



Recovery of antimony from antimony-bearing dusts through reduction roasting process under CO–CO₂ mixture gas atmosphere after firstly oxidation roasted

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Abstract: This paper mainly investigated the antimony recovery from antimony-bearing dusts through reduction roasting process after the dust firstly oxidation roasted. CO–CO₂ mixture gas was used as reducing agent, and the antimony-containing phase was reduced into Sb₄O₆, volatilized into smoke, and finally recovered through the cooling cylinder. The antimony recovery rate increased from 66.00 wt% to 73.81 wt% in temperature range of 650 to 800 °C, and decreased with temperature increased further to 900 °C due to the reduction of Sb₄O₆ to the nonvolatile Sb. Similarly, the CO partial pressure also played a double role in this test. Under optimized conditions of roasting temperature of 800 °C, CO partial pressure of 7.5 vol% and roasting time of 120 min, 98.40 wt% of arsenic removal rate and 80.40 wt% antimony recovery rate could be obtained. In addition, the “As₂O₃” product could be used for preparing ferric arsenate which realized the harmless treatment of it.

Key words: antimony-bearing dust; separation of arsenic and antimony; antimony recovery; reduction roasting; waste utilization

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1 Introduction

As a valuable metal, antimony and its compounds have been widely used in the production of ceramics, glass, paint, firework materials, and fire prevention materials etc. [1–5]. However, antimony reserves which occur chiefly as the gray sulfide mineral stibnite (Sb₂S₃) [5, 6] are very scarce. The extractable global resources of

antimony will be exhausted before 2050 if the antimony extraction rate continues to increase by the current pace [5, 7]. It is necessary to find other resources to extract antimony, in addition from the ore. There is an antimony-bearing dust generated from the reduction-smelting of non-ferrous metals, and most of which also contains other valuable metals, such as zinc, lead, copper, bismuth, and even some rare metals [8–10]. The antimony content in the dust exceeds 30 wt% in general,

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which provides the value of reutilization. Nevertheless, arsenic, a toxic element companioning with antimony [11, 12], should be firstly removed for the antimony recovery due to the similarity of their physical and chemical properties.

Main phases of arsenic and antimony existing in antimony-bearing dusts are As_2O_3 and Sb_2O_3 , respectively. The As_2O_3 is easy to volatilize and its volatilization rate outstripped 93.0 wt% in 120 min at 460 °C [13], and the Sb_2O_3 volatilization rate also exceeded 95.0 wt% in 140 min at 600 °C under nitrogen atmosphere [14]. However, when oxygen concentration exceeded 10%, PADILLA et al [15] found that the antimony volatilization was inhibited effectively by the formation of a non-volatile compound, SbO_2 . So, the arsenic could be separated effectively if the Sb_2O_3 was selectively oxidized from As_2O_3 and Sb_2O_3 to SbO_2 . Based on this, a selective oxidation roasting process for treating high As–Sb dusts was used in the studies of LI et al [16] and TANG et al [17], but their studies showed that only about 60 wt% of arsenic was removed and the antimony lost was higher than 10 wt%. The reason might be that the As_2O_3 and Sb_2O_3 were combined and transformed into a heteronuclear compound $\text{As}_x\text{Sb}_y\text{O}_6$ (where $x=1, 2$ or 3 , and $x+y=4$) during roasting process, which inhibited the arsenic volatilization and simultaneously promoted antimony volatilization at 200 to 800 °C [18–20]. A better separation rate of arsenic and antimony could be obtained from the hydrometallurgy process, in which the arsenic was selectively leached into solution and separated from the antimony using acid [21, 22], alkali [23–25], chlorination [26] or alkaline [27, 28]. The antimony was transformed into insoluble matter during the leaching process and separated from the solution by filtration [24, 29–31]. The arsenic removal rate could be up to 92 wt% using the hydrometallurgy process [23–28], but it consumes a lot of reagents and the arsenic containing wastewater poses a potential threat to the environment. Thus, a more reasonable process is urgently proposed to treat the antimony-bearing dust.

Using CuO as a weak oxidant for treating the antimony-bearing dust, ZHONG et al [32] found that about 91.50 wt% of arsenic was removed with only 8.63 wt% of antimony lost under the conditions of roasting temperature of 400 °C,

roasting time of 100 min and N_2 flow rate of 30 mL/min. A higher separation rate of arsenic and antimony was obtained. After being treated, the antimony existed in the roasted residues in the form of Sb_2O_4 , but the corresponding recovery method was not proposed in the research above. In addition, the treatment method of copper existing in the roasted residue was not also put forward. Based on the volatility of Sb_2O_3 , two stage roasting processes including oxidation and reduction for treating the antimony-bearing dust are put forward in this paper. For the first oxidation roasting stage, the process was carried out under the optimum process parameters proposed by ZHONG et al [32]. The second stage followed the first stage finished. During the second stage of reduction roasting, the CO acted as a reductant and effects of processing parameters on recovery of antimony had been investigated systematically, including roasting temperature, CO partial pressure and roasting time.

2 Experimental

2.1 Materials

The antimony-bearing dust used in this study was provided by a plant for treating tin anode slime using a pyrometallurgical process, which locates in Yunnan province, China. The chemical composition of it is presented in Table 1. Table 1 shows that the major elements presented are “As” (36.28 wt%), “Sb” (28.72 wt%) and “O” (22.35 wt%). “Others” in Table 1 is mainly composed of “Ca”, “K” and “S”, etc. Mineral constituent of the raw material was analyzed using XRD and EMPA reported in Figures 1 and 2. Figure 1 shows that the main phases are As_2O_3 , Sb_2O_3 , As_4O_6 and $(\text{Sb,As})_2\text{O}_3$. Figure 2 shows that part of arsenic and antimony exists independently in the form of white arsenic ore and valentinite respectively. Simultaneously, the combined phases of arsenic and antimony are observed, including variant white arsenic ore and altered red sulfur arsenic antimony sodium ore.

The oxidation treatment for this dust had been

Table 1 Chemical composition of antimony-bearing dust (mass fraction, %)

As	Sb	O	C	Se	Pb	F
36.28	28.72	22.35	2.52	2.46	2.06	2.05
Fe	Bi	Na	Sn	Cu	SiO ₂	Others
1.13	0.68	0.40	0.25	0.24	0.05	0.81

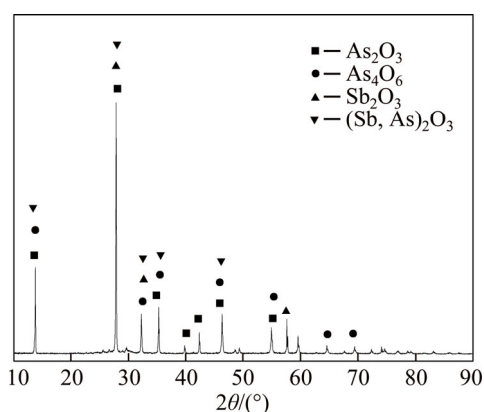


Figure 1 XRD pattern of antimony-bearing dust

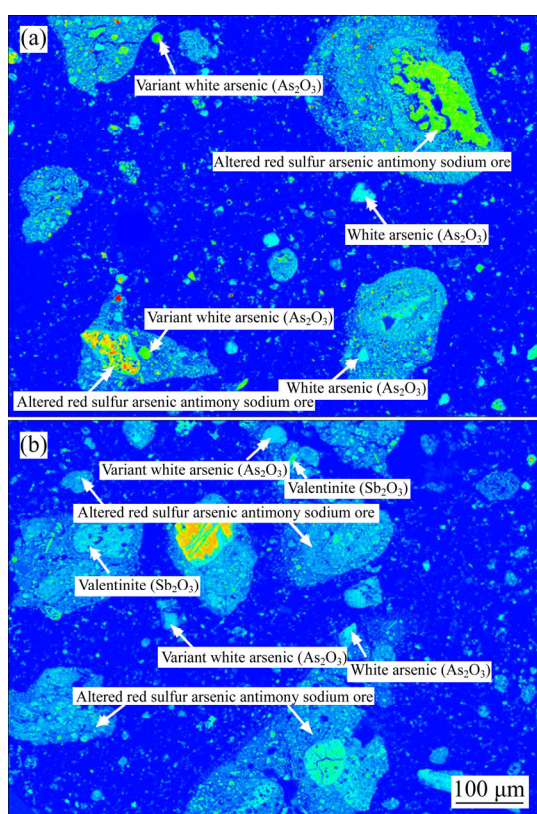


Figure 2 Mineral phase of distribution of antimony-bearing dust obtained by EPMA: (a) Concentrates with particle size of 0.075 mm; (b) Concentrates with particle size of 0.061 mm

investigated in the previous study of ZHONG et al [32], and chemical composition of the roasted residue for this roasting process is presented in Table 2. It shows that the major elements are “Sb” (36.54 wt%), “O” (26.54 wt%) and “Cu” (23.67 wt%). “Others” in Table 2 is mainly composed of “Ca”, “K” and “S”, etc. Mineral constituent of the roasted residue was characterized with XRD and EMPA. Figure 3 shows that main phases of the roasted residue are CuO, Sb₂O₄, Cu₂O

Table 2 Chemical composition of roasted residue for oxidation roasting process (mass fraction, %)

As	Sb	Cu	O	F	Pb	Fe
1.08	36.54	26.54	23.67	3.01	2.35	1.63
Se	C	Bi	Na	Sn	SiO ₂	Others
1.42	1.38	0.78	0.55	0.36	0.06	0.63

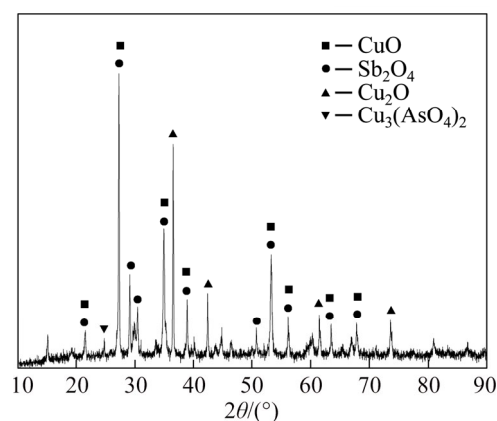


Figure 3 XRD pattern of roasted residue for oxidation roasting process

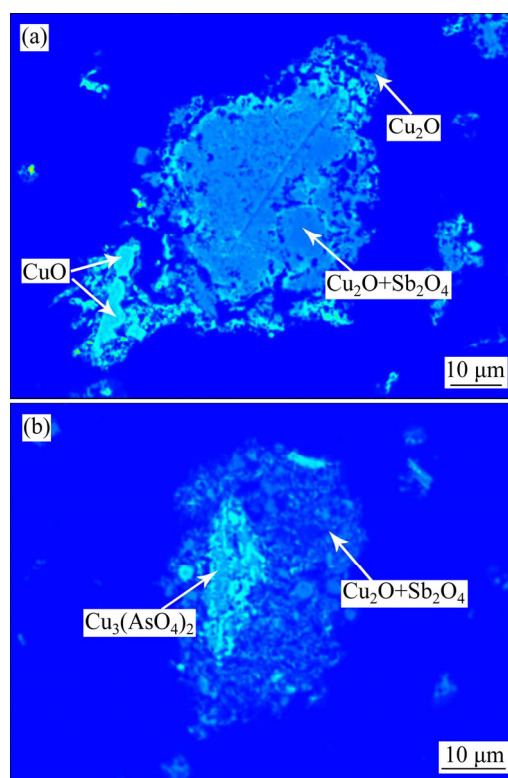


Figure 4 EPMA analysis of roasted residue for oxidation roasting process obtained: (a) 1200 X; (b) 1500 X

and Cu₃(AsO₄)₂. Figure 4 shows that most antimony phase (Sb₂O₄) coexists with copper phase (Cu₂O), and other copper exists independently in the form of Cu₂O and CuO respectively.

The CuO reagent was used as oxidant in the

oxidation roasting stage, and the purity of it is over 99.00 wt%. N_2 (purity of 99.3%), CO (purity of 99.9%) and CO_2 (purity of 99.9%) were procured from local suppliers.

2.2 Roasting experiments

In this work, two stage roasting processes including oxidation and reduction were used to deal with the antimony-bearing dust. For the purpose of separating arsenic from the dusts drastically, 30.000 g of the dust mixed with 34.54 wt% CuO was firstly roasted in the tube furnace (Figure 5) at 400 °C for 100 min with N_2 flow rate of 30 mL/min based on the previous study [32]. During this oxidation roasting process, keep the valve “14” off and “15” on. The off-gas from the reaction tube continuously passed through a water-cooled condenser (Device “10”), which collected the volatile matter, and then was directed to the solution of 1 mol/L $NaOH$ to remove harmful components. The reduction roasting followed the oxidation finished. With the temperature being raised further to a set value, the roasted residue for the oxidation roasting was further roasted in the tube furnace for 20–140 min under $CO-CO_2$ gas mixture atmosphere. The total inlet gas flow rate was fixed at 500 mL/min. After being cooled down to the room temperature under N_2 atmosphere, the roasted residue was pulled out for analysis. During the reduction roasting stage, maintain the valve “15” off and “14” on. The off-gas from the reaction tube continuously passed through a cooling cylinder (Device “12”), which collected the volatile matter,

and then was directed to the solution of 1 mol/L Na_2S to remove harmful components. At last, the volatiles in cooling cylinder (Device “12”) and water-cooled condenser (Device “10”) were put out for analysis respectively.

2.3 Characterization

Chemical composition and mineralogy of the samples were characterized by chemical analysis and electron probe microanalysis (EPMA) respectively. Especially, the “O” contents in the samples were detected by XRF analysis (MINIPAL4, PANalytical, Netherlands). Phase compositions of all the samples were detected by an XRD with a $Cu-K\alpha$ radiation (the scanning rate was $10^\circ/\text{min}$ and 2θ was $10^\circ-90^\circ$). FactSage 7.0 software was used to calculate the standard Gibbs free energy changes and equilibrium compositions of the reaction system. Mathematical expressions of volatilization rate of arsenic (R_A) and recovery rate of antimony (R_S) were defined as follows:

$$R_A = \left(1 - \frac{m_T W_{A2}}{m_C W_{A1}} \right) \times 100\% \quad (1)$$

$$R_S = \frac{m_D W_{S2}}{m_C W_{S1}} \times 100\% \quad (2)$$

where m_C stands for the mass of antimony-bearing dusts used; w_{A1} and w_{S1} stand for arsenic and antimony contents in the origin antimony-bearing dust, respectively; m_T and m_D stand for the mass of roasted residue and collected matter in device “12” (Figure 5) respectively; W_{A2} stands for the arsenic

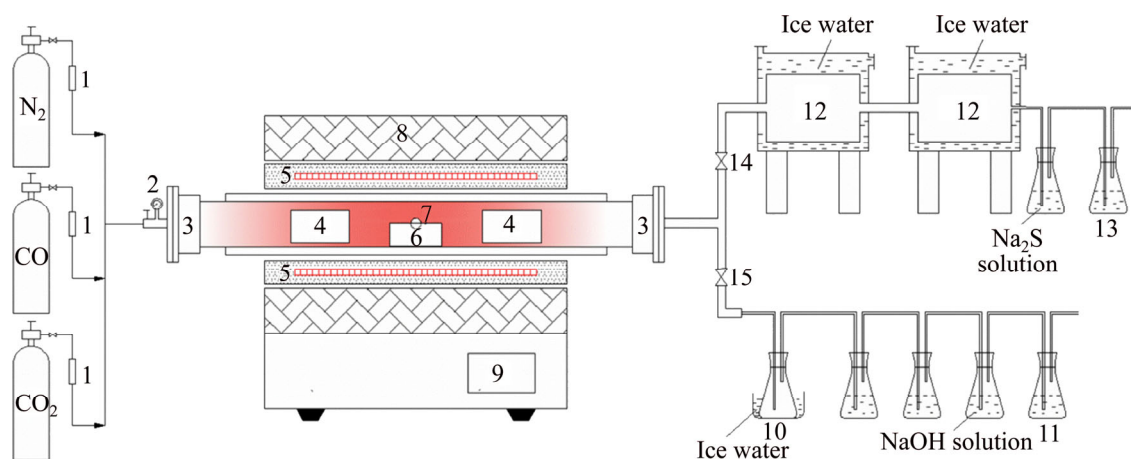


Figure 5 Experimental setup: 1–Flow meter; 2–Pressure valve; 3–Furnace cover; 4–Furnace plug; 5–Silicon carbide bar; 6–Corundum boat; 7–Thermocouple; 8–Electric furnace; 9–Control cabinet; 10–Water-cooled condenser; 11–Alkali vessel; 12–Cooling cylinder; 13–Absorbing container; 14–Valve; 15–Valve

content in the roasted residue; W_{S_2} stands for the antimony content in the collected matter in device “12” (Figure 5).

3 Thermodynamic analysis

Based on the mineral constituent of the roasted residue for the oxidation roasting process, the main reactions which may occur during the followed reduction roasting are as follows:

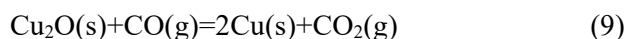
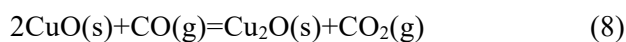
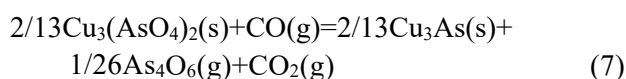
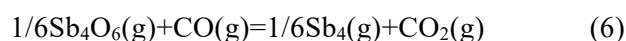
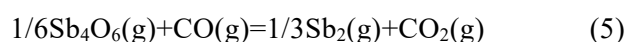
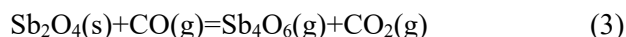


Figure 6 shows that the Sb_2O_4 can be reduced to Sb_4O_6 , and further reduced to lower valence states of antimony compounds (Sb, Sb_2 , Sb_4 , etc.). In order to increase the antimony volatilization and recovery rate, the reduction roasting process should be carried out by accurately controlling the temperature and CO partial pressure so as to increase the formation of Sb_4O_6 while avoid its further reduction.

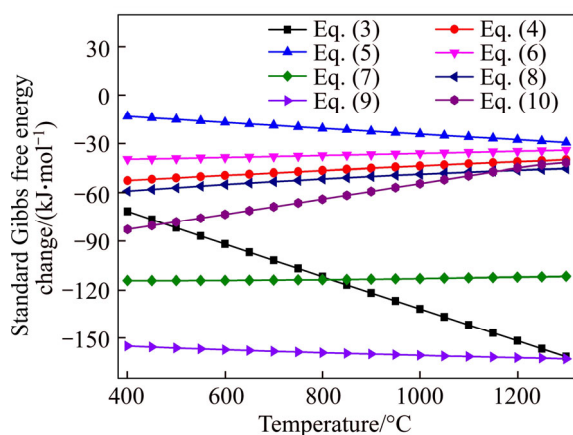


Figure 6 Standard Gibbs free energy changes of Eqs. (3)–(10) with temperature

4 Results and discussion

All of the original antimony-bearing dusts

were firstly roasted with CuO , which was carried out under the process parameters of roasting temperature of $400\text{ }^\circ\text{C}$, roasting time of 100 min, CuO amount of 34.54 wt% and N_2 flow rate of 30 mL/min [32]. Then the roasted residue for the oxidation roasting stage was further roasted under CO-CO_2 gas mixture atmosphere to recover antimony.

4.1 Effects of roasting temperature

Under roasting time of 120 min and CO partial pressure of 5 vol%, six roasting temperatures of 650, 700, 750, 800, 850 and $900\text{ }^\circ\text{C}$ were chosen for studying the effects on volatilization rates of arsenic and antimony.

Figure 7 shows that arsenic volatilization rate almost remains constant with temperature from 650 to $900\text{ }^\circ\text{C}$, which is due to most of the arsenic having been volatilized in the oxidation roasting stage [32]. Moreover, a high temperature provides a favorable kinetic condition for the selective reduction of Sb_2O_4 to Sb_4O_6 and further the Sb_4O_6 volatilization, which results in the antimony recovery rate increase with temperature from 650 to $800\text{ }^\circ\text{C}$. However, the generated Sb_4O_6 could be further reduced into nonvolatile Sb and its amount increases with temperature from 800 to $900\text{ }^\circ\text{C}$ (Figure 8), resulting in the gradual decrease of antimony recovery rate. Hence, the reduction roasting temperature is determined as $800\text{ }^\circ\text{C}$.

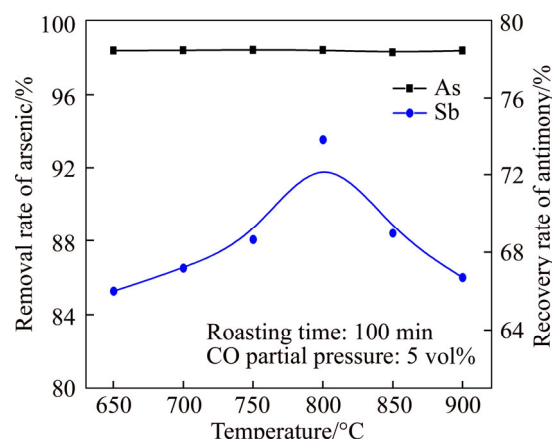


Figure 7 Effects of roasting temperature on removal rate of arsenic and recovery rate of antimony

4.2 Effects of CO partial pressure

The FactSage 7.0 was used to calculate the equilibrium of roasted products for the reduction roasting process in Gibbs free energy minimization

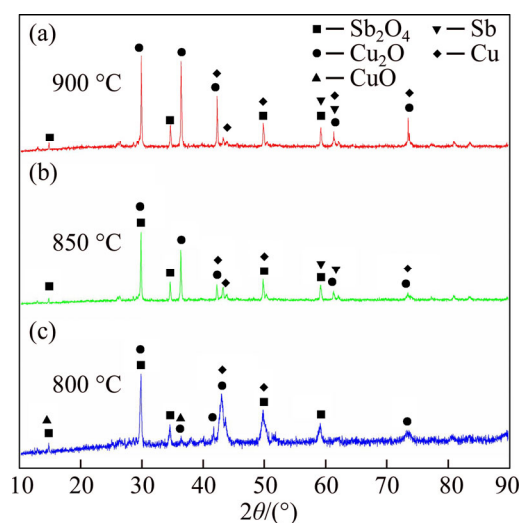


Figure 8 XRD patterns of roasted residues at 800 °C, 850 °C and 900 °C

under isothermal, isobaric and fixed mole conditions. Required data for computation were provided by FactPS database of the program.

In Equilib program of FactSage, $\text{Cu}_3(\text{AsO}_4)_2(\text{s})$ (0.0012 mol), $\text{Sb}_2\text{O}_4(\text{s})$ (0.0321 mol), $\text{CuO}(\text{s})$ (0.0602 mol) and $\text{Cu}_2\text{O}(\text{s})$ (0.0321 mol) were selected as reactant precursors, and CO-CO_2 gas mixtures was an reactant gas to strictly control the retained O_2 content in the atmosphere. Total quantity of CO and CO_2 was fixed at 2.679 mol due to the total inlet gas flow rate of 500 mL/min and roasting time of 120 min. The temperature and atmosphere pressure were fixed at 800 °C and 1.01325×10^5 Pa, respectively. This calculation was performed at antimony-bearing dusts of 30 g and CO partial pressure range of 0 to 15 vol%. The phases of $\text{Cu}_3(\text{AsO}_4)_2(\text{s})$, $\text{Cu}_3\text{As}(\text{s})$, $\text{CuO}(\text{s})$, $\text{Cu}_2\text{O}(\text{s})$, $\text{Cu}(\text{s})$, $\text{Sb}(\text{l})$ and $\text{Sb}_2\text{O}_4(\text{s})$ were assumed to be present in the roasted products, and the phases of $\text{Sb}_4\text{O}_6(\text{g})$, $\text{Sb}_2(\text{g})$, $\text{Sb}_4(\text{g})$, $\text{As}_4\text{O}_6(\text{g})$ were deemed to be volatilized and went into the smoke. The results of their equilibrium are present in Figures 9(a) and (b). Amounts of $\text{Sb}_2(\text{g})$ and $\text{Sb}_4(\text{g})$ are too little in Figure 9(a) to consider their effects during the reduction roasting. With CO partial pressure from 0 to 5 vol%, Figure 9(a) shows that $\text{Sb}_2\text{O}_4(\text{s})$ amount decreases and $\text{Sb}_4\text{O}_6(\text{g})$ amount increases attributed to the occurrence of Eq. (3). When CO partial pressure increases above 5 vol%, the $\text{Sb}(\text{l})$ phase appears going with a rapid decrease of $\text{Sb}_4\text{O}_6(\text{g})$ amount, which is related to the further reduction of

$\text{Sb}_4\text{O}_6(\text{g})$ to $\text{Sb}(\text{l})$ (Eq. (4)). Improving the $\text{Sb}_4\text{O}_6(\text{g})$ formation amount and antimony recovery rate, the reduction roasting should be performed at CO partial pressure being in the range of 3 vol% to 5 vol% seen from Figure 9(a).

With CO partial pressure being from 0 to 2 vol%, the $\text{CuO}(\text{s})$ is reduced to $\text{Cu}_2\text{O}(\text{s})$, resulting in a rapid decrease of $\text{CuO}(\text{s})$ and gradual increase of $\text{Cu}_2\text{O}(\text{s})$ in Figure 9(b). When CO partial pressure is above 2 vol%, the $\text{Cu}(\text{s})$ phase appears accompanying with a rapid decrease of $\text{Cu}_2\text{O}(\text{s})$ amount attributed to the further reduction of $\text{Cu}_2\text{O}(\text{s})$ to $\text{Cu}(\text{s})$.

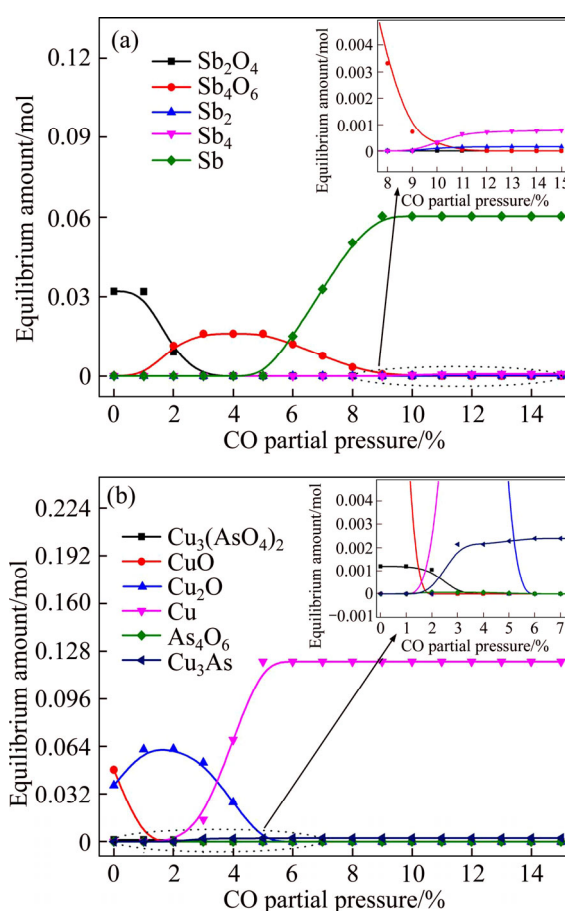


Figure 9 Equilibrium amounts of species in roasted products as function of CO partial pressure: (a) Antimony phases; (b) Copper and arsenic phases

The CO partial pressure ranging from 1.25 vol% to 15.0 vol% was selected to investigate its effects on volatilization rates of arsenic and antimony, and the results are shown in Figure 10. Obviously, the CO partial pressure hardly affects the arsenic removal rate due to its little content in the roasted residue for the oxidation roasting. The

recovery rate of antimony increases from 48.10 wt% to 80.41 wt% with CO partial pressure from 1.25 vol% to 7.50 vol%. However, the Sb(I) is formed at CO partial pressure of 7.5 vol% and its amount increases with CO partial pressure (Figure 11), resulting in the recovery rate of antimony decreasing gradually. Hence, the CO partial pressure is fixed at 7.5%. During this roasting stage, the copper phases are mainly transformed into Cu and Cu₂O (Figure 10), and they can be recycled into this two stage roasting processes after it reoxidized to CuO.

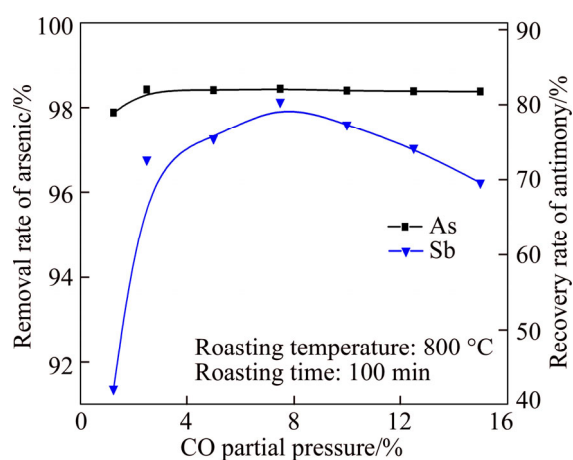


Figure 10 Effects of CO partial pressure on removal rate of arsenic and recovery rate of antimony

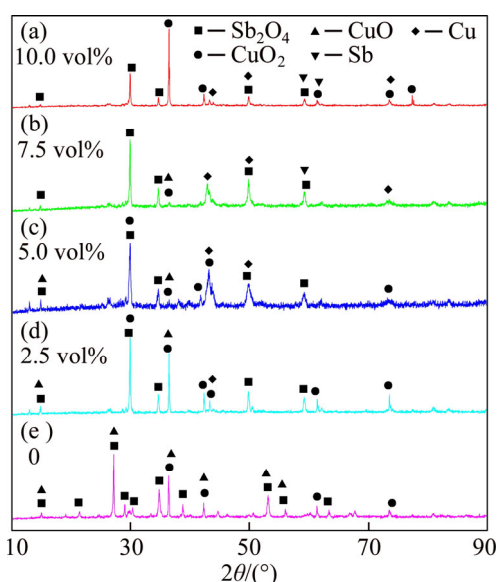


Figure 11 XRD patterns of roasted residues under different CO partial pressures

4.3 Effects of roasting time

The effect of roasting time was studied under the following conditions: 800 °C for roasting temperature and 7.5 vol% for CO partial pressure.

Figure 12 reveals that the removal rate of arsenic is almost unchanged during this text. Simultaneously, the recovery rate of antimony increases gradually in the primary 120 min, from 61.0 wt% to 80.4 wt%, and then remains nearly constant. To decrease the process energy consumption and improve antimony recovery rate, the roasting time is fixed at 120 min.

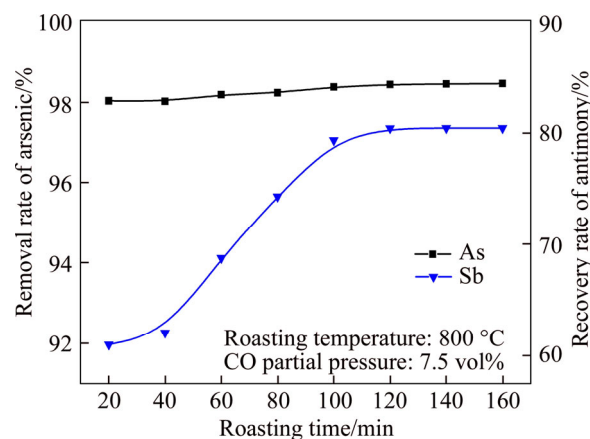


Figure 12 Effects of roasting time on removal rate of arsenic and recovery rate of antimony

Based on the discussion above, it can be concluded that recovering antimony from the antimony-bearing dust through reduction roasting under CO–CO₂ mixture gas atmosphere after oxidation roasted is viable. Under conditions of roasting temperature of 800 °C, CO partial pressure of 7.5 vol% and roasting time of 120 min, 98.40 wt% of arsenic removal rate and 80.40 wt% antimony recovery rate could be obtained. Meanwhile, the products of As₂O₃ and Sb₂O₃ could be collected from the water-cooled condenser (device “10” in Figure 5) and cooling cylinder (device “12” in Figure 5) respectively, and XRD patterns of them are shown in Figures 13 and 14

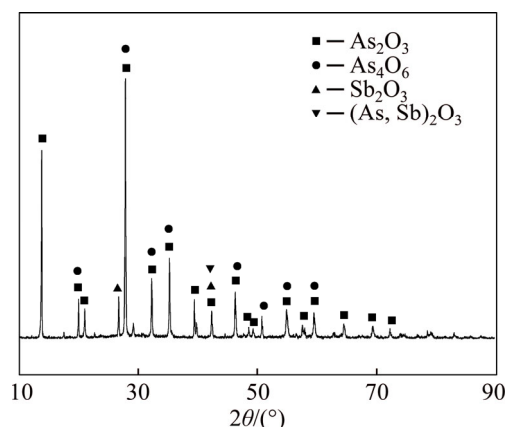


Figure 13 XRD pattern of product in water-cooled condenser (device “10” in Figure 5)

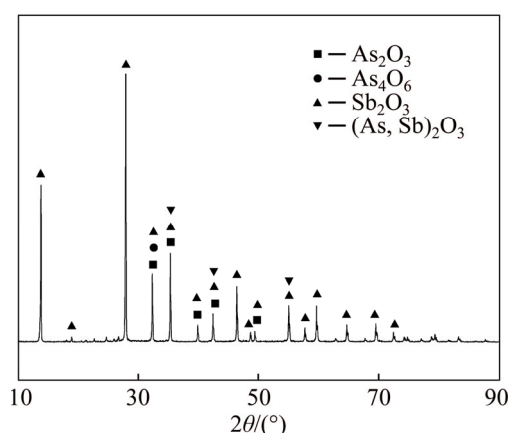


Figure 14 XRD pattern of product in cooling cylinder (device “12” in Figure 5)

respectively. In addition, the “ As_2O_3 ” product can be used for preparing ferric arsenate which realizes the harmless treatment of it [33, 34]. Meanwhile, this process can obtain a high antimony recovery rate.

5 Conclusions

The effective recovery of antimony from the antimony-bearing dust through reduction roasting under $\text{CO}\text{--}\text{CO}_2$ mixture gas atmosphere after oxidation roasted is feasible. Several parameters of reduction roasting stage were studied, i.e., the roasting temperature, CO partial pressure and roasting time.

The recovery rate of antimony increases from 66.00 wt% to 73.81 wt% with temperature from 650 to 800 °C, and decreases with temperature increased further to 900 °C due to the reduction of Sb_4O_6 to the nonvolatile Sb. Similarly, the recovery rate of antimony increases substantially with the CO partial pressure range of 1.25 vol% to 7.5 vol%, and then decreases gradually when the CO partial pressure is over 7.5 vol%. Under optimized conditions of roasting temperature of 800 °C, CO partial pressure of 7.5 vol% and roasting time of 120 min, 98.40 wt% of arsenic removal rate and 80.40 wt% antimony recovery rate could be obtained. In addition, the products of “ As_2O_3 ” can be used for preparing ferric arsenate which realized the harmless treatment of it, and the copper existed in the roasted residue in the form of Cu and Cu_2O could be recycled into this two stage roasting processes after it is reoxidized.

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中文导读

含锑烟尘氧化焙烧处理后 CO–CO₂ 混合气体中锑资源的还原焙烧法回收

摘要: 研究主要针对含锑烟尘经氧化焙烧处理后 CO–CO₂ 混合气体中锑资源的还原焙烧法回收进行了探讨。以 CO–CO₂ 混合气体作为还原剂, 过程中锑物相还原为 Sb₄O₆ 并进入气相, 最后通过冷凝收尘方式实现其回收。温度由 650 °C 升高至 800 °C 时, 锑回收率从 66.00 wt% 增至 73.81 wt%, 当温度进一步升高到 900 °C 时, Sb₄O₆ 被进一步还原为非挥发性金属锑, 锑回收率降低。同样, CO 分压对锑的挥发回收亦起双重作用。在最优焙烧条件下, 即焙烧温度 800 °C、CO 分压 7.5 vol% 及焙烧时间 120 min 时, 锑烟尘中砷挥发率可达 98.40 wt%, 同时锑回收率亦可达 80.40 wt%。此外, 挥发脱除的“As₂O₃”烟尘可用于制备砷酸铁, 以实现其无害化处理。

关键词: 含锑烟尘; 砷锑分离; 锑回收; 还原焙烧; 废物利用