Journal of Hazardous Materials 286 (2015) 545–552

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Case study of polychlorinated naphthalene emissions and factors influencing emission variations in secondary aluminum production

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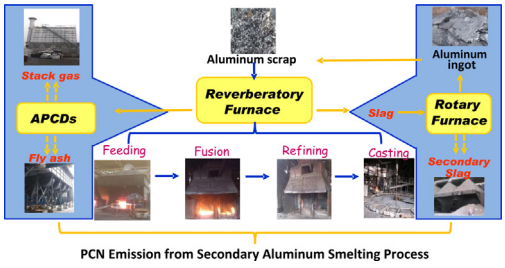
HIGHLIGHTS

- Variations in PCN emissions from different smelting stages were observed.
- Factors influencing PCN emission levels and profiles were identified.
- Addition of chloride additives possibly promote PCN formations.
- Emission factors for gaseous and various solid discharges were derived.
- This study is helpful for developing better control strategies for PCN reduction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form
17 December 2014
Accepted 4 January 2015
Available online 6 January 2015

Keywords:
Secondary aluminum production
Smelting stages
Polychlorinated naphthalene
Solid residues
Chloride additives

ABSTRACT

Secondary aluminum production has been recognized as an important source of polychlorinated naphthalenes (PCNs). Large variations in PCN emissions as the smelting process proceeds have not been determined. In this study, solid and gaseous discharges, including fly ash, slag, and stack gas samples collected from four secondary smelting plants during different smelting stages were analyzed for PCNs. The average emission factor of $\sum_{1-8}$PCNs to air was calculated to be 17.4 mg t^{-1}, with a range of 4.3–29.5 mg t^{-1}. The average emission factors of $\sum_{1-8}$PCNs from fly ash and slag were 55.5 ng t^{-1} and 0.13 ng t^{-1}, respectively. The derived emission factors may enable a more accurate estimation of annual emissions and a more comprehensive knowledge of the distribution of PCNs emitted from secondary aluminum production. The emission levels and characteristics of PCNs during different smelting stages were compared. Possible factors, including the organic impurities from aluminum scrap, fuel, and chloride additives, which could contribute to variations in PCN emissions and characteristics were discussed. These results may provide useful information for developing better control strategies for reducing PCN emissions in secondary aluminum production.

1. Introduction

Polychlorinated naphthalenes (PCNs) are persistent organic pollutants (POPs), and are ubiquitous in environmental matrices and biota [1–3]. It has recently been proposed that PCNs be included in Annexes A, B, and/or C of the Stockholm Convention on Persistent Organic Pollutants. The main sources of PCNs are the historical manufacture of technical PCN mixtures, impurities in commercial polychlorinated biphenyl mixtures and other chemicals, and unintentional production and release from industrial thermal processes [4–6]. The production and use of technical PCNs was banned in the United States and Europe in the 1980s. Currently, the major contrib-

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http://dx.doi.org/10.1016/j.jhazmat.2015.01.009
0304-3894/

utors to PCN emissions are thermal-related industries, including waste incineration, coking processes, and metallurgical processes such as secondary nonferrous smelting, iron ore sintering, and steelmaking using electric arc furnaces [7–11]. However, investigations on developing control measures aimed at reducing PCN emissions from these industrial processes are still scarce.

The decreasing costs and increasing availability of aluminum products for use in food packaging, construction, transportation, electrical applications, consumer durables, machinery and industry use forecast a growing disposal burden of aluminum scrap. Secondary aluminum smelting can dispose of aluminum scrap in an economical and recyclable way, because aluminum scrap can be recycled without any loss of quality and the production of secondary aluminum requires only 5–20% of the energy required for the production of primary aluminum from bauxite [12]. Under these circumstances, the activity rate for global secondary aluminum production has been significant in recent years. China is the largest aluminum-producing country, accounts for ~34% of global aluminum production, with a secondary aluminum production of ~3 000 000 t a^{-1} during 2011–2013 [13]. There are large discrepancies in the scales and technologies for secondary aluminum production in China; therefore, an investigation of PCN emissions from the Chinese secondary aluminum industry would facilitate an evaluation of the release of PCNs from secondary aluminum smelting processes on a global scale.

In our previous study, atmospheric emission factors and total PCN emissions from secondary aluminum production in China were investigated [14]. Large variations in PCN concentrations were observed, from 98.9–2245 ng m^{-3}, from secondary aluminum production in China [14]. However, the reasons for the large variations in PCN emission concentrations have not been considered in previous research. PCN emissions and characteristics at different smelting stages may differ depending on the operating conditions and the feedstock composition during secondary aluminum smelting process. Studies conducted to investigate PCN emissions and characteristics at different smelting stages could; therefore, facilitate understanding of the formation mechanisms of PCNs. PCNs can bind to particles and also partition into the gas phase because of their semi-volatility [9,14,15]. However, the field data from most previous investigations focusing on gaseous emissions are unavailable for assessing the integrated emission of PCNs in all discharges. Furthermore, disregarding the solid residues that are produced in the system would result in an insufficient risk assessment and inappropriate disposal, which could cause potential risks to the environment and involved workers.

In this study, fly ash from a bag filter, slag from smelting of aluminum scrap, secondary slag from secondary rotary smelting of slag, and stack gas at different smelting stages were collected from four secondary aluminum smelting plants. To the best of our knowledge, investigations of the presence of PCNs in various discharges from secondary aluminum smelting processes or other metallurgical processes are scarce. The aim was to obtain a comprehensive knowledge of the overall PCN emission distribution in secondary aluminum smelting processes. The results from this study could provide useful information for obtaining comprehensive information on PCN emission distributions, understanding PCN emission mechanisms, and developing better control strategies for PCN emissions in secondary aluminum production.

2. Experimental

2.1. Plant information

Four typical plants in China (denoted by AL1–AL4) were selected, based on their different operating technologies, including furnace type, fuel, and raw materials. In the secondary production of aluminum, scrap can be melted in gas- or oil-fired reverberatory furnaces in all the plants investigated. The reverberatory furnace production is the traditional technology for secondary aluminum production in China because of its high volumetric processing rate, and low operating and maintenance costs. Light oil, natural gas, or coal gas was used as fuel to melt the raw materials. The raw materials, which are a complex combination of all types of collected aluminum scraps, are loaded into melting furnaces. A significant amount of raw materials, including foils, extrusions, turnings, and borings from metal manufacturing processes, are defined as “clean aluminum scrap” in this study. Typical sources of raw materials also include “dirty aluminum scrap” from the recycling of consumer products. The air pollution control devices used in all the plants investigated were bag filters. Bag filters, which are bag-shaped dust collectors made of fabric filters, are widely used as air pollution control devices (APCDs) in industrial plants for capturing entrained particulate matter from flue gases. The four plants included the largest secondary aluminum plant in Asia, which uses advanced technologies, and three smaller-scale plants, which use traditional technologies; these plants are distributed across China.

2.2. Sample collection

The samples for this study were collected in June 2013. The stack gas samples were collected using an automatic isokinetic sampling system. The sampling point was set downstream of all air pollution control devices. Briefly, the sampling train consisted of a heated probe, a filter box equipped with a silica glass microfiber thimble (25 mm i.d., 90 mm length; Whatman International Ltd., Whatman, UK), a water-cooled Amberlite XAD-2 adsorbent trap (Supleco International Ltd., Varina, USA), an Isotack Basic (TCR Tecora, Italy) pump and an Isofrost cooler (TCR Tecora, Italy). Particles in the stack gas were trapped by the silica glass microfiber thimble. Gases were cooled in a condensing system and then adsorbed in a trap with Amberlite XAD-2 resin. Four distinct smelting stages are involved in secondary aluminum smelting: feeding (FD), fusion (FS), refining (RF), and casting (CS). Aluminum scrap is usually smelted and refined in a reverberatory furnace. Once smelted, the flux, which usually consists of NaCl and KCl, is added to remove some impurities from the molten aluminum [16–18]. In this study, 15 stack gas samples and eight residue samples were collected. In plant AL1, three stack gas samples were collected during the FD, FS, and RF stages, and in AL2, three stack gas samples were collected in the FD, FS, and CS stages, based on the limited scope for sampling in the plants. Three mixed gas samples were collected from AL3 and four mixed gas samples were collected from AL4, because several furnaces were in operation simultaneously at these plants. Fly ash samples were collected simultaneously from the bag filter outlets at all four plants. Slag samples were collected from the reverberatory furnace before the slag was shifted to the rotary furnace for secondary smelting at plants AL1 and AL2. Secondary slag samples were collected at the bottom of the rotary furnace, after secondary smelting was completed, at plants AL1 and AL2. All solid samples were homogenized before analysis. Basic information on the secondary aluminum smelting plants is shown in Table 1.

2.3. Analytical methods

The stack gas samples and solid residue samples (2 g) were pretreated and analyzed for PCNs by isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry [9,19]. The stack gas samples and residues were spiked with a mixture of $^{13}C_{10}$-labeled PCN internal standards (ECN-5102, tetra- to octa-CN mixture comprising $^{13}C_{10}$–CN-27, -42, -52, -67, -73, and -75, Cambridge Isotope Laboratories, Andover, MA, USA). The stack gas samples were directly Soxhlet extracted with toluene