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Distribution of Polybrominated Diphenyl Ethers (PBDEs) in a Fly Ash Treatment Plant

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ABSTRACT

PBDES are used as the flame retardants and have adverse effects on human health. Electric arc furnaces (EAF) are one of major emission source of PBDEs. The PBDE contents in the fly ashes of an EAF (29.3 ng/g) examined in this study were one to three orders higher than those in environmental soils. EAF fly ash treatment plants are established to resolve the disposal of this material, and also to recover the remaining iron or zinc from it. However, very little is known about the fate of PBDEs in EAF fly ash treatment plants. The EAF fly ash treatment plant investigated in this work can be divided into three sub-systems, including a pelletizer, reducing furnace and submerged arc furnace (SAF). The fly ash generated from the pelletizer process exhibited the highest PBDE content (7.69 ng/g), and contributed about 91% of the total PBDE inputs (4.40 g/day). The total PBDE concentrations in the stack flue gases of the pelletizer, reducing furnace and SAF were 24.5, 2.88 and 4.71 ng/Nm^3, respectively. The high PBDE concentrations of the pelletizer resulted from not only the thermal desorption of lighter brominated congeners, but also fugitive particles of EAF fly ashes. Together, the three stacks accounted for 40.8% of the total PBDE outputs, revealing that the air pollution control devices deployed in the current study were not very effective with regard to removing PBDEs from the flue gas. The PBDE output/input ratio of the EAF fly ash treatment plant was 0.0378, and thus most PBDEs introduced into the system were decomposed. The EAF fly ash treatment plant examined in this work is thus a reliable facility with regard to the disposal of this material.

Keywords: Fly ash treatment plant; PBDEs; Mass distribution; Stack flue gas.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs), structurally similar to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), have been extensively used as brominated flame retardants (BFRs) in a large variety of consumer products. However, animal and epidemiological studies show PBDEs exposure can cause liver toxicity, developmental neurotoxicity, and may relate to metabolic obesity (Herbstman *et al.*, 2007; Main *et al.*, 2007; U.S. EPA, 2009). Therefore, commercial penta-BDE, octa-BDE and deca-BDE mixtures have been banned within the European Union (European Court of Justice, 2008), while commercial penta-BDE and octa-BDE mixtures have also been included in the list of persistent organic pollutants (POPs) contained in the Annex A chemicals (elimination) in the Stockholm Convention in May 2009. In the U.S., no new manufacturing or importing of the commercial penta-BDE and octa-BDE mixtures has been allowed since January 1, 2005, while deca-BDE mixtures are set to be voluntarily phased out by December 2012. Nevertheless, the use of PBDEs is still not restricted in Taiwan.

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Steel is the world's most used, fabricated and recycled metal. According to a report from the Steel Recycling Institute, about 30% of the world's steel requirement is produced via melting scrap metals in electric arc furnaces (EAFs) (World Steel Association, 2010). In Taiwan, EAF processes account for around 47% of all steel production (Kao *et al.*, 2011). However, the scrap materials used in EAFs are often contaminated with plastics, paints, oils and coatings that contain chlorine and bromine. Furthermore, the smelting conditions of EAFs are conducive to the formation of PCDD/Fs, polybrominated dibenzo-*p*-dioxins and debenzofurans (PBDD/Fs) and PBDEs (Wang *et al.*, 2003; Lee *et al.*, 2004; Lee *et al.*, 2005; Wang *et al.*, 2010b). The thermal desorption of the commercial PBDE mixtures during scrap charging contribute PBDEs and PBDD/Fs to the stack flue gases of the EAFs (Wang *et al.*, 2010b). Odabasi *et al.* (2009) also reported that scrap charging emits mostly particle phase PBDEs, while the melting and high temperature operation emits gas phase ones. Not only the stack flue gases but also the fly ashes of EAFs, which are collected by air pollution control devices (APCDs) like bag filters, have been noted to be important sources of PCDD/Fs, PBDD/Fs and PBDEs (Wang *et al.*, 2003; Lee *et al.*, 2004; Lee *et al.*, 2005; Wang *et al.*, 2010a, b). The PBDE contents in EAF fly ash had been reported to be as high as 50.1 ng/g (Lin *et al.*, 2012) and 205 ng/g (Cetin and Odabasi, 2008), which are much higher than those in woodland (180 and 710 ng/kg) and grassland (440 ng/kg) soils (Harrad and Hunter, 2006).

There are 170,000 tonnes of EAF fly ash discharged annually in Taiwan (Lin *et al.*, 2008), and thus fly ash treatment plants have been established to deal with the disposal of the ashes, and also to recover the remaining iron or zinc from them. However, compared to EAFs and sinter plants, EAF fly ash treatment plants exhibit much higher PCDD/F, PBDD/F and PBDE emission factors (4.99 μg I-TEQ/tonne-product, 0.101 μg TEQ/tonne-product and 1010 μg/tonne-product) (Wang *et al.*, 2010b), and thus clarifying the fate of PBDEs in EAF fly ash treatment plants is a critical task. As yet, very little is known about the fate of PBDEs in EAF fly ash treatment plants. In this study, the stack flue gases, raw materials and the ashes in different units of an EAF fly ash treatment plant were sampled to investigate their PBDE characteristics. Furthermore, the formation and depletion of PBDEs in the EAF fly ash treatment plant system were also clarified. With better understanding their fate and distribution, appropriate control strategies to decrease the PBDEs emitted from EAF fly ash treatment plant can be adopted.

MATERIALS AND METHODS

Basic Information Concerning the EAF Fly Ash Treatment Plant

The EAF fly ash treatment plant investigated in this work produces 51.5 tonnes of steel per day. Its process flow is illustrated in Fig. 1, which shows that the plant can be divided into three sub-systems, the pelletizer, reducing furnace and submerged arc furnace (SAF). For the pelletizer sub-system, the oxidized iron scraps (24.5 tonnes/day), EAF fly ashes (136 tonnes/day), carbon powders (28.1 tonnes/day) and binders (3.95 tonnes/day) are pelleted together to make the size of the raw materials uniform prior to feeding into the furnace. Oxidized iron scraps are first dried in the dryer, and then mixed with carbon powders, binders and EAF fly ashes, which are the major raw material of this metallurgical system. The resulting pellets (193 tonnes/day) then undergo a reduction process by using a reducing furnace to become reduced pellets (136 tonnes/day). After that, the reduced pellets (136 tonnes/day) are mixed with coke (7.10 tonnes/day) and flux (12.7 tonnes/day), and then melted in the SAF under a high voltage electric arc. The pellets and reduced pellets, which are the products of sub-systems A and B, respectively, and also the raw materials of its next sub-system, are not sampled for the PBDE measurements in this work, because they are in the closed tubes. The PBDE contents of the final product, the steel ingots, are also not analyzed, because the material is too hard to grind, and it is assumed that they contain no PBDEs.

Each sub-system owns its stack. Bag filters are used as air pollution control devices (APCDs) for the pelletizer and reducing furnace, while a gravity settling chamber (GSC) and a bag filter are deployed for the SAF.

Sampling Procedures

All the stack flue gas, raw material and ash samplings, as well as chemical analyses, were carried out by our accredited laboratory, which specializes in PCDD/F sampling and analyses. The stack flue gases were collected isokinetically according to U.S. EPA Modified Method 23. The sampling train adopted in this study is comparable with that specified by U.S. EPA Modified Method 5. The sampled flue gas volumes were normalized to the dry conditions of 760 mmHg and 273 K, and denoted as Nm^3. The collection time for each stack flue gas sample lasted for about three hours. To obtain representative samples, the feeding raw materials, bottom residues of SAF, and fly ashes from the gravity settling chamber and bag filters were sampled simultaneously with the stack flue gas samples. After the coarse solids were ground to particles with a diameter of less than 1 mm, the raw material and ash samples were well-mixed and diagonally sectioned. 10 g of raw materials, 5 g of bottom residues and fly ashes were sampled for PBDE analyses.

Analytical Procedures

The samples were analyzed for 30 PBDE congeners. Prior to analysis, each sample was spiked with a known amount of the $^{13}C_{12}$-labeled internal standard to the extraction thimble. Toluene was added to fill the reservoir approximately 2/3 full, and the heat source was adjusted to cause the extractor to cycle three times per hour. After being extracted for 24 hours, the extract was concentrated and treated with concentrated sulfuric acid, and this was followed by a series of sample cleanup and fractionation procedures. The eluate was concentrated to approximately 1 mL and transferred to a vial. The concentrate was further concentrated to near dryness using a stream of nitrogen.

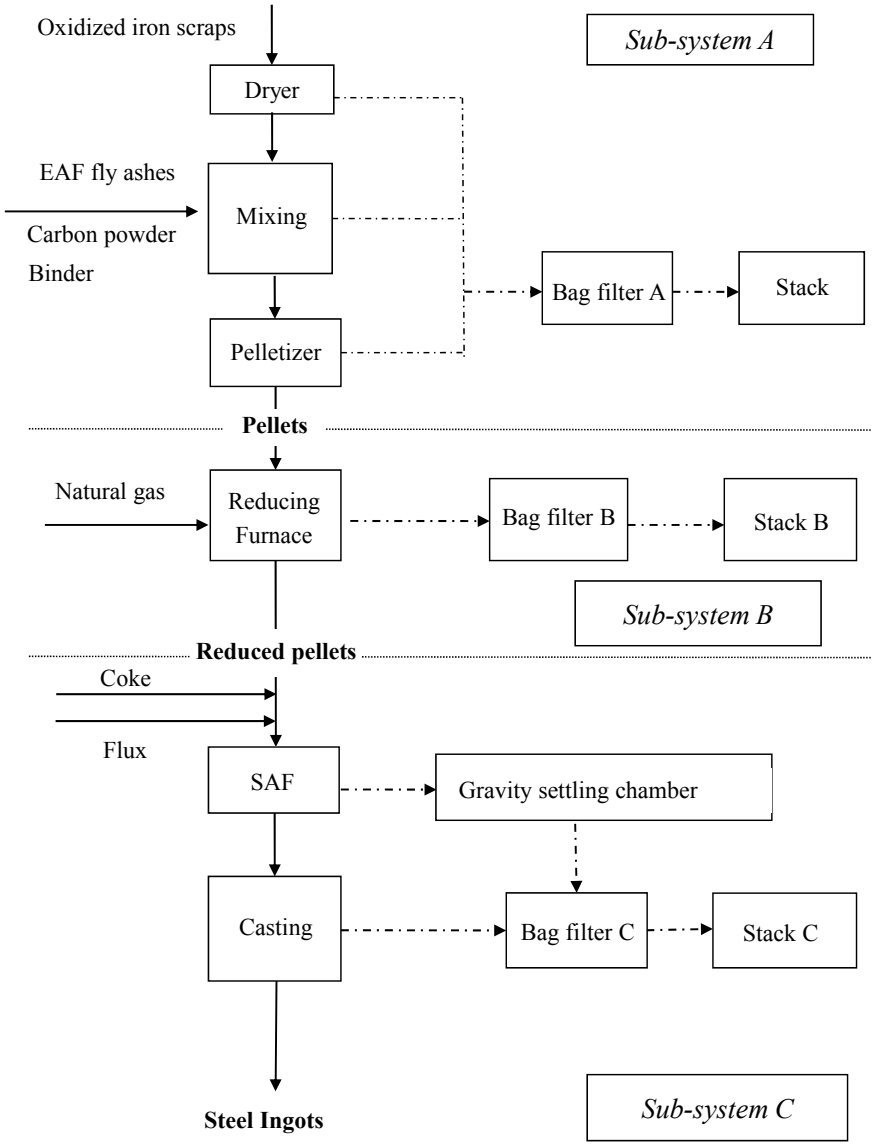

Fig. 1. The process flow of the EAF fly ash treatment plant.

Immediately prior to analysis, the standard solution for recovery checking was added to the sample.

A high-resolution gas chromatography/high-resolution mass spectrometer (HRGC/HRMS) was used for PBDE measurement. 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 μm) (J&W Scientific, CA), and with a splitless injection (injector at 250°C, transfer glass line at 280°C). The injection volume was 2 μL. The column oven temperature program was set according to the following parameters: initial oven temperature began at 100 °C (held for 4 min), then increased at 40 °C/min to 200°C (held for 3.5 min), and finally increased at 10 °C/min to 325°C (held for 2.5 min). Helium at a flow rate of 1.0 mL/min was the carrier gas. The HRMS (Micromass Autospec Ultima, Manchester, UK) mass spectrometer was equipped with a positive electron impact (EI+) source. The selected ion monitoring mode was used with a resolving power of 10,000. The detailed analytical procedures are given in our previous works (Wang *et al.*, 2010a, 2011).

RESULTS AND DISCUSSION

PBDE Characterization of the Feeding Raw Materials

The total PBDE contents in the feeding raw materials of the EAF fly ash treatment plant are listed in Table 1, and were 15.2 ng/g for oxidized iron scraps, 29.3 ng/g for EAF fly ashes, 0.738 ng/g for carbon powders, 0.372 ng/g for binders, 1.16 ng/g for coke and 0.291 ng/g for flux. The oxidized iron scraps contained much lower PBDE contents than the scrap raw materials for an aluminum recycling plant, which had 245–67450 ng/g (Sinkkonen *et al.*, 2004). The PBDE contents in the EAF fly ashes (29.3 ng/g) obtained in this study are lower than that (50.1 ng/g) reported in Lin *et al.* (2012), but were still one to three orders higher than those in reference soils, which were ranged from 0.038–3.8 ng/g (BDE-209 included) (Sellström *et al.*, 2005; Harrad

Table 1. PBDE contents in the feeding materials.

PBDEs (ng/g)	Oxidized iron scrap	EAF fly ashes	Carbon powders	Binders	Coke	Flux
BDE-7	0.000106	0.00459	0.000107	0.000491	0.000106	0.000106
BDE-15	0.00133	0.0228	0.000831	0.00128	0.00102	0.00267
BDE-17	0.00133	0.111	0.000442	0.00297	0.000440	0.00161
BDE-28	0.00161	0.147	0.000383	0.00283	0.00120	0.00149
BDE-49	0.00536	0.398	0.000693	0.00356	0.00204	0.000869
BDE-71	0.000385	0.0657	0.000386	0.000383	0.000384	0.000384
BDE-47	0.0247	1.53	0.0114	0.0119	0.0201	0.0162
BDE-66	0.00244	0.268	0.000292	0.00173	0.00137	0.000291
BDE-77	0.000482	0.0565	0.0000555	0.000310	0.000296	0.0000552
BDE-100	0.00522	0.454	0.00200	0.00170	0.00299	0.00227
BDE-119	0.00133	0.0773	0.00133	0.00132	0.00133	0.00133
BDE-99	0.0214	2.65	0.00739	0.00367	0.0144	0.00898
BDE-85	0.000886	0.130	0.0000641	0.000346	0.000857	0.0000639
BDE-126	0.000213	0.0160	0.0000262	0.0000260	0.0000261	0.0000261
BDE-154	0.0112	0.545	0.000426	0.00122	0.00342	0.00211
BDE-153	0.0344	1.02	0.00125	0.00303	0.00835	0.00522
BDE-139	0.00194	0.126	0.000154	0.000153	0.000618	0.000153
BDE-140	0.00224	0.113	0.000233	0.000232	0.000913	0.000232
BDE-138	0.00298	0.186	0.000253	0.000964	0.00134	0.000252
BDE-156	0.0000764	0.00855	0.0000766	0.0000761	0.0000763	0.0000763
BDE-184	0.00447	0.105	0.000243	0.000242	0.000243	0.000243
BDE-183	0.0756	1.34	0.00558	0.00547	0.0137	0.00698
BDE-191	0.00425	0.142	0.000652	0.000648	0.00208	0.000649
BDE-197	0.0857	1.03	0.00809	0.0115	0.0313	0.00140
BDE-203	0.0591	0.906	0.00939	0.0114	0.0356	0.00870
BDE-196	0.0530	0.757	0.0114	0.00986	0.0325	0.00766
BDE-208	0.242	1.15	0.0294	0.0152	0.0517	0.00959
BDE-207	0.552	2.22	0.0648	0.0322	0.109	0.0201
BDE-206	0.535	1.50	0.0520	0.0203	0.0715	0.00312
BDE-209	13.5	12.3	0.528	0.227	0.752	0.188
Σ_{2-8} BDEs	0.402	12.2	0.0632	0.0773	0.177	0.0700
Σ_{9-10} BDEs	14.8	17.1	0.674	0.295	0.984	0.221
Total PBDEs (ng/g)	15.2	29.3	0.738	0.372	1.16	0.291

and Hunter, 2006; Leung *et al.*, 2007). Therefore, the EAF fly ashes need to be well disposed to prevent their PBDEs discharging to the environment. For the other feeding raw materials, their PBDE contents (0.291–1.16 ng/g) are close to those of the aforesaid reference soils.

The PBDE congener profiles of the feeding raw materials are illustrated in Fig. 2. The most dominant PBDE congeners were the highly brominated-substituted ones, namely BDE-209, -208, -207 and -206. Among the low to medium brominated congeners, BDE-47 and BDE-99 were relatively dominant. BDE-209 was the most dominant in all samples, and contributed 88.8% for oxidized iron scraps, 42.0% for EAF fly ashes, 71.6% for carbon powders, 61.0% for binders, 64.8% for coke and 64.6% for flux. The PBDE congener profiles of the EAF fly ashes leaned more to the lighter brominated congeners (e.g., BDE-47 5.2% and BDE-99 9.0%) compared to the other raw materials. The more abundant BDE-47 and -99 of the EAF fly ashes may be attributed to the thermal desorption occurring on the EAF feeding periods, because the feeding scraps contained the commercial penta-BDE mixtures as impurities.

PBDE Characterization of the Bottom and Fly Ashes Generated from the EAF Fly Ash Treatment Plant

The PBDE contents in the bottom and fly ashes generated from the three sub-systems of the EAF fly ash treatment plant are listed in Table 2, and were 7.69 ng/g for fly ashes collected by the bag filter of pelletizer and 0.774 ng/g for fly ashes collected by the bag filter of reducing furnace. For the SAF sub-system, the PBDE contents in the bottom ashes and fly ashes collected by GSC and bag filter were 0.345 ng/g, 0.600 ng/g and 0.489 ng/g.

Among these ash samples, the fly ash from the pelletizer process exhibited the highest PBDE content, while the others had PBDE contents ranging from 0.345 ng/g to 0.774 ng/g. This is because the fly ash from the pelletizer only underwent the mixing process, and the PBDEs of the EAF fly ashes were retained. For the other ash samples, the extremely high temperature in the processes leads to effective PBDE destruction (Artha *et al.*, 2011). In our previous study, the effects of temperature on the formation mechanisms of PBDEs occurring in the processes of heating fly ash were investigated. Compared to PBDE contents of the fly ashes

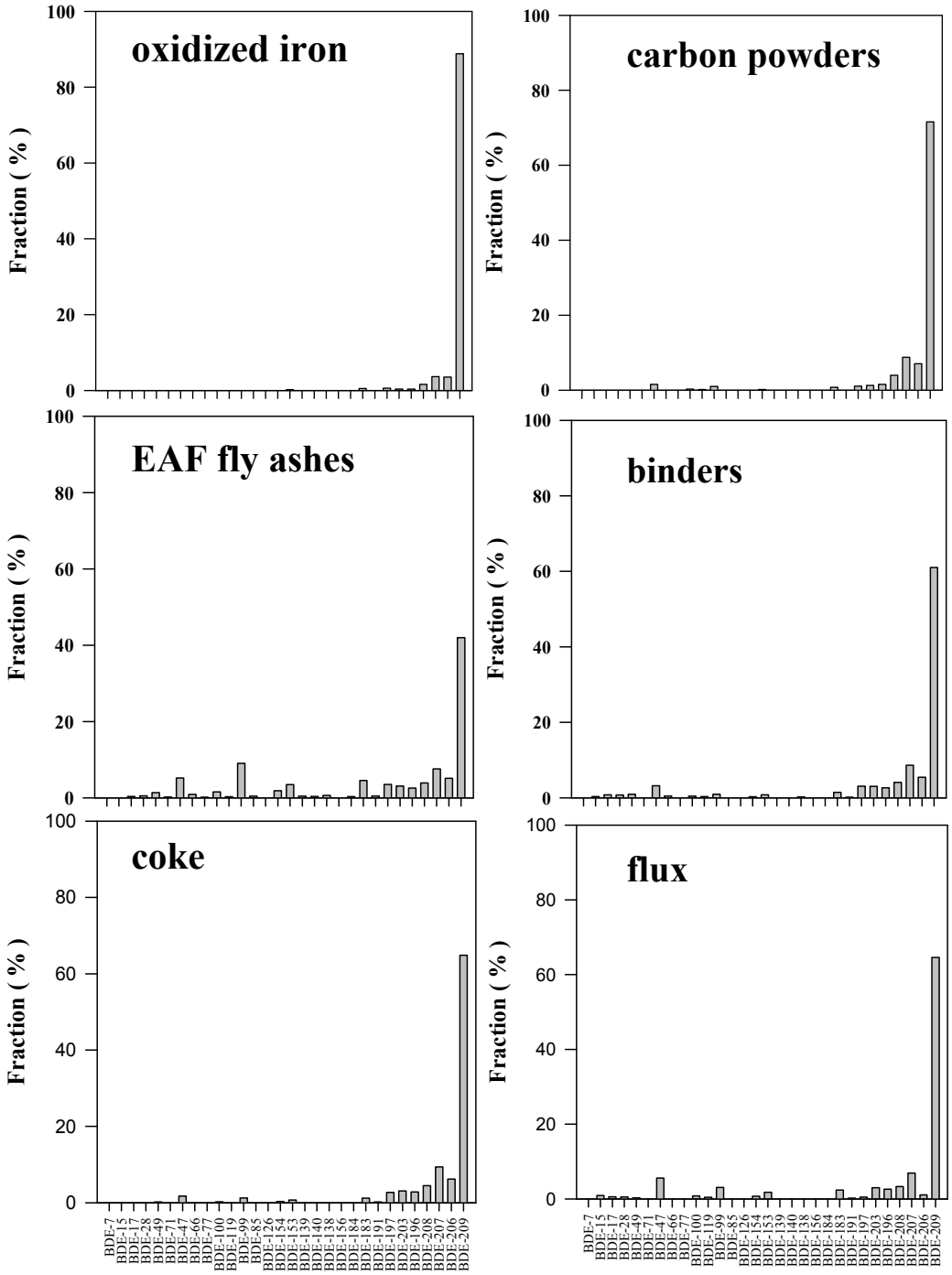

Fig. 2. PBDE congener profiles of the feeding raw materials.

during the temperature window of formation, the PBDE contents during the heating temperature at 900°C–1450°C dramatically decreased, and remained at the level of 0.253–0.389 ng/g (Artha *et al.*, 2011).

Fig. 3 shows the PBDE congener profiles of the bottom and fly ashes generated in the EAF fly ash treatment plant. The PBDE congener profile in the fly ash collected by the bag filter of the pelletizer is very close to that of the EAF fly ashes. For the other ash samples which were generated at extremely high temperatures, BDE-209 was highly dominant, and contributed 58.0%–77.0% of total PBDEs.

PBDE Characterization of the Stack Flue Gases

The total PBDE concentrations in the stack flue gases of the three sub-systems of the EAF fly ash treatment plant are listed in Table 3, and were 24.5 ng/Nm^3 in the stack flue gases of the pelletizer, 2.88 ng/Nm^3 in the stack flue gases of the reducing furnace, and 4.71 ng/Nm^3 in the stack flue gases of the SAF. The stack flue gases of the pelletizer had much higher PBDE concentrations than the reducing furnace and SAF. Furthermore, the pelletizer had more Σ_{2-8} BDEs (17.2 ng/Nm^3) than Σ_{9-10} BDEs (7.30 ng/Nm^3), while the reducing furnace and SAF were more abundant in Σ_{9-10}

Table 2. PBDE contents in the bottom and fly ashes generated from the EAF fly ash treatment plant.

PBDEs (ng/g)	Pelletizer	Reducing furnace	SAF		
	Fly ashes of bag filter A	Fly ashes of bag filter B	bottom ash	Fly ashes of GSC	Fly ashes of bag filter C
BDE-7	0.00280	0.00687	0.000105	0.000107	0.000107
BDE-15	0.0143	0.00324	0.0026	0.00160	0.00131
BDE-17	0.0430	0.00373	0.00138	0.000442	0.00117
BDE-28	0.0517	0.00528	0.00235	0.00112	0.00200
BDE-49	0.150	0.00854	0.000340	0.00133	0.00228
BDE-71	0.0124	0.000383	0.000380	0.000386	0.000386
BDE-47	0.395	0.0374	0.0221	0.0132	0.0199
BDE-66	0.0667	0.00490	0.000288	0.000860	0.00131
BDE-77	0.0175	0.00102	0.0000547	0.000156	0.000223
BDE-100	0.142	0.00847	0.00317	0.00187	0.00268
BDE-119	0.0143	0.00132	0.00131	0.00133	0.00133
BDE-99	0.606	0.0390	0.0103	0.00765	0.0104
BDE-85	0.0327	0.00181	0.0000632	0.000367	0.000463
BDE-126	0.00526	0.000026	0.0000258	0.0000262	0.0000262
BDE-154	0.143	0.00707	0.00235	0.00135	0.00178
BDE-153	0.292	0.0144	0.00330	0.00349	0.00337
BDE-139	0.0365	0.00135	0.000152	0.000657	0.000447
BDE-140	0.0352	0.00131	0.000230	0.000233	0.000562
BDE-138	0.0419	0.00182	0.000249	0.000563	0.000253
BDE-156	0.00148	0.00148	0.0000755	0.0000766	0.0000766
BDE-184	0.0344	0.000242	0.000240	0.000243	0.000243
BDE-183	0.362	0.0239	0.00248	0.00508	0.00617
BDE-191	0.043	0.00222	0.00854	0.000652	0.000652
BDE-197	0.238	0.0187	0.00138	0.00928	0.00848
BDE-203	0.281	0.0187	0.00105	0.0105	0.00815
BDE-196	0.199	0.0161	0.00678	0.00948	0.00662
BDE-208	0.262	0.0213	0.00974	0.0136	0.0125
BDE-207	0.430	0.0434	0.0184	0.0243	0.0287
BDE-206	0.348	0.0306	0.0192	0.0283	0.0306
BDE-209	3.39	0.449	0.226	0.462	0.337
Σ_{2-8} BDEs	3.26	0.229	0.0713	0.0720	0.0803
Σ_{9-10} BDEs	4.43	0.544	0.274	0.528	0.409
Total BDEs (ng/g)	7.69	0.774	0.345	0.600	0.489

BDEs, which accounted for 83.4% and 84.1% of total PBDEs, respectively. The PBDE concentration of the pelletizer was comparable to the concentrations found in the stack flue gases of other metallurgical processes, such as EAFs (15.7–19.4ng/Nm^3), sinter plants (22.2–35.2 ng/Nm^3) (Wang *et al.*, 2010b) and secondary aluminum smelters (45.0 ng/Nm^3) (Wang *et al.*, 2010a), while those of the reducing furnace and SAF were much lower.

The PBDE congener profiles in the stack flue gases of the three sub-systems of the EAF fly ash treatment plant are shown in Fig. 3. The more dominant lighter brominated congeners, especially BDE-99 and BDE-47, in the stack flue gases of the pelletizer perhaps resulted from the fact that the preheating drying of scrap and pelletizing process enhanced the thermal desorption of lighter brominated congeners which are contained in the scrap and EAF fly ashes. Furthermore, the great similarity of congener profile between the stack flue gases of the pelletizer and the feeding EAF fly ashes suggests that there are still fugitive particles of EAF fly ashes in the stack flue gases, although bag filter was deployed. Therefore the high PBDE concentrations in the stack flue gases of the pelletizer resulted from not only the thermal desorption of lighter brominated congeners, but also fugitive particles of EAF fly ashes. The highly brominated-substituted congeners, namely BDE-209, -208, -207 and -206, were the most dominant in the stack flue gases of the reducing furnace and SAF, and this is consistent with combustion processes preferring the formation of highly brominated congeners (Wang *et al.*, 2010b).

Inputs and Outputs of PBDEs in the EAF Fly Ash Treatment Plant

The inputs and outputs in the EAF fly ash treatment plant, as well as their corresponding PBDE inputs and outputs, are listed in Table 4. Among the PBDE inputs, the EAF fly ashes were the greatest PBDE contributor, and contributed 3.99 g PBDEs per day, that is, about 91% of the total PBDE inputs (4.40 g/day). The oxidized iron scraps contributed 8.5%, and the other raw materials had less than 1% contribution.

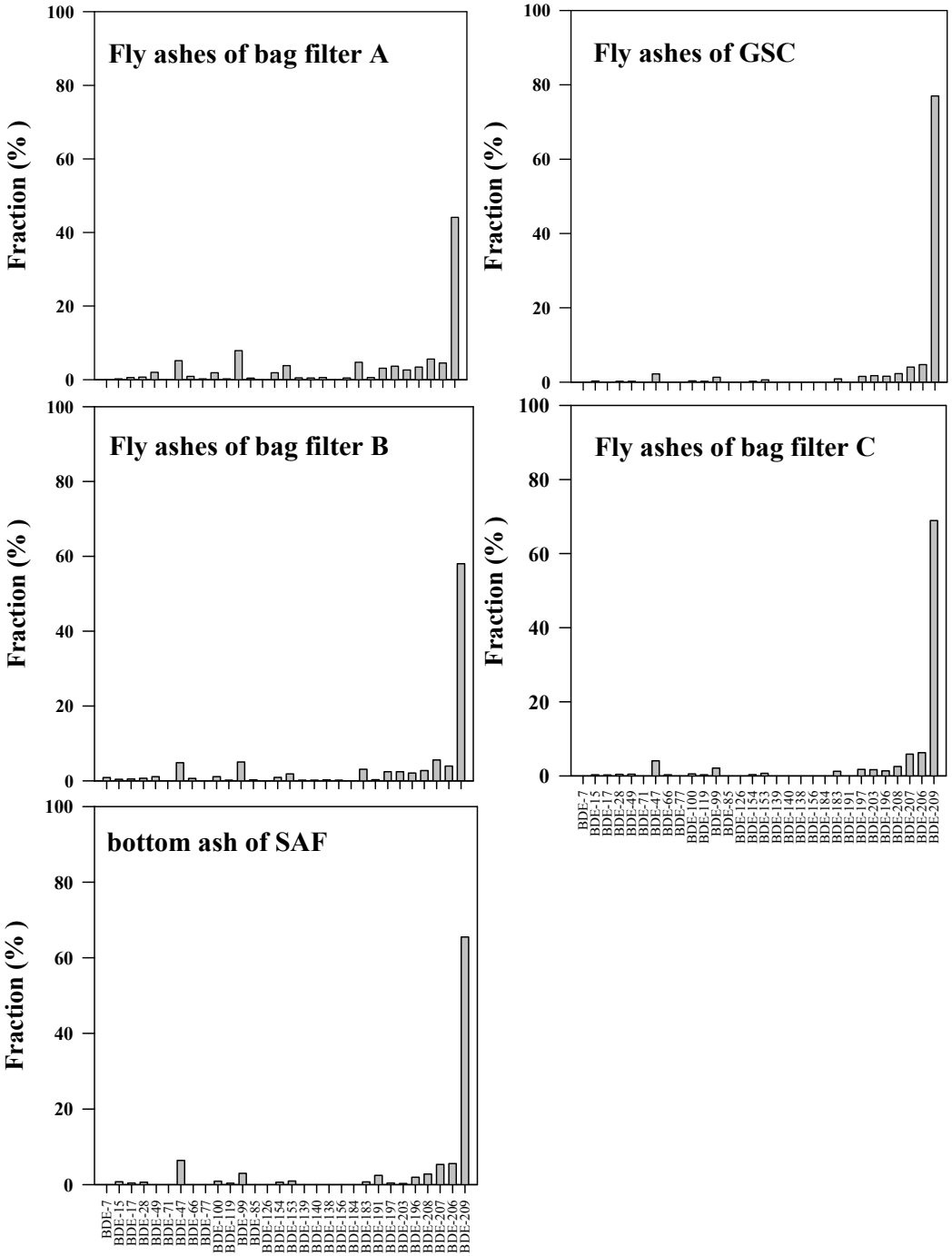

Fig. 3. PBDE congener profiles of the bottom and fly ashes generated from the EAF fly ash treatment plant.

For the PBDE outputs, the fly ashes collected by the bag filter of the pelletizer (0.0812 g/day) were the greatest PBDE contributor, and represented about 49% of the total PBDE outputs (0.166 g/day). Together, the three stacks accounted for 40.8% of the total PBDE outputs, and thus 40.8% of the total PBDEs discharged by the EAF fly ash treatment plant were emitted to the atmosphere. Compared to another EAF fly ash treatment plant deploying a dual bag filter system coupled with activated carbon injection as APCDs, only 0.0307% of the total PCDD/F I-TEQ were discharged by stack flue gases (Lin *et al.*, 2008), revealing that the deployed APCDs in the current study are not very effective in removing PBDEs from the flue gas. Among the three stacks, the stack of the SAF was the greatest PBDE emitter, at 0.0359 g/day and 21.7% of the total PBDE outputs, while for the stack of the pelletizer emitted the least amount of PBDEs, at only 9.2% of the total, although it exhibited the highest PBDE concentrations.

The PBDE emission factors to the atmosphere of the pelletizer, reducing furnace and SAF were 0.0794, 0.0851 and 0.231 mg/tonne-feedstock. The higher PBDE emissions from the stack of the SAF could be related to precursor

Table 3. PBDE concentrations in the stack flue gases of the EAF fly ash treatment plant.

PBDEs (ng/Nm^3)	Stack A of the pelletizer (n = 3)		Stack B of the reducing furnace (n = 3)		Stack C of the SAF (n = 3)	
	Concentration	RSD (%)	Concentration	RSD (%)	Concentration	RSD (%)
BDE-7	0.00339	25.1	0.00197	118	0.00485	12.9
BDE-15	0.0100	6.8	0.00517	14.3	0.0108	4.8
BDE-17	0.0128	80.9	0.00195	41.6	0.0107	19.7
BDE-28	0.0371	79.1	0.00615	45.7	0.0138	14.1
BDE-49	0.0747	92.9	0.00108	0.1	0.0173	12.8
BDE-71	0.0196	111	0.00121	0.1	0.00215	61.2
BDE-47	4.31	118	0.0536	54.6	0.159	3.0
BDE-66	0.00635	17.6	0.000911	0.1	0.0117	23.3
BDE-77	0.000230	0.7	0.000173	0.1	0.000170	0.4
BDE-100	1.66	127	0.0226	116	0.0291	1.7
BDE-119	0.137	136	0.00416	0	0.00420	0.4
BDE-99	6.87	130	0.0778	37.5	0.121	3.8
BDE-85	0.282	141	0.00216	128	0.000200	0.5
BDE-126	0.000110	0.5	0.0000820	0.1	0.0000800	0.4
BDE-154	0.919	135	0.0193	38.0	0.0155	16.8
BDE-153	1.64	137	0.0369	34.2	0.0254	28.2
BDE-139	0.0765	140	0.000820	32.2	0.000480	0.5
BDE-140	0.000970	0.5	0.000729	0.1	0.000730	0.4
BDE-138	0.115	140	0.000789	0.1	0.000800	0.4
BDE-156	0.000320	0.5	0.000514	75.4	0.000240	0.4
BDE-184	0.00102	0.6	0.000761	0.1	0.000770	0.3
BDE-183	0.0257	83.7	0.0282	59.3	0.0468	20.2
BDE-191	0.00272	0.6	0.00204	0.8	0.00205	0.5
BDE-197	0.0453	84.7	0.0407	31.1	0.0406	9.0
BDE-203	0.429	126	0.0690	43.5	0.122	19.5
BDE-196	0.492	108	0.0856	19.2	0.112	30.6
BDE-208	0.327	84	0.0628	23.7	0.181	28.2
BDE-207	0.566	77.5	0.120	28.4	0.207	25.4
BDE-206	2.05	119	0.137	18.4	0.216	35.9
BDE-209	4.36	7.1	2.09	35	3.35	44.7
Σ_{2-8} BDEs	17.2	126	0.464	22.8	0.752	10.2
Σ_{9-10} BDEs	7.30	44.4	2.41	32.8	3.96	42.3
Total PBDEs (ng/Nm^3)	24.5	102	2.88	29.2	4.71	37.1

Table 4. PBDE inputs and PBDE outputs of the EAF fly ash treatment plant.

Sub-systems	Inputs		Outputs	
	Feeding material	PBDE amounts (g/day)	Output media	PBDE amounts (g/day)
Pelletizer	Oxidized iron scraps	0.372	Fly ashes of bag filter A	0.0812
	EAF fly ashes	3.99	Stack A	0.0153
	Carbon powders	0.0208	Pellets	
	Binder	0.00147	(product of this sub-system)	-
Reducing furnace	Pellets	-	Fly ashes of bag filter B	0.00266
			Stack B	0.0165
			Reducing pellets	
			(product of this sub-system)	-
SAF	Reducing pellets	-	Bottom ash of SAF	0.00414
	Coke	0.00824	Fly ashes of GSC	0.00503
	Flux	0.00370	Fly ashes of bag filter C	0.00501
			Stack C	0.0359
			Steel ingots (Final product)	-

formation and de novo synthesis that occurred during the cooling process of the flue gas due to using coke as an auxiliary fuel and deploying GSC as one of the APCDs (Lin *et al.*, 2008; Wang *et al.*, 2010a; Artha *et al.*, 2011). The

PBDE emission factor to the atmosphere of the whole system, that is, the EAF fly ash treatment plant, was 0.318 mg/tonne-feedstock. The arithmetic means and geometric means of the PBDE emission factor from the stack flue gases of six EAFs (18 stack flue gas samples) were 0.531 and 0.215 mg/tonne-feedstock, respectively, in an earlier study (Wang *et al.*, 2010a), which are comparable to those of the EAF fly ash treatment plant in this study.

The PBDE output/input ratio of the EAF fly ash treatment plant was 0.0378 (= 0.166/4.40), and the corresponding destruction and removal efficiency (DRE) was 96.2% (= (4.40–0.166)/4.40 × 100%), revealing that most PBDEs introduced into the system were decomposed. The results obtained in this study are comparable to the DREs of 98.9% for PBDEs (Lin *et al.*, 2012) and 99.6% for PCDD/Fs (Lin *et al.*, 2011) which were both obtained from a laboratory scale thermal treatment system for EAF fly ash, revealing that the EAF fly ash treatment plant examined in the current work is a reliable facility, not only with regard to recovering the remaining iron or zinc, but also to resolving the issue of disposing EAF fly ashes.

CONCLUSIONS

The elevated PBDE concentrations in the stack flue gases of the pelletizer (24.5 ng/Nm^3) resulted from not only the thermal desorption of lighter brominated congeners, but also fugitive particles of EAF fly ashes. BDE-209, -208, -207 and -206 were the most dominant congeners in the stack flue gases of the reducing furnace and SAF, indicating that the related combustion processes preferred the formation of highly brominated congeners. The PBDE emission factors to the atmosphere of the pelletizer, reducing furnace and SAF were 0.0794, 0.0851 and 0.231 mg/tonne-feedstock. The higher PBDE emissions from the stack of the SAF could be related to the precursor formation and de novo synthesis that occurred during the cooling process of the flue gas, due to the use of coke as an auxiliary fuel and deploying GSC as one of the APCDs. The PBDE output/input ratio of the EAF fly ash treatment plant was 0.0378, and the corresponding DRE was 96.2%. These values are comparable to those obtained from a laboratory scale thermal treatment system for EAF fly ash, revealing that the EAF fly ash treatment plant examined in this work is reliable for both recovering the remaining iron, and also resolving the disposal of the EAF fly ashes.

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