Emissions of Polybrominated Diphenyl Ethers during the Thermal Treatment for Electric Arc Furnace Fly Ash

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ABSTRACT

This study investigated the fate of polybrominated diphenyl ethers (PBDEs) in a thermal treatment system that was employed to recover the metals from the electric arc furnace (EAF) fly ash. After 1450°C thermal treatment, the content of PBDEs in the EAF fly ash (50128 ng/kg) was greatly reduced by 98.9%, based on the solid destruction efficiency (SDE). The sums of five PBDE contents in ingot and slag were 86.0 and 32.3 ng/kg, respectively, revealing that the residual PBDE content in slag was much lower than those in woodland (180 and 710 ng/kg) and grassland (440 ng/kg) soils (Harrad and Hunter, 2006). With this PBDE level, the slag can be either safely disposed of in landfills or utilized as construction material. After the 1450°C thermal treatment and 1200°C secondary combustion, 95.8% of the PBDEs were destroyed or removed without air pollution control devices (APCDs). The PBDE concentrations in cooling unit and filter (APCDs) were 8810 and 327 pg/Nm^3, respectively, while that in the PUF cartridges (final emission) was 13009 pg/Nm^3. However, the PBDE concentration of the untreated flue gas was 22.1 ng/Nm^3, which is still higher than that measured in the exhausts from various stationary sources (15.7–46.7 ng/Nm^3) (Wang *et al.*, 2010a, c). Fortunately, the concentration of PBDEs can be effectively reduced to a much lower level (13.0 ng/Nm^3) in the flue gas. In addition, after the Pearson correlation analyses, the logarithm contents of PBDEs and PCDD/Fs showed a statistically high correlation ($r = 0.930$–1.000). Consequently, thermal treatment with APCDs can effectively reduce the PBDEs in EAF fly ash, while the heavy metals can also be recovered.

Keywords: PBDEs; EAF fly ash; Thermal treatment; Emissions.

INTRODUCTION

Electric arc furnace (EAF) fly ash collected in the bag filters has been categorized as hazardous waste owing to its high contents of both heavy metals and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Ward *et al.*, 2002; Lee *et al.*, 2004; Gass *et al.*, 2005; Lee *et al.*, 2005; Li *et al.*, 2007b; Lin *et al.*, 2007; Wang *et al.*, 2008; Wang *et al.*, 2010b). EAFs are one of the important parts in iron/steel smelter plants, and are employed for the recycling of scrap iron and steel. However, because the raw materials in an EAF contain paints, oils and coals, the emissions from such plants, which contain pollutants such as PCDD/Fs, PAHs, heavy metals, have become a main problem, and considerable attention has been focused on controlling and reducing these pollutants (Cetin and Odabasi, 2007, 2008; Odabasi *et al.*, 2009; Wang *et al.*, 2010f; Wu *et al.*, 2010; Chiu *et al.*, 2011; Kuo *et al.*, 2011). Recent studies that investigate emissions of PCDD/Fs from EAF plants have shown that polybrominated diphenyl ethers (PBDEs) are also very important pollutants in the stack flue gases produced by metallurgical processes (Cahill *et al.*, 2007; Choi *et al.*, 2008; Odabasi *et al.*, 2009; Wang *et al.*, 2010e). PBDEs, which are structurally similar to PCDD/Fs, have been extensively used as brominated flame retardants (BFRs) in various fire retarding materials over the past few decades, and are emitted during the steel production process, because ferrous scrap used as raw material always contains impurities like plastic and foam (Alcock *et al.*, 2003; Sinkkonen *et al.*, 2004; Choi *et al.*, 2008).

Our recent studies found that a large amount of PBDEs can be emitted from the stack flue gases of sinter plants, and that they can form during the combustion processes through similar conditions to those required to produce PCDD/Fs (Wang *et al.*, 2010a; Wang *et al.*, 2010b). The results of these earlier works also revealed that metallurgical facilities are not only important sources of PCDD/Fs, but also emit significant amounts of PBDD/Fs and PBDEs. Furthermore,

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most of the PCDD/Fs and PBDEs remaining in the EAF fly ash in the stack flue gas can be captured by bag filters, since the PBDEs in the feeding materials can reform or be incompletely destroyed during the combustion process (Wang *et al*., 2010a; Artha *et al*., 2011).

In Taiwan, EAFs release 170,000 tons of EAF fly ash annually. A dedicated EAF fly ash treatment plant was set up to treat and recover metals via a thermal process in 1999 (Li *et al*., 2007b). Recent studies have examined the PCDD/F contents in the raw materials, output products, stack flue gas, neighboring atmospheric environments and the indoor or outdoor air of workplaces (Li *et al*., 2007b; Yu *et al*., 2010). The results show that the Waelz process had a positive but minor effect in reducing the total PCDD/F mass, while it actually increased the toxicity (total PCDD/F I-TEQ), and thus had adverse effects. Moreover, it is more difficult to decompose the aromatic rings of PCDD/Fs than to dechlorinate from the high-chlorinated congeners to the low-chlorinated ones in Waelz process. Therefore, the low-chlorinated congeners with higher toxicity were accumulated and increased the overall toxicity. (Wang *et al*., 2003; Lee *et al*., 2005; Li *et al*., 2008; Shih *et al*., 2008; Shih *et al*., 2009; Chiu *et al*., 2011; Kuo *et al*., 2011). Searching for new methods to treat EAF fly ash thus becomes essential.

Vitrification has been used to successfully treat the hazardous materials in fly ash, sludge and so on (Li *et al*., 2007a; Chou *et al*., 2009; Kuo *et al*., 2009). There are three kinds of vitrification based on the heat source: electric melting, burner melting and blast melting. While electric melting furnace is an expensive technology, due to the high cost of the equipment and significant energy consumption, they are widely regarded as a clean technology, because they can destroy toxic organics, stabilize heavy metals, and recover useful metals during the melting process (Kuo *et al*., 2004; Yang *et al*., 2008; Wang *et al*., 2009).

PBDEs have been shown to act as the raw materials for forming PBDDs via the bromophenol pathway (Gullett *et al*., 2010; Wang *et al*., 2010a), In addition, similar to PCDD/Fs, PBDEs can also be formed by de novo synthesis and precursor mechanisms during thermal processes (Lenoir *et al*., 1994; Alcock *et al*., 2003; Wang *et al*., 2010a; Wang *et al*., 2010b; Artha *et al*., 2011). Moreover, bromine-chlorine exchange reactions have been shown to occur under various conditions during the forming of PBDDs and PBDEs, such as when fly ash is treated in a municipal waste incinerator at 300°C (Thoma *et al*., 1987; Thoma *et al*., 1987; Zier *et al*., 1991; Luijk *et al*., 1994; Wang *et al*., 2010a; Liu *et al*., 2011). However, the decomposition, formation and transformation of PBDEs without the need for any auxiliary fuels is not well understood, not is the relationship between the PBDEs and PCDD/Fs during the treatment of EAF fly ash. Therefore, in this study a thermal treatment was employed to treat the EAF fly ash. The PBDE contents/concentrations in the process of vitrifying the EAF fly ash were determined, including the raw materials (EAF fly ash and cullet) and products (slag, ingot, cooling unit, filter and PUF cartridge) in the system. The fate of PBDEs was examined with the mass balance calculation, as well as the relationship between PBDEs and PCDD/Fs in the raw materials and products. The results of this study have considerable value with regard to planning new control strategies for EAF fly ash treatment plants.

MATERIALS AND METHODS

Raw Materials

The untreated EAF fly ash used in the current study was collected from an iron manufacturing plants in southern Taiwan. The cullet that was used as the additive for vitrification reaction in the thermal process was obtained by grinding down the waste glass from lab glassware, which was not contaminated by any chemicals. Both the EAF fly ash and cullet powders were sieved out with a 150 μm metallic sieve before the thermal treatment. A specific mass ratio of the EAF fly ash and cullet (7:3), which was recommended by previous studies (Li *et al*., 2003; Li *et al*., 2007a), was utilized to adjust the basicity (CaO/SiO_2 in mass) of the mixture.

Melting System

As shown in Fig. 1, the melting system consisted of (1) a high temperature furnace, (2) a secondary combustion chamber (SCC) and a two-stage air pollution control device (APCD), including (3) a cooling unit for collecting the condensed water containing dissolved PBDEs and a certain amount of dust, (4) a filter for collecting particulate matters, and (5) three glass cartridges plugged with polyurethane foam (PUF) to collect the residual PBDEs in the flue gas. More details of this system have been 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 seconds. The experiments with each were 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 PBDEs.

Analytical Procedures of PBDEs

Both the slag and ingot were ground down to particles around 150 μm in diameter, like the EAF fly ash and cullet. Furthermore, all of the solid-like samples were analyzed following U.S. EPA Method 1614. Samples collected from the cooling unit were divided into two parts. The first one, called solution A, was collected directly using a condenser, and was aqueous solution containing dissolved PBDEs and a certain amount of solid dusts. The mean collected volume of solution part A was 11 mL. The other part was solution B, which was collected by washing the cooling tube with *n*-hexane. Normally, the volume of solution B was 200 mL. Solutions A and B were mixed together, the particulates were filtered out, and the mixture was then shaken for the liquid/liquid extraction and PBDEs analyses. Solution B accounted for the major part (> 96% in mass) of the PBDEs mass collected from the cooling unit. These results were very similar to those obtained in Lee *et al.* (2008).
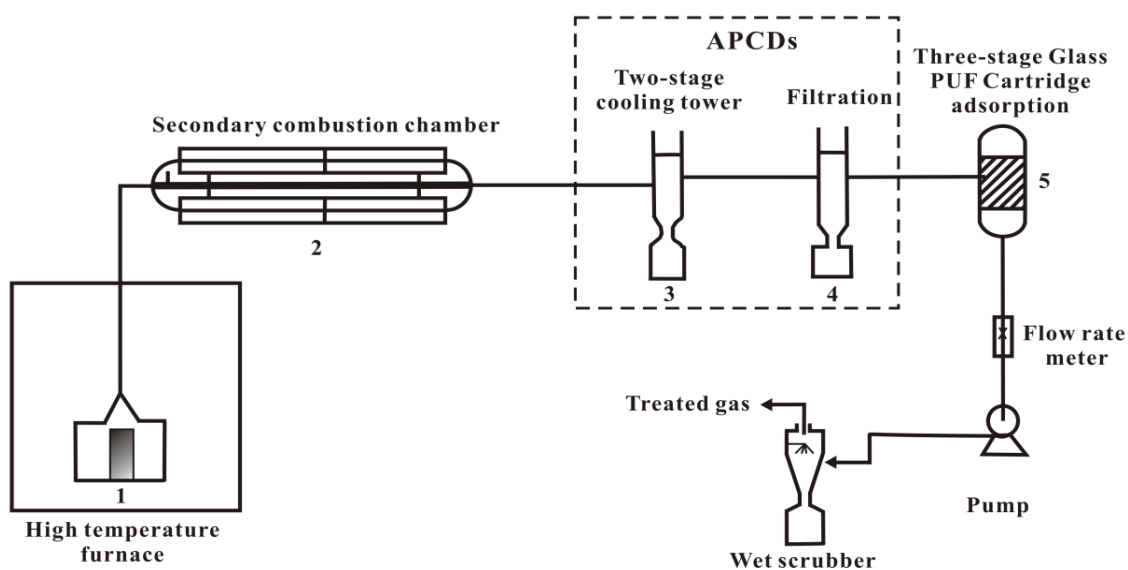
Fig. 1. Sketch of the thermal system.

Instrumental Analysis of PBDEs

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PBDEs analyses. The HRGC (Hewlett-Packard 6970 Series gas chromatograph, CA) was equipped with a DB-5HT capillary column (L = 15 m, i.d. = 0.25 mm, film thickness = 0.1 mm) (J & W Scientific, CA), while the HRMS (Micromass Autospec Ultima, Manchester, UK) had a positive electron impact (EI$^+$) source. The selected ion monitoring (SIM) analyzer mode was used, with a resolving power of 10,000. The electron energy and source temperature were specified at 35eV and 250°C, respectively. More detailed instrumental analysis parameters of the PBDEs are given in our previous works (Chao *et al.*, 2007; Wang *et al.*, 2010a; Wang *et al.*, 2010a; Wang *et al.*, 2010b; Wang *et al.*, 2010c). Details of the quality assurance and quality control (QA/QC) are described in the supporting information, which included field and laboratory blanks, as well as the recoveries of the surrogate and internal standards. The results showed that all the recoveries met the acceptance criteria for PBDEs.

RESULTS AND DISCUSSION

PBDE Contents in EAF Fly Ash and Cullet

This study examined the destruction efficiency, distribution and fate of PBDEs in the thermal treatment of EAF fly ash. The total contents (n = 5) of PBDEs with thirty congeners in the EAF fly ash and cullet were first determined, as shown in Table 1. The contents of individual PBDE congeners in the EAF fly ash were between 3.25 (BDE-156) and 30576 ng/kg (BDE-209), whereas those in cullet were between 0.0125 (BDE-126) and 84.5 ng/kg (BDE-209). The total PBDE contents (n = 5) in EAF fly ash was 50128 ng/kg, which was much higher than that (n = 5) in the cullet (120 ng/kg), indicating that it cannot be directly disposed of into the soil, which was measured at 3550–6620 ng/kg in the preliminary sampling by our research group in Taiwan . In comparison, the Σ_7PBDE (BDE-28, -47, -100, -99, -154, -153, -209) contents in the EAF fly ash (39805 ng/kg) in this study

only accounted for 19.4% (39805/205000) of the dry weight in the bag filter dust of a steel plant (205000 ng/kg) (Cetin and Odabasi, 2007). However, the amount of these seven PBDE congeners was still 47.4 (39805/840) and 2.14 (39805/18600) times that in general suburban and urban soils, respectively (Cetin and Odabasi, 2007). Because there are no solid pollution standards regulated by the Taiwan EPA for PBDEs, the PBDE contents of EAF fly ash has to be compared with those in background soils. When compared to various backgrounds, the sum (9099 ng/kg) of five PBDE contents (BDE-47, -99, -100, -153 and -154) in the EAF fly ash are 20.7, 50.6 and 12.8 times those in grassland soil (440 ng/kg) and woodland soil (180 ng/kg) in the UK, and the woodland soil (710 ng/kg) in Norway, respectively (Jamshidi *et al.*, 2007). Therefore, the EAF fly ash cannot be directly disposed of into the soil.

Wang *et al.* (2010a) reported that the total PBDE contents in the fly ash from two MSWIs fed with 40/60 and 80/20 municipal/industrial waste were 25500 and 332 ng/kg, respectively. In the same study, the total PBDE contents in the bottom ash from those two MSWIs were 186000 and 20400 ng/kg, respectively. Compared with the above results, the PBDE contents in the EAF fly ash collected in the present study was 1.97–151 times those in the MSWI fly ashes, revealing that the fly ash from metallurgical processes contain more PBDEs than those from either normal industrial or municipal waste. The operating temperature of an MSWI ranges from 900 to 950°C, while the EAF was operated at more than 3000°C in the current study. Generally, the higher temperature will help to decompose the PBDE molecules; however, the EAF fly ashes still contained higher amount of PBDEs than that from MSWI (lower temperature) in the current research. This conflicting result could be attributed to there were more PBDE mixtures, including paint, plastic, lubricant and other commercial materials, in the metal crap than in the municipal waste. The PBDEs in such materials could diffuse during the preheating process, and further condense onto the surface of EAF fly ash or be emitted to the atmosphere (Odabasi *et al.*, 2009; Wang *et al.*, 2010c). Nevertheless, the co-fuel, e.g. coal, was reported to be one

Table 1. PBDE contents in the raw materials.

PBDEs (ng/kg)		EAF fly ash (n = 5)			Cullet (n = 5)		
		Ranges	Mean	RSD (%)	Ranges	Mean	RSD (%)
di-	BDE -7	20.1–27.3	24.0	14.1	0.0409–0.0680	0.0532	21.9
	BDE -15	24.4–37.8	30.5	16.4	0.314–0.482	0.397	18.7
tri-	BDE -17	93.7–148.2	120	19.8	0.402–0.722	0.553	25.2
	BDE -28	108–163	130	16.5	0.719–1.22	0.953	21.9
tetra-	BDE -49	320–471	418	14.3	0.572–0.836	0.727	16.0
	BDE -71	49.0–85.2	62.0	23.2	0.159–0.244	0.188	19.0
	BDE -47	1949–3306	2651	20.0	5.80–9.53	7.74	20.1
	BDE -66	238–282	261	7.53	0.556–0.665	0.606	8.25
	BDE -77	34.9–55.3	46.6	18.3	0.0212– 0.0304	0.0258	15.9
penta-	BDE -100	597–689	633	5.65	0.639–0.918	0.768	15.6
	BDE -119	36.8–62.1	51.6	21.4	0.557–0.784	0.695	13.7
	BDE -99	3613–4701	4104	10.3	1.68–2.33	1.99	12.2
	BDE -85	127–188	168	15.2	0.0221–0.0351	0.0286	21.2
	BDE -126	16.3–25.8	22.6	17.7	0.0101–0.0161	0.0125	20.4
hexa-	BDE -154	434–776	633	21.3	0.364–0.553	0.444	17.5
	BDE -153	886–1231	1078	12.3	0.437–0.797	0.584	28.5
	BDE -139	102–141	114	14.2	0.0666–0.0972	0.0818	15.8
	BDE -140	52.6–80.9	72.2	16.2	0.0864–0.125	0.106	16.0
	BDE -138	103–152	121	16.0	0.0885–0.142	0.120	23.4
	BDE -156	2.88–3.64	3.25	8.92	0.0294–0.0487	0.0360	24.3
hepta-	BDE -184	74.0–97.6	84.6	10.9	0.0961–0.155	0.120	19.5
	BDE -183	698–1034	874	14.2	0.952–1.55	1.14	21.6
	BDE -191	61.1–85.6	72.7	12.3	0.230–0.393	0.323	20.4
octa-	BDE -197	475–807	612	24.9	0.582–0.791	0.656	12.0
	BDE -203	478–595	549	10.3	0.823–1.30	0.989	23.0
	BDE -196	453–730	536	20.7	0.763–1.13	1.00	14.5
nona-	BDE -208	1375–1956	1522	16.3	2.97–4.34	3.56	15.9
	BDE -207	2303–3522	2648	19.0	5.01–7.55	5.85	18.3
	BDE -206	1540–2481	1911	18.2	4.34–7.73	6.07	25.2
deca-	BDE -209	22405–37665	30576	20.9	59.5–97.2	84.5	17.7
Total PBDEs		42621–56540	50128	13.0	94.1–135	120	12.9

of the PBDE sources through de novo synthesis and precursor mechanisms on the surface of the EAF fly ash (Artha *et al.*, 2011). With regard to the potential environmental impact, Cetin and Odabasi (2007) showed that the Σ_7PBDE content in the soil around a steel plant was 22000 ng/kg, which is even higher than that in the MSWI fly ash. Once PBDEs, especially BDE-209, contaminate the soil by atmospheric sedimentation, they will be hazardous to humans and the environment for more than 20 years (Sellstrom *et al.*, 2005). Therefore, the PBDEs in the EAF fly ash should be carefully treated.

The PBDE congener profiles for EAF fly ash and cullet are illustrated given Fig. 2. Each selected congener was normalized by dividing its content by the summation of the thirty congeners. The PBDE congener profiles in EAF fly ash and cullet were similar to those in the fly ash and bottom ash of MSWIs (Wang *et al.*, 2010a; Artha *et al.*, 2011). The most dominant PBDE congeners in EAF fly ash and cullet were highly brominated substituted congeners, including BDE-209, BDE-206, BDE-207 and BDE-208. The contents of the three major commercial PBDEs in the global market (*penta-*, *octa-* and *deca-*BDE) were 4979, 1697 and 30576 ng/kg in the EAF fly ash, accounting for 9.93, 3.39 and 61.0% of the total 30 PBDEs in mass, respectively. Therefore, the commercial PBDEs, especially *deca-*BDE, account for a

large part of the total PBDE contents in EAF fly ash. Among the lower brominated-substituted congeners, BDE-47 and BDE-99 were more abundant than the others. Moreover, the PBDE congener profiles obtained in this study were also close to those collected by an electronics recycling facility in a computer laboratory, and inside and outside a dismantling hall (Cahill *et al.*, 2007). Therefore, it can be concluded that most of the PBDE in EAF fly ash comes from the commercial mixtures in the raw metal scraps.

PBDE Contents in Ingot and Slag

Ingot and slag were the two major products after the thermal treatment in this study. The total PBDE contents (n = 5) in ingot and slag after the thermal treatment at 1450°C were 1296 and 386 ng/kg, respectively, as shown in Table 2. The amount of PBDE congeners in ingot ranged from 0.0987 (BDE-126) to 990 ng/kg (BDE-209), while that in slag ranged from 0.0767 (BDE-126) to 276 ng/kg (BDE-209). In comparison, the total PBDE contents in ingot and slag were much lower than those in untreated EAF fly ash (50128 ng/kg), revealing that the 1450°C thermal treatment could significantly reduce the amount of PBDEs in EAF fly ash. To examine the efficiency of reducing PBDEs with a high temperature furnace, the solid destruction efficiency (SDE) was defined, as shown in Eq. (1), below.
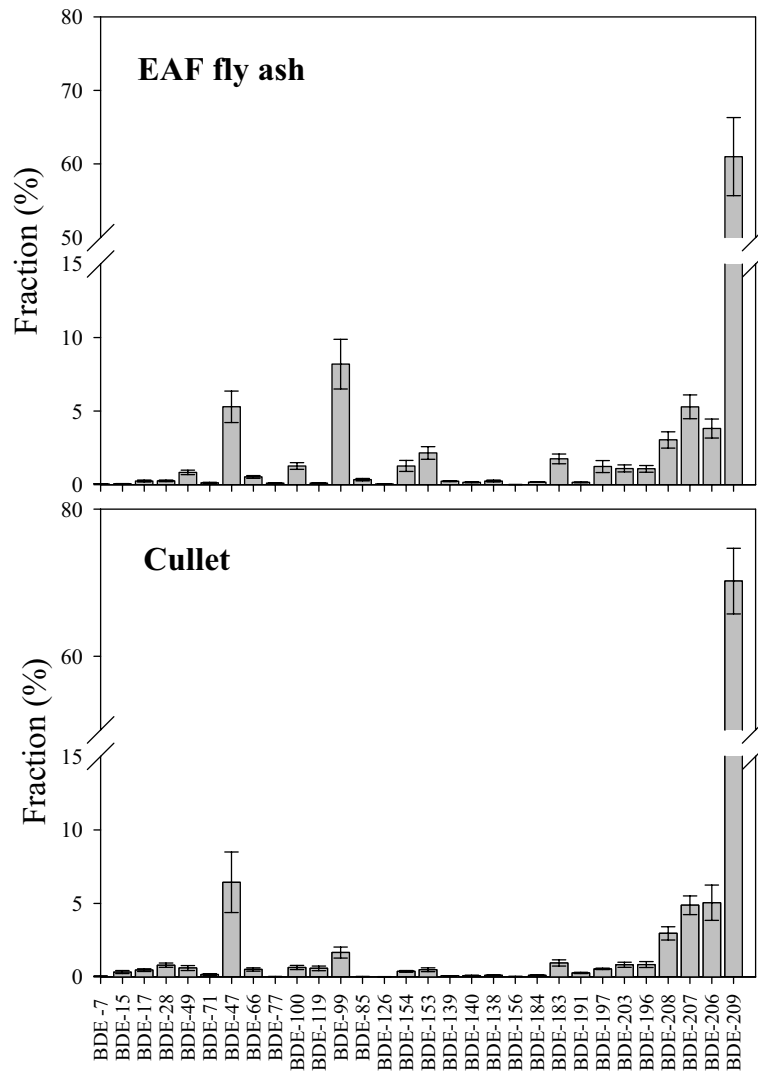
Fig. 2. Congener profiles of PBDEs in the EAFs fly ash and cullet.

$$SDE\ (\%) = [1 - (M_1 + M_2/M_0] \times 100\% \tag{1}$$

where M_1 and M_2 are the total PBDE masses in ingot and slag, respectively; and M_0 is the sum of total PBDE masses in both untreated EAF fly ash and cullet. The PBDE masses in the media (EAF fly ash, cullet, ingot and slag) were calculated based on their masses and the PBDE contents. The SDE of total PBDEs was 98.9%, while those of the individual 30 congeners ranged from 94.2% (BDE-119) to 99.9% (BDE-85). These results indicate that most of PBDEs in solid products were eliminated.

In order to further dispose of the slag produced from the EAF fly ash thermal treatment, the PBDE contents need to be compared with the background soils, although there are no regulations of this in Taiwan. The total amount of PBDE remaining in the slag was 386 ng/kg, much lower than that measured in the suburban soil in southern Taiwan (3550–6620 ng/kg). For the commercial Σ_7PBDEs (BDE-28, -47, -100, -99, -154, -153, -209), the amount remaining in the slag was 310 ng/kg, significantly lower than the amount in both suburban soil (840 ng/kg) and urban soils (18600 ng/kg) reported by Cetin and Odabasi (2007). Nevertheless, as noted

previously, the sum of the five residual PBDEs (32.31 ng/kg) in the slag produced in the present study was also less than in the natural ground soil (grassland: 440 ng/kg in UK; woodland: 180 ng/kg in UK; woodland: 710 ng/kg in Norway) (Harrad and Hunter, 2006). This indicates that the slag produced by the thermal treatment could be directly disposed of in a landfill or reused as a raw material in manufacturing without serious risk. Additionally, the sum of the five PBDEs (BDE-47, -99, -100, -153 and -154) in ingot was 86 ng/kg, less than in the background soils. Therefore, the thermal treatment that was used to recover the metals, e.g. zinc or iron, produces a low level of PBDE emissions.

The congener profiles of PBDEs in ingot and slag are shown in Fig. 3. The highly brominated-substituted PBDEs (BDE-209, -206, -207 and -208) were the major congeners in ingot and slag. These four congeners are also the major components in commercial *nona*- and *deca*-BDE flame retarding materials, and were commonly survive combustion (Wang *et al.*, 2010a). Additionally, the high BDE-209 content found in our results might be due to the combustion reaction, since PBDEs and PBDD/Fs formed by combustion processes prefer highly brominated congeners (Wang *et al.*, 2010c).

Table 2. PBDE contents in ingot and slag.

PBDEs (ng/kg)		Ingot (n = 5)			Slag (n = 5)		
		Ranges	Mean	RSD (%)	Ranges	Mean	RSD (%)
di-	BDE -7	0.328–0.422	0.377	9.24	0.191–0.335	0.245	24.6
	BDE -15	1.55–2.36	1.92	19.4	1.39–2.04	1.82	14.7
tri-	BDE -17	1.19–2.09	1.52	23.3	0.896–1.34	1.17	15.4
	BDE -28	1.29–1.78	1.50	12.4	1.81–2.81	2.18	17.3
tetra-	BDE -49	2.59–3.60	3.18	14.1	1.83–3.13	2.24	24.1
	BDE -71	1.09–1.77	1.49	19.0	0.709–1.00	0.846	14.2
	BDE -47	30.6–39.9	36.5	10.6	14.1–21.9	8.60	21.9
	BDE -66	2.46–3.90	3.35	17.5	2.34–3.29	2.88	15.3
	BDE -77	0.155–0.251	0.196	22.4	0.112–0.143	0.132	9.18
penta-	BDE -100	6.59–10.83	9.18	18.8	0.852–1.45	1.14	24.7
	BDE -119	3.78–5.80	4.95	18.3	2.63–4.11	3.25	18.5
	BDE -99	25.8–40.0	31.2	16.9	6.50–10.5	18.6	17.4
	BDE -85	0.202–0.292	0.252	14.9	0.150–0.192	0.174	10.3
	BDE -126	0.0724–0.126	0.0987	19.4	0.0657–0.0830	0.0767	8.79
hexa-	BDE -154	3.40–6.19	4.26	26.8	0.762–1.31	1.10	21.0
	BDE -153	3.74–5.50	4.88	14.6	2.61–3.52	2.87	13.1
	BDE -139	0.476–0.673	0.546	15.3	0.330–0.491	0.404	18.0
	BDE -140	0.709–1.07	0.897	18.0	0.486–0.695	0.624	13.3
	BDE -138	0.809–1.19	1.01	16.5	0.476–0.771	0.639	19.0
	BDE -156	0.265–0.342	0.295	10.6	0.164–0.219	0.190	11.4
hepta-	BDE -184	0.666–1.11	0.791	22.9	0.473–0.720	0.641	17.4
	BDE -183	6.95–11.3	8.40	20.4	5.32–7.62	6.33	16.0
	BDE -191	1.873–.07	2.62	20.0	1.26–1.94	1.55	18.0
octa-	BDE -197	4.45–6.27	5.15	14.6	3.01–3.52	3.18	7.12
	BDE -203	8.43–13.1	10.9	16.9	4.27–6.34	5.73	15.2
	BDE -196	7.68–9.73	8.61	10.7	4.22–5.74	4.82	12.7
nona-	BDE -208	20.8–34.2	26.4	21.1	5.81–8.95	7.42	16.2
	BDE -207	45.8–79.8	61.7	20.7	8.77–12.5	10.6	15.6
	BDE -206	61.8–85.9	74.2	13.2	17.0–25.0	20.2	17.0
deca-	BDE -209	775–1171	990	17.8	211–354	276	23.1
Total PBDEs		1090–1478	1296	13.7	323–456	386	15.1

On the other hand, BDE-47 and BDE-99 had relatively high mass ratios among the low brominated-substituted congeners. In comparison, the PBDE congener profiles of both ingot and slag were similar to those in the EAF fly ash. The higher fractions of high brominated PBDEs might be due to the incomplete destruction of commercial PBDE mixtures, even when the operating temperature was as high as 1450°C. Additionally, the low brominated congeners could be formed from the destruction of the high brominated ones, the de novo synthesis and the precursor condensation on the surface of the EAF fly ash (Artha *et al*., 2011). Notably, the BDE-47/BDE-99 mass ratio in slag and EAF fly ash were both smaller than one, and were 0.462 (8.6/1.86, Table 2) and 0.646 (2651/4104, Table 1), respectively. These ratios reveal that the more volatile low brominated-substituted congener tends to evaporate into a gaseous phase, whereas the higher brominated-substituted congener tends to stay in the solid phase, which is also found in the previous research (Hassanin *et al*., 2004; Harrad *et al*., 2006).

PBDE Concentrations in Cooling Unit, Filter and PUF Cartridge

The thermal treatment system for EAF fly ash using a high temperature furnace produced two products, the solid and gaseous dominant phases. Even though most of the PBDEs in the EAF fly ash were decomposed or removed during the thermal process, and more valuable products were produced with a lower toxicity (i.e. ingot and slag), the potential of PBDE pollution in the flue gas still needed to be determined to avoid secondary pollution. Therefore, a secondary combustion chamber (SCC) was installed after the high temperature furnace, and this further destroyed the PBDEs and their precursors at 1200°C. Additionally, the surviving PBDEs remaining from the SCC were collected in the air pollution control devices (APCDs,), namely a cooling unit and filter. Finally, the PBDEs in the APCDs were 100% captured in the PUF cartridge.

The PBDE concentrations in the cooling unit, filter and PUF cartridge are listed in Table 3. The total PBDE concentrations (n = 5) in each APCD and PUF cartridge were 8810, 327 and 13009 pg/Nm^3, respectively. The table also shows that the concentration of individual 30 PBDE congeners ranged from 0.0682 to 5778 pg/Nm^3 in the cooling unit, 0.0722–240 pg/Nm^3 in the filter and 0.0697–12211 pg/Nm^3 in the PUF cartridge. The sum of the PBDE concentrations in the cooling unit, filter and PUF cartridge was 22146 pg/Nm^3, and this was determined as the total amount of PBDEs in the untreated flue gas leaving the SCC, whereas that in the PUF cartridge represented the PBDE levels in the flue gas treated by the cooling unit and filter.
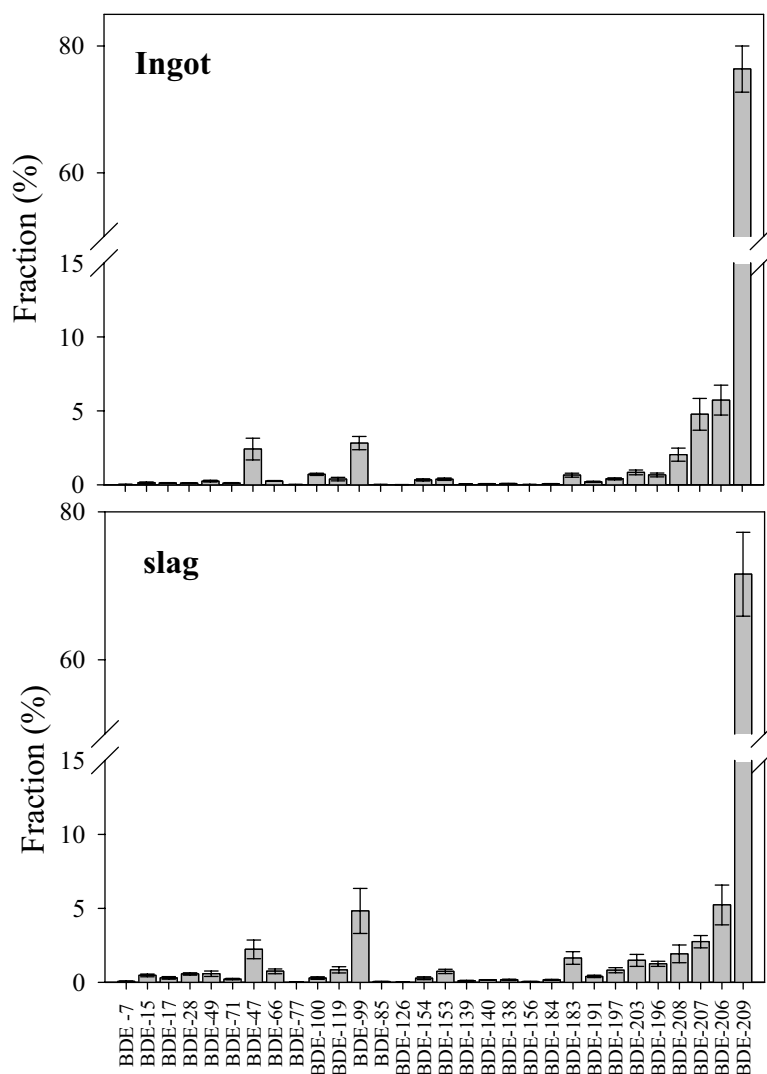
Fig. 3. Congener profiles of PBDEs in the slag and ingot.

Since there are still no PBDE emissions standards in Taiwan, the emission levels in the flue gas were thus compared with the atmospheric or emission results in previous studies. The total PBDE concentrations in the flue gas of EAFs, EAF fly ash treatment plant (Waelz process), sinter plant (Wang *et al.*, 2010c), secondary smelters, coal power plant, unleaded gas-fueled vehicles, diesel-fueled vehicles, wood chips boiler (Wang *et al.*, 2010b) and MSWI (Wang *et al.*, 2010a) are 15.7, 15.7, 35.2, 45.0, 33.5, 16.8, 46.7, 29.1 and 26.1 ng/Nm^3, respectively. The results show that the total PBDE concentration in the untreated flue gas in this study (22.1 ng/Nm^3) was still higher than those in EAFs and EAF fly ash treatment plants, but lower than the other plants listed above. Moreover, the PBDE concentration in the PUF cartridge (13.0 ng/Nm^3), which is considered as being from the treated emissions, was much lower than those in all of the eight sources given above, even though they are employed APCDs (e.g., a bag filter and activated carbon injection system) to treat the stack flue gas. Therefore, the thermal treatment with APCDs in the present work avoided secondary pollution in the flue gas.

The PBDE congener profiles in the cooling unit, filter and PUF cartridge are shown in Fig. 4. The highest four brominated-substituted congeners, BDE-209, -206, 207 and 208, were the major species in all three APCDs, indicating incomplete combustion of the PBDE flame retardant. On the other hand, the mass fractions of the low brominated-substituted congeners were decreased significantly from the cooling unit to the filter and PUF cartridge. This might be due to the PBDEs reformation through the de novo synthesis and precursor mechanisms. Artha *et al.* (2011) focused on the PBDE formation mechanisms in combustion reactions, and found two temperature ranges (400°C and 650–850°C) in which PBDEs reformation took place. The cooling unit used in the present study contained a two-stage cooling tube, and this could effectively reduce the flue temperature into the ranges at which reformation could take place. The high temperature flue gas with the residual PBDEs, aromatic hydrocarbon and their precursors first left from the 1200°C SCC and entered the cooling unit. Furthermore, enormous amounts of key brominated aromatic precursors for PBDEs were formed in the higher-temperature region (about 750°C), and subsequently condensed or adsorbed onto the surface of the fly ash during the cooling down to 400°C, and thus the

Table 3. PBDE concentrations in the flue gas collected in cooling unit, filter, and PUF cartridge.

PBDEs (pg/Nm³)		Cooling unit (n = 5)		Filter (n = 5)		PUF cartridge (n = 5)	
		Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)
di-	BDE -7	26.5	17.4	0.257	19.6	1.24	20.5
	BDE -15	196	15.0	0.458	13.1	17.0	22.5
tri-	BDE -17	92.6	22.9	1.09	23.7	2.49	20.1
	BDE -28	140	16.9	1.01	12.0	4.81	13.5
tetra-	BDE -49	84.9	23.3	0.776	18.2	0.964	16.2
	BDE -71	7.28	12.9	0.841	15.7	1.00	22.4
	BDE -47	550	21.0	6.50	19.4	28.3	20.1
	BDE -66	50.8	14.4	0.702	14.6	1.59	13.7
	BDE -77	4.30	22.2	0.141	16.2	0.137	13.2
penta-	BDE -100	75.2	6.89	1.17	22.6	1.25	12.8
	BDE -119	11.5	20.8	3.65	11.0	3.31	18.6
	BDE -99	277	23.2	9.99	20.3	11.2	6.58
	BDE -85	7.33	16.0	0.150	23.3	0.171	17.4
	BDE -126	0.0682	7.85	0.0722	7.78	0.0697	10.8
hexa-	BDE -154	32.6	17.1	1.02	16.0	1.27	8.67
	BDE -153	72.9	10.6	3.11	19.5	3.31	15.1
	BDE -139	0.390	18.7	0.411	12.2	0.415	10.4
	BDE -140	0.591	16.8	0.575	16.9	0.587	17.0
	BDE -138	3.53	13.6	0.647	20.7	0.643	12.3
	BDE -156	0.198	17.3	0.180	16.6	0.199	19.5
hepta-	BDE -184	0.659	17.7	0.659	17.6	0.678	13.9
	BDE -183	69.1	22.6	5.56	18.6	6.89	13.0
	BDE -191	1.50	11.1	1.76	19.4	1.78	19.9
octa-	BDE -197	39.8	15.8	4.02	18.5	3.76	13.1
	BDE -203	68.0	12.8	2.79	19.5	9.19	18.9
	BDE -196	44.2	23.2	1.85	14.7	10.1	21.4
nona-	BDE -208	270	22.3	7.49	8.23	125	7.55
	BDE -207	325	11.8	10.6	17.8	174	23.1
	BDE -206	579	17.7	19.3	17.6	387	21.0
deca-	BDE -209	5778	16.7	240	17.5	12211	6.59
Total PBDEs		8810	10.8	327	13.5	13009	5.88

low brominated-substituted PBDE reformed. Furthermore, the amount of low brominated-substituted congeners decreased from the cooling unit to the filter, and this may be due to the rapidly decreasing temperature. Finally, very little reformation of PBDEs was found when the temperature decreased to much less than 300°C, based on the low mass fraction of the low-brominated PBDEs found in the PUF cartridges.

The PBDE congener profiles in the cooling unit, filter and PUF cartridge were compared with those in the stack flue gases (Wang *et al.*, 2010a; Wang *et al.*, 2010b; Wang *et al.*, 2010c). First of all, the congener profile in the cooling unit was very close to those in both carbon steel and stainless steel EAFs of metallurgical facilities, secondary smelter plants and EAF fly ash treatment plants employing the Waelz process. Additionally, the PBDE congener profile in the filter was similar to those in MSWI and coal power plants. Nevertheless, the individual PBDE congeners had very similar distributions in the PUF cartridges, wood chip boilers, unleaded gas-fueled vehicles and diesel-fueled vehicle emissions. These results further indicate that the PBDEs tend to be reformed by both de novo synthesis in the low temperature flue gas and precursor condensation on the surface of fly ash, whereas that the congeners in the PUF cartridge do not show any potential for (low-brominated) PBDE reformation. However,

the total PBDE emissions from a thermal treatment system equipped with a cooling unit and filter (13.0 ng/Nm³) could be lower than those from a stationary plant, although the PBDEs might be reformed in the APCDs.

Fate and Mass Distribution of PBDEs in the Thermal Treatment System

The PBDE mass fractions (MFs) in various media in the current thermal treatment were calculated by Eq. (2) and shown in Fig. 5.

$$MF_i = (M_1/M_0) \times 100\%, \qquad i = 1, 2, 3, 4, 5 \qquad (2)$$

where M_0, M_1, M_2, M_3, M_4 and M_5 are the total PBDE masses in the (EAF fly ash + cullet), ingot, slag, cooling unit, filter and PUF cartridge, respectively.

Based on the mass distributions, the MFs of total PBDE masses in the ingot, slag, cooling unit, filter and PUF cartridge were 0.66, 0.42, 1.23, 0.05 and 1.81%, respectively. These results revealed that the PBDE contents of the EAF fly ash were significantly reduced during the thermal treatment. However, the APCDs still collected some mass of total PBDEs, and this also needs to be discussed.

In the current thermal treatment system, the total PBDE mass emitted from the SCC (M_{SCC}) was assumed to be
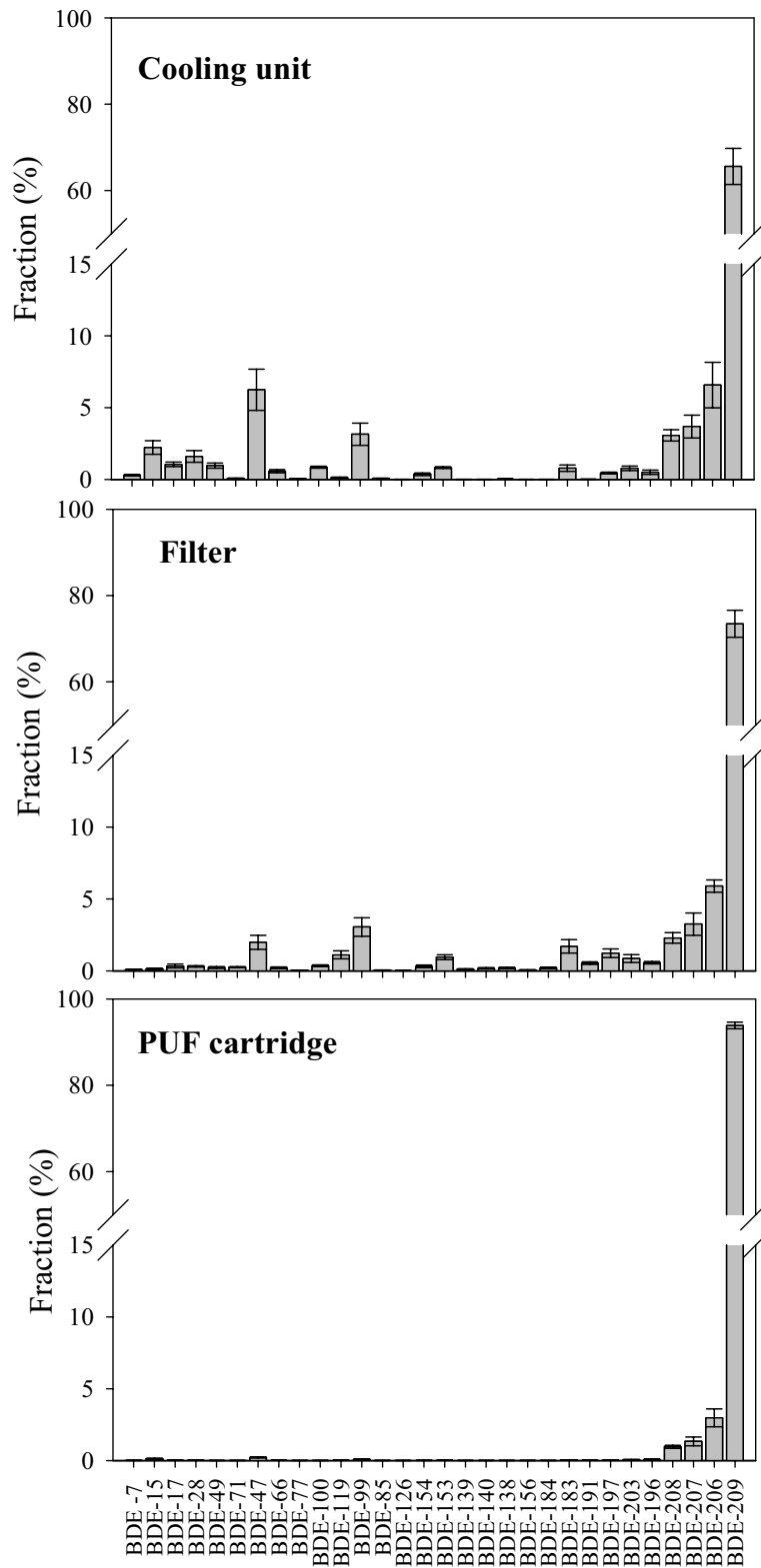
Fig. 4. Congener profiles of PBDEs in the cooling unit, filter and PUF cartridge.

completely captured by the cooling unit, filter and PUF cartridge. M_{SCC} was thus equal to the sum of M_3, M_4 and M_5. The total PBDE mass distributions (MD_i, %) of individual APCDs were then determined by Eq. (3) and are further illustrated in Fig. 6.

$$MD_i = (M_i / M_{SCC}) \times 100\%, \qquad i = 3, 4, 5 \qquad (3)$$

where M_3, M_4, M_5 and M_{SCC} have the same definitions as above. Based on the Eq. (3), the PBDE masses was distributed at 39.8, 1.48 and 58.7% into the cooling unit (MD_1), filter
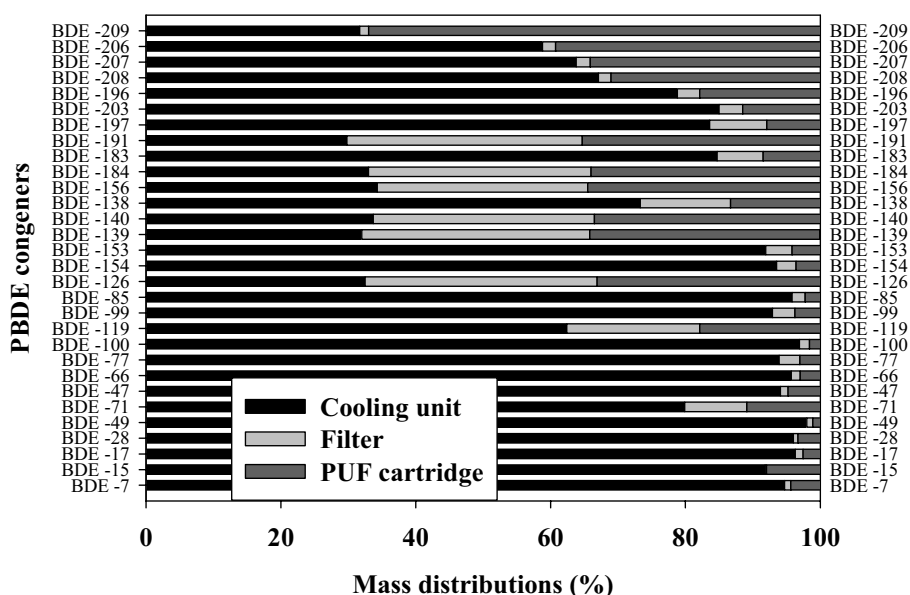
Fig. 5. Mass fractions of PBDEs in the cooling unit, filter and PUF cartridge.
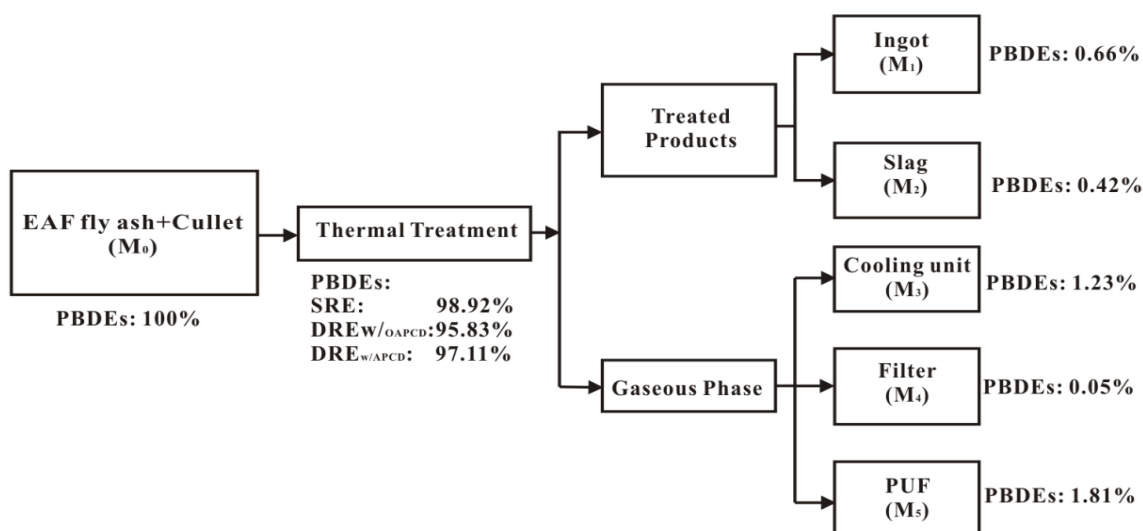
Fig. 6. PBDE mass fractions in the thermal treatment system.

(MD_2) and PUF cartridge (MD_3), respectively. Specifically, the low-brominated substituted PBDEs were highly distributed in the cooling unit instead of in the filter or PUF. However, the total PBDE mass in the PUF cartridge was 1.47 times (5.87/3.98) that in the cooling unit, while the main contributive species is BDE-209. The low brominated PBDEs are the main group in the cooling unit (MD_1 region), whereas the high brominated PBDEs are the dominant species in the PUF cartridge (MD_3 region). These results could be attributed to that the fact that the lower brominated-substituted congeners were formed by the de novo synthesis and precursor mechanisms in the cooling unit, which covered the whole reaction temperature range (400°C and 650–850°C) for PBDE reformation. In the cooling unit, some of the low brominated congeners were dissolved and suspended in the cooling liquid, while the some of them were adsorbed on the inner cooling tube wall and further washed out by *n*-hexane. Moreover,

the highly brominated-substituted congeners could be emitted directly to the filter and finally collected by the PUF cartridge, because these have very low solubility in water. Nevertheless, the de novo synthesis and precursor mechanisms were not effective in the PUF cartridge, since the conditions were assumed to have cooled down to approximately 4°C after the cooling unit. The highly brominated-substituted congeners thus dominated the PBDEs in the PUF cartridge. Therefore, the above results emphasize the importance of APCDs, especially for the more toxic low brominated PBDEs in the present thermal treatment system.

To evaluate the overall reduction of PDBEs in the thermal treatment, the PBDE masses in ingot, slag, cooling unit, filter, and PUF cartridge were considered as the residual output masses. The PBDE mass destruction removal efficiencies (DRE) of this thermal treatment without APCDs ($DRE_{W/O}$) were thus defined by the following equation:

$$DRE_{W/O}\,(\%) = [1 - (M_1 + M_2 + M_3 + M_4 + M_5)/M_0] \times 100\%$$
$$= [1 - (MF_1 + MF_2 + MF_3 + MF_4 + MF_5)] \times 100\%$$
(4)

where M and MF have the same definitions as in Eq. (2). According to the above definition, the $DRE_{W/O}$ of the total PBDEs was 95.8%, while the individual congeners presented a range from 90.9% (BDE-7) to 99.6% (BDE-139), although BDE-15 was 46.6%. Moreover, the low brominated-substituted PBDE congeners had lower $DRE_{W/O}$ values than the highly brominated ones. This might be due to the reformation process, as discussed previously. Generally, the PBDEs in the EAF fly ash were significantly decomposed by the thermal treatment; however, the PBDE concentrations emitted from the SCC were still higher than those for the EAFs and EAF fly ash treatment plants (Waelz process). In order to reduce the PBDE emission concentrations, APCDs (cooling unit and filter) were installed. Furthermore, the PBDE mass DREs of the overall treatment with APCDs were defined by Eq. (5), as follows:

$$DRE_W\,(\%) = [1 - (M_1 + M_2 + M_3)/M_0] \times 100\%$$
$$= [1 - (MF_1 + MF_2 + MF_3)] \times 100\%$$
(5)

where M and MF had the same definitions as in Eq. (2). The PBDE masses in ingot, slag and PUF are taken as the residual mass of emissions, while the PBDE masses in the APCDs (cooling unit and filter) are considered as being removed. Based on Eq. (5), the DRE_W of total PBDEs was 97.1%; meanwhile, those of individual PBDE congeners were in the range of 91.3% (BDE-15) to 99.9% (BDE-85), meaning that there was a greater reduction in PBDEs after installing the APCDs.

Consequently, the thermal treatment with APCDs undertaken in the current study has significant effects in reducing most of the PBDEs congeners. The low toxic recovery of metals from EAF fly ash is a key attraction of the thermal treatment process presented in this work, and similar results were reported in a previous study that focused on the thermal treatment process for decomposing the PCDD/F contents in EAF fly ash (Lin *et al.*, 2011).

Relationship between PBDE Contents and PCDD/F or their I-TEQ Contents

PBDEs and PCDD/Fs have been reported to be the major two persistent organic pollutant (POP) emissions in flue gases from various sources, such as MSWI plants, sinter plants, EAF fly ash treatment plants (Waelz process), secondary smelter plants, power plants and so on. Additionally, the formation mechanism of these POPs are very similar, and might occur in similar emissions (Odabasi *et al.*, 2009; Wang *et al.*, 2010a; Wang *et al.*, 2010b; Wang *et al.*, 2010d; Wang *et al.*, 2010f; Hsieh *et al.*, 2011). In order to evaluate the correlation between PBDEs and PCDD/Fs or their I-TEQ contents in this thermal treatment system, the ratios between PBDEs and PCDD/Fs or their I-TEQ contents were analyzed, including PBDEs/(PCDD/Fs), PBDEs/(PCDD/F I-TEQ), log PBDEs/(log PCDD/Fs) and log PBDEs/(log PCDD/F I-TEQ) (as shown in Fig. 7). The contents and concentrations of PCDD/Fs and their I-TEQ in the EAF fly ash, cullet, ingot, slag, cooling unit, filter and PUF cartridge were measured at same

conditions that the PBDEs were also determined (as listed in Table 4). Fig. 7 shows that the logarithms of total PBDE contents were statistically highly correlated with the logarithms of total PCDD/Fs. This might be due to the similar formation (de novo synthesis and precursor condensations) and destruction (debromination/dechloridation) mechanisms of PBDEs and PCDD/Fs in the thermal treatment process presented in this work.

Pearson correlation was also employed to analyze the statistical relationships among PBDE, PCDD/Fs and PCDD/F I-TEQ. The resulting correlation *r* values of total PBDE contents in the raw materials, solid products and gaseous phase with those of total PCDD/Fs and PCDD/F I-TEQ were 1.000 and 0.998, respectively. Moreover, the *r* values of total log PBDEs in the raw materials, solid products and gaseous phase with those of total log PCDD/Fs and log PCDD/F I-TEQ were 0.972 and 0.930, respectively. These results support the previous finding that the total PBDE contents were statistically highly correlated with those of total PCDD/Fs or total PCDD/F I-TEQ, and these results remained the same after using logarithm transformations.

Since a linear correlation has been found between the log PBDE and log PCDD/F contents, the ratio of log PBDEs/(log PCDD/Fs) could be used to evaluate the emissions from one to another (PBDEs and PCDD/Fs) in an emission source to reduce the monitoring cost or increase the accuracy.
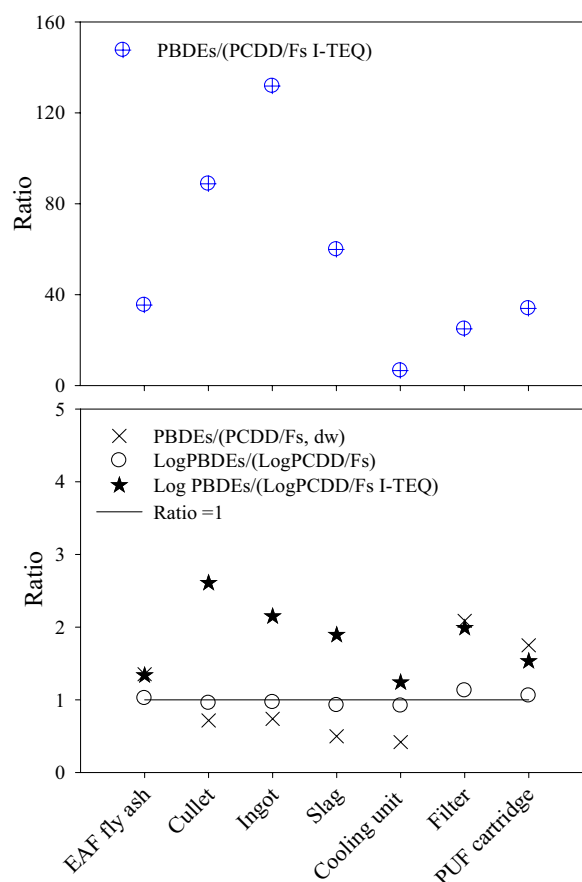

Fig. 7. The relationships between the PBDEs and PCDD/Fs or I-TEQs of the raw materials, solid products and gaseous phase.

Table 4. The mass of PBDEs, PCDD/Fs and PCDD/Fs I-TEQ in various media.

Emissions, pg	EAF fly ash	Cullet	Ingot	Slag	Cooling unit	Filter	PUF cartridge
PBDEs	1406595	1447	9240	5846	17298	642	25542
PCDD/Fs	1040231	2021	12508	11734	41286	308	14591
PCDD/Fs I-TEQ	39682	16.3	70.1	97.7	2632	25.8	753

CONCLUSIONS

1. The total PBDE content in EAF fly ash was 50128 ng/kg, which was much higher than in the previous studies. Fortunately, the five PBDE contents (BDE-47, -99, -100, -153 and -154) in ingot (86.0 ng/kg) and slag (32.3 ng/kg) were much less than those in the background soils (440 ng/kg in woodland soils and 180 ng/kg grassland soils in UK; 710 ng/kg in woodland soils in Norway) after the thermal treatment.

2. The total PBDE concentration in the untreated flue gas was 22146 pg/Nm^3, which was still higher than that measured from EAF fly ash treatment plants (15.7 ng/kg) and sinter plants (15.7 ng/kg). Fortunately, the concentration in the PUF cartridge was reduced to 13009 pg/Nm^3 when APCDs were installed. It was much lower than the content in all the other plants.

3. With regard to the mass balance, the total PBDE mass fractions of the ingot, slag, cooling unit, filter and PUF cartridge were 0.66, 0.42, 1.23, 0.05 and 1.81%, respectively. The reformation of PBDE congeners was found in the cooling unit through de novo synthesis and precursor condensation.

4. The overall destruction removal efficiency of the total PBDEs was 97.1 or 95.8%, depending on whether the APCDs were installed or not. All the results indicate that the thermal treatment process presented in this work is effective in reducing the PBDEs and recovering metals from the EAF fly ash.

5. The results of the mass ratio and Pearson correlation analyses suggest that the ratio of log PBDEs/(log PCDD/Fs) could be used to evaluate the emissions from one to the other (PCDD/Fs and PBDEs) from the emission sources.

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