Formation and emission of brominated dioxins and furans during secondary aluminum smelting processes

Mei Wang, Guorui Liu^{*}, Xiaoxu Jiang, Sumei Li, Wenbin Liu, Minghui Zheng

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

HIGHLIGHTS

- PBDD/F emissions from different secondary aluminum smelters were investigated.
- The raw material composition significantly influenced PBDD/F emissions.
- The feeding–fusion stage was the main stage in which PBDD/Fs were emitted.
- Effective metal scrap pretreatments can significantly decrease PBDD/F emissions.
- The more-brominated PBDD/F congeners were dominant.

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ABSTRACT

Secondary aluminum smelting (SAI) processes have previously been found to be important sources of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs). It is crucial that the key factors that influence the formation and emission of PBDD/Fs are identified to allow techniques for decreasing PBDD/F emissions during SAI processes to be developed. In this study, stack gas samples were collected from four typical secondary aluminum smelters that used different raw materials, and the samples were analyzed to allow differences between PBDD/F emissions from different SAI plants to be assessed. The composition of the raw materials was found to be one of the key factors influencing the amounts of PBDD/Fs emitted. The PBDD/F emission factors (per tonne of aluminum produced) for the plants using 100% (Plant1), 80% (Plant2), and 50% (Plant3) dirty aluminum scrap in the raw material feed were 180, 86, and 14 $\mu\text{g t}^{-1}$, respectively. The amounts of PBDD/Fs emitted at different stages of the smelting process (feeding–fusion, refining, and casting) were compared, and the feeding–fusion stage was found to be the main stage in which PBDD/Fs were formed and emitted. Effective aluminum scrap pretreatments could significantly decrease PBDD/F emissions. Much higher polybrominated dibenzofuran concentrations than polybrominated dibenzo-*p*-dioxin concentrations were found throughout the SAI process. The more-brominated congeners (including octabromodibenzo-*p*-dioxin, octabromodibenzofuran, heptabromodibenzo-*p*-dioxins, and heptabromodibenzofurans) were the dominant contributors to the total PBDD/F concentrations. The results could help in the development of techniques and strategies for controlling PBDD/F emissions during metallurgical processes.

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1. Introduction

Secondary aluminum smelters primarily recover aluminum from new and used scrap and dross containing aluminum (Ba et al., 2009). Scrap metal and metal waste may also contain organic

materials, such as paints, plastics, and solvents (Kevorkjian, 2010). Secondary aluminum smelting (SAI) may lead to the unintentional formation of persistent organic pollutants (POPs), including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polybrominated dibenzo-*p*-dioxins and polybrominated dibenzofurans (PBDDs and PBDFs, together called PBDD/Fs), and dioxin-like compounds (such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs)), because of the incomplete combustion of impurities in the raw materials (Hu et al., 2013a).

^{*} Corresponding author.

E-mail address: grliu@rcees.ac.cn (G. Liu).

Unintentionally produced POPs can form through reactions between inorganic or organically bound halogen atoms and carbon from organic material in scrap metal or other materials (such as partially burnt fuels or the reductants) (Weber and Kuch, 2003; Altarawneh et al., 2009; Ortuño et al., 2014). This process can be catalyzed by aluminum, copper, and other metals (Weber et al., 2001; Ryu et al., 2003; Fujimori et al., 2009, 2013).

The formation and emission of PCDD/Fs, PCBs, and PCNs during SAI processes have previously been studied in detail, and SAI has been found to be an important source of these chlorinated compounds (Chen et al., 2004; Lee et al., 2005; Li et al., 2007; Ba et al., 2010; Hu et al., 2014; Jiang et al., 2015). Ba et al. (Ba et al., 2009, 2010) measured PCDD/F, dioxin-like PCB, and PCN emissions from Chinese secondary aluminum metallurgical plants and estimated that the total amounts of PCDD/Fs, dioxin-like PCBs, and PCNs emitted to the atmosphere in 2007 were 7.3, 0.53, and 0.39 g toxic equivalents (TEQ), respectively. Grochowalski et al. (Grochowalski et al., 2007) found much higher concentrations of PCDD/Fs (0.030–0.58 ng International TEQ Nm⁻³), PCBs (0.0080–0.054 ng World Health Organization TEQ Nm⁻³), and hexachlorobenzene (11–23 ng Nm⁻³) in flue gases at a SAI in Poland than in flue gases produced during other industrial thermal processes. Daily inhaled doses of PCDD/Fs, dioxin-like PCBs, and PCNs in SAI plants that exceed the tolerable daily intake recommended by the World Health Organization have been found (Hu et al., 2013a). Lee et al. (Lee et al., 2009) measured PCDD/F concentrations in serum from 134 workers in electric arc furnace, secondary copper smelting, and SAI plants. The highest PCDD/F concentrations were found in the serum samples from the SAI workers. The studies described above showed that SAI plants are important sources of unintentionally produced chlorinated POPs.

Intensive studies of PCDD/F, PCB, and PCN emissions during SAI processes have been performed (Chen et al., 2004; Lee et al., 2005; Li et al., 2007; Ba et al., 2010; Hu et al., 2014; Jiang et al., 2015), but emissions of the toxic brominated analogs of these pollutants, particularly PBDD/Fs, have been investigated in few studies. PBDD/Fs are the brominated analogs of PCDD/Fs, so PBDD/Fs have similar physicochemical properties, toxicities, and environmental behaviors to PCDD/Fs (Behnisch et al., 2003; Birnbaum et al., 2003; Olsman et al., 2007; Samara et al., 2009). PBDD/Fs have recently been found in various environmental matrices (Haglund et al., 2007; Li et al., 2008; Chang et al., 2013; Zacs et al., 2013). It has previously been suggested that polybrominated diphenyl ethers (PBDEs) are important precursors of PBDD/Fs in industrial thermal processes (Sakai et al., 2001; Weber and Kuch, 2003; Olsman et al., 2007; Duan et al., 2011; Altarawneh and Dlugogorski, 2013; Sindiku et al., 2014). Significant amounts of PBDEs have been found in the raw materials of SAI plants. For example, Sinkkonen et al. (Sinkkonen et al., 2004) screened four raw scrap material samples from a SAI plant for persistent halogenated aromatic compounds and found PBDEs in all of the samples, at concentrations of 250–67,000 ng g⁻¹. The presence of bromine-containing materials and various nonferrous metals in the raw materials used in the SAI process naturally means that the formation of PBDD/Fs during the SAI process should be considered.

Although PBDD/Fs are believed to be formed during SAI processes, few data on PBDD/F emissions from secondary aluminum metallurgical facilities have been reported. To the best of our knowledge, only one study of PBDD/Fs in stack gas samples from only one SAI plant has been published (Du et al., 2010). However, the effects of factors that could affect PBDD/F emissions (e.g., the smelting techniques used, the furnace capacity, the raw materials, and the fuel) were not thoroughly investigated in that study. More case studies are therefore needed to allow PBDD/F emissions during SAI processes to be systematically evaluated.

China is the world's largest producer and consumer of aluminum, accounting for roughly 40% of global aluminum production (Chen and Shi, 2012; Lo and Wang, 2013). Secondary aluminum production in China increased dramatically after 2000, and now accounts for roughly 22% of the total amount of aluminum produced, producing three million tonnes in 2009 (Chen and Shi, 2012; Lo and Wang, 2013). Investigating PBDD/F emissions from typical Chinese SAI plants is therefore likely to be important to allow a preliminary estimate of global PBDD/F emissions from SAI plants to be made.

In this study, PBDD/F emissions from four typical SAI plants with different furnace capacities and using different raw materials were investigated. The primary objective was to estimate PBDD/F emissions from typical SAI plants in China. A further objective was to identify the factors that influence PBDD/F emissions. The results of this study will provide helpful information to develop and implement measures to control PBDD/F emissions.

2. Materials and methods

2.1. Sample collection

Secondary aluminum production in China is mostly performed using reverberatory furnaces because such furnaces have simple structures, are easy to operate, and are suitable for large-scale production (Hu et al., 2013b; Jiang et al., 2015). Scrap containing aluminum is the main raw material used in Chinese SAI plants. Fabric bag filters are widely used as air pollution control devices in Chinese SAI plants (Ba et al., 2010; Hu et al., 2013b; Jiang et al., 2015). Four typical Chinese SAI plants with reverberatory furnaces and bag filter air pollution control devices were studied. The plants, labeled Plant1, Plant2, Plant3, and Plant4, were selected because they used different mixtures of raw materials. The raw material used in Plant1 and Plant4 was 100% dirty aluminum scrap (used and discarded material, such as appliances, aluminum foil, automobile and airplane parts, aluminum sidings, and beverage cans). The raw material used in Plant2 and Plant3 contained 80% and 50% dirty scrap, respectively. The remaining 20% of the raw material used in Plant2 was copper-clad aluminum wire. The remaining 50% of the raw material used in Plant3 was clean aluminum scrap (pre-consumer scrap material, such as waste from the drilling and machining of aluminum castings, waste from fabrication and manufacturing operations, and dross skimmed off molten aluminum during the smelting process). Additional information on the plants is given in Table S1.

A total of 15 stack gas samples from different smelting stages were collected from the four SAI plants. The samples were collected using an automatic isokinetic sampling system (Isostack Basic; TCR Tecora, Fontenay sous Bois, France) that has been used in previous studies (Liu et al., 2009, 2010). The sampling system consisted of Isostack Basic pumps, Isofrost coolers, a heated titanium probe, a filter box with a Whatman quartz microfiber thimble filter (GE Healthcare Bio-Sciences, Pittsburgh, PA, USA), and a water-cooled Amberlite XAD-2 (Supelco, Bellefonte, PA, USA) adsorbent trap. The quartz fiber filter was used to collect the particle-bound pollutants and the XAD-2 adsorbent resin was used to trap the vapor-phase pollutants. ³⁷Cl₄-labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was spiked into the resin prior to sampling to allow the sampling efficiency to be evaluated. After collection, each sample was wrapped tightly in aluminum foil and packed in a sealed polyethylene bag to prevent it becoming contaminated or material being lost.

2.2. Analytical procedures

Thirteen 2,3,7,8-brominated PBDD/F congeners were identified

and quantified in this study (17 2,3,7,8-chlorinated PCDD/F congeners are generally quantified) because several $^{13}\text{C}_{12}$ -labeled compounds that would ideally be used as internal standards are currently not commercially available. The PBDD/F congeners were identified and quantified using an isotope dilution high-resolution gas chromatography combined with high-resolution mass spectrometry method. Full details of the analytical methodology have been published previously (Wang et al., 2015). Briefly, each stack gas sample was spiked with a mixture of $^{13}\text{C}_{12}$ -labeled PBDD/F internal standards (EDF-5408; Cambridge Isotope Laboratories, Andover, MA, USA), then Soxhlet extracted for approximately 24 h with 250 mL of toluene. The extract was concentrated using a rotary evaporator and then subjected to a series of clean-up steps, including a multilayer silica gel column and a basic alumina column. A silica gel column impregnated with active carbon was then used to separate the PBDD/Fs from other compounds. The fraction containing PBDD/Fs was concentrated to approximately 20 μL using a rotary evaporator and then under a gentle stream of N_2 . Then, $^{13}\text{C}_{12}$ -labeled PBDD/F injection standards (EDF-5409; Cambridge Isotope Laboratories) were added to allow the internal standard recoveries to be calculated. The extract was then analyzed for PBDD/Fs using a Trace GC Ultra gas chromatograph coupled to a DFS mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with an electron impact ion source. The mass spectrometer was operated in selected ion monitoring mode with a resolution of approximately 10,000. The PBDD/F congeners were separated on a DB-5 MS capillary column (15 m long, 0.25 mm i.d., 0.1 μm film thickness; Agilent Technologies, Santa Clara, CA, USA). The electron energy was 45 eV and the source temperature was 280 $^{\circ}\text{C}$.

2.3. Quality assurance and quality control

The $^{37}\text{Cl}_4$ -labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin recoveries were 93–105%, indicating that the sampling efficiency was satisfactory. The $^{13}\text{C}_{12}$ -labeled PBDD/F internal standard recoveries were 24–115%, and met the requirements for the trace analysis of dioxins and dioxin-like compounds in environmental samples. The 2,3,7,8-brominated PBDD/F congeners were identified using the isotope dilution method. Three quality control criteria were used when identifying each target compound: (a) the retention time was matched to the corresponding $^{13}\text{C}_{12}$ -labeled standard; (b) the signal-to-noise ratio was higher than 3; and (c) the ratio between the areas of the quantification and identification ion peaks was within $\pm 15\%$ of the theoretical value. One blank sample was included in each batch of samples analyzed. The 1,2,3,4,6,7,8-heptabromodibenzofuran (HpBDF) and octabromodibenzofuran (OBDF) concentrations were a little higher than the detection limits but were less than 2% of the concentrations in the stack gas samples. The stack gas sample volumes were normalized to “dry standard conditions” of 273 K and 101.3 kPa, the units for which are labeled Nm^3 .

3. Results and discussion

3.1. PBDD/F and PBDE emissions during the SAI processes

The PBDD/F concentrations found in the stack gas samples from the four plants are shown in Table 1. The PBDD/F concentrations in the samples from the different plants varied widely, from 144 to 4573 pg Nm^{-3} . The highest PBDD/F concentrations were found in the samples from Plant1, for which the mean concentration was 3578 pg Nm^{-3} (range 1937–4573 pg Nm^{-3}). The mean PBDD/F concentration in the samples from Plant2 was 1049 pg Nm^{-3} (range 729–1467 pg Nm^{-3}). The PBDD/F concentrations were much lower in the samples from Plant3 than in the samples from Plant1 and

Plant2, the mean being 272 pg Nm^{-3} and the range being 259–296 pg Nm^{-3} . The PBDD/F concentrations were lower in the samples from Plant4 than in the samples from the other plants, the mean being 171 pg Nm^{-3} and the range being 144–206 pg Nm^{-3} .

The results of previous studies in which PBDD/F concentrations were measured in stack gases emitted from SAI plants and other industrial thermal processes are summarized in Table 2 (Du et al., 2010; Wang et al., 2010a, 2010b; Drage et al., 2014; Li et al., 2015; Wang et al., 2015). Very few studies of PBDD/Fs unintentionally released from SAI plants have been performed, and, to the best of our knowledge, only one such study has been published (Du et al., 2010). The mean PBDD/F concentration in the stack gas samples collected in that study was 560 pg Nm^{-3} . The PBDD/F concentrations we found (144–4573 pg Nm^{-3}) were much higher than the concentrations that have previously been found in stack gases produced by municipal solid waste incinerators and converter steelmaking processes (Wang et al., 2010a, 2010b; Li et al., 2015) and were higher than or comparable to the concentrations that have previously been found in stack gases produced during iron ore sintering processes, secondary copper smelting processes, and electric arc furnace processes (Du et al., 2010; Wang et al., 2010b, 2015). These results show that SAI plants are important sources of PBDD/F emissions.

There are currently no internationally agreed toxic equivalency factors for PBDD/F congeners relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. It has been suggested by a number of researchers and by the World Health Organization that PCDD/F toxic equivalency factors should be used for the PBDD/Fs (WHO, 1998; Wang et al., 2010a; Ren et al., 2011). The PCDD/F toxic equivalency factors shown in Table S2 were therefore used to calculate the PBDD/F TEQ in this study. The PBDD/F TEQ concentrations in the stack gas samples from the four SAI plants were 0.0039–0.053 ng TEQ Nm^{-3} (see Table S3). The highest PBDD/F TEQ concentrations were found in the stack gas samples from Plant1, for which the mean was 0.043 ng TEQ Nm^{-3} (range 0.024–0.053 ng TEQ Nm^{-3}). The mean PBDD/F TEQ concentration in the Plant2 stack gases was 0.030 ng TEQ Nm^{-3} (range 0.015–0.042 ng TEQ Nm^{-3}). The PBDD/F TEQ concentrations in the Plant3 and Plant4 stack gases were 0.013–0.019 and 0.0039–0.0079 ng TEQ Nm^{-3} , respectively. The concentrations in the stack gases from all four plants were below 0.1 ng TEQ Nm^{-3} , which is the regulatory limit for dioxin emissions from some industrial sources (Liu et al., 2013, 2015).

It is widely recognized that PBDEs are important precursors of PBDD/Fs formed during industrial thermal processes (Weber and Kuch, 2003; Olsman et al., 2007; Altarawneh and Dlugogorski, 2013; Sindiku et al., 2014). Altarawneh and Dlugogorski (2013) performed a detailed mechanistic and kinetic study of the formation of PBDD/Fs from PBDEs, and found that the loss of ortho Br or H atoms from a PBDE, followed by a ring-closure reaction, is the most accessible pathway for the production of PBDFs via modest reaction barriers. Weber and Kuch (2003) stated that PBDD/Fs can be formed from PBDEs via the simple intramolecular elimination of HBr. In this study, the PBDE concentrations were also determined, and they are shown in Table S4. The PBDE concentrations in the samples from the four plants ranged from 7.8 to 102.1 ng Nm^{-3} . The dominant PBDE congener was BDE-209, and the next most dominant congeners were BDE-99 and BDE-47. The PBDE concentrations were much (about 5–244 times) higher than the PBDD/F concentrations in the stack gas samples. The PBDE emissions at different smelting stages in Plant1 and Plant2 followed similar patterns to the PBDD/F emissions. It has been suggested in several studies that BDE-209 could be transformed into OBDF or HpBDFs (Ren et al., 2011; Vetter et al., 2015). It can be seen from Fig. S1 that BDE-209 emissions at different smelting stages in Plant1 and Plant2 followed similar patterns to the OBDF and HpBDF emissions. The high

Table 1

Polybrominated dibenzo-*p*-dioxin (PBDD) and polybrominated dibenzofuran (PBDF) concentrations (pg Nm⁻³) in the stack gases emitted from the secondary aluminum smelting plants.

Plant		∑PBDDs	∑PBDFs	Ratio ^a	∑PBDD/Fs
Plant1	FF ^b	105	4468	0.02	4573
	RE ^c	64	4156	0.02	4221
	CA ^d	74	1863	0.04	1937
Plant2	FF1	525	865	0.61	1390
	FF2	574	893	0.64	1467
	RE	398	553	0.72	950
	CA	331	398	0.83	729
Plant3	Mix1	103	193	0.53	296
	Mix2	81	192	0.42	274
	Mix3	83	178	0.47	261
	Mix4	65	194	0.34	259
Plant4	Mix1	46	160	0.29	206
	Mix2	44	130	0.34	173
	Mix3	45	120	0.38	164
	Mix4	39	104	0.38	144

^a Ratio calculated as ∑2,3,7,8-PBDDs/∑2,3,7,8-PBDFs.

^b FF, feeding-fusion.

^c RE, refining.

^d CA, casting.

Table 2

Polybrominated dibenzo-*p*-dioxin and dibenzofuran (PBDD/F) concentrations found in stack gases from different industrial thermal processes.

Industrial thermal processes	Number of samples	PBDD/F concentration (pg Nm ⁻³)		Reference
Municipal solid waste incinerators	7	65–88	tetra- to octa-	(Wang et al., 2010a)
Converter Steelmaking Processes	15	36–183	tetra- to octa-	(Li et al., 2015)
Electric arc furnaces	6	20–2780	tetra- to octa-	(Wang et al., 2010b)
Iron ore sintering process	5	183–3010	tetra- to octa-	(Wang et al., 2010b)
Iron ore sintering process	15	370–710	tetra- to hexa-	(Drage et al., 2014)
Secondary copper smelting process	8	115–559	tetra- to octa-	(Wang et al., 2015)
Secondary copper smelting process	1	2500	tetra- to hexa-	(Du et al., 2010)
Secondary aluminum smelting	1	560	tetra- to hexa-	(Du et al., 2010)
Secondary aluminum smelting	15	144–4573	tetra- to octa-	This study

concentrations of PBDE congeners (including BDE-209) may therefore have provided abundant brominated precursors for the formation of PBDD/Fs, especially OBDF and HpBDFs, during the SAI processes.

3.2. PBDD/F emissions from different stages of the SAI processes

There are three distinct stages in the SAI process, feeding–fusion (FF), refining, and casting. Raw materials are first added to the furnace and heated by burning fuel. When the raw material has almost melted, alloying agents (zinc, copper, magnesium, or silicon) are added to modify the strength and ductility of the final product. The refined liquid aluminum is poured into molds or casting machines to produce aluminum ingots. PBDD/Fs may be formed and emitted during each smelting stage because of the incomplete combustion of organic and bromine-containing material (Sinkkonen et al., 2004). Different amounts and profiles of PBDD/Fs may be emitted at different stages of the smelting process. Plant1 and Plant2 each had only one furnace operating during the sampling period. This made it possible to examine the different amounts and profiles of PBDD/Fs emitted during the different smelting stages in these plants without interference from other furnaces sharing the same air pollution control devices. Separate stack gas samples were collected while the FF, refining, and casting processes were being performed in Plant1 and Plant2.

The PBDD/F concentrations in the samples from Plant1 and Plant2 while the different smelting processes were being performed are shown in Fig. 1. The highest PBDD/F concentrations (4573 and 1467 pg Nm⁻³ in the Plant1 and Plant2 samples, respectively) were found during the FF process at both plants. The

raw materials were melted in the FF process using heat supplied by burning fuel. The raw materials were added to the furnace in several batches, and the unsteady conditions that would have occurred each time raw material was added could have led to the incomplete combustion of fuel or organic impurities in the raw materials. It has previously been found that PBDD/Fs can easily form when an unsteady state occurs during an industrial thermal process (Weber and Kuch, 2003; D'Silva et al., 2004). The FF stage took 4–6 h in Plant1 and Plant2. The duration of the FF stage and the conditions under which it was performed make it unsurprising

Fig. 1. Polybrominated dibenzo-*p*-dioxin (PBDD) and polybrominated dibenzofuran (PBDF) concentrations in stack gases produced during different stages of the smelting process in Plant1 and Plant2 (FF = feeding–fusion, RE = refining, and CA = casting).

that large amounts of PBDD/Fs were formed and emitted while the FF stage was performed. The PBDD/F concentrations were slightly lower in the samples collected during the refining stage (4221 and 950 pg Nm⁻³ for the Plant1 and Plant2 samples, respectively) than in the samples collected during the FF stage. Some organic impurities in the raw materials would still have been present in the

respectively. Therefore, we attempted to determine whether PBDD/F emissions were affected by the composition of the raw material used. To achieve this, we estimated PBDD/F emission factors for Plant1, Plant2, and Plant3 from the PBDD/F concentrations in the stack gas samples, the stack gas flow rates, and the aluminum production capacities using Equation (1).

$$\text{Emission factor (ng t}^{-1}\text{)} = \frac{\left(\text{Concentration in stack gas (ng Nm}^{-3}\text{)} \times \text{Stack gas flow rate (Nm}^3 \text{ h}^{-1}\text{)}\right)}{\text{Aluminum production capacity (t h}^{-1}\text{)}} \quad (1)$$

furnace during the refining stage because the furnace contents will have been insufficiently mixed for the organic material to have been completely removed during the FF stage. Alloying agents are added to the liquid layer of aluminum during the refining stage to modify the strength and ductility of the aluminum produced. PBDD/Fs may therefore be produced during the refining stage because of the presence of organic impurities and metal oxides. Almost all of the organic impurities in the raw material will have been removed in the FF and refining processes, so very little organic material will be present during the casting stage. The PBDD/F concentrations were lower in the stack gas samples collected during the casting stage (1937 and 729 pg Nm⁻³ in the Plant1 and Plant2 samples, respectively) than in the samples collected during the FF and refining stages.

The results and information presented above lead us to suggest that variations in PBDD/F emissions during SAI processes may be related to the different smelting stages. PBDD/F emissions during SAI were found to occur mainly during the FF stage. These results may be useful in the development of techniques for decreasing PBDD/F emissions during SAI processes.

3.3. Influence of the raw material composition on PBDD/F emissions

The raw materials, smelting technique, and furnace capacity might influence emissions of unintentionally produced POPs during an industrial thermal process (Li et al., 2007; Ba et al., 2009; Wang et al., 2010b; Hu et al., 2014; Li et al., 2015; Wang et al., 2015). Identifying the effects of key factors on PBDD/F emissions could allow steps to be taken to significantly decrease PBDD/F emissions from SAI plants. We therefore investigated the influences of the raw materials, smelting techniques, and furnace capacities used in the plants on the PBDD/F concentrations in the stack gas samples. No significant correlation was found between the furnace capacity and the PBDD/F concentration. The relationships between the PBDD/F concentrations and the scrap pre-treatments and raw material compositions that were used were assessed.

In our previous studies, we found that using raw materials with different compositions can cause different amounts and profiles of PCDD/Fs, PCBs, and PCNs to be emitted during secondary metal smelting processes (Hu et al., 2013b; Jiang et al., 2015). Few studies of the influences of different raw material compositions in metal smelting processes on PBDD/F emissions have been performed. Plant1, Plant2, and Plant3 all had bag filter air pollution control devices and used similar furnaces and raw material pretreatment techniques. The most obvious difference between the three plants was the raw material used. Dirty scrap aluminum contributed 100%, 80%, and 50% of the raw materials used in Plant1, Plant2, and Plant3,

The PBDD/F emission factors were in the range 14–180 μg t⁻¹. The PBDD/F emission factors for Plant1, Plant2, and Plant3 are shown in Fig. 2A. It can be seen from Fig. 2A that Plant1, which used only dirty aluminum scrap as a raw material, had the highest PBDD/F emission factor, 180 μg t⁻¹. Dirty aluminum scrap typically contains relatively large amounts (18–20% by weight) of organic residues, such as plastics, paints, and solvents (Kevorkjian, 2010). Using raw materials with higher organic residue contents will lead to more PBDD/Fs being emitted during the smelting process. It is therefore not surprising that relatively large amounts of PBDD/Fs were found in the stack gas samples from Plant1. The PBDD/F

Fig. 2. Relationships between the dirty aluminum scrap contents of the raw materials used in Plant1, Plant2, and Plant3 and (A) the polybrominated dibenzo-*p*-dioxin and dibenzofuran (PBDD/F) emission factors and (B) the sums of the octabromodibenzofuran (OBDF), 1,2,3,4,6,7,8-heptabromodibenzofuran (HpBDF), octabromodibenzo-*p*-dioxin (OBDD), and 1,2,3,4,6,7,8-heptabromodibenzo-*p*-dioxin (HpBDD) contributions to the total PBDD/F concentrations.

emission factor for Plant2, which used 80% dirty aluminum scrap and 20% copper-clad aluminum wire as its raw material, was $86 \mu\text{g t}^{-1}$, and this was lower than the emission factor for Plant1. Plant3, which used 50% dirty aluminum scrap and 50% clean aluminum scrap as its raw material, had the lowest PBDD/F emission factor, $14 \mu\text{g t}^{-1}$. The PBDD/F emission factor increased as the dirty aluminum scrap content of the raw material increased. These results indicate that the composition of the raw material used in a SAI plant is one of the key factors influencing PBDD/F emissions from the plant. The composition of the raw material, especially the proportion of secondary materials (such as dirty aluminum scrap) with high organic impurity contents, should be given careful consideration when evaluating PBDD/F emissions from SAI plants.

3.4. Effect of scrap pretreatment on decreasing PBDD/F emissions

The scrap pretreatment process generally involves sorting, washing, depitching, crushing, and drying the scrap to remove contaminants and prepare the material for smelting. In the sorting process, aluminum is separated from other metals and non-metallic materials such as plastics and paint. The scrap is then washed to remove dirt and oil, then the depitching process removes paint and other coatings from the surfaces of the aluminum. The scrap is crushed to break it into small pieces to improve the efficiency at which iron can later be removed using magnets. The aluminum scrap will still contain some organic contaminants, and these are removed by drying the scrap in rotary dryers.

All of the feed materials used in the plants we studied were pre-cleaned, but different pretreatment techniques were used in the different plants. The feed materials used in Plant4 were subjected to a series of standardized pretreatments that included manual and magnetic separation, washing, depitching, crushing, and tumble drying at about 400°C . The feed materials used in Plant1, Plant2, and Plant3 were not effectively pretreated but were simply dried at a relatively low temperature, $150\text{--}200^\circ\text{C}$. Plant4 and Plant1 used only dirty aluminum scrap as the raw material. The mean PBDD/F concentration in the stack gas from Plant4, in which the raw materials were pretreated effectively, was 171 pg Nm^{-3} , which was significantly (a factor of 20) lower than the mean concentration in the stack gas from Plant1 (3577 pg Nm^{-3}), in which the raw materials were only dried at a low temperature. The PBDD/F concentrations were also markedly lower in the stack gas from Plant4 than in the stack gas from Plant2 and Plant3 (the concentrations were 1049 and 272 pg Nm^{-3} in the samples from Plant2 and Plant3, respectively), which used raw materials containing 50–80% dirty aluminum scrap that was not pretreated effectively. It has been shown that the incomplete combustion of organic impurities in raw materials leads to the unintentional production of POPs during a number of industrial thermal processes (Fiedler, 2007; Gullett et al., 2009; Li et al., 2015). Effective pretreatment of scrap metal can significantly decrease the organic impurity content of the raw material, meaning that smaller amounts of PBDD/Fs will be formed through the incomplete combustion of organic impurities during smelting. Our results clearly indicate that the effective pretreatment of scrap aluminum has an important role to play in decreasing PBDD/F emissions during SAI processes.

3.5. Congener profiles of the PBDD/Fs in the stack gas samples

The tetra- to octa-brominated PBDD/F homolog profiles, shown in Fig. S2, were evaluated to improve our understanding of the PBDD/F emissions from the SAI plants we studied. The hepta- and octa-brominated PBDD/Fs were the main homologs in the stack gas samples from all of the plants, together contributing 97–98%,

84–94%, 64–81%, and 86–90% of the total PBDD/F concentrations in the samples from Plant1, Plant2, Plant3, and Plant4, respectively. It can be seen from Fig. S2 that the relative contributions of the tetrabrominated PBDD/F homologs were higher in the Plant3 samples (12–15%) than in the samples from Plant1 (0.20–0.39%), Plant2 (0.70–3.7%), and Plant4 (1.0–3.2%). The PBDF concentrations were much higher than the PBDD concentrations in the stack gas samples, the PBDFs contributing 94–99%, 55–97%, 65–68%, and 73–90%, of the total PBDD/F concentrations in the stack gas samples from Plant1, Plant2, Plant3, and Plant4, respectively.

The PBDD/F congener profiles can help identify the PBDD/F formation mechanisms and sources. We selected thirteen 2,3,7,8-substituted PBDD/F congeners to “fingerprint” the PBDD/Fs produced during SAI processes. The concentration of each PBDD/F congener was normalized to the total 2,3,7,8-substituted PBDD/F concentration to allow the PBDD/F patterns to be compared effectively. The PBDD/F congener profiles in the stack gas samples from the SAI plants we studied are shown in Fig. 3. As is shown in Fig. 3, the more brominated PBDD/F congeners (OBDF, 1,2,3,4,6,7,8-HpBDF, octabromodibenzo-*p*-dioxin (OBDD), and 1,2,3,4,6,7,8-heptabromodibenzo-*p*-dioxin (HpBDD)) were the dominant congeners in the samples from all of the plants. The contributions of the PBDD and PBDF congeners to the total 2,3,7,8-substituted PBDD/F concentrations in the Plant2 samples increased as the degree of bromination increased, and OBDD and OBDF contributed more than the other congeners to the total 2,3,7,8-substituted PBDD/F concentrations. The Plant4 samples had similar tetra- to octa-brominated PBDD and tetra- to hexa-brominated PBDF congener patterns to the Plant2 samples, but OBDF contributed significantly less than 1,2,3,4,6,7,8-HpBDF to the total PBDD/F concentrations in the Plant4 samples than in the Plant2 samples. The Plant1 samples did not have the same congener pattern, the hepta- to octa-brominated PBDF congeners contributing far more than the tetra- to hexa-brominated PBDD/F congeners to the total 2,3,7,8-substituted PBDD/F concentrations. The most abundant congener in the Plant3 samples was OBDF, and the next most abundant were 1,2,3,4,6,7,8-HpBDF, OBDD, and 1,2,3,4,6,7,8-HpBDD.

The PBDD/F congener profiles in samples from waste incinerators, secondary copper production plants, iron ore sintering plants, and electric arc furnaces (used to produce steel) have previously been found to be dominated by the more brominated PBDFs, particularly OBDF and 1,2,3,4,6,7,8-HpBDF (Wang et al., 2010b; Wyrzykowska-Ceradini et al., 2011; Li et al., 2015; Wang et al., 2015). The PBDD/F congener profiles in our SAI samples were similar to the profiles that have been found in samples from waste incinerators, secondary copper production plants, iron ore sintering plants, and electric arc furnaces, suggesting similar PBDD/F formation mechanisms occur in the processes performed in each of these types of plant.

As described above, we concluded that using raw materials with different compositions caused there to be different PBDD/F concentrations in stack gases produced by the SAI plants. The more brominated PBDD/F congeners were the dominant contributors to the total 2,3,7,8-substituted PBDD/F concentrations in the stack gas samples. We evaluated the influence of the raw materials used on the PBDD/F congener patterns by estimating the contributions of the more brominated PBDD/F congeners (OBDF, 1,2,3,4,6,7,8-HpBDF, OBDD, and 1,2,3,4,6,7,8-HpBDD) to the total 2,3,7,8-substituted PBDD/F concentrations in the samples from Plant1, Plant2, and Plant3. The relationship between the sums of the contributions of OBDF, 1,2,3,4,6,7,8-HpBDF, OBDD, and 1,2,3,4,6,7,8-HpBDD to the total 2,3,7,8-substituted PBDD/F concentrations and the dirty aluminum scrap contents of the raw materials for Plant1, Plant2, and Plant3 is clearly shown in Fig. 2B.

Fig. 3. Polybrominated dibenzo-*p*-dioxin and dibenzofuran congener profiles in the stack gas samples from the secondary aluminum smelting plants (BDD = bromodibenzo-*p*-dioxin, BDF = bromodibenzofuran, Te = tetra, Pe = penta, Hx = hexa, Hp = hepta, O = octa).

The sum of the OBDF, 1,2,3,4,6,7,8-HpBDF, OBDD, and 1,2,3,4,6,7,8-HpBDD contributions to the total 2,3,7,8-substituted PBDD/F concentration was 98% for Plant1, which used only dirty aluminum scrap as its raw material. The sum of the OBDF, 1,2,3,4,6,7,8-HpBDF, OBDD, and 1,2,3,4,6,7,8-HpBDD contributions to the total 2,3,7,8-substituted PBDD/F concentration was lower, at 89%, for Plant2, which used 80% dirty aluminum scrap and 20% copper-clad aluminum wire as its raw materials. The sum of the OBDF, 1,2,3,4,6,7,8-HpBDF, OBDD, and 1,2,3,4,6,7,8-HpBDD contributions to the total 2,3,7,8-substituted PBDD/F concentration was lower still, at 75%, for Plant3, which used 50% dirty aluminum scrap and 50% clean aluminum scrap as its raw materials. We concluded that the contribution of the more brominated PBDD/F congeners (the hepta- and octa-brominated PBDD/Fs) increased as the dirty aluminum scrap content of the raw material increased at the plants we studied. It is therefore clear that using raw materials with different compositions can affect both the amounts of PBDD/Fs emitted and the congener patterns of the PBDD/Fs emitted during SAI processes.

4. Conclusions

We measured PBDD/F emissions and the PBDD/F congener patterns in stack gases produced in four typical SAI plants in China. High PBDD/F concentrations were found in the stack gas samples, but the PBDD/F concentrations and congener profiles varied widely. The composition of the raw materials used in a SAI plant was found to be a key factor influencing the amounts of PBDD/Fs emitted and the PBDD/F congener profiles. PBDD/F emission factors were derived for the plants using different proportions of dirty aluminum scrap in their raw material feeds. Larger amounts of PBDD/Fs were found to be emitted during the FF stage than in the other stages. We found that effectively pretreating aluminum scrap can significantly decrease the amounts of PBDD/Fs emitted. Different PBDD/F congener profiles were found in the samples from the SAI plants using raw materials with different compositions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.11.109>.

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