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Reduction in toxicity and generation of slag in secondary lead process

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A B S T R A C T

This paper focuses on the improvement of a secondary lead recycling processing plant, giving special attention to the generation of lead slag. The study was conducted using two different industrial rotary furnaces that together produce three different slag types, which depend on charge composition and lead-containing raw material obtained from a lead-acid battery recycling process. First, characterization of three slag types from different batches was performed, and such characterization included chemical, mineralogical, and structural analyses. By analyzing these data and the operational conditions of the process, it was possible to identify certain deficiencies in the recycling process and implement modifications in order to improve it. A reduction of up to 25% in the quantity of slag generated could be achieved with certain charges. In addition to this process improvement, it was possible to reduce the toxicity of the slag produced when processing a charge containing the same proportion of paste and grid as the lead-acid battery. This improvement lessens the overall environmental impact of the process. By applying this methodology, it was possible to determine some principles of cleaner production in the lead recycling process. So, waste generation could be reduced via improvements in the process and slag characteristics were modified to decrease its toxicity (as determined by lead content in leaching tests).

1. Introduction

Secondary lead recycling using lead-acid battery scraps as raw material generates a large amount of solid waste in the foundry stage, during which the lead is reduced to its metallic form. The impurities present in the lead-containing raw materials, together with other materials added to promote the necessary reactions in the process, constitute the slag. It is not possible to ascertain the precise quantity of slag generated in the world, but it is estimated that the annual production from primary and secondary lead processes is 3 Mt (Rodriguez-López, 1999).

In the U.S., per example, between 1999 and 2006, lead recovery and recycling was stagnant at steady values, but lead consumption increased at an annual growth rate of 2.25%. In light of increased lead prices, it makes economic and environmental sense to maximize lead recovery and recycling by establishing a strong ecologic interface between stakeholders and consumers (Genaidy et al., 2008). In China, an increasing number of enterprises have begun to produce secondary lead, and the scale of production has expanded from tens of tons to tens of thousands of tons. The flourishing development of electric bicycles, electric tricycles, and photovoltaic energy systems should provide ongoing opportunities for the lead-acid battery industry (Chen et al., 2009).

In Brazil, lead is produced entirely from secondary processes, mainly from the recycling of lead-acid battery scrap. The slag generated in the rotary furnaces is classified as hazardous waste in accordance with Brazilian norm ABNT NBR 10004 (Associação Brasileira de Normas Técnicas (ABNT), 2004) and is disposed of in landfills.

Dahodwalla and Heart (2000) discussed the environmental problems caused by the lead-acid battery manufacturing industry and investigated some of the cleaner production options that can be applied to alleviate these problems. However, they did not discuss options for changing the smelting stage.

Other researchers have performed analyses of secondary lead process and suggested some possible improvements. Lewis and Beautement (2002) studied a secondary lead process with the aims of characterizing the waste, minimizing waste production through process improvement, modifying the waste, and identifying slag treatment methods. Suggested process improvements to reduce the quantity of generated waste included the adjustment of the Fe:S and Fe:Na molar ratios and the adjustment of the coke quantity. Suggestions for modification of the waste included the possibility of reducing the presence of zinc by avoiding the processing galena concentrates and lead slag.

Genaidy et al. (2009) have published research on pollution prevention as well as waste minimization practices and

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technologies for secondary lead smelters. By dividing the smelting process into pre-, in-, and post-processing, the efforts were concentrated on improving the operation at the pre-processing stage. They concluded that the adoption of cleaner technologies at this stage can significantly improve the smelter performance from both an economic and an environmental perspective.

Other studies characterized the slag generated in a lead recycling process from a treatment or disposal perspective. Coya et al. (2000) evaluated the toxicity of the leachate produced from lead slags collected on different dates. The waste samples were collected from the edge of the deposits; three samples were taken for the 6-month-old slag together with one sample that had undergone a month less of aging and one sample of recent slag. After the leaching process, the toxicity of leachate was determined using a bioluminescence assay and analysis of its heavy metal content. The authors reported that, for the slag to be classified as non-eco-toxic, either a minimum aging time is necessary for the slag to leach under natural conditions or the slag must be subject to a washing process that reduces its soluble components.

De Angelis et al. (2002) studied the performance of products arising from the stabilization/solidification of secondary lead slag into a Portland cement matrix. The goal of the study was to permit stabilized waste to be disposed of according to current legislation and also to obtain a recyclable material. The results showed that only a limited amount of slag can replace siliceous sand, if problems caused by the interactions of lead with cement components are to be avoided.

Lassin et al. (2007) used previous characterizations of a secondary lead slag to construct a physicochemical model of slag behavior, and then used the model to carry out sensitivity analyses with various landfill scenarios. This resulted in proposed adjustments to the process to facilitate the recovery of the residual heavy metals and the upgrading of the co-products generated by inerting the slag. Their results showed that only the elimination of the sulfur could conceivably allow for disposal in a waste landfill, guaranteeing reasonable safety. Only after a stage of stabilization and solidification can this waste be landfilled with an optimal degree of safety.

Seignez et al. (2008) have studied the leaching behavior of lead slags from blast furnaces in pure water and open flow experiments. The pollutant release at conditions found in landfills was determined and the understanding of such mechanisms was improved. Lead was found to be strongly released in open flow conditions.

Smaniotto et al. (2009) presented a new methodology for the extraction of lead from slag produced in secondary lead smelters. The complexing agent (EDTA) was used to promote a complexation reaction with the lead salts present in the waste. The developed method has been considered as a promising route for the treatment of the lead contained in such slags.

It is known (Seadon, 2010) that the understanding of the process as a system and taking into consideration material flows is a way of reducing the waste generation and improving the sustainability of a process. The analysis of one of the goals of the latest National Waste Plan of Finland (Lilja and Liukkonen, 2008), per example, showed a relative reduction of hazardous waste generation by 15% over the period 1992 to 2005. An interview done in twelve selected companies verified that all stated waste minimization as part of their environmental policy. Of the listed actions, 44% could classify as technology changes, 34% as changes in the working methods and 22% were related to changes in the material inputs. Yet, changes related to hazardous compounds in products were mentioned.

In this work, we attempted to achieve some principles for cleaner production in the lead recycling process by reducing waste generation through improvements in the process and material inputs and by modifying slag hazardous compounds in order to decrease its toxic effects. Initially, samples of three slag types generated from two different secondary lead production plants were analyzed, taking into consideration the charge formulation corresponding to each sample. As a result of this analysis, and by the identification of some process deficiencies, modifications in the smelting process charge were studied in order to reduce the environmental toxicity of the slag. The assessments were made in accordance with Brazilian norm ABNT NBR 10005 (Associação Brasileira de Normas Técnicas (ABNT), 2004) concerning the leaching test procedure and consideration was given to the quantity of slag generated in each batch.

1.1. Description of the recycling process

As stated above, the principal raw material used in the secondary lead industry is the lead-acid battery scrap. When an acid-lead battery reaches the end of its useful life, it becomes an extremely hazardous waste and must be recycled. As seen in Fig. 1, the first stage of its recycling process is grinding and separation of the following different materials:

- Discharged paste, containing lead sulfate (its main compound) and lead oxides;
- Grids and connectors, materials composed mainly of metallic lead;
- Separators, materials composed of plastic, rubber, or cellulose, which prevent contact between the positive and negative plates of the battery;
- Battery casings, materials composed of polypropylene.

The paste, grids, connectors, and (in most cases) the separators, go to the next stage of the recycling process, where batches of metallic lead is produced in rotary furnaces.

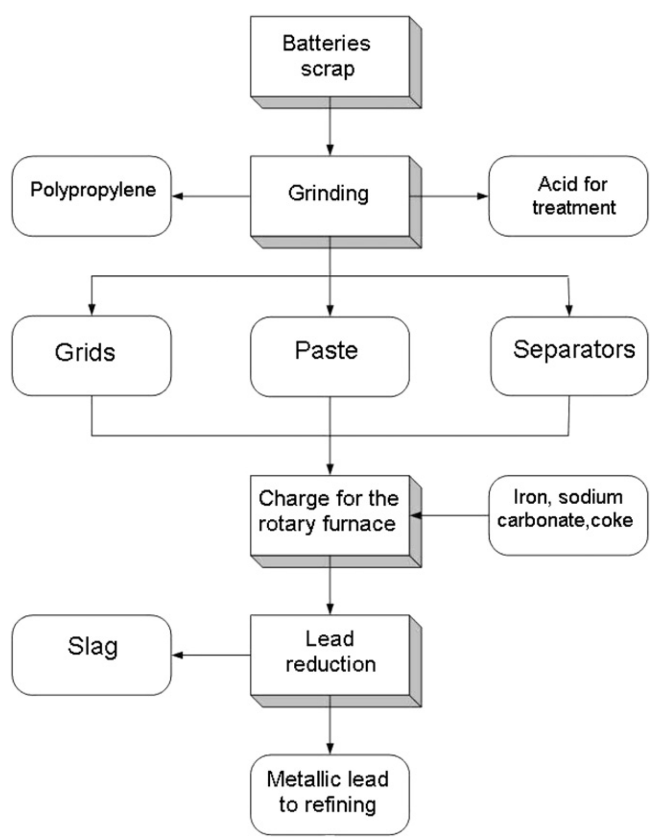

Fig. 1. Flow sheet diagram for secondary lead processing.