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

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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 (SAl) 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 SAl 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 SAl 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 μg 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 SAl 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.

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 (Kevorkjjan, 2010). Secondary aluminum smelting (SAl) 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).

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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 SAl processes have previously been studied in detail, and SAl 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 SAl in Poland than in flue gases produced during other industrial thermal processes. Daily inhaled doses of PCDD/Fs, dioxin-like PCBs, and PCNs in SAl 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 SAl plants. The highest PCDD/F concentrations were found in the serum samples from the SAl workers. The studies described above showed that SAl plants are important sources of unintentionally produced chlorinated POPs.

Intensive studies of PCDD/F, PCB, and PCN emissions during SAl 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 SAl plants. For example, Sinkkonen et al. (Sinkkonen et al., 2004) screened four raw scrap material samples from a SAl 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 SAl process naturally means that the formation of PBDD/Fs during the SAl process should be considered.

Although PBDD/Fs are believed to be formed during SAl 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 SAl 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 SAl 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 SAl plants is therefore likely be important to allow a preliminary estimate of global PBDD/F emissions from SAl plants to be made.

In this study, PBDD/F emissions from four typical SAl plants with different furnace capacities and using different raw materials were investigated. The primary objective was to estimate PBDD/F emissions from typical SAl 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 SAl plants. Fabric bag filters are widely used as air pollution control devices in Chinese SAl plants (Ba et al., 2010; Hu et al., 2013b; Jiang et al., 2015). Four typical Chinese SAl 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 SAl 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. $^{37}Cl_4$-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