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Recovery of lead from lead paste in spent lead acid battery by hydrometallurgical desulfurization and vacuum thermal reduction

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ABSTRACT

Lead sulfate, lead oxides and lead metal are the main component of lead paste in spent lead acid battery. When lead sulfate was desulfurized and transformed into lead carbonate by sodium carbonate, lead metal and lead oxides remained unchanged. Lead carbonate is easily decomposed to lead oxide and carbon dioxide under high temperature. Namely, vacuum thermal process is the reduction reaction of lead oxides. A compatible environmental process consisted of hydrometallurgical desulfurization and vacuum thermal reduction to recycle lead was investigated in this research. Lead paste was firstly desulfurized with sodium carbonate, by which, the content of sulfur declined from 7.87% to 0.26%. Then, the desulfurized lead paste was reduced by charcoal under vacuum. Under the optimized reaction conditions, i.e., vacuum thermal reduction at temperature 850 °C under 20 Pa for 45 min, a 22.11×10^{-2} g cm^{-2} min^{-1} reduction rate, and a 98.13% direct recovery ratio of fine lead (99.77%) had been achieved, respectively.

1. Introduction

Lead production is composed of primary production and secondary production, as with other metals. About 30% from lead ore mining has become the source of battery manufacturing industry, and the lead acid battery represents about 60% of batteries sold in the entire world (Ellis and Mirza, 2010; Kreusch et al., 2007).

With the wide application of lead acid battery, spent lead acid battery has become a serious problem to environmental protection and human health. Though spent lead acid battery can be a contaminant if not handled properly, it is also an important resource. In the next several years, the total lead production will increase, while the level of primary lead production remains static as of the last 10 years. In other words, all the growth will be supported by secondary output. Therefore, secondary lead production will play an essential role in sustainable development of lead industry. With the rapid development of economy and improvement of people's living standard, the number of automobile per capita is increasing quickly in China. The growth in the demand of lead acid batteries, due to the increase in the number of automotive vehicles, more and more stringent environmental regulations, created the need to design processes for both batteries production and lead recycling in order to minimize their impact on the environment and human health (Kuijp et al., 2013; Chen et al., 2012).

There are four main components in spent lead acid battery: polymeric containers, lead alloy grids, waste acids and pastes. Among them, the pastes mainly comprise lead oxide (~9%), lead dioxide (~28%), lead sulfate (~60%) and a small amount of lead (~3%) (Zhu et al., 2012a). Commonly, lead from battery scrap has been smelted in blast furnace, electric furnace, reverberatory furnace or rotary furnace, usually to produce antimonial lead bullion and soda slags or mattes (Ahmed, 1996; Ramus and Hawkins, 1993). Although lead recovery from spent lead acid batteries is carried out by pyrometallurgical processes which comprise over 90% of the recovery technology, decomposition of lead sulfate needs high carbothermic reduction temperature of over 1000 °C, causing environmental problems due to the emission in the atmosphere of lead particulates (30–50 kg/t) and sulfur dioxide (about 70 kg/t) (Sonmez and Kumar, 2009; Sobanska et al., 1999). As a result, there has been a large development in less pollutant processes such as hydrometallurgical approaches, or electrowinning routes in recent years. Generally, hydrometallurgical approaches for desulfurization of spent lead acid battery paste convert sulfur ($PbSO_4$) in the paste into soluble sulfates (Na_2SO_4, etc.) by reacting with alkaline reagents such as NaOH, Na_2CO_3, K_2CO_3 or $(NH_4)_2CO_3$ solutions (Lyakov et al., 2007; Morachevskii et al., 2001), or organic reagents such as $C_6H_8O_7 \cdot H_2O$ (Zhu et al., 2013), or ethanolamine (Begum et al., 1989). The traditional treatment methods are smelting, and dissolution by acid digestion followed by electro-winning (Ferracin et al., 2002). In addition, the electro-hydrometallurgical metal lead recovery route has been studied and several pilot plants have been proposed (Soundarrajan et al., 2012).

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In China, there are about 300 secondary lead plants, with more than 80% of raw materials coming from battery scrap, and the scale of these plants differs from tens of tons to thousands of tons per year. Most of these plants use backward technologies such as small reverberatory and blast furnaces, leading to serious issues with contamination and safety (Chang et al., 2009). Therefore, an effort must be made to find more advanced technology without a negative impact on the environment for recycling spent lead acid batteries.

The vacuum thermal recycling process makes use of advantages of the vacuum, because in the vacuum all elements evaporate at a significantly lower temperature which results in saving of energy and material use, and the hermetic construction prevents the contamination of gases by heavy metals for which costly treatment of waste gases can hence be avoided. And a more important point is that attainability of good vacuum in the system also helps to prevent formation of oxides. This paper reports a recovery of lead contained in spent lead acid battery using hydrometallurgical desulfurization and vacuum thermal reduction. The spent lead pastes are converting sulfur ($PbSO_4$) to soluble sulfates (Na_2SO_4) by reacting with alkaline reagents Na_2CO_3. As both of the conversion of lead sulfate into carbonate and the decomposition of lead carbonate can take place easily, the reduction of oxidized compound of lead is particularly discussed in this study.

2. Experimental

2.1. Experimental materials

Analytical grade lead oxide and spent lead acid battery were used as experimental materials. Before desulfurization, the battery paste was washed by distilled water to remove acid. The battery pastes were rinsed by filtration for about 10 min. The amounts of water required to rinse 1 kg of battery pastes are about 300–400 ml. The chemical composition of spent lead acid battery paste is given in Table 1. Fig. 1 presents the X-ray diffraction (XRD) pattern of the lead paste before desulfurization, which shows the major phases in lead paste to be $PbSO_4$, PbO_2, PbO and Pb. Analytically pure sodium carbonate was used in the desulfurization process, and the reductant used in the vacuum thermal reduction process was charcoal.

2.2. Methods

The decomposition of $PbSO_4$ from pastes requires high temperature, which results in high energy consumption and emission problem of SO_2, sulfur should first be removed before pastes are reduced under vacuum. In order to convert $PbSO_4$ to $PbCO_3$ by reaction (1), a mixture of paste, sodium carbonate and water in the mass ratio of 100:28:250 (molar ratio $Na_2CO_3/S = 1.1$, solid/liquid ratio 500 g/L) was vigorously stirred for 0.5 h at 80 °C using a magnetic stirrer. After completion of the desulfurization reaction, the filtered solids were washed with distilled water (about 300 ml/kg), dried at 105 °C for 24 h, and then they were made into pellets (Lyakov et al., 2007; Lin and Qiu, 2011).

Hydrometallurgical removal of sulfur involves conversion of lead sulfate to carbonate or hydroxide, which helps to avoid formation of off-gases containing sulfur and reduce pollution dramatically. The reaction (1) is based on the fact that $PbCO_3$ ($K_{sp} = 7.4 \times 10^{-14}$) is more insoluble than $PbSO_4$ ($K_{sp} = 1.6 \times 10^{-8}$). The Eh–pH diagram of Pb–C–S–H_2O is shown in Fig. 2 which is drawn by HSC 5.1. Fig. 2 shows that $PbCO_3$ or the compound of $PbCO_3$ and $Pb(OH)_2$ are the predominant equilibrium species when the pH of the system is above 7. The desulfurization rate of lead paste was calculated through the following Eq. (2).

$$PbSO_4(s) + Na_2CO_3(aq) = PbCO_3(s) + Na_2SO_4(aq) \tag{1}$$

$$\text{Desulfurization rate } (\%) = \frac{m_1 w_1 - m_2 w_2}{m_1 w_1} \tag{2}$$

where m_1 is the mass of original paste sample, w_1 is the mass percentage of S of origin paste sample, m_2 is the mass of desulfurized paste sample, and w_2 is the mass percentage of S of desulfurized paste sample.

Desulfurized paste mainly consists of Pb, PbO, PbO_2 and $PbCO_3$. When heated, $PbCO_3$ was thermally decomposed into oxide of lead

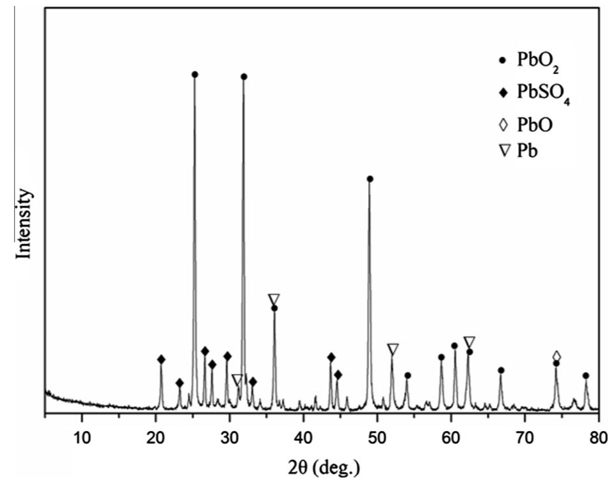

Fig. 1. XRD pattern of the initial spent lead acid battery.

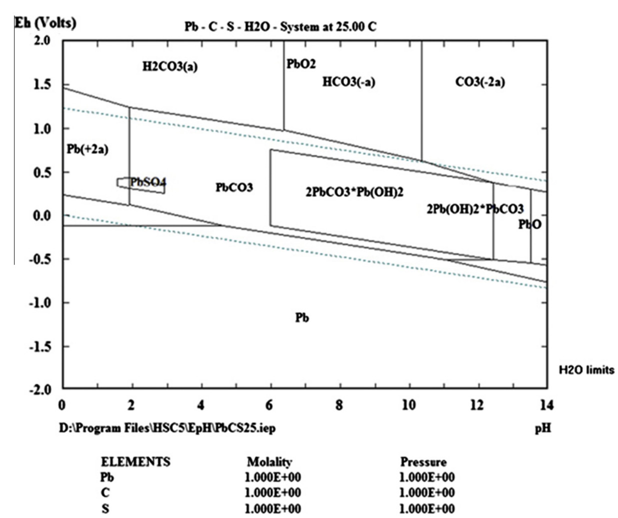

Fig. 2. Eh–pH diagram of $PbSO_4$ desulfurization with Na_2CO_3.

Table 1
Chemical composition of spent lead acid battery paste.

Element	Pb	Sb	Fe	Zn	Bi	Cu	Ag	As	S
Content (%)	68.670	0.029	0.015	0.016	0.011	5.3×10^{-3}	1.7×10^{-3}	6.8×10^{-3}	7.870