



Fate of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans during the Thermal Treatment of Electric Arc Furnace Fly Ash

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ABSTRACT

Thermal treatment is often employed to recover the metals contained in electric arc furnace (EAF) fly ash, which is considered a major source of PCDD/Fs. After the present treatment, the mass and volume of untreated material (EAF fly ash + cullet) were significantly reduced by 44.2 and 89.2%, respectively; meanwhile the density increased significantly by 476%. These results indicate that the mass and volume of EAF fly ash can be effectively reduced to benefit the further disposal in landfill. Additionally, this study also investigated the fate of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) during the thermal treatment. For the EAF fly ash with an original PCDD/F content of 1414 ng I-TEQ/kg, 99.58% solid destruction efficiency (SDE) was achieved with thermal treatment at 1450°C. The total PCDD/F I-TEQ contents in ingot and slag were thus reduced to 9.83 and 6.44 ng I-TEQ/kg, respectively. The residual PCDD/F I-TEQ content in slag was far below the soil disposal limit in Taiwan (1000 ng I-TEQ/kg). After PCDD/Fs were decomposed in a secondary combustion chamber at 1200°C, the thermal treatment without air pollution control devices (APCDs) displayed an overall 91.28% destruction removal efficiency (DRE_{W/OAPCD}). Furthermore, the total PCDD/F I-TEQ concentrations in the cooling unit, filter and PUF cartridge were reduced to 1340, 131 and 383 pg I-TEQ/Nm³, respectively. Notably, their total amount, 1736 pg I-TEQ/Nm³, exceeded the emission limit in Taiwan (400 or 1000 pg I-TEQ/Nm³). The cooling unit and filter used as APCDs in this study could significantly lower the PCDD/F I-TEQ. The amount of residual PCDD/Fs captured in the PUF cartridge, was low enough (< 400 pg I-TEQ/Nm³) to be directly emitted into the atmosphere. Consequently, the thermal treatment with APCDs in this study was able to effectively reduce the PCDD/F contents in EAF fly ash, while the metal contents were recovered as the ingot.

Keywords: PCDD/Fs; EAF fly ash; Thermal treatment.

INTRODUCTION

Electric arc furnace (EAF) fly ash is one of by-products from both iron sintering or steel manufacturing, and has been described in detail by previous studies (Wang *et al.*, 2003a; Wang *et al.*, 2003b; Cieplik *et al.*, 2006; Shih *et al.*, 2008; Shih *et al.*, 2009). It is a major feedstock in iron smelter plants via recycling waste iron and steel scraps, although the raw materials used in the sintering processes contain paints, oils and coatings, and these materials are composed mainly of heavy metals and PCDD/Fs, which are then captured by the bag filters. Therefore, EAF fly ash is categorized as a

hazardous waste. Iron ore sintering is one of the major sources of airborne emissions of PCDD/Fs in many areas (Ward *et al.*, 2002; Kim *et al.*, 2003; Gass *et al.*, 2005; Li *et al.*, 2007c). For example, sinter plants were reported to account for approximately 3.2% of total dioxin emissions in Japan, and for 19.6 and 59% in Europe and Taiwan, respectively (Lahl, 1993, 1994; Quass *et al.*, 2000; Kumagai *et al.*, 2002; Wang *et al.*, 2003a). In Taiwan, after a more stringent regulatory limit was introduced in 2001 for municipal waste incinerators (0.1 ng I-TEQ/Nm³), sinter plants, and especially EAF fly ash, have become the most important source of PCDD/F emissions (Wang *et al.*, 2003a).

The Waelz rotary kiln process (Waelz process) is an appropriate method that has been broadly used for treating EAF fly ash and recover heavy metals (i.e. zinc oxide) in many places around the world for several decades. There were 13 EAF factories in Taiwan that utilize the Waelz process to deal with the EAF fly ash recovery (Li *et al.*, 2007c). However, the Waelz process has been identified as a new source of potentially high PCDD/F emissions in both France and Germany (Everaert and Baeyens, 2002). In Taiwan,

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EAFs emit 170,000 tons of fly ash annually, and thus an EAF fly ash treatment plant has been operating in the centre of Taiwan to treat and recover zinc from EAF fly ash via a thermal process since 1999 (Li *et al.*, 2007c). Some recent studies have examined the PCDD/F contents in the raw materials, output products, stack flue gas, vicinity atmosphere and the indoor air of workplaces (Lin *et al.*, 2010a; Wang *et al.*, 2010b; Wu *et al.*, 2010; Hsieh *et al.*, 2011). The Waelz process has a positive but minor effect with regard to the depletion of total PCDD/F mass. In addition, the total PCDD/F I-TEQ emissions had adverse health effects on employees in the affected workplaces during the treatment process (Wang *et al.*, 2003a; Wang *et al.*, 2010a). Moreover, the Waelz process increased the fraction of low-chlorinated congeners, because it is more difficult to decompose the aromatic rings of PCDD/Fs than to dechlorinate from the high-chlorinated congeners to the lower ones (Lee *et al.*, 2005; Li *et al.*, 2007c; Li *et al.*, 2008; Shih *et al.*, 2008; Shih *et al.*, 2009; Yu *et al.*, 2010; Chiu *et al.*, 2011; Kuo *et al.*, 2011). Therefore, the PCDD/F formation, emission, transportation, reduction and risk assessment for the Waelz process need to be evaluated, (Huang *et al.*, 2011), and to treat EAF fly ash needs to be developed.

There are several methods for treating hazardous solid waste, including acid leaching, cementation, sintering and vitrification (Cheeseman *et al.*, 2005; Park *et al.*, 2005; Wu and Ting, 2006; Browsers *et al.*, 2007; El-Nadi *et al.*, 2007). The vitrification approach has been shown to successfully treat hazardous materials, such as fly ash and sludge (Li *et al.*, 2007a; Chou *et al.*, 2009; Kuo *et al.*, 2009; Wang *et al.*, 2010c). There are three kinds of vitrification depending on the heat source: electric melting, burner melting and blast melting. Electric melting furnaces are usually considered as a cleaner technology, although they are more expensive, due to the high equipment cost and energy consumption. Vitrification can destroy toxic organic compounds, stabilize heavy metals and recover precious metals by the melting process (Kuo *et al.*, 2004; Yang *et al.*, 2008; Wang *et al.*, 2009a; Chuang *et al.*, 2010).

Considerable research has examined the reaction mechanisms of PCDD/Fs in the Waelz process, and the results indicate that PCDD/Fs are mainly formed by the de novo synthesis from carbon sources and inorganic chloride (Huang and Buekens, 1996; Buekens *et al.*, 2001; Wang *et al.*, 2009b; Lin *et al.*, 2010b; Chen *et al.*, 2011). However, the formation and transformation reactions of PCDD/Fs in the vitrification process, which do not need any auxiliary fuel, are still not well understood. In this study, thermal treatment equipment was employed to treat the EAF fly ash, and the PCDD/F contents/concentrations in the EAF fly ash, cullet, slag, ingot, cooling unit, filter and PUF cartridge were all determined. The congener profiles were then derived and analyzed, while the fate of the PCDD/Fs was discussed based on mass balance calculations. The results of this study have considerable importance, and can provide useful information that can aid in developing better control strategies for EAF fly ash treatment plants.

EXPERIMENTAL SECTION

Raw Material

The EAF fly ash used in the current study was collected from an iron and steel manufacturing plant in southern Taiwan. Cullet was obtained by grinding down the waste glass from common lab glassware, which was not contaminated by other chemicals. Both the EAF fly ash and cullet powders were sieved out using a #100 mesh (with 150 μm pore diameter) metallic sieve before use. Based on our previous studies (Li *et al.*, 2003; Li *et al.*, 2007a), the sieved EAF fly ash and cullet were mixed homogeneously in the mass ratios of 7:3 to adjust the basicity (CaO/SiO_2 in mass) of the mixture.

Melting System

As shown in Fig. 1, the melting system consists of (1) a high temperature furnace, (2) a secondary combustion chamber (SCC) and a set of air pollution control devices (APCDs), which included (3) a cooling unit for collecting the

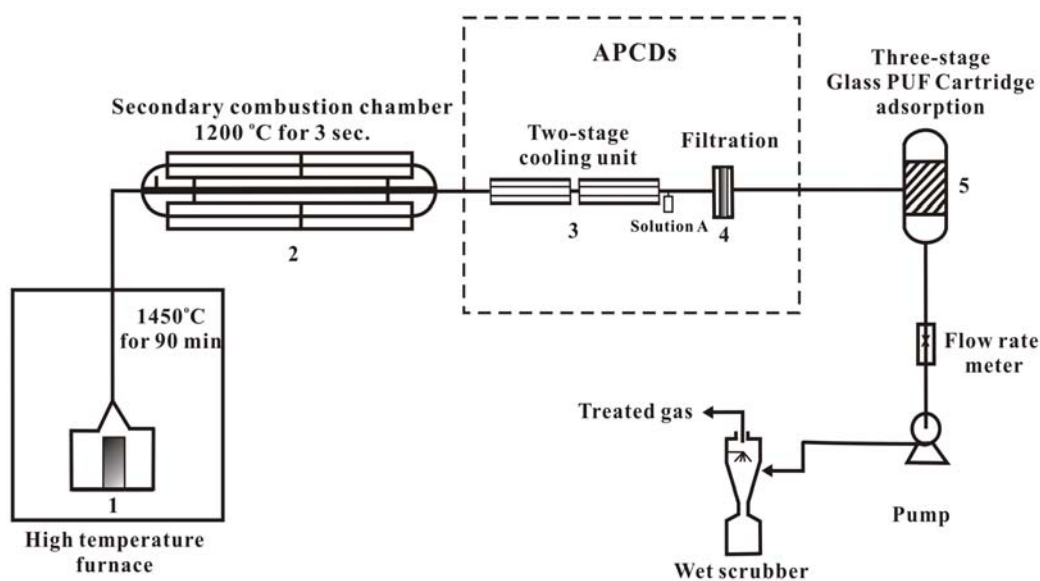


Fig. 1. Sketch of the thermal system.

condensed water containing dissolved PCDD/Fs and a certain amount of dust, and (4) a filter for collecting particles and (5) three glass cartridges plugged with polyurethane foam (PUF) to collect the residual gaseous PCDD/Fs. More details of this system are given in our previous studies. (Lai *et al.*, 2007; Lee *et al.*, 2008).

EAF fly ash (28.0 g) and cullet (12.0 g) were well mixed and put into a graphite crucible, which was further placed in the high temperature furnace. The inside diameter and the height of crucible were 70 and 95 mm, respectively. The high temperature furnace temperature was raised by 6 °C/min from the room temperature and maintained at 1,450°C for 1.5 hrs. The gaseous products from the high temperature furnace were further introduced into the SCC, which was fixed at 1,200°C throughout. The pumping flow rate was controlled at 6.0 L/min and the retention time of the gas stream in the SCC was approximately 3 s. Each previous batch experiment was repeated five times for consistency. After the thermal treatment, the samples collected from slag, ingot, cooling unit, filter and the PUF cartridge were further analyzed for PCDD/Fs.

PCDD/F Analysis

Both the slag and ingot were ground down to around 150 µm diameter (#100 mesh sieve), the same as that of EAF fly ash and cullet. Furthermore, all of the solid-like samples were analyzed using USEPA Method 1613B.

Samples collected from the cooling unit were divided into two parts. The first one was called solution A, which was collected directly via a condenser, and it was aqueous solution that contained dissolved PCDD/Fs and a certain amount of solid dusts. The mean collected volume of solution part A was 11 mL. The other part was called solution B, which was collected via tube washing by using *n*-hexane. The volume of solution B was 200 mL. Solutions A and B were mixed together, the particulates were filtered out, and then shaken for the liquid/liquid extraction and then the PCDD/F analyses. Solution B accounted for the major part (> 96% in mass) of the PCDD/F mass collected from the cooling unit, while the PCDD/F mass contributed by solution A was less than 4% in mass of the total amount (the sum of the mass from solutions A and B). These results were very similar to those obtained in Lee *et al.* (2008).

The PCDD/Fs were analyzed in the Super Micro Mass Research and Technology Center in Cheng Shiu University, Taiwan. Each sample was spiked with a known standard and subsequently extracted for 24 hours with toluene by a Soxhlet extractor. The extract was then concentrated and treated with sulfuric acid, which was followed by a series of clean-up and fractionation procedures. A specific amount of standard solution was added to the sample before PCDD/F analysis to estimate the recovery of overall analysis process. A high resolution gas chromatograph with a mass spectrometer (HRGC/MS) was used to determine the concentrations of 17 individual PCDD/Fs. The HRGC was equipped with a DB-5 fused silica capillary column ($L = 60$ m, i.d. = 0.25 mm, film thickness = 0.25 µm) and splitless injector. The oven temperature was programmed from the initial temperature at 150°C. There were three thermal gradients set as 1.5 °C/min, 30 °C/min and 1.5 °C/min from the initial condition (150°C) to 220, 240 and 310°C. Helium

with over 99.99995% purity was used as the carrier gas. The HRMS was equipped with a positive electron impact (EI+) source. The analyzer mode was selected ion monitoring (SIM) with the resolving power set at 10000. The electron energy and the source temperature were set at 35 eV and 250°C, respectively. The recoveries for the 17 individual PCDD/Fs compounds were 81–116%, which met the criteria of 70–130%. This recovery demonstrates that negligible PCDD/F breakthrough occurred. The recoveries of the PCDD/F internal standard solutions were all within their corresponding recovery criteria. The detailed instrumental analysis parameters of PCDD/Fs are given in our previous works (Wang *et al.*, 2003a; Lee *et al.*, 2008).

RESULTS AND DISCUSSION

The Effects of the Thermal Treatment on EAF Fly Ash Mass, Volume and Density

Thermal treatment was utilized in the current study to treat the EAF fly ash for mass, volume and toxicity reduction, and therefore it is important to analyze the changes in mass, volume and density after the treatment. The masses of EAF fly ash, cullet, ingot and slag were 28.1, 12.0, 6.86 and 15.5 g, respectively. The mass of the input material (EAF fly ash + cullet) was reduced by 44.2%, as determined by $(40.1 - 22.36)/40.1$, after the thermal treatment. The volumes of EAF fly ash, cullet, ingot and slag were 25.2, 10.9, 0.90 and 3.00 cm³, respectively. A significant 89.2%, $(36.1 - 3.9)/36.1$, volume reduction from the untreated EAF fly ash + cullet was achieved by the thermal treatment. Additionally, the densities of the EAF fly ash, cullet, ingot and slag were 1.1138, 1.1083, 7.6247 and 5.1778 g/cm³, respectively. Notably, the density increased from the untreated EAF fly ash + cullet (2.2221 g/cm³) to the ingot + slag (12.8025), representing a 476% increase. According to the above results, the mass and volume of EAF fly ash can be effectively reduced to benefit subsequent disposal in landfill. The metals in EAF fly ash were concentrated into the ingot, as could be seen by the high increase in density.

Contents of PCDD/Fs in EAF Fly Ash and Cullet

In order to estimate the efficiency of thermal treatment, the PCDD/Fs in EAF fly ash and cullet were first analyzed. The contents of PCDD/Fs in EAF fly ash and cullet are shown in Table 1. Total PCDD/F I-TEQ content was defined by summing up the contents of seventeen congeners and multiplying these by their own International Toxicity Equivalent Factors (I-TEFs). The means ($n = 5$) of the total PCDD/F contents in EAF fly ash and cullet were 37072 and 168 ng/kg, respectively; while the means ($n = 5$) of total I-TEQ contents were 1414 and 1.40 ng I-TEQ/kg, respectively. In contrast to the results of previous studies, the total PCDD/F I-TEQ content in the EAF fly ash of the present study was slightly higher than that reported by Li *et al.* (2007c, 945 ng I-TEQ/kg), and much higher than that reported by Giugliano *et al.* (2002, 194 ng I-TEQ/kg) in fly ash from a municipal solid waste incinerator. Notably, the total PCDD/F I-TEQ in the EAF fly ash found by the present study exceeded the soil pollution standard set by Taiwan's EPA (1000 ng I-TEQ/kg), and thus needs further treatment before disposal.

Table 1. PCDD/F contents in EAF fly ash and cullet.

PCDD/Fs (ng/kg)	EAFs fly ash (n = 5)			Cullet (n = 5)		
	Range	Mean	RSD (%)	Range	Mean	RSD (%)
2,3,7,8-TeCDD	17.7–19.7	18.7	10.9	0.0430–0.0450	0.0441	4.90
1,2,3,7,8-PeCDD	180–210	196	15.3	0.0880–0.0921	0.0901	4.51
1,2,3,4,7,8-HxCDD	245–265	255	7.54	0.183–0.198	0.191	7.89
1,2,3,6,7,8-HxCDD	810–839	825	3.60	0.282–0.293	0.287	3.94
1,2,3,7,8,9-HxCDD	1039–1092	1065	4.95	0.620–0.635	0.627	2.44
1,2,3,4,6,7,8-HpCDD	6001–6602	6301	9.52	9.39–9.70	9.55	3.21
OCDD	6721–6813	6767	1.35	85.3–88.7	87.0	3.90
2,3,7,8-TeCDF	20–234	217	15.4	0.176–0.182	0.179	3.38
1,2,3,7,8-PeCDF	449–484	466	7.57	0.416–0.438	0.427	5.17
2,3,4,7,8-PeCDF	853–956	904	11.4	0.372–0.395	0.383	6.19
1,2,3,4,7,8-HxCDF	1095–1170	1132	6.64	1.16–1.21	1.18	4.54
1,2,3,6,7,8-HxCDF	1145–1225	1185	6.79	1.19–1.29	1.24	7.86
1,2,3,7,8,9-HxCDF	1762–1837	1800	4.13	1.71–1.79	1.75	4.51
2,3,4,6,7,8-HxCDF	235–284	259	18.9	0.250–0.257	0.253	2.95
1,2,3,4,6,7,8-HpCDF	5090–5317	5204	4.36	21.9–22.8	22.4	3.93
1,2,3,4,7,8,9-HpCDF	1757–1855	1806	5.43	3.73–3.89	3.81	4.06
OCDF	8234–9109	8671	10.1	37.2–39.9	38.6	7.00
PCDDs	15021–15834	15427	5.27	96.1–99.5	97.8	3.43
PCDFs	20850–22438	21644	7.34	68.8–71.6	70.2	3.92
PCDDs/PCDFs ratio	0.700–0.730	0.713	4.97	1.35–1.44	1.40	5.82
Total PCDD/Fs	35944–38199	37072	6.08	166–170	168	2.30
PCDDs ng I-TEQ/kg	384–417	401	8.12	0.380–0.385	0.382	1.30
PCDFs ng I-TEQ/kg	970–1055	1013	8.38	0.962–0.985	0.974	2.31
PCDDs/PCDFs (I-TEQ) ratio	0.390–0.400	0.395	4.36	0.389–0.396	0.393	1.63
Total ng I-TEQ/kg	1357–1471	1414	8.09	1.34–1.37	1.36	1.94

The PCDDs/PCDFs ratio in EAF fly ash was 0.713, and thus the PCDFs content was higher than that of PCDDs. The reason for this might be that the PCDFs were reformed by the de novo synthesis in the EAF fly ash, and collected by bag filter after the arc furnace operation.

The congener profiles of PCDD/Fs in EAF fly ash and cullet are shown in Fig. 2. Each selected congener was normalized by dividing its content by that of the sum of the 17 PCDD/F congeners. The high-chlorinated PCDDs (1,2,3,4,6,7,8-HpCDD and OCDD) and PCDFs (1,2,3,4,6,7,8-HpCDF and OCDF) were the major PCDD/F congeners in both EAF fly ash and cullet; however, the fractions of low-chlorinated PCDD/Fs in EAF fly ash were relatively higher than those in the cullet. The higher low-chlorinated PCDD/F fractions (Fig. 2) and low PCDDs/PCDFs (< 1) might be the sign of de novo synthesis in the EAF fly ash production. In addition, the PCDD/F congener profile obtained from this study for EAF fly ash closely resembles that reported by Li (Li et al., 2007c), which also focused on EAF fly ash analysis.

PCDD/F Contents in Slag and Ingot

Table 2 showed the PCDD/F contents in ingot and slag after treatment of EAF fly ash at 1450°C. The means of total PCDD/F contents in ingot and slag were 1754 and 774 ng/kg, while the total PCDD/F I-TEQ in them was 9.83 and 6.44 ng I-TEQ/kg, respectively. In comparison, both PCDD/F and its I-TEQ contents in ingot and slag were much lower than those in untreated EAF fly ash (37072 ng/kg and 1414 ng I-TEQ/kg), indicating that thermal treatment of EAF fly ash at 1450°C could significantly lower the PCDD/Fs.

In order to recover the slag from the thermal treatment of EAF fly ash, the PCDD/F contents need to be reduced to meet the soil disposal limit in Taiwan (1000 ng I-TEQ/kg). The solid destruction efficiency (SDE) achieved by the high temperature furnace was thus defined as below to examine the efficiencies of PCDD/F reduction.

$$\text{SDE (\%)} = [1 - \sum M_i / \sum M_j] \times 100\% \quad (1)$$

where $\sum M_i$ was the total PCDD/F I-TEQ mass in slag and ingot; $\sum M_j$ was the total PCDD/F I-TEQ mass in untreated EAF fly ash and cullet.

The PCDD/F I-TEQ masses of EAF fly ash, cullet, ingot and slag were calculated based on their masses and PCDD/F I-TEQ contents. SDE of PCDD/F I-TEQ was thus determined as 99.58%. Moreover, the residual PCDD/F content in slag (6.44 ng I-TEQ/kg) was far below the soil disposal limit in Taiwan (1000 ng I-TEQ/kg). Slags produced after the treatment of EAF fly ash at 1450°C can be undoubtedly used in secondary backfill.

Fig. 3 shows the congener profiles of PCDD/Fs in ingot and slag. The fractions of low-chlorinated PCDD/Fs (2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF) were very low after thermal treatment (SDE = 98.2–99.8%). On the other hand, the fractions of high-chlorinated (OCDD and OCDF) were very high, indicating that certain residual contents still remained in ingot (933 and 505 ng/kg) and slag (388 and 189 ng/kg). Regarding the reduction of OCDD

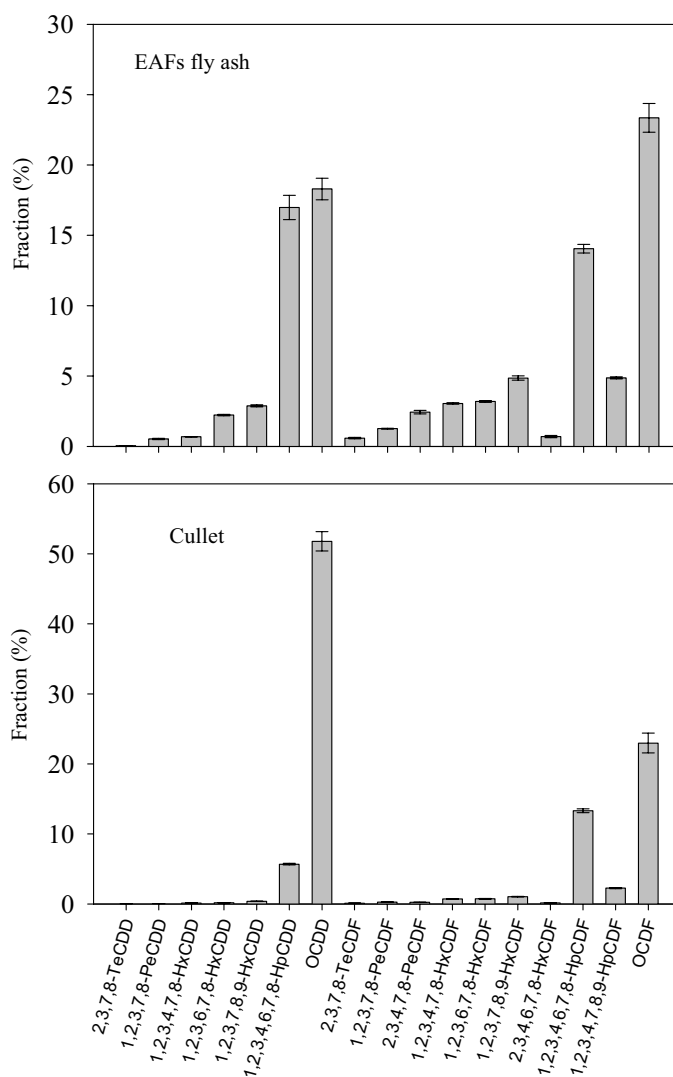


Fig. 2. Congener profiles of PCDD/Fs in the EAFs fly ash and cullet.

and OCDF contents during thermal treatment, that of OCDF was greater (SDE = 97.3%) than that of OCDD (93.4%).

Fig. 3 also shows the dominant congeners in ingot and slag were 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF, which were very close to those in cullet. Moreover, the dechlorination of high-chlorinated PCDD/Fs was not significant in the solid phase transformations, because relatively lower fractions of low-chlorinated PCDD/Fs were found in the products. (Kim *et al.*, 2005; Lundin and Marklund, 2007)

In addition, the ratios of PCDDs/PCDFs were 1.29 and 1.45 in ingot and slag (Table 2), respectively, revealing that the contents of PCDDs were higher than those of PCDFs. The above ratio of slag (1.45) was very close to that of the cullet (1.40), probably because the cullet is the major component in slag (12.03 g cullet/15.16 g slag = 79.4%). Nevertheless, those higher PCDDs/PCDFs (> 1) might be due to the precursor condensation of PCDD/F formation. Interestingly, the ratios of PCDD/PCDF (I-TEQ) were 0.590 and 0.383 in ingot and slag, respectively, representing that there was more PCDF I-TEQs than PCDD I-TEQs in ingot and slag. These differences in the ratios of PCDDs/PCDFs

(> 1) and PCDD/PCDF (I-TEQ) (< 1) might be because there was more highly toxic PCDFs (low-chlorinated congeners) than higher toxicity PCDDs (low-chlorinated congeners). The PCDF I-TEQ contents thus became higher and further reduced the PCDD/PCDF (I-TEQ). Nevertheless, the higher ratio of PCDFs survival was caused by the closed-shell configuration of the electron resonance process, which makes them more chemically stable than PCDDs in low-chlorinated congeners (Visez and Sawerysyn, 2005). Huang and Buekens (1995) concluded that the ratio of PCDDs/PCDFs was usually smaller than one in de novo synthesis experiments. On the other hand, PCDD/Fs have been reported to be produced by a precursor condensation pathway with a large ratio of PCDDs/PCDFs (Huang and Buekens, 1996; Buekens *et al.*, 2001). Therefore, the dominant pathway of PCDD/F formation in the present study might be precursor condensation (ratios of PCDDs/PCDFs = 1.29 and 1.45 in ingot and slag) from chlorophenol, chlorophenoxy, and graphite carbon, whereas the de novo synthesis showed no significant effect on PCDD/F formations in the treated products. In the de novo synthesis, the low-chlorinated PCDD/Fs were prior products formed

Table 2. PCDD/F contents in ingot and slag.

PCDD/Fs (ng/kg)	Ingot (n = 5)			Slag (n = 5)		
	Range	Mean	RSD (%)	Range	Mean	RSD (%)
2,3,7,8-TeCDD	0.339–0.365	0.352	7.24	0.204–0.216	0.210	5.63
1,2,3,7,8-PeCDD	0.789–0.841	0.815	6.34	0.401–0.429	0.415	6.55
1,2,3,4,7,8-HxCDD	1.38–1.46	1.42	5.75	0.892–0.943	0.918	5.57
1,2,3,6,7,8-HxCDD	3.26–3.39	3.33	3.93	1.46–1.51	1.48	3.37
1,2,3,7,8,9-HxCDD	5.07–5.34	5.21	5.14	2.90–2.98	2.94	2.75
1,2,3,4,6,7,8-HpCDD	93.5–98.1	95.8	4.81	43.2–45.7	44.4	5.67
OCDD	923–943	933	2.18	376–340	388	6.11
2,3,7,8-TeCDF	0.603–0.649	0.626	7.32	0.583–0.616	0.600	5.57
1,2,3,7,8-PeCDF	1.98–2.06	2.02	4.11	1.73–1.84	1.78	5.98
2,3,4,7,8-PeCDF	2.08–2.15	2.12	3.41	1.63–1.70	1.67	3.67
1,2,3,4,7,8-HxCDF	7.03–7.28	7.16	3.52	5.73–6.11	5.92	6.53
1,2,3,6,7,8-HxCDF	7.13–7.42	7.28	4.04	6.16–6.51	6.34	5.61
1,2,3,7,8,9-HxCDF	10.1–10.7	10.4	6.04	8.95–9.37	9.16	4.60
2,3,4,6,7,8-HxCDF	1.91–1.98	1.94	3.61	1.49–1.55	1.52	3.46
1,2,3,4,6,7,8-HpCDF	150–154	152	2.89	100–104	102	3.76
1,2,3,4,7,8,9-HpCDF	25.5–27.2	26.3	6.38	17.0–18.1	17.6	6.16
OCDF	494–515	505	4.09	187–191	189	2.18
PCDDs	1030–1049	1040	1.87	426–451	438	5.61
PCDFs	703–726	714	3.32	333–338	336	1.55
PCDDs/PCDFs ratio	1.44–1.47	1.46	2.51	1.27–1.35	1.31	6.13
Total PCDD/Fs	1734–1774	1754	2.27	762–786	774	3.08
PCDDs ng I-TEQ/kg	3.60–3.69	3.65	2.45	1.76–1.81	1.78	2.63
PCDFs ng I-TEQ/kg	6.14–6.23	6.18	1.41	4.63–4.69	4.66	1.36
PCDDs/PCDFs (I-TEQ) ratio	0.581–0.599	0.590	3.03	0.378–0.388	0.383	2.53
Total ng I-TEQ/kg	9.77–9.89	9.83	1.15	6.40–6.49	6.44	1.40

by the substitution of chlorine onto the residual carbon (graphitic structure). The extremely low fractions of low-chlorinated PCDD/Fs (Fig. 3) thus again supported the previous conclusion of non-significant de novo synthesis during solid phase transformation.

PCDD/F Concentrations in Cooling Unit, Filter and PUF Cartridge

Even though most of the PCDD/Fs in the EAF fly ash were destroyed or removed by the high temperature furnace to produce more valuable and lower toxicity products (ingot and slag), there was still a certain amount of PCDD/Fs in the flue gas. Therefore, a secondary combustion chamber (SCC), that could decompose most of the PCDD/Fs and their precursors at 1200°C, was installed after the high temperature furnace. Furthermore, the surviving PCDD/Fs leaving from the SCC were collected in the air pollution control devices (APCDs, cooling unit and filter), and 100% of the penetrating PCDD/Fs from the cooling unit and filter could be eventually be captured.

Table 3 shows the PCDD/F concentrations in the cooling unit, filter and PUF cartridge. As shown in this table, the total PCDD/F I-TEQ concentrations in each APCDs and PUF cartridge were 1340, 13.1 and 383 pg I-TEQ/Nm³, respectively. The sum of the PCDD/F I-TEQ concentrations in the cooling unit, filter and PUF represent the PCDD/Fs in untreated flue gas leaving from the SCC. Unfortunately, this concentration was 1736 pg I-TEQ/Nm³, which was significantly higher than the regulated standards in Taiwan (1000 and 400 pg I-TEQ/Nm³), and thus a set of APCDs needed to be installed. After two APCDs (cooling unit and

filter) were used, the PCDD/F I-TEQ concentration in the filter was equal to that captured in PUF cartridge (383 pg I-TEQ/Nm³), and was low enough (< 400 pg I-TEQ/Nm³) to be directly emitted into the atmosphere. Therefore, the APCDs used in the present study could effectively reduce the PCDD/F I-TEQ concentration in flue gas to meet the regulated standards in Taiwan. Nevertheless, the potential of treated exhaust gas to exceed the limits in Taiwan could be reduced by further installing an activated carbon injection system before the filter, as this approach has been widely used as a APCD for PCDD/F reduction.

Most of the high PCDD/F I-TEQ contributive sources examined in the literature are equipped with an activated carbon injection system in their APCDs to alleviate the PCDD/F loading, e.g. a EAF fly ash treatment plant using the Waelz process (Li *et al.*, 2007c; Li *et al.*, 2008), a secondary smelting plant (Li *et al.*, 2007b), and a coal-fired plant (Lin *et al.*, 2007). The concentrations of the total PCDD/F I-TEQ in the stack flue gas of these plants were 5.24 (EAF fly ash treatment plant), 1.50 (secondary smelting plant) and 0.036 (coal power plant) ng I-TEQ/Nm³, respectively. The results show that the total PCDD/F I-TEQ concentrations in the current research (0.0383 ng I-TEQ/Nm³) were slightly higher than those of the coal power plant, but much lower than those from EAF fly ash treatment and secondary smelting plants. The thermal treatment employed in this study is thus a potentially promising process for reducing the PCDD/F emissions in flue gas.

The PCDDs/PCDFs ratios of the cooling unit, filter and PUF cartridge were 0.245, 0.201 and 0.289, respectively, significantly different from those of the treated products

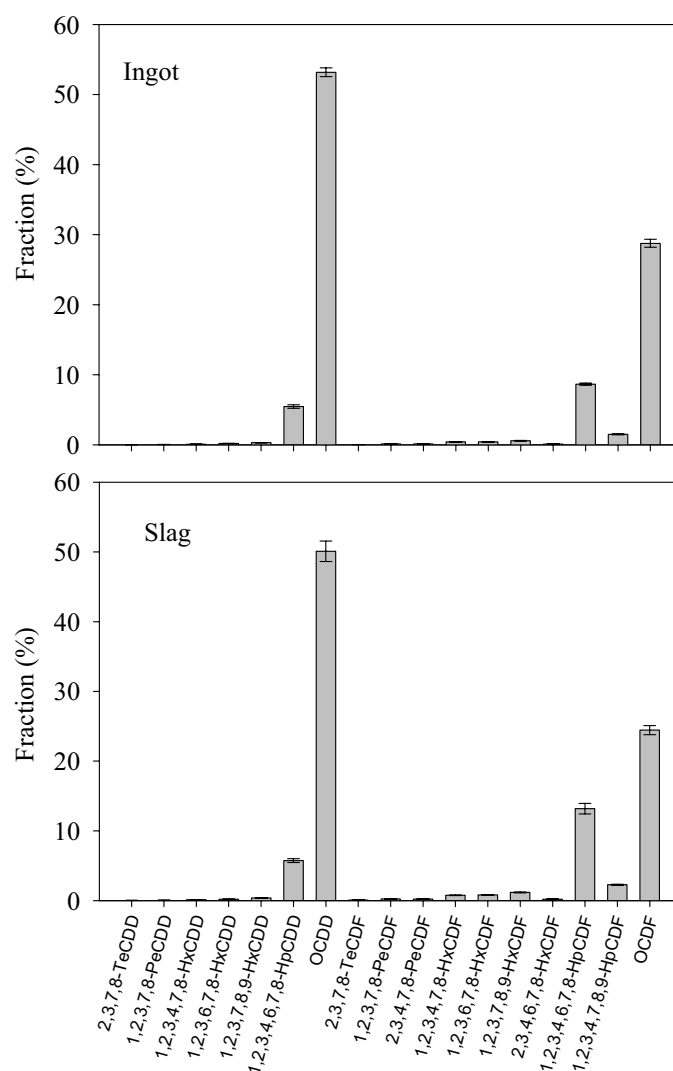


Fig. 3. Congener profiles of PCDD/Fs in slag and ingot.

Table 3. PCDD/F concentrations in cooling unit, filter and PUF cartridge.

PCDD/Fs (pg/Nm ³)	Cooling unit (n = 5)		Filter (n = 5)			PUF cartridge (n = 5)			
	Range	Mean RSD (%)	Range	Mean RSD (%)		Range	Mean RSD (%)		
PCDDs	4100–4176	4138	1.84	25.9–26.5	26.2	2.31	1637–1691	1664	3.19
PCDFs	16745–1703	16890	1.72	129–132	130	2.04	5685–5850	5768	2.86
PCDDs/PCDFs ratio	0.242–0.248	0.245	2.35	0.198–0.204	0.201	2.82	0.281–0.296	0.289	5.16
Total PCDD/DFs	20872–21183	21027	1.48	155–158	157	1.80	7356–7507	7432	2.02
PCDDs pg I-TEQ/Nm ³	144–146	145	1.40	1.53–1.59	1.56	3.54	45.9–47.8	46.8	4.08
PCDFs pg I-TEQ/Nm ³	1181–1210	1196	2.37	11.4–11.8	11.6	3.40	331–342	337	3.38
PCDDs/PCDFs (I-TEQ) ratio	0.119–0.123	0.121	3.51	0.131–0.140	0.135	6.53	0.137–0.142	0.139	3.69
Total pg I-TEQ/Nm ³	1327–1354	1340	2.01	12.9–13.3	13.1	2.70	377–390	383	3.26

(ingot: 1.29; slag: 1.45). These results indicate that the concentrations of PCDFs in the APCDs and PUF were significantly higher than those of PCDDs, whereas the opposite results were found in the ingot and slag. The discrepant results between the treated products and flue gases might be due to the different formation pathways. A series of two cooling tubes was employed in the cooling unit to cool down the flue gas after the SCC. Furthermore, the unburned carbon with degenerate graphitic structures

(soot) might drive the de novo synthesis during the cooling process (450°C down to 250°C) (Hu *et al.*, 2009). However, the residual carbon structures in slag and ingot might be relatively stable. Notably, it was the different process of PCDD/F formation in solid products that caused the residual carbon structure (amorphous) in slag too be too stable to start the formation process, even when the temperature of the high temperature furnace cooled down to the de novo synthesis reaction range (250–450°C). Additionally, the

smaller amounts of chlorophenol and chlorophenoxy derived by PCDD/F dechlorination and decomposition reacted with each other due to the presence of a catalytic transition metal, such as copper, to reform PCDD/Fs in the solid products.

The PCDD/F congener profiles in the cooling unit, filter and PUF cartridge are shown in Fig. 4. The congener profiles

in the APCDs and PUF cartridge were quite similar. The dominant congeners in APCDs and PUF cartridge were 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF and OCDF. These results were different from those reported by Li et al. (Li et al., 2007c; Li et al., 2008),

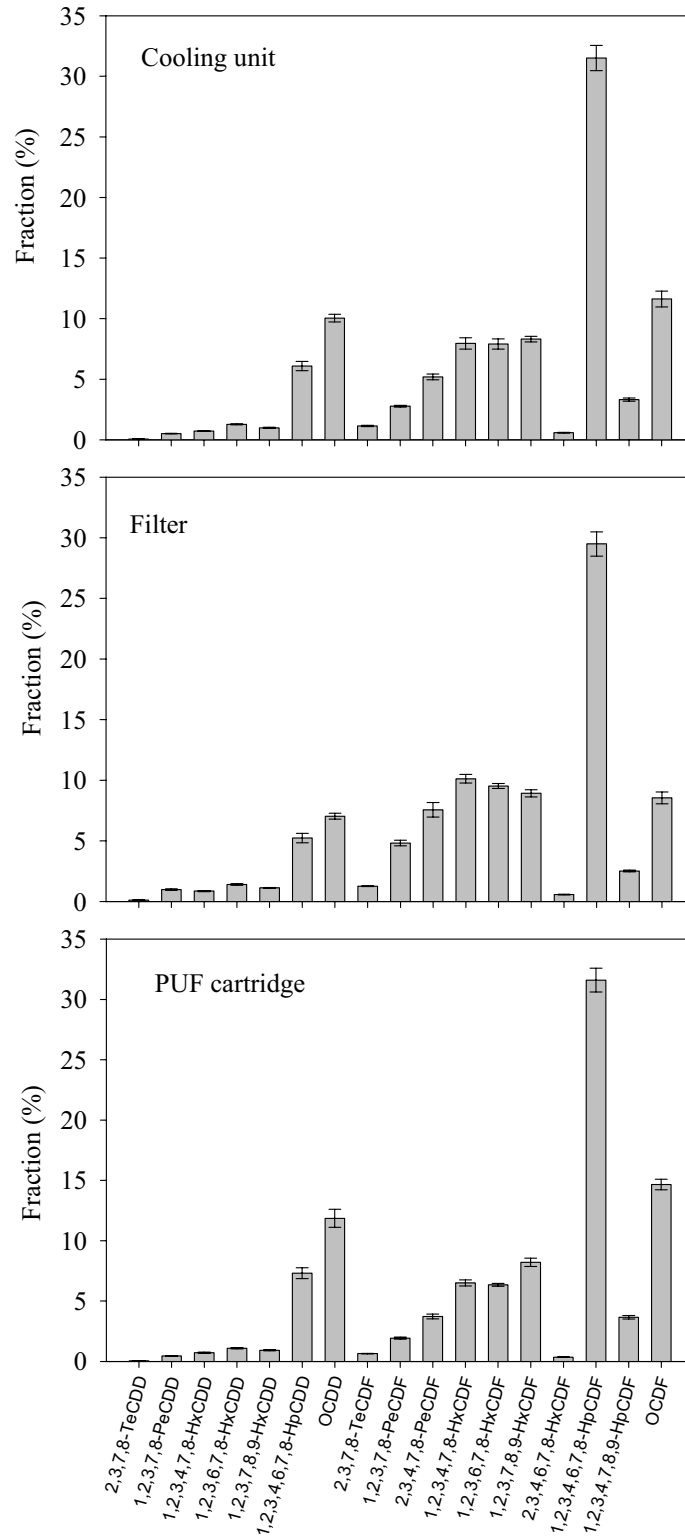


Fig. 4. Congener profiles of PCDD/Fs in the cooling unit, filter and PUF cartridge.

which indicated that OCDD was the most dominant congener in the stack flue gas produced by a Waelz rotary kiln process. Additionally, the relatively higher fractions of the low-chlorinated PCDD/Fs might have resulted from the de novo synthesis, and there is some support for this from the low PCDDs/PCDFs ratios, as mentioned above.

Fate and Mass Distribution of PCDD/Fs in the Thermal Treatment System

The PCDD/Fs and their I-TEQ mass fractions (MFs) in various media in the current thermal treatment are shown in Fig. 5, as calculated based on Eq. (2).

$$MF_i = (M_i / M_0) \times 100\%, \quad i = 1, 2, 3, 4, 5 \quad (2)$$

where M_0 , M_1 , M_2 , M_3 , M_4 and M_5 are the total PCDD/Fs or their I-TEQ mass in (EAF fly ash + cullet), ingot, slag, cooling unit, filter and PUF cartridge, respectively.

With respect to the mass distribution, the MFs of total PCDD/Fs in slag, ingot, cooling unit, filter and PUF cartridge were 1.13, 1.20, 3.96, 0.03 and 1.40%, respectively, while the MFs of total PCDD/F I-TEQ in these media were 0.25, 0.18, 6.63, 0.06 and 1.60%, respectively. These results indicate that the PCDD/F contents and their toxicities in the EAF fly ash were significantly reduced during the thermal treatment, whereas the APCDs still collected a certain mass of total PCDD/Fs and I-TEQs. Thus, the mass distribution in APCDs needed to be further discussed.

In the current study, the total PCDD/F I-TEQ mass escaping from the SCC (M_{sc}) was assumed to be completely collected in the cooling unit, filter and PUF cartridge. M_{sc} was thus equal to $M_3 + M_4 + M_5$. The individual removal efficiency of APCDs for total PCDD/F I-TEQ mass (RE_i , %), i.e. the mass distribution (as listed in Table 4), was then determined by the following equation.

$$RE_i = (M_i / M_{sc}) \times 100\%, \quad i = 3, 4, 5 \quad (3)$$

According to this equation, the individual removal

efficiency of the cooling unit (RE_1), filter (RE_2) and PUF cartridge (RE_3) for total PCDD/F I-TEQ masses were 77.2, 0.755 and 22.1%, respectively. These results indicate that most of the total PCDD/F I-TEQ mass was removed by the cooling unit, and little collected in either the filter or PUF cartridge. As mentioned in the experimental section, less than 3% of PCDD/Fs mass was collected in solution A, while the solution B has the main contribution (> 97%) for the cooling unit. This might be due to the low solubility of the PCDD/Fs in water, which was the major content in solution A. Additionally, the PCDD/F I-TEQ mass was adsorbed or reformed by the de novo synthesis on the inner cooling tube wall and further washed out by *n*-hexane, resulting in the higher contribution (> 97%) in solution B. However, the relatively high PCDD/F I-TEQ mass fraction of the cooling unit again emphasized the importance of APCDs in the current system.

For the overall thermal treatment without the use of APCDs, the PCDD/F masses in ingot, slag, cooling unit, filter, and PUF were all considered as the residual mass output. The PCDD/Fs and their I-TEQ mass destruction removal efficiencies in the treatment without APCDs ($DRE_{W/OAPCD}$) were thus defined by the Eq. (4):

$$\begin{aligned} DRE_{W/OAPCD} (\%) &= [1 - (M_1 + M_2 + M_3 + M_4 + M_5) / M_0] \\ &\quad \times 100\% \\ &= [1 - (MF_1 + MF_2 + MF_3 + MF_4 + MF_5)] \\ &\quad \times 100\% \end{aligned} \quad (4)$$

where M and MF have the same definitions as in the Eq. (2). The $DRE_{W/OAPCD}$ of total PCDD/Fs and their I-TEQ were 92.28% and 91.28%, respectively, indicating that both PCDD/F content and toxicity of the EAF fly ash was significantly reduced by the thermal treatment. However, the PCDD/F I-TEQ concentration emitted from the SCC exceeded the emission limit, which has been discussed in the previous section. Therefore, the PCDD/F.

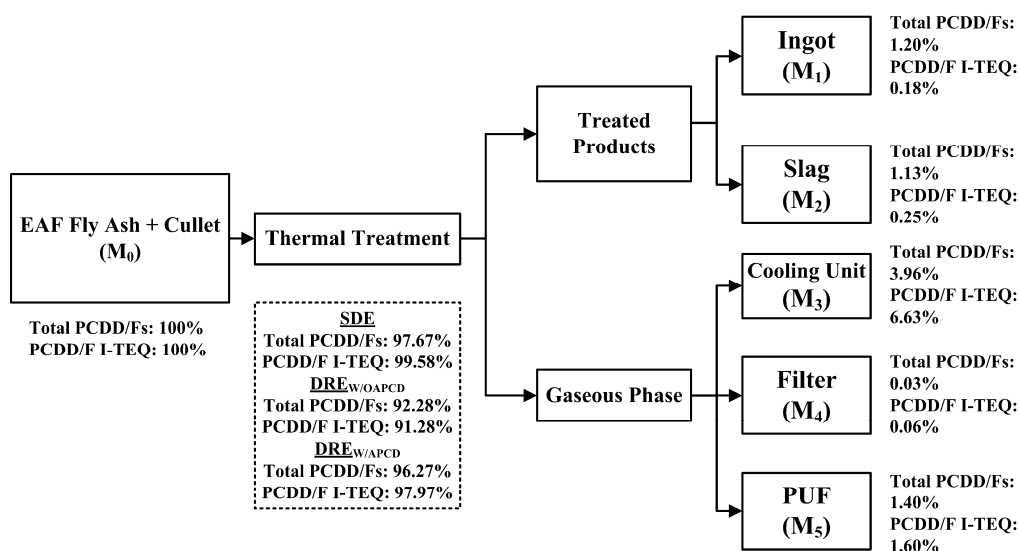


Fig. 5. PCDD/F and their I-TEQ mass fractions in the thermal treatment system.

Table 4. Mass distributions (%) of PCDD/Fs in cooling unit, filter and PUF cartridge.

PCDD/Fs (n = 5)	Cooling unit (%)	Filter (%)	PUF Cartridge (%)	Total (%)
2,3,7,8-TeCDD	79.8	0.991	19.2	100
1,2,3,7,8-PeCDD	75.2	1.08	23.7	100
1,2,3,4,7,8-HxCDD	73.2	0.652	26.1	100
1,2,3,6,7,8-HxCDD	76.3	0.625	23.1	100
1,2,3,7,8,9-HxCDD	74.7	0.635	24.7	100
1,2,3,4,6,7,8-HpCDD	69.9	0.447	29.6	100
OCDD	70.3	0.366	29.3	100
2,3,7,8-TeCDF	82.6	0.681	16.7	100
1,2,3,7,8-PeCDF	79.5	1.02	19.5	100
2,3,4,7,8-PeCDF	79.1	0.856	20.0	100
1,2,3,4,7,8-HxCDF	77.0	0.730	22.2	100
1,2,3,6,7,8-HxCDF	77.4	0.694	22.0	100
1,2,3,7,8,9-HxCDF	73.7	0.588	25.7	100
2,3,4,6,7,8-HxCDF	82.2	0.603	17.2	100
1,2,3,4,6,7,8-HpCDF	73.5	0.512	26.0	100
1,2,3,4,7,8,9-HpCDF	71.7	0.404	27.9	100
OCDF	68.9	0.377	30.7	100
PCDDs	71.0	0.450	28.6	100
PCDFs	74.1	0.572	25.3	100
Total PCDD/Fs	73.5	0.547	26.0	100
PCDDs I-TEQ	74.9	0.808	24.2	100
PCDFs I-TEQ	77.5	0.749	21.8	100
Total I-TEQ	77.2	0.755	22.1	100

and their I-TEQ mass destruction removal efficiencies after the overall treatment with APCDs ($DRE_{W/APCD}$) were thus derived using Eq. (5).

$$DRE_{W/APCD} (\%) = \left[1 - \frac{(M_1 + M_2 + M_5)}{M_0} \right] \times 100\% \quad (5)$$

$$= \left[1 - \frac{(MF_1 + MF_2 + MF_5)}{M_0} \right] \times 100\%$$

In Eq. (5), the PCDD/Fs and their I-TEQ masses in ingot, slag and PUF were considered as the residual mass of emissions, while the PCDD/F masses in APCDs (cooling unit and filter) were considered as removed. Based on Eq. (5), the $DRE_{W/APCD}$ of total PCDD/Fs and PCDD/F I-TEQs were 96.27 and 97.97%, respectively, showing the significant enhancement of PCDD/Fs reduction by installing APCDs in the thermal treatment system.

Consequently, the thermal treatment approach using APCDs presented in the current study has a obvious effect with regard to the destruction of total PCDD/Fs and PCDD/F I-TEQ, and this may result not only the dechlorination of the highly chlorinated congeners, but also the decomposition of aromatic rings in PCDD/Fs. Nevertheless, the recovery of the metals from the EAF fly ash is the key point in this treatment process.

CONCLUSIONS

1. The total PCDD/F I-TEQ in untreated EAF fly ash (1414 ng I-TEQ/kg) was higher than the soil disposal standard in Taiwan (1000 ng I-TEQ/kg), while the figures for the treated product, slag (6.44 ng I-TEQ) and ingot (9.83 ng I-TEQ) were all far below this.
2. The total PCDD/F I-TEQ concentration in the untreated flue gas was 1740 pg I-TEQ/Nm³, which exceeded the

limit for either existing or newly constructed fly ash treatment plants in Taiwan (1000 and 400 pg I-TEQ/Nm³, respectively). Fortunately, this was well below the limits if we also considered the concentration (0.0383 ng I-TEQ/Nm³) in the PUF cartridge for the flue gas treated by APCDs.

3. In the mass balance, the total PCDD/F I-TEQ mass fractions of the products, including slag, ingot, cooling unit, filter and PUF cartridge, were 0.25, 0.18, 6.63, 0.06 and 1.60%, respectively. The cooling unit accounted for the highest contribution of PCDD/F I-TEQ throughout the thermal treatment process presented in this work.
4. The total PCDDs were higher than PCDFs in solid products (PCDDs/PCDFs > 1, precursor condensation dominated), while PCDFs became the major congeners (PCDDs/PCDFs < 1, de novo synthesis dominated) in the gaseous phases.
5. The thermal treatment method presented in this work is an effective technology to decompose PCDD/Fs and recover the metals from the EAF fly ash. The destruction removal efficiencies for the total PCDD/Fs and I-TEQ were 92.3 and 91.0% after vitrification at 1450°C.
6. The thermal treatment method presented in this work not only enhanced the dechlorination of the high-chlorinated congeners, but also decomposed the aromatic rings of PCDD/Fs. Therefore, the above results suggest that a set of simple APCDs is needed to provide an economic EAF fly ash retreatment process that can meet local regulatory standard.

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