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Studies on mathematical modeling of the leaching process in order to efficiently recover lead from the sulfate/oxide lead paste

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ABSTRACT

Increasing global lead consumption has been mainly supported by the acid battery manufacturing industry. As the lead demand will continue to grow, to provide the necessary lead will require an efficient approach to recycling lead acid batteries. In this paper was performed a mathematical modeling of the process parameters for lead recovery from spent lead-acid batteries. The results of the mathematical modeling compare well with the experimental data. The experimental method applied consists in the solubilisation of the sulfate/oxide paste with sodium hydroxide solutions followed by electrolytic processing for lead recovery. The parameters taken into considerations were NaOH molarity (4 M, 6 M and 8 M), solid/liquid ratio - S/L (1/10, 1/30 and 1/50) and temperature (40 °C, 60 °C and 80 °C). The optimal conditions resulted by mathematical modeling of the electrolytic process of lead deposition from alkaline solutions have been established by using a second-order orthogonal program, in order to obtain a maximum efficiency of current without exceeding an imposed energy specific consumption. The optimum value for the leaching recovery efficiency, obtained through mathematical modeling, was 89.647%, with an error of $\delta_y = 3.623$ which leads to a maximum recovery efficiency of 86.024%. The optimum values for each variable that ensure the lead extraction efficiency equal to 89.647% are the following: 3 M - NaOH, 1/35 - S/L, 70 °C - temperature.

1. Introduction

The annual production of lead in the last 10 years has grown rapidly; from 6.7 million tons in 2004 to 10.6 million tons in 2015, with a peak of 11.15 million tons in 2013. Lead consumption has increased due to predominant use in lead-acid batteries (Statista, 2016). In some countries, the use of lead in lead-acid battery production has significantly exceeded the world average consumption (76.7% in 2012). For example, lead fraction used for battery production in the US was 86%. Due to the progressive exhaustion of lead ore, lead-acid batteries industry pays very much attention to recycling processes, mainly because lead acid batteries are products that contain a very high amount of lead (International Lead and Zinc Study Group, 2016).

Lead containing waste is generated in various forms and arises from various life stages of multiple industries. On one hand, waste laden lead represents a potential threat to the environment because of heavy metals that can be dispersed in the environment (Chia-ho et al., 2012; Ferella et al., 2016). On the other hand, waste laden lead represents a secondary source for lead recovery. In the last years new leaching technologies have been proposed for lead recovery (Tang and Steenari, 2016; Sasai et al., 2008; Wang and Zhu, 2012; Matsumoto et al., 2012; Okada et al., 2012). As a result, the degree of recycling of materials containing lead is growing. About 85% of commercial products containing lead can be recycled (Siegmund, 2000).

Lead batteries represent a recycling success story of our time, as more than 99% of all battery lead is recycled. Compared to 55% of aluminum soft drink and beer cans, 45% of newspapers, 26% of glass bottles and 26% of tires, lead-acid batteries top the list of the most highly recycled consumer product (Battery Council International, 2016).

Lead-acid batteries contain a number of heavy metals and toxic chemicals (Recknagel et al., 2014) that can be hazardous to human health and to the environment. These particular batteries contain lead (Almeida et al., 2006), a highly toxic metal and sulphuric acid, a corrosive electrolyte solution. Disposing them by the same process as regular trash has raised concerns over soil contamination

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and water pollution (Bernardes et al., 2004). Some batteries are recycled more readily than others (Lin and Qiu, 2011), such as lead–acid automotive batteries (nearly 90% are recycled). These are recycled by grinding them, neutralizing the acid, and separating the polymers from the lead. The recovered materials are used in a variety of applications, including new batteries (Battery recycling in USA, 2008; Fisher et al., 2006).

As defined by the World Commission on Environment and Development (1987), sustainable development is "development to ensure the needs of the present without compromising the ability of future generations to satisfy their own needs" (Report of the World Commission on Environment and Development, accessed 2016). Sustainable development aims to find the optimal interaction between economic, technologic and human-environmental systems.

Increasing consumption of energy and raw materials is directly related to population explosion through a powerful increase in consumption. Unfortunately for the moment human activities are likely to use large amounts of resources (Overconsumption? Our use of the world's natural resources, accesed 20016) and energy, returning to the environment waste and heat loss.

It is known that metals recycling (UNEP, 2011) are the most developed recycling industries. In the case of lead, at an annual global production of about 8,000,000 tons, over 50% represent recyclability rate from consumption. It is worth to mention that today the major fraction of lead is used in lead-acid batteries.

Obtaining lead by mining activity (Zheng et al., 2013) of known reserves (in the 0–300 m depth) is becoming increasingly expensive, because the minimum content of metal has dropped to 0.10–0.25%.

Lead price, is around 1800 $/ton. Meanwhile, the prices of waste lead-acid automotive batteries (Recycler's World, accessed 2016) range between: 250 $/ton (Philippines, Manila Port), 350 $/ton (South Africa, Gauteng Durban) and 750 $/ton (Tunisia, Bou Argoub Tunis).

In order to eliminate the shortcomings of the traditional pyrometallurgical processes applied to spent lead-acid batteries new hydrometallurgical procedures (De Angelis et al., 2002; Lin and Qiu, 2011; Quirijnen, 1999) as the one applied in the present work have been devised. The hydrometallurgical technologies for recovering lead (Sonmez and Kumar, 2009; Zabaniotou et al., 1999) from the spent lead-acid car batteries differ mainly by the leaching agent used to dissolve lead from the waste pastes (Buzatu et al., 2013, 2015).

Table 1
Lead compounds identified in the sulfate-oxide paste.

Compound name	Chemical formula	S-Q (wt%)
Anglesite	$PbSO_4$	38
Lanarkite	Pb_2SO_5	36
Plattnerite	PbO_2	9
Lead oxide sulfate Hydrate	$(PbO)_3(Pb(SO_4))(H_2O)$	6
Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	4
Scrutiny	PbO_2	3
Litharge	PbO	2
Lead	Pb	2

The hydrometallurgical procedure consists in subjecting the solid paste resulted from spent lead-acid batteries to a leaching process in sodium hydroxide followed by the recovery of pure metallic lead by means of the electrolysis of these solutions (Roche and Toyne, 2004; Swanson, 2005; Valdez, 1997). A small amount of undissolved paste is separated by filtration and further recycled in order to recover the components of the crushed batteries (Volpe et al., 2009; Chen et al., 2016). Lead dissolution in sodium hydroxide is one of the latest procedures for lead recovery from spent lead-acid batteries. This procedure offers a twofold advantage: firstly the environment pollution may be kept under control and secondly the same procedure may be applied to processing other type of lead wastes such the volatile dust resulting from lead extraction processes (Lead and Zinc, 2013) from primary sources.

In order to facilitate the dissolution of lead the reduction of PbO_2 is mandatory. As a reducing agent a material containing PbS should be used, such as matte, volatile dusts or lead concentrates. The pH of the reaction is controlled by the addition of acid drained from the battery. The reaction which takes place is the following:

$$4PbO_2 + PbS + 4H_2SO_4 \rightarrow 5PbSO_4 + 4H_2O \quad (1)$$

The desulphation of the paste is carried in alkaline environment (NaOH) according to the reaction:

$$PbSO_4 + 2NaOH \rightarrow PbO + Na_2SO_4 + H_2O \quad (2)$$

The desulphated paste (containing mainly lead oxide), is leached with sodium hydroxide. The resulting sodium plumbite is then subjected to electrolysis:

$$PbO + 2NaOH + H_2O \rightarrow PbNa_2(OH)_4 \quad (3)$$

Table 2
Rational composition of sulfate/oxide wastes from dismantling lead-acid batteries.

Elements	Pb (%)	Fe (%)	Sb (%)	Si (%)	Ca (%)	As (%)	Cu (%)	S (%)	O_2 (%)	Sn (%)	Na (%)	Ba (%)	C (%)	H_2O (%)	Others (%)	Total (%)
Compounds																
PbO	13.19								1.020							14.210
PbO_2	18.35								2.837							21.187
$PbSO_4$	38.69							5.98	11.96							56.630
Pb met.	2.820															2.820
$Fe_2(SO_4)_3$		0.09						0.08	0.153							0.323
Na_2SO_4								0.02	0.032		0.02					0.072
$BaSO_4$								0.009	0.019			0.041				0.069
Sn(SO4)$_2$								0.01	0.020	0.02						0.050
SiO_2				0.11					0.126							0.236
CaO					0.022				0.009							0.031
$CuSO_4$							0.032	0.01	0.032							0.074
As_2O_3						0.025			0.008							0.033
Sb_2O_3			0.41						0.081							0.491
C													0.88			0.880
H_2O														0.29		0.290
Others															2.670	2.670
Total	73.05	0.09	0.410	0.110	0.022	0.025	0.032	6.109	16.279	0.02	0.020	0.041	0.880	0.290	2.670	100.000

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