Resources, Conservation and Recycling xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Resources, Conservation and Recycling

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

Full length article

Integrated assessment of process pollution prevention and end-of-pipe control in secondary lead smelting

Yanping Li[a,b,*,1], Zhen Su[c,1], Qi Qiao[b], Xuewen Hu[b], Si Wan[c], Ruonan Zhao[b]

[a] College of Water Sciences, Beijing Normal University, Beijing 100875, China
[b] Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[c] Hunan Province Research Institute of Non-Ferrous Metals, Changsha 410015, China

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 23 October 2015
Accepted 4 November 2015
Available online xxx

Keywords:
Integrated assessment
Process pollution prevention
End-of-pipe control
Secondary lead smelting
Substance flow analysis (SFA)

ABSTRACT

Based on the Conservation Law, the equations and variables of the process pollution prevention and EPC were established for a given product process. The eco-efficiency indicator including resource efficiency (r) and environmental efficiency (q) is pointed out as the integrated assessment of the process pollution prevention and end-of-pipe control. Substance Flow Analysis (SFA) was adopted to account all the integrated assessment indicators for three typical secondary lead smelting technologies: *Mixed smelting process (MSP)*, *Pre-desulfurization smelting process (PDSP)* and *Hydro-metallurgical smelting process (HMP)*. Based on the site monitoring and statistical data collection, there are 15 secondary lead production enterprises covering all the three smelting processes and 87.67% production capacity of sec-lead production of China in 2014. The result of integrated assessment shows us that lead pollution emission load is the result of co-control of process pollution prevention and end-of-pipe control. The environmental efficiency of different technology is *PDSP* > *HSP* > *MSP* without any process pollution prevention or end-of-pipe control. The effect of process pollution prevention improving the eco-efficiency varies due to different technology along with *HSP* > *PDSP* > *MSP* and for different sub-process of different technology. Under the co-control of process pollution prevention and end-of-pipe control, the *HSP* will be the best available smelting technology for secondary smelting industry.

1. Introduction

Frequent events of lead pollution (Hu and Chen, 1999; Shen et al., 1996; Li et al., 2009) have aroused great attention not only from the public but also the Chinese government because of the severe risk to ecosystems and human healthy. It's proved that lead-rich fly ash or dust can be inhaled and penetrating deep into the lungs and even the blood stream (Goyal and Small, 2005; Shen et al., 1996). Moreover, lead-contaminated soil and water may be an additional risk of lead poisoning via ingestion (Gottesfeld and Pokhrel, 2011; Liang and Mao, 2014). Zheng et al. (2010) pointed out that the concentration of lead in environment around the lead and zinc smelting and the secondary lead smelting is several times higher than the average level. Therefore, lead-pollution prevention now has become an indispensable part of the goals of most smelting because of external pressure (laws, the demands of customers, etc.) or pursuing more profit through environmental performance improvement.

Typically, there are two fundamental types of abatement measure mitigating the adverse environmental impacts of production: "Process-Pollution-Prevention (PPP)" and "End-of-Pipe Control (EPC)". Depending on the type of production process, PPP reduce resource use and/or pollution by reuse and recycling solution during the process of production, while EPC curb emissions through the installation of purification and detoxification unit at the end of production. Thus the PPP is generally seen as being superior to EPC for both environmental and economic reasons (Frondel et al., 2007; Hilson, 2003). However, the establishment of PPP is often hampered by substantial investment, the nature of the environmental problem and the type of regulation involved (Hilson, 2000; Olajire, 2010). Besides, the frequently imposed regulations, like "Lead & zinc Industrial Pollutant Emission Standards", cannot be achieved at present without end-of-pipe equipment (Tian et al., 2014). Therefore, companies in practice usually pursue the integrated pollution prevention of these two solutions.

This study aims to assess the difference contribution of PPP and EPC to the lead pollution of secondary lead smelting with the

* Corresponding author. Tel.: +86 10 84920936.
E-mail address: leeyp@craes.org.cn (Y. Li).
[1] Yanping Li and Zhen Su are the co-first author.

http://dx.doi.org/10.1016/j.resconrec.2015.11.005

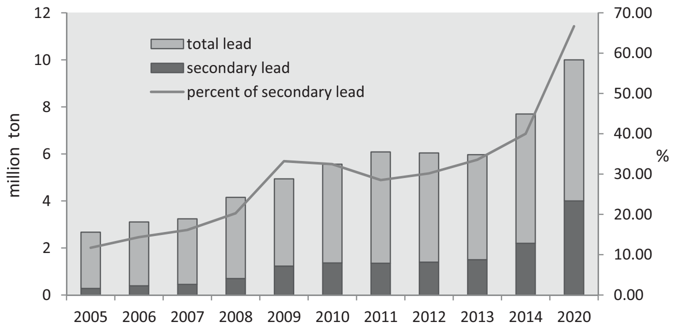

Fig. 1. Development of secondary lead production of China from 2005 to 2020.

following reasons: first, lead smelting is the main pollutant emissions of heavy metals and main emission source of children's blood lead. Compared with numerous researches on primary lead smelting pollution prevention (Bai et al., 2015; Cai et al., 2009; Zhang et al., 2012), there are fewer study on secondary lead smelting let alone on different smelting processes. Second, with the rapid growth of secondary lead output in China which is predicted to reach 70% of the total lead production in the Thirteen Five nonferrous Development Plan in 2020 (Fig. 1), the pressure on pollution prevention of it will be increasingly prominent and serious, especially more than 80% material from waste lead-acid battery (Tian et al., 2014) managed as the hazard waste made it necessary to assess the secondary environmental pollution. Finally, it's urgent and necessary to carry out integrated assessment to meet the whole process environmental supervision on secondary lead process. We'll carry out assessment of the lead pollution load during the whole production process by integrated assessment method.

2. Secondary lead smelting

For secondary lead smelting, the recycling process consists of two stages, namely, physical separation and chemical separation. Typically, the spent lead-acid batteries (LAB) are drained of the electrolyte and crushed into small pieces for further processing through manual or mechanical dismantling, followed by the washing and gravity separation in hydro-separator to isolate lead-containing component and other materials. Three streams are then obtained: lead-containing materials (25–29% lead, 35–55% PbO_2/$PbSO_4$), polypropylene scraps (5–8%), and sulfuric acid (11–28%) (Jolly and Rhin, 1994; Sonmez and Kumar, 2009). It should be mentioned that the lead-containing materials usually come from grids and posts and electrode paste. At the chemical stage, the lead-containing materials are reduced to metallic lead through pyro-metallurgical or hydro-metallurgical methods (Andrews et al., 2000; Genaidy et al., 2009). Pyro-metallurgical techniques reduce all metallic compounds to their metallic or reduced forms by means of heating (>1200 °C) and use of fluxing and reducing agents. In some practices, desulfurization and neutralization steps are needed prior to smelting (Ellis and Mirza, 2010). Following is a refining step at which specific reagents are added to the molten lead at appropriate temperatures (>320 °C) to remove other unwanted metals. As for hydro-metallurgical technology, it directly reduce all the lead compounds to metallic lead via electrolysis that deposits lead on electrodes, which is subsequently shaken off, collected and pressed to form platelets of pure lead. In comparison, hydro-metallurgical method is superior in terms of the lead purity of product and environmental hazard. However, its production out-put is much less than that of pyro-metallurgical process.

2.1. Secondary lead smelting process

Currently, pyro-metallurgical approach is still the dominant operation for lead production in China and only a few companies take the hydro-metallurgical method. In this study, three main practices for secondary lead smelting are investigated and they are denoted as "*Mixing smelting process*" "*Pre-desulfurization smelting process*" and "*Hydro-metallurgical process*", respectively, according to the different processing ways for lead paste.

Fig. 2(A) shows the technology of *Mixing smelting process*. This is an improved technology used for secondary lead smelting but based on the equipment and processes for primary lead smelting. It is featured in the component of feed material, constituting not only spent lead-acid batteries but also lead concentrate. On the whole, eight sub-process units are involved: two physical-separation units (battery breaking/hydro-separation and pelletization), and six chemical-separation units (refining and alloying, bottom-blowing smelting, reduction smelting, fuming, electrolysis and ingot casting). At the very beginning, spent lead-acid batteries are mechanically broken and hydrodynamically separated as lead grid and lead paste. For lead grid, which is usually of high lead content (>90%), is sent to the refining kettles to remove the residual impurities and then lead alloy can be obtained by adjusting some other trace elements to produce alloys as per customer requirements and cast into ingot for shipment. While for the lead paste, it will be mixed with the lead concentrate and other burdening (limestone or quartzite) with appropriate ratio and fed into the pelletization process. Afterwards, the lead pellets are transported to the bottom-blowing furnace and reduction furnace at which units different forms of lead compounds are converted to lead bullion. The obtained lead bullion is then moved to electrolytic refining process. To put it simply, lead bullion is first pressed as anode plate while refined lead serves as cathode plate, and then through the potential between the electrodes, lead from anode plate will deposit on cathode plate that can be casted into ingot for sale. Meanwhile, other mixed metals like copper, tin, antimony, silver, etc. can be separated from lead. One thing should be mentioned is that the presence of lead concentrate during the smelting will lead to the formation of zinc oxide that is usually sold to zinc smelters as raw materials (Harrison and Williams, 1981). Fig. 2(B) shows the *Pre-desulfurization smelting process*. As can be seen, in this case the processing object is only spent lead-acid batteries and the process units are less than the former technique. Six processes are included, one physical-separation unit (battery breaking/hydro-separation) and five chemical-separation units (desulfurization, refining and alloying, smelting, electrolysis and ingot casting). The manner to treat lead grid is the same. But the lead paste should first be desulfurized and then added into furnace for smelting. The reason for desulfurization is that desulfurized paste is beneficial to reduce energy consumption and pollution generation. After smelting, the acquired lead bullion should be electrolyzed to produce refined lead product as described before. For *Hydro-metallurgical process* (Fig. 2C). It has six process units. The biggest difference is that lead paste undergoes a full hydro-metallurgical process. More specifically, after the completion of desulfurization process, lead paste then bears leaching operation to obtain lixivium that is rich in lead. Since the most commonly used leaching agent is silicofluoric acid, the resulting lixivium is lead fluorosilicate. Afterwards, the electrolysis unit that uses graphite as anode and refined lead as cathode is carried out to acquire final product.

2.2. Environmental pollution of secondary lead smelting

To a large degree, EPC for secondary lead enterprise is mandatory to meet the environmental laws and regulations. The forms of lead emission include liquid, slag and gas. During the process,