Recovery of Sb and Fe from Sb-bearing Slags through a Reduction Roasting Process with Low Density Polyethylene

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A novel method for treating the Sb-bearing slag using LDPE as a reductant under N₂ atmosphere is proposed. The H₂, CH₄ and C₂ (C₂H₆, C₂H₄, C₂H₂) are released quickly during the LDPE pyrolysis process, and some of them have escaped off the roasting system before the reaction with the Sb-bearing slag. The Sb, Pb and Fe phases in the original Sb-bearing slag could be selectively reduced to Sb₄O₆, Pb and Fe₃O₄ respectively by the pyrolysis gas at roasting temperature of 1 000°C and LDPE amount of 25 wt%. The Sb₄O₆ could be separated and recovered effectively with the volatilization rate of 93.51% accompanying the Pb volatilization rate was only around 0.68% and the Fe phase was almost transformed into Fe₃O₄ retaining in the residue. Then the Fe₃O₄ can be separated and collected from the roasted residues using magnetic separation process.

KEY WORDS: Sb-bearing slag; LDPE; selective reduction; Sb separation; Fe recovery.

1. Introduction

The Sb has a variety of industrial application, especially for manufacture of flame retardant, sliding bearing and welding flux.^{1–3)} Due to the depletion of antimony primary ore resource, recovery of it from secondary resources has gained attention, such as from Sb-bearing slags, As–Sb dust and Sb alloy scraps.^{4–6)} The corresponding processing methods existed mainly consists of pyrometallurgical and hydrometallurgical processes, and the separation of Sb from As and/or Pb compounds is the key problem. A high separation rate of As from Sb phases could be obtained in the previous researches. For the hydrometallurgy process, the As was selectively leached into solution and separated from Sb phases using alkali,^{7,8)} hot water,⁹⁾ or by chlorination.¹⁰⁾ Meanwhile, the Sb was transformed into insoluble matter and separated by filtration. The arsenic removal rate also reached above 90 mass% through a selective oxidation roasting process with CuO,¹¹⁾ MnO₂⁶⁾ and Fe₂O₃,⁵⁾ and the Sb was oxidized to Sb₂O₄ and remained in the roasted residue. The traditional treatment of Pb–Sb alloy for separating Sb is blowing smelting in reverberatory furnace, in which the Sb volatilizes in the form of Sb₂O₃. There exists many shortcomings in this conventional method, such as high energy consumption and low separation efficiency between

Sb and Pb.¹²⁾ Many researchers developed some other methods to resolve this problem, such as vacuum distillation, reducing-matting smelting and leaching technology in chloride system.¹³⁾ However, there still exist some problems for them being applied in the industry containing high power consumption and expensive production. Based on the difference in vapor pressure of substances in Sb-bearing slags, Qiu Keqiang and Zhang Rongliang found that the Sb₂O₃ could be separated from PbO and SnO₂ through vacuum evaporation process at temperature of 893 K and pressure of 250 Pa. However, the results showed that the evaporation rate of Sb was only 59.15%.¹⁴⁾ As an intermediate produced from pyrometallurgy of jamesonite, the Sb-rich oxidizing slag is mainly composed of Sb and Pb oxides, as well as Sn, Fe, and As *etc.* This Sb-rich oxidizing slag is now mainly processed by smelting reduction method. However, it increases energy consumption and decreases the recovery rates of Sb and Pb obviously due to repeated smelting. Meanwhile, an ultrasound-assisted HCl–NaCl leaching method was employed to recover Pb and Sb from this Sb-rich oxidizing slag in the research of Rong Liang Zhang *et al.*, and they found that increasing ultrasonic power could augment the leaching rate or accelerate the procedure. However, the recovery rates of Sb and Pb were also relatively low in this process, which were around 85% and 75% respectively.¹⁵⁾

Plastics are a standard group of synthetic or natural materials with carbon and hydrogen as major element. They

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are highly durable, strong, elastic and cheap to produce, which make them an ideal choice for packaging and storage applications.¹⁶⁾ The global production of plastics keeps increasing and so does the waste generation. These plastics are abundantly present in municipal solid waste. Plastic recovery can be divided into material recycling and energy recovery, which depends on the plastics types, segregation from other materials, and cost aspects of process. Thermal degradation of plastics is of increasing concern for recycling them in the form of energy through the conversion to gas, liquid and solid products.¹⁷⁾ Low and high density polyethylene (LDPE & HDPE) and polypropylene (PP) are the three major kinds.¹⁸⁾ Due to the lack of management from the governing organizations, the plastic waste goes to dumping sites along with other waste materials.¹⁹⁾ The disposal of them is currently a challenge because the dumping of them in landfills is no longer permitted in some countries. Most of them are recycled or recovered, and the gasification or pyrolysis, seems to be the future for them treatment.^{20,21)} The composition of pyrolysis products is widely different due to the thermal behavior and reactivity of these plastics, which are mainly determined by the virgin materials, the reactor type, or the applied process parameters.²²⁾

In the pyrolysis of LDPE type plastic wastes, around of 30.9% gas was yielded at 600°C, and H₂, CH₄ and C₂–C₄ hydrocarbons made for 58.3%, 20.3% and 21.4% respectively.²³⁾ There is a dramatic increase in gas yield with increasing temperature. At pyrolysis temperature of 740°C, there was an almost complete conversion of the LDPE to gas.²⁴⁾ The products of the LDPE pyrolysis can be used as reductant, but little attention has been given to it. A novel method for treating Sb-bearing slag using LDPE under N₂ atmosphere is proposed in this paper. Here, the “Sb” phases are reduced and then volatilized in the form of Sb₄O₆. Meanwhile, the “Fe” and “Pb” phases in the slag are reduced Fe₃O₄ and metallic Pb respectively and remain in the residue, and they can be separated and recovered using a general magnetic separation method.

2. Materials and Methods

2.1. Experimental Materials and Analyses

The Sb-bearing slag used in this study was supplied by a plant for treating high As–Sb dust using pyrometallurgical processes locating in Yunnan province of China. The LDPE was obtained from Shengwang Ltd. in China. Nitrogen (purity of 99.99%) was procured from local supplier.

The composition of the slag was characterized by chemical analysis, and the result is presented in **Table 1**. It shows that the slag mainly comprises 42.04 wt.% Sb, 21.31 wt.% Fe and 6.24 wt.% Pb, which are all valuable to be recovered. The “Others” in Table 1 are mainly composed of “O”, “Ca”, and “Si”, etc. X-ray diffraction (XRD, Rigaku, TTR-III) study with 2θ varying from 10 to 90° using Cu Kα radiation (λ=1.54Å at 40 kV and 200 mA) at a scan-

ning rate of 10°/min was carried out to determine the phases in the slag. The XRD spectrum in **Fig. 1** indicates that the slag mainly comprises Sb₂O₄, Sb₆O₁₃, Pb₂Sb₂O₇, PbSb₂O₆, Fe₂O₃ and FeSbO₄. An electron probe microscopic analysis (EPMA-JAX8230, JEOL, Japan) was carried out to detect the elemental distribution in various phases of the slag. **Figure 2** and **Table 2** show the focal points of analysis in the raw material. It can be seen that the major phases present include Fe₂O₃, and coexistent phases of Pb–Sb–O, Fe–Sb–O and Pb–Sb–Fe–O, which is consistent with the XRD result in Fig. 1.

2.2. Experimental Methods

The experiment was carried out in a tube furnace (GSL-1500X, Hefei Kejing Materials Technology Co. Ltd., China), and the roasting temperature was measured by a Pt–Rh thermocouple and controlled by a KSY Intelligent Temperature Controller (accuracy ± 1 K). The LDPE addition amount was given based on the quality ratio of it to the slag in all the tests.

The slag was firstly grounded and sieved to yield a particle size below 74 μm, and then mixed thoroughly with a given amount of LDPE at a particle size of 1–3 mm. For each experiment, 6 g of samples (mixture of the dust and LDPE) were used. The N₂ (150 ml/min) was sent into the furnace during the preheating and experimental process. The reactor containing the sample was weighed and placed in the constant temperature zone of the furnace when the furnace temperature reached a desired value and then held for a pre-set time. After a required time, the sample was cooled in N₂ atmosphere, weighed when the temperature reached room temperature, and prepared for analysis. The gases evolved throughout were collected in a Teflon gas sample bag and analyzed off-line by Agilent 7890A GC. The volatilization rates, α and β, for antimony and lead respectively, were calculated through Eqs. (1) and (2).

$$\alpha = \left(1 - \frac{m \times w_A}{m_R \times w_{AR}} \right) \times 100\% \quad \text{..... (1)}$$

$$\beta = \left(1 - \frac{m \times w_P}{m_R \times w_{PR}} \right) \times 100\% \quad \text{..... (2)}$$

Fig. 1. X-ray diffraction pattern of the Sb-bearing slag.

Table 1. Chemical composition of the Sb-bearing slag.

Components	Sb	Fe	Pb	Bi	Cu	Others
Wt (%)	42.04	21.31	6.24	0.57	0.22	29.12

where m_R and m stand for total mass of the raw materials and roasted residues, respectively; w_{AR} and w_{PR} are mass contents of Sb and Pb in the raw materials, and w_A and w_P are mass contents of Sb and Pb in the roasted residues, respectively.

3. Thermodynamic Analysis

3.1. LDPE Pyrolysis

It is well-known that the polymer degradation in LDPE by thermal cracking is carried out according with a radical chain mechanism, which proceeds via a random chain scission to form primary radicals. This process includes chain initiation (a), chain reaction (b, c, d, e), and chain termination (f)²⁵⁾ as shown in Fig. 3. Meanwhile, the alkanes and alkenes can further decompose into char and hydrogen

(g).²⁶⁾ Pyrolysis temperature is one of the most important operating parameters affecting the products composition. Higher temperature enhances bond breaking and favors the production of smaller molecules. As shown in Fig. 4, the mole fraction of C_2 (C_2H_6 , C_2H_4 , C_2H_2) decreases while the C_1 (CH_4) mole fraction increases with temperature before 1 000°C. Then the C_1 (CH_4) mole fraction decrease with

Table 2. Elemental analysis of different points corresponding in Fig. 2 (mole%).

Elements/Mole fraction	O	Fe	Sb	Pb
pt1	41.45	58.55		
pt2	49.66	19.10	20.04	11.20
pt3	56.90		26.55	16.55
pt4	61.74	22.62	15.64

Fig. 4. Mole fraction changes of pyrolysis gas with temperature. (Online version in color.)

Fig. 2. EPMA-EDS analysis of the Sb-bearing slag. (Online version in color.)

Fig. 3. Thermal degradation mechanism of LDPE.

temperature being higher than 1 000°C due to its decomposition to H_2 .

3.2. Reactions between the LDPE and Sb-bearing Slag

The LDPE is assumed to be thermally decomposed firstly and then reacted with the Sb-bearing slag. Selecting the pyrolysis products of LDPE in Fig. 4 and components existing in the Sb-bearing slag (Fig. 1) as reactant precursors, the FactPS, FTOxid and FTOxCN databases of FactSage 7.0 were used to calculate the reaction equilibrium between the LDPE and Sb-bearing slag by minimizing Gibbs free energy under isothermal, isobaric and fixed-mole conditions. The phases of $O_2(g)$, $Pb(s)$, $PbO(s)$, $Sb_2O_4(s)$, $Sb_4O_6(g)$, $Sb(s)$, $Fe_2O_3(s)$, $Fe_3O_4(s)$, $FeO(s)$, and $Fe(s)$ were assumed to be present in the roasted products, and the other generated phases with low contents or outside the scope of this work are not shown in the output results (Fig. 5) due to their little contents. Figure 5 shows that with the increase of pyrolysis

gas amount from 0 to 0.5, the $Sb_2O_4(s)$ amount decreases while $Sb_4O_6(g)$ and $Sb(s)$ amounts increase attributed to the reduction between pyrolysis gas and $Sb_2O_4(s)$, and the $Sb_4O_6(g)$ is the main reduction product at pyrolysis gas amount of 0.5 and 900–1 100°C. As the pyrolysis gas amount increases over 0.5, the $Sb_4O_6(g)$ will be reduced into Sb and the Sb amount increases obviously. In addition, the Pb -containing phases are almost reduced to $Pb(s)$ with the pyrolysis gas amount of 0.5 and 0.75 at temperature of 700–900°C and 1 000–1 100°C respectively, and the iron phases are almost transformed to $Fe_3O_4(s)$ with the pyrolysis gas amount of 0.5 at temperature of 700–1 000°C. The Sb phases can be separated effectively from the slag in the form of $Sb_4O_6(g)$ at temperature of 900°C and pyrolysis gas amount of 0.5 from the point of view of thermodynamics, while the Fe and Pb phases are transformed to $Fe_3O_4(s)$ and $Pb(s)$ respectively which could be separated and recovered by a general magnetic separation process.

Fig. 5. Equilibrium phases of the Sb-bearing slag roasted with LDPE at different temperatures. (Online version in color.)

4. Results and Discussion

4.1. Effect of Roasting Temperature

Under N_2 flow rate of 150 ml/min, roasting time of 60 min and LDPE amount of 15.0 wt%, five roasting temperatures of 700°C, 800°C, 900°C, 1 000°C and 1 100°C were chosen for studying the effects on the volatilization rate of Sb and phase transformation of Pb and Fe. In addition, a contrast experiment using 15.0 wt% coke with a particle size of 1–3 mm as reductant was also carried out.

With 15.0 wt% coke used as reductant, the Sb- and Pb-containing phases in the original slag are mainly reduced to Sb, Pb and $FeSb_2$ as shown in Fig. 6. As a result, the α is small, ranging from 0% to 13.51% with temperature from 700°C to 1 100°C and β is lower than 1.00% (Fig. 7). When the LDPE was roasted with the Sb-bearing slag at 700–1 100°C, it would pyrolyze and release CH_4 , H_2 and C_2 (C_2H_6 , C_2H_4 , C_2H_2) quickly as reported in Fig. 4. Due to a fast pyrolysis rate of the LDPE at 700–1 100°C,²⁴ some pyrolysis gases had escaped off the roasting system (Fig. 8(B) at 900°C) before the reduction reaction with the Sb-bearing slag, and it causes some Sb and Pb phases in the original Sb-bearing slag might only be reduced to Sb_4O_6 (g) and PbO (g) respectively. Correspondingly, α increases from 60.34% to 83.49% and β increases from 30.17% to 40.13% with temperature from 700°C to 900°C (Fig. 7).

Fig. 6. X-ray diffraction patterns of the roasted residues with 15 wt% coke added at different roasting temperatures for 60 min.

Figure 8 shows the tail gas compositions when the Sb-bearing slag was roasted with 15 wt% coke and 15 wt% LDPE respectively. The carrier gas N_2 (150 ml/min) accounts for a lower proportion when the Sb-bearing slag was roasted with LDPE compared to that with coke, and simultaneously volume fractions of CH_4 , H_2 and C_2 in Fig. 8(B) increase from 22% to 27%, 16% to 19% and 4% to 10% respectively with roasting time from 10 to 30 min. Massive metallic Pb were generated (Fig. 9) at 1 000°C and it results the Pb volatilization rate (β) decreases sharply to 1.37% as shown in Fig. 7. The Sb was produced with temperature increased to 1 100°C (Fig. 9), and the α also decreases. In addition, the Fe mainly exists in form of Fe_3O_4 in the roasted residue as shown in Fig. 9, which could be recovered by a general magnetic separation process. The roasting temperature should be fixed at 1 000°C to improve the separation rate of Sb from the Sb-bearing slag.

4.2. Effect of LDPE Addition Amount

The effect of LDPE amount is studied at temperature of 1 000°C, roasting time of 60 min and N_2 flow rate of 150 ml/min. With the increase of LDPE amount from 5 wt% to 25 wt%, the $Pb_2Sb_2O_7$ and $PbSb_2O_4$ amounts decrease and disappear at LDPE dosage of 25 wt% as shown in Fig. 10. Correspondingly, the α increases from 78.47% to 93.50%

Fig. 7. Effects of roasting temperature on volatilization rates of Sb and Pb. (Online version in color.)

Fig. 8. Compositions of the tail gases with the Sb-bearing slag roasted with 15 wt% coke (A) and 15 wt% LDPE (B) respectively at 900°C. (Online version in color.)

Fig. 9. X-ray diffraction patterns of the roasted residues at different temperatures with 15 wt% LDPE added for 60 min.

Fig. 10. X-ray diffraction patterns of the roasted residues with different LDPE amounts at 1000°C for 60 min.

(Fig. 11) through Eqs. (3) and (4). However, increasing the LDPE dosage to 35 wt% and 45 wt% respectively, the metallic Sb will be formed and increases (Fig. 10), and it causes the α decreases (Fig. 11). More metallic Pb phases are formed with LDPE dosage from 5 wt% to 45 wt% seen from Fig. 10, and it results in the β decreasing from 6.43% to 0.38% obviously (Fig. 11). For increasing the volatilization rate of Sb, the suitable LDPE amount is 25 wt%.

4.3. Effect of Roasting Time

Figure 12 shows that the PbSb_2O_4 amount in roasted residues decreases and metallic Pb amount increases with roasting time, and the PbSb_2O_4 disappears at roasting time of 60

Fig. 11. Effects of LDPE amount on volatilization rates of Sb and Pb at 1000°C for 60 min. (Online version in color.)

Fig. 12. X-ray diffraction patterns of roasted residues at 1000°C with 25 wt% LDPE for different roasting time.

Fig. 13. Effects of roasting time on volatilization rates of Sb and Pb at 1000°C with 25 wt% LDPE added. (Online version in color.)

min. Correspondingly, the α reaches a maximum of 93.51% at this roasting time and then becomes almost constant with roasting time increase (Fig. 13). The β is lower than 1% and

Fig. 14. Element distribution of the roasted residue obtained by EPMA. (Online version in color.)

remains nearly constant with roasting time changing (Fig. 13). Considering α and β , it is concluded that 60 min is an appropriate roasting time.

For increasing the Sb separation rate from the Sb-bearing slag, this roasting process with LDPE should be carried out at a roasting temperature of 1 000°C, LDPE dosage of 25 wt%, and roasting time of 60 min. Under these optimum conditions, the volatilization rate of Sb is approximately 93.51% and that of Pb is only around 0.68% (Fig. 13), and meanwhile the Fe component in the slag is almost transformed into Fe_3O_4 (Fig. 12). **Figure 14** shows that most Fe_3O_4 in the roasted residue are distributed independently from Pb phases. This Fe_3O_4 can be separated and recovered from the roasted residues using magnetic separation process, thereby rendering Fe and Pb in the Sb-bearing slag resource utilization.

5. Conclusions

The effective separation of Sb from Sb-bearing slag through a reduction roasting process using LDPE was feasible. The factors of roasting temperature, LDPE addition amount and roasting time played significant roles.

During the LDPE pyrolysis process, the C_2 (C_2H_6 , C_2H_4 , C_2H_2) mole fraction decreases while the C_1 (CH_4) and H_2 mole fractions increase with temperature. The Sb can be separated from the Sb-bearing slag in the form of Sb_4O_6 (g) at temperature of 900°C and LDPE pyrolysis gas amount of 0.5 from the point of view of thermodynamics. Some pyrolysis gas of LDPE will escape off the roasting system before the reaction with the Sb-bearing slag, and this results some Sb and Pb phases in the original Sb-bearing slag might only be reduced to Sb_4O_6 (g) and PbO (g) respectively. Volatilization rate of Sb could be increased obviously with a certain LDPE addition. At roasting temperature of 1 000°C, LDPE dosage of 25 wt% and roasting time of 60 min, the volatilization rate of Sb is approximately 93.51% and that of Pb is only around 0.68%, and meanwhile the Fe component is almost transformed to Fe_3O_4 . This Fe_3O_4 can be separated and collected from the roasted residues using magnetic separation process.^{27,28)}

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