

Application of a Sulfur Removal Hydrometallurgical Process in a Lead-Acid Battery Recycling Plant in Costa Rica

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Abstract

This study presents the implementation of a desulphurization process for lead recycling under different chemical and physical conditions using pyro-metallurgical processes. Desulphurization was done using a hydrometallurgical process using sodium carbonate as a desulphurization agent and different lead-bearing loads compositions. Waste characterization included: SO₂ concentrations in the stack emissions, total lead content in the furnace ash, the total lead content in the slag, and the toxicity characteristic leaching procedure (TCLP). A significant reduction in SO₂ emissions was achieved (~55% reduction) where mean SO₂ concentrations changed from 2193 ± 135 ppm to 1006 ± 62 ppm after the implementation of the modified processes. The desulfurized lead paste (*i.e.* the metallic fraction lead of the battery) of the modified process exhibited an improvement in the concentration of the lead in the TCLP test, with an average value of 1.5 ppm which is below US EPA limit of 5 ppm. The traditional process TCLP mean value for the TCLP was 54.2 ppm. The total lead content in the bag house ashes shows not significant variations, when comparing the desulphurization (67.6% m/m) and non-desulphurization process (64.9% m/m). The total lead mean content in the slag was higher in the desulphurization process (2.49% m/m) than the traditional process (1.91% m/m). Overall, the implementation of a new desulphurization method would potentially increase the operation costs in 10.3%. At the light of these results, a combination of hydrometallurgical and pyro-metallurgical processes in the recycling of lead-acid batteries can be used to reduce the environmental impact of these industries but would increase the operational costs of small lead recyclers.

Keywords

Lead-Acid Battery Recycling, Hydrometallurgical and Pyro-Metallurgical Processes, Hazardous Waste Management

1. Introduction

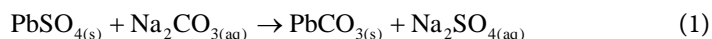
Lead-acid batteries belong to a group of commercial products that can become a potential hazardous waste after their use. Lead recovery from lead-acid batteries is the type of business that combines environmental protection and economic profits. The largest component of the lead-acid battery is the so-called metallic fraction lead or lead paste (60% - 75%) that is obtained during the processing of battery scrap. The other components are comprised of electrolytes and various types of plastics. Lead paste is primarily a mixture of PbSO_4 , PbO_2 , Pb_2O , Pb_2O_3 and metallic lead. PbSO_4 is the main lead carrier in the battery paste (40%). It is formed during the battery operation as a result of the reaction of metallic Pb and PbO_2 with the electrolyte (*i.e.* aqueous solution of sulphuric acid IV) [1] [2] [3].

Raw lead is obtained by melting the metallic fraction to achieve a reduction of the lead compounds (*i.e.* mainly PbSO_4 and PbO) [1] [4] [5]. At the smelting step, named pyro-metallurgical process, the lead compounds are reduced to metallic lead by smelting the battery paste (*i.e.* lead oxides with a small amount of lead sulfate) using reducing agents rich in carbon, cast iron (Fe), and sodium carbonate (Na_2CO_3) for the removal of other metals (e.g. Cu, Sn, As, Ag) in the oxide form. This reduction process leads to the formation of sulfides, named lead slag, as well as other gases and particulate matter emissions. The equipment used is a rotary furnace, short or long, to minimize the amount of waste, along with emissions control systems, such as bag houses for the filtration and recovery of the lead-rich particulate matter [6].

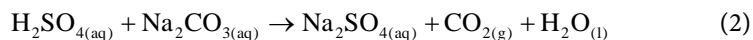
As a result of the battery paste melting process, a fraction of the sulfur is transferred into the slag in the form of sulfides, and the remaining large portion is oxidized to sulfur dioxide. Recently, national and international environmental agencies have updated the environmental legislation and have implemented new emissions limits that seek a reduction of the SO_2 emissions into the atmosphere. For example, the Basel Convention has enforced secondary lead producers to take actions in order to decrease SO_2 emissions. One available method to prevent large SO_2 emissions relies on the desulphurization of the battery paste before melting [1] [2] [3] [4]. The most common process in desulphurization of battery paste includes the application of caustic soda (NaOH) or sodium carbonate (Na_2CO_3) solutions. [1] [5]-[10].

The sodium carbonate method is commonly used for desulphurization of battery paste when the sulfur content is less than 1%. This method converts the sulfur present in the paste into sodium sulphate using sodium carbonate as a desulphurization agent. Consequently, a desulphurized paste and soluble sodium sulphate is obtained. Equation (1) describes the chemical reaction in the desul-

phurization step [1] [4] [5]:



To achieve high efficiency in the desulphurization process, the reaction must be carried out using an excess of carbonate. Therefore, an excess of sodium carbonate is added and later neutralized according to Equation (2) [1] [4] [5]:



There is only one major organization, PB Metals S.A., producing lead metal in Costa Rica. PB Metals uses only scrap battery. The production capacity of PB Metals during 2016 is 4500 ton per year of secondary lead, being this production exported entirely to Colombia. This study presents the implementation of a desulphurization process of lead paste under different chemical and physical conditions in a smelting furnace, before its conversion into metallic lead. The aims of the study was: i) to implement a desulphurization process for lead paste using a hydrometallurgical process and sodium carbonate as desulphurization agent, ii) to make a waste characterization of the traditional process (*i.e.* the pyrometallurgical process) and the hydrometallurgical modified process which includes total lead content in the sulphidic slag, the lead content in the bag house ashes, the toxicity characteristic leaching properties of the slag using the TCLP test, and the SO₂ concentrations in the stack emissions, iii) to estimate the change in operational costs after the implementation of the new hydrometallurgical process (Figure 1).

2. Materials and Methods

The experimental approach of this work was similar to that reported by Lewis and Beutement (2002) [11] that used a characterization of the waste to facilitate the overall process understanding and to aid the identification of process defi-

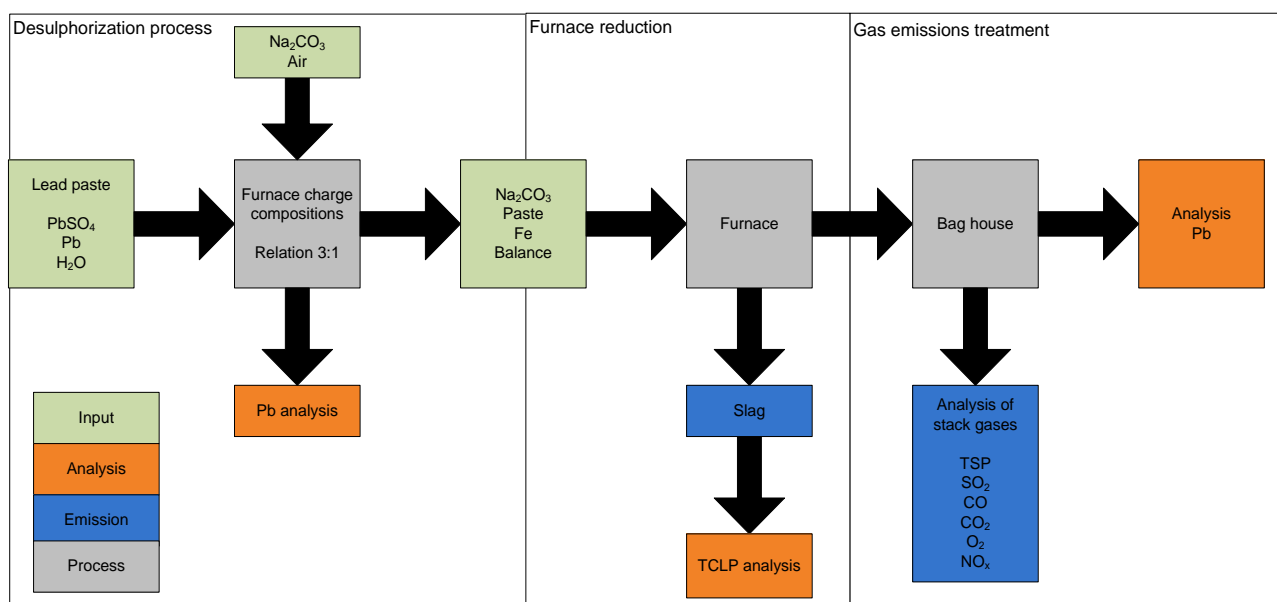


Figure 1. Schematic diagram of the experimental process in PB Metal S.A.

ciencies. However, because of the limited budget available, we decided to focus our work on tracking the losses of lead, namely the amount of lead present in the bag house dust and stack particulate matter, along with the analysis of the slag (total lead content and TCLP). We define as start point the former furnace's charge composition used in RNP, which was defined as the percentage of anthracite (coke), cast iron and sodium carbonate.

The furnace compositions correspond to [8]-[8]-[5], [7.4]-[7.4]-[5.3] and [5]-[5]-[3]; these numbers indicate the percentage of Na_2CO_3 , cast iron (Fe) and anthracite in each charge, respectively. For example, a furnace's charge named [8]-[8]-[5] was composed with 8% Na_2CO_3 , 8% Fe and 5% anthracite. The rest of the charge was composed of lead containing materials, formed mainly of metallic lead and lead paste. The final charge was mixed thoroughly and dries in an open air container before being introduced into the furnace. Desulfurized lead paste (hydrometallurgical process) and non-desulfurized lead paste (pyro-metallurgical process) were evaluate separately.

Typically, the composition of each charge was at least 79% in lead bearing materials. The optimization of the process was carried out by varying the amount of these materials in order to achieve a more efficient reduction process in the furnace (*i.e.* a lesser amount of lead lost during the process). PB Metals operates under a batch production system, where every batch requires 4 hours to be completed. In this study, we had only one furnace available. Desulphurization of the lead paste was achieved by using a hydrometallurgical process and sodium carbonate as the desulphurization agent. The waste characterization of the traditional process (pyro-metallurgical only) and the hydrometallurgical modified process included the total lead content in the sulphidic slag, the lead content in the bag house ashes, the TCLP test, and SO_2 concentrations in the stackremissions. The analyses of the bag house ashes and the slag were done by acid digestion and atomic absorption (AA). In each case, 0.5 - 1.0 g of the solid material was homogenized and acid digested in a microwave digestion system CEM MARS 5 (CEM, USA). An atomic absorption spectrophotometer ZEEnit 700P was used for the lead quantitative analysis (Analytical Jena, Germany). The bag house dust and the slag were collected after every batch was completed. The toxicity characteristic leaching procedure (TCLP) was applied to the slag according to United States Environmental Protection Agency (US-EPA) Method 1311 [12].

The stack gas analyses were done according to US-EPA stationary source emissions test methods [12]. A TESTO 350 (Testo AG, Germany) flue gas analyzer was used for the analysis of SO_2 concentrations and flue gas concentrations, whereas an APEX XC-522 isokinetic sampler (Apex Instruments, USA) was used for the total suspended particulate matter (TSP) sampling. Stack gas and particulate matter sampling was carried out during the furnace operation and until every batch was completed. The lead content in the particulate matter (P-Pb) matter was extracted by acid digestion and analyzed by atomic absorption (AA) as described above.

3. Results and Discussion

Table 1 shows the results the SO₂ analysis in the stack emissions for each process, namely for the processes using desulfurized lead paste and non-desulfurized lead paste.

SO₂ emissions were reduce 47%, 86% and 21% for the furnace charge compositions [5]-[5]-[3], [7.4]-[7.4]-[5.3] and [8]-[8]-[5], respectively, when using the desulfurized lead paste. The results indicate an acceptable efficiency for the implemented desulphurization process. The second furnace charge composition (*i.e.* [7.4]-[7.4]-[5.3]) showed a major decrease in the SO₂ concentrations related with a better furnace efficiency. This composition was formerly identified by PB Metals as the most efficient composition to recover lead. For the [8]-[8]-[5] charge composition, the SO₂ emissions decrease was close to 20%, which could be explained by a deficient Na₂CO₃ agitation process or because an excess of lead paste in the furnace charge. The excess of lead paste in the initial charge leads to a less PbCO₃ formation and an increase of the SO₂ content [14]. According to Costa Rica's environmental regulations, the SO₂ concentration in the stack emissions from furnace charge composition [7.4]-[7.4]-[5.3] and [8]-[8]-[5] (under desulphurization conditions) are according to the permissible limits (maximum value 2500 mg/Nm³); nevertheless, in the second and third furnace charge composition using the non-desulfurized lead paste the values are close to the limit (2500 mg/Nm³). In the case of the charge composition [5]-[5]-[3], only when the desulfurized lead paste was used, the country regulatory standards were met.

Table 2 shows the total lead content in the bag house ashes. There was not a significant variation of the total lead content when comparing the 3 furnace charge compositions for both processes (with desulphurization and without desulphurization). However, the total lead content in the bag house were greater for those furnace charges that used desulfurized lead paste. The small increase of the lead content when using the desulfurized lead paste for the individual

Table 1. SO₂ analysis in the stack emissions for each evaluated process and furnace charge composition.

Furnace Charge Composition	Non-desulfurized lead paste	Desulfurized lead paste	ΔSO ₂
	SO ₂ [mg/Nm ³]	SO ₂ [mg/Nm ³]	SO ₂ [mg/Nm ³]
[5]-[5]-[3]	3064 ± 189	1643 ± 101	-1421 ± 101
[7.4]-[7.4]-[5.3]	2149 ± 133	299 ± 18	-1850 ± 134
[8]-[8]-[5]	1366 ± 84	1078 ± 67	-288 ± 18

Table 2. Total lead content in the bag house ashes expressed in % m/m.

Furnace Charge Composition	Non-desulfurized lead paste	Desulfurized lead paste	Δ% Pb
	% m/m	% m/m	
[5]-[5]-[3]	74.1	76.2	2.1
[7.4]-[7.4]-[5.3]	65.3	67.5	2.2
[8]-[8]-[5]	55.2	59.2	4.0

charges could be related with the increase of the lead oxides content during the desulphurization stage. In general the lead concentration was stable ($\Delta\%$ Pb < 5%) in every single charge.

For pyro-metallurgical processes, the Basel Convention has set a total lead content in the ash of approximately 65% m/m [13]. In the case of the furnace charge composition [7.4]-[7.4]-[5.3] with and without the desulfurized paste, our results are very close to the Basel Convention limit of 65% m/m. The [8]-[8]-[5] furnace composition with the non-desulfurized paste presents the lowest lead concentration in the ash, with a valued of 55.2%. In the case of the formula [5]-[5]-[3], the concentrations are over the limit for both processes, with 74.1% (without desulphurization) and 76.2% (with desulphurization). It's important to point out that the small increase of the lead content when using the desulfurized paste could be related with the increase of the lead oxides during the desulphurization process [14].

Table 3 shows the total lead concentrations in the slag. In the non-desulfurized lead paste, the lead concentrations were 1.95%, 1.92%, and 1.87, for the formulas [5]-[5]-[3], [7.4]-[7.4]-[5.3], and [8]-[8]-[5], respectively. In the case of the desulfurized lead paste, the values between each single formula used were also very similar. In general, there is a small increase in the lead concentration when using the desulfurized paste.

Calvo *et al.* [14] concluded that a slag with high content of Fe_2O and Fe_3O (named as magnetite) increases the slag viscosity making the lead decantation less efficient, therefore the lead remains in the slag. According to the authors, one reason of this phenomenon could be associated with the furnace operation, related with a low reduction potential in the furnace, increasing the content of magnetite and hence the slag lead content. However, Calvo *et al.* [14] recommended values between 2% and 3% of lead concentration in the slag as a permissible mean concentration values. Based on this premise, PB Metals furnace operation has an acceptable performance.

Table 4 presents the lead concentrations in the slag lixiviate (TCLP test). The

Table 3. Total lead content in the sulphidic slag expressed in % m/m.

Furnace Charge Composition	Non-desulfurized lead paste	Desulfurized lead paste
	$\pm 0.05\%$ (m/m)	$\pm 0.05\%$ (m/m)
[5]-[5]-[3]	1.95	2.76
[7.4]-[7.4]-[5.3]	1.92	2.65
[8]-[8]-[5]	1.87	2.05

Table 4. Lead concentration in the slag lixiviates based on the TCLP test.

Furnace Charge Composition	mg/L Pb	
	Non-desulfurized lead paste	Desulfurized lead paste
[5]-[5]-[3]	56.2	1.61
[7.4]-[7.4]-[5.3]	52.8	Not detected
[8]-[8]-[5]	53.5	Not detected

non-desulfurized paste lead content was very high compared with the US-EPA limit (5 ppm) showing a mean of 54.2 ppm.

In the case of the desulfurized paste, the TCLP values obtained for the 3 furnace charges compositions were under the US-EPA limit of 5 ppm. The difference between both processes could be associated to the decrease of sulfate content (SO_4^{2-}) during the desulphurization process as well as the decrease of FeS. This situation allows the slag to tolerate more easily acid conditions. Once the FeS is solubilized, the lead retained in the slag will be released. Therefore when using desulfurized paste, a low concentration of FeS in the slag is obtained (comparing with the non-desulfurized paste), hence a greater lead concentration is retained in the slag, providing a lower lead lost, because there is a small quantity of lead in the cationic form to be lixiviated.

Finally, an economic evaluation of both processes was done in order to establish the feasibility of using the new hydrometallurgical process in PB Metals. Using the furnace charge composition [7.4]-[7.4]-[5.3] as reference, the implementation of the hydrometallurgical process involves an increase of $\sim 10\%$ in the operational costs (*i.e.* about US \$ 200 per charge). Based on historic records available at the company, the [7.4]-[7.4]-[5.3] furnace formula has overall lead recovery efficiency of 70%. We estimated that the desulphurization process increased this efficiency in only 1% when the same formula was used meaning that the increment in the operational costs cannot be compensated directly from the increment in the lead production. Another issue is the increment in the processing time of the lead bearing materials. The desulphurization process takes about 5 hours for completion, which means that PB Metals would need to increase the existing lead inventories to be able to feed the furnace at the same rate they do now. Nevertheless, the hydrometallurgical process implementation could also provide environmental benefits for PB Metals, for example, a decrease in the treatment costs of the sulphidic slag, the largest contributor to waste material [11].

4. Conclusions

Based on the analysis of SO_2 of the stack emissions, the desulphurization process was highly effective for the evaluated furnace charge compositions. According to Costa Rica's environmental regulation, the SO_2 emissions from furnace charge composition [7.4]-[7.4]-[5.3] and [8]-[8]-[5] (under desulphurization conditions) are according to the permissible limits (2500 mg/Nm^3). Nevertheless, for the case of the non-desulfurized lead paste, the values are very close to the limit for second and third furnace charge composition. The results of the total lead content in the baghouse ash indicate that there was not a significant variation of the total lead content when comparing the selected furnace charge compositions for both processes (with desulphurization and without desulphurization). However, the total lead content in the bag house was greater for each furnace charge with the desulfurized lead paste. For similar processes, the Basel Convention recommends a total lead content in the ash of approximately 65% (m/m). In the case of

the furnace charge composition [7.4]-[7.4]-[5.3] with and without the desulfurized paste, the results are very close to the Basel Convection limit. The lead concentrations in the slag lixiviate (TCLP test) for the non-desulfurized paste was very high compared with the US-EPA limit (5 ppm) showing an average of 54.2 ppm. In the case of the desulfurized paste, the TCLP values obtained for the evaluated furnace charges composition were under the US-EPA recommended limit.

Despite the fact that the implementation of this hydrometallurgical process before the traditional pyro-metallurgical process could lead to an increment in the operational costs of for PB Metals, it should not be overlooked the related environmental benefits of its application. In the future, the combination of both processes could also render economic benefits, for example, a reduction in the treatment of hazardous waste like the sulphidic slag [15].

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