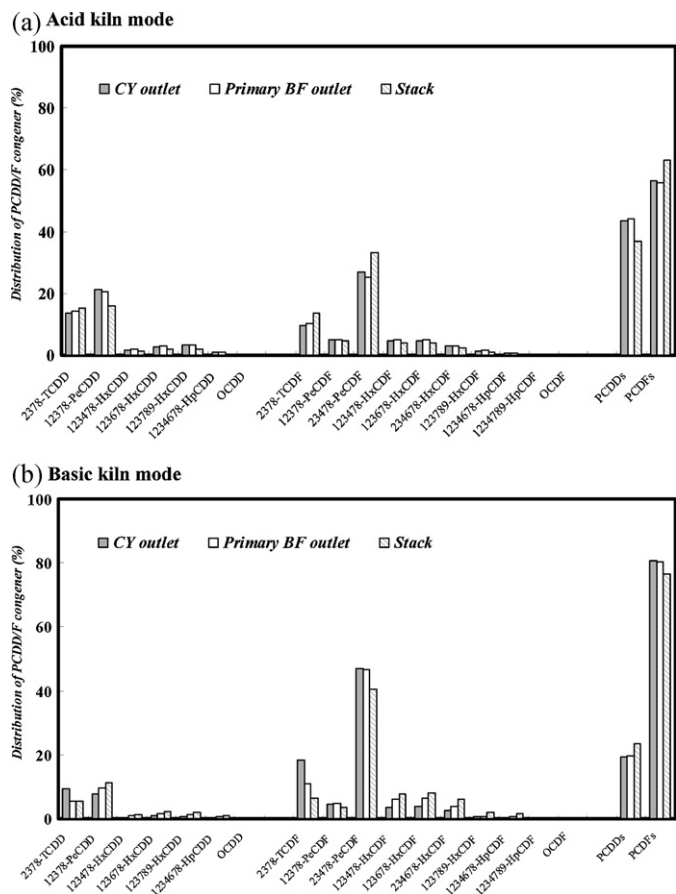


Fig. 2. TEQ distributions of PCDD/F congeners in flue gases at different sampling points in flue gases of the Waelz plant investigated operated in (a) acid and (b) basic kiln modes.

sampling points. Major contributors include 2,3,4,7,8-PeCDF (25–33%), 1,2,3,7,8-PeCDD (16–21%) and 2,3,7,8-TCDD (14–15%). If we compare the distributions of PCDD/F congeners in stack gases observed between the Waelz plant investigated in this study and EAF of an earlier study [3,11], 1,2,3,7,8-PeCDD (based on TEQ) is quite unique and can serve as the indicator for the flue gas emitted from the Waelz plant. Distribution of 1,2,3,7,8-PeCDD (based on TEQ) measured in the stack gases of MWI and EAF is generally about 5–10% by Hell et al. [19], but that observed in the stack gases of the Waelz plant exceeds 15%. That may be attributed to the different formation mechanisms among waste incineration, steel-making and Waelz processes, even though the literature indicates de novo synthesis is always the major formation pathway of PCDD/Fs evaluated with 9 kinds of industries, including municipal solid waste incinerators, industrial waste incinerator, ferrous and non-ferrous smelting processes [20]. By changing over to the basic kiln mode, the distribution of PCDDs in flue gases decreased from 37–44% to 19–23% at different sampling points of the Waelz plant. Additionally, the significantly lower distribution of 2,3,7,8-TCDD (6–8%) was observed during the basic kiln mode. As the $\text{Ca}(\text{OH})_2$ was applied to replace SiO_2 as part of the input material, around 90% of the most toxic dioxin congener (2,3,7,8-TCDD) formation was effectively inhibited (decreased from 17.5 to 1.69 ng I-TEQ/Nm³). Hence, the ratio of the mass concentration to the I-TEQ concentration measured in the flue gas at CY outlet decreases from 7.8 (acid kiln mode) to 5.9 (basic kiln mode). Fig. 3 shows that lower PCDD/F concentration in the flue gas was observed as the Waelz plant was operated in the basic kiln mode, especially vapor-phase PCDD/Fs. At CY outlet, significantly lower vapor-phase PCDD/F concentration in the

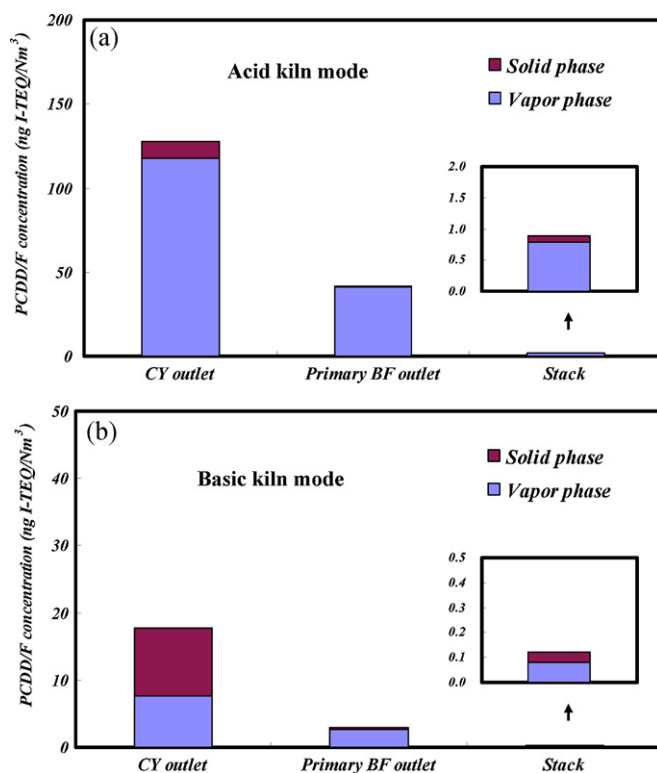


Fig. 3. Average concentrations of vapor/solid-phase PCDD/Fs ($n=3$) in flue gases of the Waelz plant investigated operated in (a) acid and (b) basic kiln modes.

basic kiln mode was observed compared with the acid operation. This is attributed to the fact that vapor-phase PCDD/F formation was effectively inhibited since HCl in the flue gas was effectively removed by reacting with basic substances in the basic kiln mode.

3.2. Comparison of PCDD/F removal efficiencies with the adsorbent injection + DBF system

In 2007, the adsorbent injection + DBF technology was applied at the Waelz plant investigated to meet the PCDD/F emission standard of 1.0 ng I-TEQ/Nm³. In practice, the carbon-type adsorbent was mixed with part of the fly ash collected by CY, and then injected into the flue gas of secondary BF inlet. The injection rate of adsorbent in DBF system was controlled at 13 kg/h (around 175 mg-AC/Nm³) as the Waelz plant was operated in acid kiln mode. Previous study indicates 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 [12]. To better control the PCDD/F emission and decrease the adsorbent consumption, the injection rate of adsorbent in DBF system was reduced to 7 kg/h (around 95 mg-AC/Nm³) as the Waelz plant was operated in basic kiln mode. The mixing rate of adsorbent and CY ash was regulated according to the flue gas conditions such as particulate matter concentration, temperature, filter loading and pressure drop observed in the filter bag.

For the PCDD/F congeners removal efficiencies, over 98% removal efficiencies of PCDD/F congeners based on TEQ in vapor and solid phases achieved with ACI + DBF system at the Waelz plant operated in acid and basic kiln modes. In addition, the AC injection rate (7 kg/h) in the Waelz process operated with basic process is lower than that (13 kg/h) with acid process. However, the PCDD/F removal efficiencies achieved with ACI + DBF system is not suffered even though lower AC injection rate is injected at basic kiln modes. On the other hand, the potential of PCDD/F formation in fly ash may

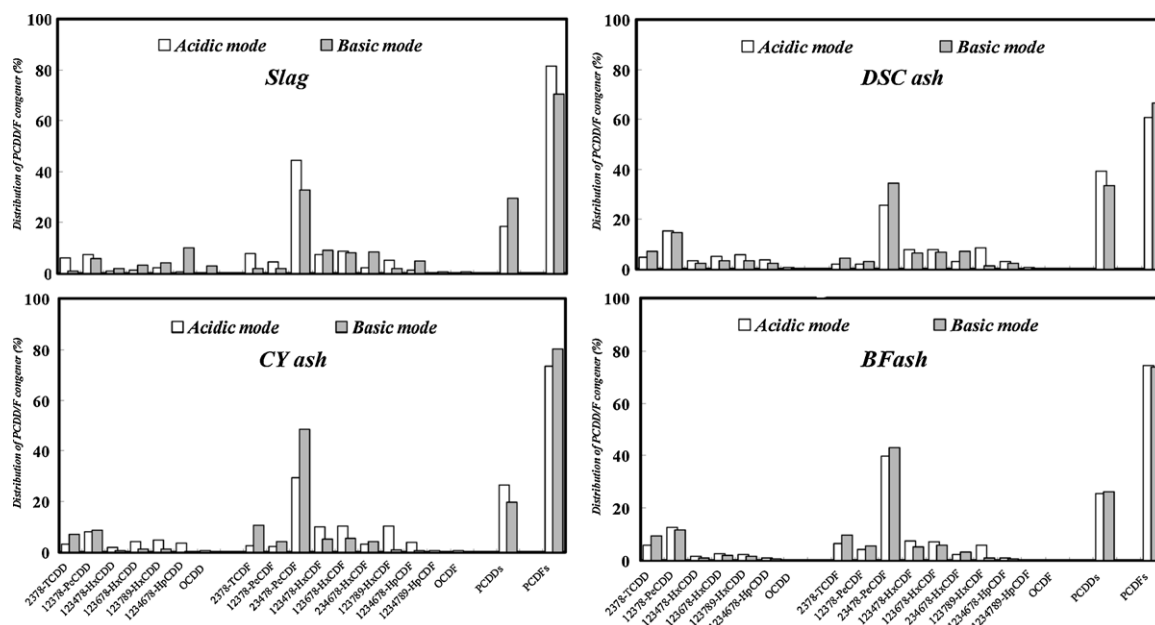


Fig. 4. Distribution of PCDD/F congeners in fly ash collected from different APCDs with acid and basic operating modes of Waelz process.

be further reduced with decreasing carbon supply from AC injection [14].

3.3. PCDD/F TEQ flows in the Waelz process operated in acid and basic kiln modes

Table 2 lists the PCDD/F concentrations of input material, slag, DSC ash, CY ash and BF ash of the Waelz plant investigated during different operating modes. As the Waelz plant was operated in the acid kiln mode, the PCDD/F concentrations of 1st and 2nd BF ash of the Waelz plant were 13.2 and 105 ng I-TEQ/g, respectively. PCDD/F concentrations were significantly higher than that of the ash samples collected at typical MWIs and EAFs, ranging from 0.3 to 10 ng I-TEQ/g [21,3]. As the Waelz plant was operated in the basic kiln mode, the PCDD/F concentrations of 1st and 2nd BF ash decreased to 2.92 and 12.3 ng I-TEQ/g, respectively. In the meantime, the PCDD/F concentrations of slag and DSC ash also significantly decreased from 0.017 to 0.002 ng I-TEQ/g and from 3.57 to 0.964 ng I-TEQ/g, respectively. The significant decrease of PCDD/F concentrations measured in ash samples of the Waelz process is attributed to the fact that basic substances added with the input material in the Waelz process can react with metal catalysts and HCl and thus effectively suppress PCDD/F formations. Fig. 4 shows the PCDD/F congener distributions based on TEQ concentration in ash samples (slag, DSC ash, CY ash and BF ash) collected at the Waelz plant investigated with acid and basic operating modes. PCDFs account for 60–80% of total PCDD/Fs at all ash samples. In slag samples, the lower distributions of 2,3,7,8-TCDD and 2,3,4,7,8-PeCDF were observed during the basic mode operation. The decreasing trends of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDF were also observed in the measurement conducted in flue gas sampling. In addition, the distributions of PCDD/F congeners in CY and BF ashes were similar to that of the flue gas sampled at CY outlet and stack, respectively. However, the significant difference between acid and basic kiln modes is found at lowly chlorine-substituted PCDD/Fs. As the Waelz plant is operated in the basic mode, the HCl in flue gases can react with basic substances. Hence, the chlorinated level of aryl compounds may be decreased, and then the distribution of highly chlorinated PCDD/Fs (6–8Cl) is further decreased. Additionally, the ratios of total toxicity concentration to total mass concentration calculated from results of

Table 2 is increased from 0.05, 0.04, and 0.12 in DSC ash, CY ash and BF ash, respectively, with the acid operating mode to 0.07, 0.14 and 0.14 with basic operating mode. That is attributed to the fact that the TEQ values of lowly chlorinated PCDD/F congeners (4–5Cl) are higher than those of highly chlorinated PCDD/F congeners (6–8Cl). Based on the operating data and the sampling results of flue gas and fly ash, the flows and emission factors of PCDD/Fs of the Waelz process can be calculated as follows:

$$\text{PCDD/F mass flow in stack gas (ng I-TEQ/kg EAF-dust treated)} = [\text{Average flue gas flow rate (Nm}^3/\text{h)} \times \text{PCDD/F concentration (ng I-TEQ/Nm}^3\text{)}] \div \text{capacity of EAF-dust treated (kg EAF-dust/h)}$$

$$\text{PCDD/F mass flow in ashes (ng I-TEQ/kg EAF-dust treated)} = [\text{PCDD/F concentrations in ashes (ng I-TEQ/g)} \times \text{product of ashes (kg/h)} \times 10^3 \text{ (g/kg)}] \div \text{capacity of EAF-dust treated (kg EAF-dust/h)}$$

Fig. 5 shows the PCDD/F mass flows on the basis of treating one kg of EAF dust at the Waelz plant investigated with acid/basic kiln operation, respectively. During the acid kiln operation, PCDD/F discharged via stack gas was 5.47 ng I-TEQ/kg EAF-dust treated. At this operating mode, the PCDD/Fs emitted via stack gas with adsorbent injection + DBF at the Waelz process investigated were significantly higher than that measured at typical waste incineration processes (0.3–0.9 ng I-TEQ/kg waste treated) [22]. Even though the adsorbent injection + DBF system adopted in the Waelz plant removed over 99% PCDD/Fs from flue gases, significant amount of PCDD/Fs was discharged via BF ash of the Waelz process (538 ng I-TEQ/kg EAF-dust treated) and this issue should be further addressed. Fortunately, the total PCDD/F emission flow (including stack gas and ash) was 640 ng I-TEQ/kg EAF-dust treated, which was lower than the input flow (1180 ng I-TEQ/kg EAF-dust treated) of this facility. Significantly higher PCDD/F mass flow observed in BF ash was attributed to the fact that the DBF system transfers the vapor-phase PCDD/Fs from flue gas to solid phase (BF ash) in the

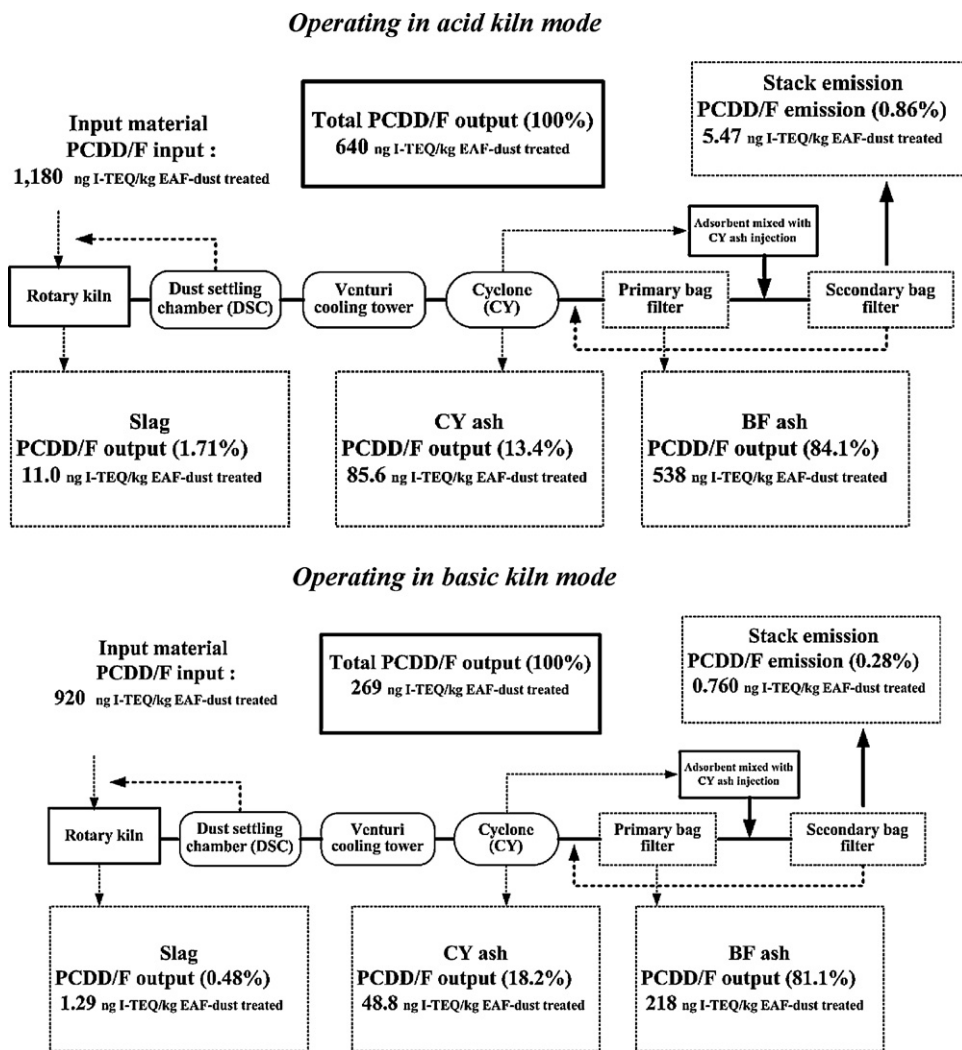


Fig. 5. PCDD/F TEQ flows in the Waelz process operated in acid and basic kiln mode, respectively.

Waelz plant. By changing over to the basic operation, the PCDD/Fs (0.760 ng I-TEQ/kg EAF-dust treated) emitted via the stack gas at this facility were significantly lower than that measured at the acid kiln mode. It is interesting to note that the total PCDD/F emission flow in this facility with the basic operation mode was dramatically decreased from 640 to 269 ng I-TEQ/kg EAF-dust treated, especially significant reduction in BF ash discharge (from 538 to 218 ng I-TEQ/kg EAF-dust treated) was observed.

4. Conclusions

Acid kiln mode was adopted originally in the Waelz plant investigated in this study. For effectively decreasing PCDD/F emission of stack and ash (product), the basic kiln mode was tested and the characteristics of PCDD/F emission were evaluated in this study. The potential of PCDD/F formation was significantly reduced with the basic kiln mode compared with the acid kiln mode via adding $\text{Ca}(\text{OH})_2$. PCDD/F concentration of the flue gas at cyclone outlet with the basic kiln mode had been significantly lower than that with the acid kiln mode and PCDD/F concentrations in fly ashes sampled from the DSC, CY, PF and SF were also decreased with the basic kiln mode. Total PCDD/F emission on the basis of treating one kg of EAF dust in the basic operation mode was 269 ng I-TEQ/kg EAF-dust treated which was significantly lower than that in the acid mode (640 ng I-TEQ/kg EAF-dust treated). As a result, the Waelz plant

operated in the basic kiln mode further reduced the total PCDD/F emissions.

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