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Recycling of a secondary lead smelting matte by selective citrate leaching of valuable metals and simultaneous recovery of hematite as a secondary resource

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A new recycling process, according to the zero-waste concept, was investigated for an iron rich waste stream, more specifically a secondary lead smelting matte. The process consists of a selective citrate leaching of Pb, Cu, Ni and Zn in combination with a roasting step, leading to a simultaneous recovery of hematite as a secondary iron resource. The parameters, such as leaching time, leaching temperature, H_2O_2 concentration and roasting temperature, were experimentally optimized. The maximum Pb leaching efficiency was 93% and the leachability of Cu (33%) and Zn (11%) increased slightly in the presence of 0.5 M H_2O_2 in 1 M citrate at 25 °C and pH 5.5. Importantly, almost no Fe was leached (<0.6%) from the iron rich matrix material at this condition allowing for a maximal recovery of hematite as a secondary resource after further treatment (i.e. roasting or sulfur removal). The leachability of Pb, Cu, Ni and Zn was strongly affected by the roasting temperature. Maximum leaching efficiency in 1 M citrate (25 °C, L/S ratio 10, pH 6.5) was 93% for Pb, 80% for Cu and 60% for Zn at a roasting temperature of 600 °C, while for Ni the maximum leaching efficiency of 53% was reached after roasting at 650 °C. Furthermore, when oxidative roasting was applied, the leaching residue consists dominantly of hematite (Fe_2O_3) with minor quantities of $PbSO_4$, which can be used as pig iron ore (Fe >60 wt%).

1. Introduction

The total annual production of lead worldwide is >11.3 million tonnes, of which >60% is produced from recycled scrap mainly composed of lead acid batteries (US geological survey, 2015). Nearly 95% of all discarded batteries are currently recycled by pyrometallurgical methods (Zhang et al., 2016). At the smelting step of the recycling process, the lead compounds are reduced to metallic lead and a great amount of slags is generated. For each tonne of metallic lead produced, 100–350 kg of slag is generated that contains approximately 5% of lead compounds and hazardous minor elements such as copper, tin, antimony, nickel and zinc (Shu et al., 2015).

In the pyrometallurgical processing of Pb, two types of slags are generated, namely carbonate based (Na_2CO_3), also known as the soda slag, and calcium iron silicate based (Ellis and Mirza, 2010; Ettler and Johan, 2014). The first process is based on the production of a desulfurized paste from crushed and separated car batteries, which is subsequently introduced into rotary furnaces, where Na_2CO_3 is used as a fluxing agent for the reducing fusion. Today, about 80% of lead smelters, among which 19 are based in Europe, apply this technology. In contrast, the second technology (4 smelters in operation in Europe today) is based on smelting entire batteries in shaft furnaces fired with coke and supplemented with Fe (iron scrap) and Ca (calcite) additives (Ettler and Johan, 2014). The silicate slags have become more prevalent in recent years to mitigate issues related to the leachability of residual elements within the slag (Ellis and Mirza, 2010).

Most of the research on lead smelting slag has focused on the leachability of metals in inorganic (Ettler et al., 2003; Lassin et al., 2007) or organic solution (Ettler et al., 2004) in order to estimate the slag-water interactions during waste disposal. The performance of products from the stabilization/solidification of slags from lead batteries recycled into a Portland cement matrix has also been evaluated (Angelis et al., 2002). In the perspective of only lead recovery, fly ash enriched with lead in the forms of $PbSO_4$ (anglesite) and Pb_2OSO_4 (lanarkite), formed as an intermediate in waste lead-acid battery smelting, was recycled by hydro-electrometallurgy in NaOH or HNO_3 (Chen et al., 2016). Furthermore, Shu et al. (2015) studied HNO_3-NaCl leaching from lead slag, with recovery of lead oxide powder by reaction with sodium oxalate and followed by calcination to produce active materials for new lead acid batteries.

In hydrometallurgical processes, carboxylic acids have been proposed as an alternative, probably less expensive and environmentally

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friendly leaching agent (Aydoğan et al., 2007). Organic acids such as citric/citrate and acetic acid have been used for their ability to solubilize lead from sulfides (PbS) (Aydoğan et al., 2007; Zárate and Lapidus, 2015) in the presence of H_2O_2 or lead pastes ($PbO/PbO_2/PbSO_4$) (Zhang et al., 2016; Sonmez and Kumar, 2009; Zhu et al., 2013; Zárate and Lapidus, 2014). However, there are hardly any studies aimed at leaching valuable metals, other than Pb, from lead smelting residues as well as matrix valorization in view of recycling accoding to the zero-waste concept. By combining selective leaching, to recover valuable metals and remove heavy metal contaminants, and matrix valorization, a (near) zero-waste solution could be created for secondary lead smelting residues. The zero-waste concept (Curran and Williams, 2012; Zaman, 2015) envisions a closed-loop use of all available resources and thus embraces the full recovery and valorization of both metals and matrix material from metal production and processing residues. In order to reduce the current waste production to zero, industrial symbioses and development of new (recycling) technologies need to be stimulated (Curran and Williams, 2012). Although at its infancy, the application of the zero-waste principle to metal containing mineral waste materials is gaining growing interest in the scientific literature. For instance, Binnemans et al. (2015) emphasized the need for "new metallurgical systems" to allow for the zero-waste valorization of low-grade rare earth element containing mineral waste materials, such as phosphogypsum and bauxite residue. Whereas, Kim et al. (2016) have proposed a process to fully recycle stainless steel slag by a combination of chromium extraction and subsequent carbonation of the mineral residue to new building applications.

In this study, the leaching behavior of the valuable metals Pb, Cu, Ni, and Zn from secondary lead smelter residues were investigated in citrate solution. Furthermore, the effects of phase differences (sulfides or sulfates), obtained through oxidative roasting of the smelting residues, on the metal leachability were studied. The experimental process optimization aims to simultaneously extract valuable metals and valorize the mineral matrix of the residues.

2. Experimental

2.1. Materials

The lead smelting residues were collected at a lead smelting company. The residue was produced in a shaft furnace fired with coke and loaded with a charge composed of lead scrap, iron scrap (flux), and lime (additive). The smelted and molten residues which consist of two layers, i.e., matte (sulfur-rich layer, more dense) and slag (oxides), were tapped off into a cone-shaped pot, cooled, turned over and physically separated. The >15 cm size fraction of the slag phase is reused in the process and the remainder of the slag and matte are currently disposed. In this study, the disposed matte was used as sample. A representative sample of the matte was collected according to the Flemish standards CMA/1/A.14 and CMA/1/A.15 (2012).

A total of 16 individual scoops (4 L each) were taken at different locations across the material heap (estimated volume 40 m^3). The samples were transported to the laboratory in 20 L buckets (each containing 4 scoops) and subsequently mixed prior to further treatment.

Representative samples for analysis were obtained after crushing, grinding and sieving below 125 μm of the material. The chemical (Table 1) and mineralogical compositions (Fig. 1) of the samples were determined. The matte mainly consists of FeS (troilite) and FeO (wüstite) as iron phases, and metallic lead, PbS (galena) and PbO (litharge) as lead phases. The material also contains minor amounts of Fe_2SiO_4 (fayalite) and Fe_3O_4 (magnetite).

Table 1
Chemical composition of the matte sample.

wt%	Fe	Pb	Cu	Ni	Zn	Sn	Si	S
Matte	49.9	7.04	1.33	0.17	0.48	0.23	3.3	20

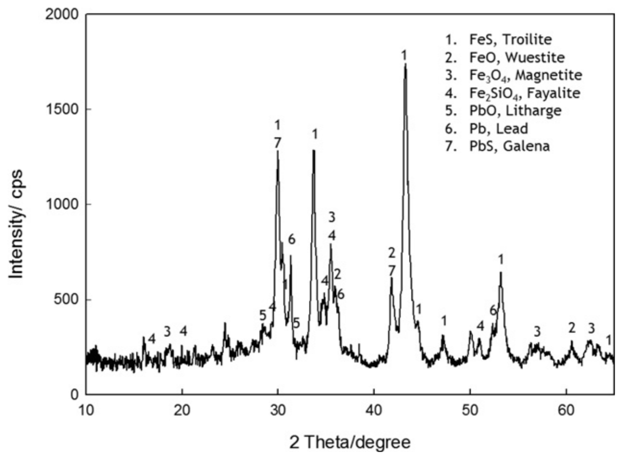

Fig. 1. XRD patterns of the matte materials.

2.2. Roasting and leaching

Roasting was carried out in an alumina crucible, which was placed in a temperature controlled muffle furnace (L/H 30/13, Nabertherm). The samples were heated at a rate of 2 °C/min from room temperature to the set temperature (400 °C to 700 °C) at which it was held for 2 h. Mass change during the reaction was measured by weighing the sample before and after roasting. Subsequently, the roasted samples went to the sodium citrate leaching step. The leaching behavior was compared to that of samples which did not undergo roasting.

Leaching tests were carried out in a 60 mL polytetrafluoroethylene (PTFE) bottle with cap on 2.0 g solid samples. A typical experimental procedure consisted of mixing the sample with a predetermined liquid volume to solid (L/S) mass ratio 10. The bottle consists of 1 M sodium citrate in the presence or absence of H_2O_2, which was heated and stirred at 200 rpm in a water shaking bath. A 1 M HNO_3 solution was used to adjust the acidity of the solution.

The reagents used in this study were H_2SO_4 (95%, VWR), HNO_3 (65%, Merck), H_2O_2 (35%, Merck), and $Na_3C_6H_5O_7 \cdot 2H_2O$ (Merck) with analytical grade.

2.3. Analytical methods

After each leaching experiment, the slurry was filtered by filter paper (Whatman) of 0.45 μm pore size and the obtained filtrate was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Elemental) to determine the amount of metal extraction. The obtained solid residues were analyzed by X-ray fluorescence (XRF, Thermo Scientific) and X-ray diffraction (XRD, Philips) in order to determine the chemical and mineralogical composition, respectively.

3. Results and discussion

3.1. Citrate leaching

Galena (PbS) which is a main phase of lead in the matte, can be oxidized by hydrogen peroxide according to the following reactions.

$$PbS + 2H^+ + H_2O_2 \rightarrow Pb^{2+} + S^o + 2H_2O \quad (1)$$

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O \quad (2)$$

The solubility of lead sulfate ($PbSO_4$) in water at room temperature is very low ($K_{sp} = 10^{-6.2}$) and thus it precipitates when formed according to Eq. (2). However, in concentrated citrate solutions, $PbSO_4$ forms several soluble complexes (Zárate and Lapidus, 2015; Zhu et al.,