



Removing antimony from waste lead storage batteries alloy by vacuum displacement reaction technology

Tiantian Liu, Keqiang Qiu*

College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China



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ABSTRACT

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 battery can be a contaminant if not handled properly, it is also an important resource to obtain refined lead. Nowadays, the Sb-content in lead storage batteries is about 0.5–3 wt%, which is higher than the Sb-content in the crude lead. However, there are few reports about the process of removing antimony from high-antimony lead bullion. In this study, vacuum displacement reaction technology, a new process for removing antimony from high-antimony lead melts, was investigated. During this process, lead oxide was added to the system and antimony from lead melts was converted into antimony trioxide, which easily was evaporated under vacuum so that antimony was removed from lead melts. The experimental results demonstrated that Sb-content in lead melts decreased from 2.5% to 23 ppm under following conditions: mass ratio of PbO/lead bullion of 0.33, residual gas pressure of 30 Pa, melt temperature of 840 °C, reaction time of 60 min. The distillate gotten can be used as by-product to produce antimony white. Moreover, this study is of importance to recycling of waste lead storage batteries alloy.

1. Introduction

Tremendous use of lead acid battery has produced large amount of spent batteries, resulting in serious environmental problems and global issues. Therefore, the recycling of waste lead storage battery is an important subject, not only for the environment protection, but also for the recovery of valuable materials [1,2]. These scrap lead from waste lead storage battery are usually sent to lead smelters to produce antimonial lead bullion. Then antimonial lead bullion needs to be refined further to produce fine lead. According to the reference [3,4], the Sb-content in the crude lead is usually about 0.35–0.85 wt%. Nowadays, the Sb-content in the lead storage batteries is approximately 0.5–3 wt%. However, there are few specific reports about the method of removing antimony from high-antimony lead bullion. Generally, removal of antimony from high-antimony lead bullion was treated in reference to the refining process of crude lead with lower antimony content. At present, lead produced by the pyrometallurgical refining process accounts for about 70% of the refined lead in the world and only some of countries, such as Canada, Peru, Japan and China utilize the electrolytic process to refine lead bullion [5].

The pyrometallurgical process for refining lead bullion includes oxidation refining process and basic refining process, which both are on the basis of the principle that antimony is oxidized more easily than

lead [6]. The oxidation refining mainly chooses air as oxidant which oxidizes antimony in the molten lead. Nevertheless, poor working conditions, a long time to finish the process of oxidizing refining, high fuel consumption and large loss of lead make it not popular. In the basic refining process, niter as oxidant is added into the lead melts to react with antimony. Then antimony entering the alkaline slag is separated from molten lead. But this technology also exist some shortcomings, such as large amount of reagent waste and complex subsequent treatment of metal slag [7–9]. In the process of electrolytic refining, the required antimony content of lead anode plate is approximately 0.4–0.7 wt%. When antimony content of lead anode plate is more than 1.2 wt%, antimony firmly adheres to the residual lead anode plate during the refining process, which leads to difficulty in cleaning. Therefore it must be treated by preliminary pyrometallurgical refining to reduce antimony content before the electrolytic refining, which means long process and more energy consumption. Moreover, silicofluoric acid needs to be replenished regularly during the electrolytic refining process, resulting in producing a lot of waste liquid [3].

To solve the problems in the existing process for refining crude lead from waste lead storage batteries alloy, it is very meaningful to develop a high-efficiency technology for refining high-antimony lead bullion, which eliminates much of air pollution, metal loss and process time. That is the reason why we undertook an investigation about this topic.

* Corresponding author.

E-mail address: qiuwhs@sohu.com (K. Qiu).

2. Experimental section

2.1. Materials

High-antimony lead bullion containing about 2.5% by weight antimony was used in the experiments, which was self-prepared for simplicity and convenience. When pure lead was smelted in melting furnace, a small amount of lead-antimony alloy (Sb-content 20%) was put into the molten lead to increase the antimony content to about 2.5 wt%. This melting process maintained 3 h and was stirred by a graphite rod to ensure the alloy's uniformity. By the way, real waste lead storage batteries alloy was used as the raw material in the verification experiments in order to demonstrate whether the method has perfect trust in practice. The antimony content of the homogenized sample was measured by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry). Lead oxide (analytically pure) was also used in this study.

2.2. Apparatus

The main equipment of experiment used as follows: temperature controller (TCW-32A), rotary-vane vacuum pump (2XZ-1), self-manufactured resistance furnace, vacuumeter, quartz tube, water jacketed condenser and corundum crucible. The equipment is shown in Fig. 1. The furnace temperature was controlled by a temperature controller which was connected with a thermocouple. The quartz tube was conjunct with vacuum pump and vacuumeter to make the reaction under a constant gas pressure. Meantime, the top of quartz tube was connected with water jacketed condenser, which can collect volatile substances for convenience.

2.3. Procedures

Lead oxide was placed in the bottom of corundum crucible and about 12 g of high-antimony lead bullion was added on the lead oxide (Fig. 2(a)). The corundum crucible was put into the quartz tube which was fastened in the resistance furnace and was heated to certain temperature under vacuum, the timing of the vacuum treatment process started. During vacuum displacement reaction, most of antimony trioxide and few lead were evaporated (Fig. 2(b)). After the experiment, the distillate on the water jacketed condenser was collected and weighted (Fig. 2(c)). The vacuum treatment process was showed in Fig. 2. Afterwards, the Sb-content of refined lead was detected by ICP-AES. The evaporation ratio (E) of high-antimony lead bullion was

calculated by the following formulas:

$$E(\%) = \frac{m_0 - m_1}{m_0} \times 100\% \quad (1)$$

where m_0 is the mass of lead oxide and high-antimony lead bullion before the experiment and m_1 is the mass of refined lead gained after the experiment.

3. Experimental principle and exploratory experiments

3.1. The saturation vapor pressure of Pb, Sb and their oxides

The vapor pressure of metal is the important datum for metal refining by vacuum distillation. At the same temperature, the difference in saturation vapor pressure of each substance can be used as a rough guide in determining that whose substance should exhibit preferential evaporation. According to the relationship between saturation vapor pressure and temperature [10,11], Fig. 3 is obtained.

Fig. 3 shows that the saturation vapor pressures of lead, antimony, lead oxide, antimony trioxide are proportional to the temperature. At the same temperature, the greater the saturation vapor pressure of substance, the easier it evaporates. However, antimony with higher vapor pressure can't be evaporated into gas phase under vacuum, because the binary Pb-Sb system is negative deviation system from Raoult's law [12]. Therefore, the suitable technology must be developed to resolve the problem of removing antimony from the high-antimony lead melts.

3.2. Principle of removing antimony from high-antimony lead bullion

The important observation, from Fig. 3, is that the saturated vapor pressure of antimony trioxide is much higher than not only lead but also antimony. Moreover, antimony trioxide is very easily evaporated into gas phase under vacuum. Obviously, if antimony from the high-antimony lead melts can be converted into antimony trioxide, antimony can be efficiently removed from the high-antimony lead melts. Because antimony has a higher affinity with oxygen than lead, it can react with lead oxide to be converted into antimony trioxide with good volatility. In view of the reason mentioned above, lead oxide is added into the vacuum system in this study, which can avoid introducing other impurities. Therefore, the reaction of this system is under vacuum as follows:

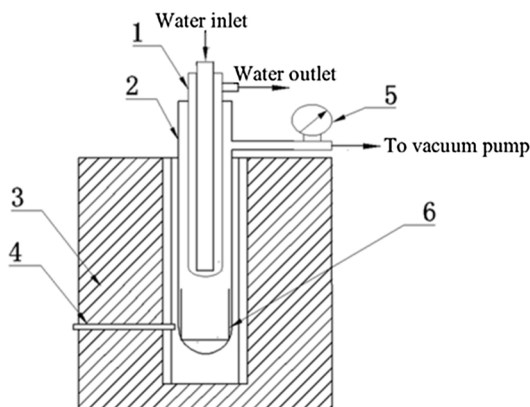
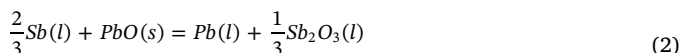


Fig. 1. The schematic illustration of apparatus: 1, water jacketed condenser; 2, quartz tube; 3, resistance furnace; 4, thermocouple; 5, vacuumeter; 6, corundum crucible.

1. Water jacketed condenser, 2. Quartz tube, 3. Resistance furnace,
4. Thermocouple, 5. Vacuumeter, 6. Corundum crucible

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