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Antimony and arsenic substance flow analysis in antimony pyrometallurgical process

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Abstract: Substance flow analysis was applied to an antimony pyrometallurgical system. By taking antimony and arsenic as the objective elements, the mass balance and substance flow charts based on the production system were established, and evaluating indicators such as the direct recovery rate, waste recovery rate, and resource efficiency were set up. The results show that the resource efficiency of antimony is 89.21%, and the recovery rates of antimony in volatilization smelting, reduction smelting, and refining are 78.79%, 91.00%, 96.06%, respectively. At the same time, for 1 t of antimony produced, 11.94 kg of arsenic is carried into the smelting system. Arsenic is a major impurity element in the smelting process. The distribution behavior of arsenic in the main process was analyzed. Based on the substance flow analysis, some recommendations for improving the resource efficiency of antimony and cleaner production were proposed.

Key words: antimony metallurgy; substance flow analysis; antimony resource efficiency; arsenic distribution behavior

1 Introduction

Antimony is an important strategic metal. Antimony metal and compounds are mainly used in producing semiconductors, far-infrared materials, lead−antimony alloys, flame retardants, catalysts, and other products. They are widely used in the military industry, electronics, aerospace, and other fields [1−3]. According to the survey data of the U.S. Geological Survey in 2021, the global antimony reserves in 2020 are 1.9 million tones, and the reserves in China are 480000 tones, accounting for 25% of the total reserves [4]. China is the largest producer of antimony products in the world [5]. With the increasing complexity of antimony resources and the extensive use of antimony−gold concentrate with high arsenic concentration, the concentrations of arsenic and antimony in arsenic-alkali residue produced in the production process have increased significantly (up to 20% arsenic and 20%−30% antimony) [6,7]. With the improvement of environmental protection requirements, it is urgent to solve the problems of efficient separation of high arsenic and antimony and final disposal of arsenic. There are many studies on smelting treatment technology [8−10] and arsenic-containing solid waste treatment [11,12]. Still, few people pay attention to the flow and distribution of antimony and arsenic in the production system. Substance flow profoundly impacts the resource efficiency and environmental load of the production system. Therefore, an in-depth analysis of the distribution behavior of antimony and impurity elements is of great significance in improving the utilization efficiency of antimony resources and reducing the emission level of pollutants.

As an analytical tool, substance flow analysis (SFA) is an important method to study substance

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flow state of a given system (production, economy, society, etc.) in a certain range. In the past few decades, SFA has been widely used to analyze the stock and flow of various metals (copper [13−15], lead [16], aluminum [17], zinc [18], indium [19], cobalt [20], etc.) In addition, SFA was applied to waste management [21,22], pollution prevention and control [23], resource recycling, and whole industry chain analysis [24,25]. In the past, most studies were focused on material flow and waste management at the regional or national level. Using SFA to track the quantity and migration of substances in the production process can determine the production efficiency of the process and reveal the ways of pollutant generation, which is conducive to the resource management and pollution control of the plant. It has important guiding significance for the efficient utilization of resources, pollutant prevention and control, and the formulation of environmental protection policies for enterprises and industries. BAI et al [26] took SFA as the research tool, established the substance flow model of a lead-smelting system, evaluated the resource utilization, circulation, and emission level of the system, and put forward some suggestions on emission control and pollution prevention of lead production enterprises. CHEN et al [27] established the mass balance and material flow chart of the tungsten hydrometallurgy system and analyzed the tungsten resource efficiency of the system and the distribution behavior of arsenic in the production process.

The researches on substance flow analysis of antimony have been mainly focused on the national stock, consumption, and circulation of antimony [28] and the environmental impact caused by the use of antimony-containing products [29,30]. There was less research on substance flow analysis of the antimony production process. In this study, SFA was applied to an antimony pyrometallurgical production system to study the substance flow of antimony and arsenic in the whole system. By setting evaluation indicators such as the metal recovery rate, waste recovery rate, resource efficiency and studying the utilization level of antimony resources, the emission characteristics of arsenic pollutants in the production process were revealed, which provided theoretical support for improving the utilization rate of resources in the smelting process and reducing the emission level of contaminants.

2 Methodology

Compared with applying SFA in global or regional large-scale systems, applying SFA to a production process is more specific. It can be used to analyze the impact of various logistics changes on environmental load and resource efficiency and then determine the key links and main factors to put forward corresponding improvement measures. The SFA model of the production process generally includes the substance flow of a unit process and the substance flow of the whole production system composed of several unit processes.

2.1 Definition of substance flows in unit process

If we define a unit process in the production system as Process *j*, the substance flow model of Process *j* can be decomposed into six substance flows. Six substance flows are explained below and shown in Fig. 1.

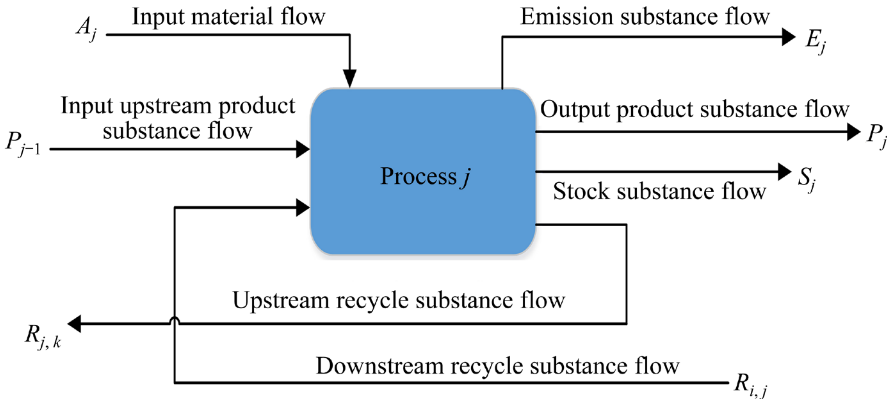


Fig. 1 Decomposition of substance flow chart of a unit process

(1) Input material flow, A_j.

(2) Input upstream product substance flow, P_{j-1}.

(3) Recycle substance flow: upstream recycle substance flow, $R_{j,k}$, meaning that the upstream processes reuse the substance flow; downstream recycle substance flow, $R_{i,j}$, meaning that the substance flow is reused from downstream back to Process *j*.

(4) Emission substance flow, E_j: This flow includes the by-products and pollutants that are discharged outside of the objective system from Process *j*.

(5) Output product substance flow, P_j.

(6) Stock substance flow, S_j: This kind of product is temporarily stocked in the warehouse and will be put into production when needed.

According to the mass-balance principle of steady-state process, a unit process *j* can be expressed as

$$A_j+P_{j-1}+R_{i,j}=P_j+R_{j,k}+E_j+S_j \tag{1}$$

2.2 Substance flows of whole system

By connecting all unit processes in a particular order, the substance flow model of the whole system can be obtained. The composition of each substance flow is as follows:

(1) Input material flow *A*:

$$A=\sum_{j=1}^{m}A_j \tag{2}$$

(2) Recycle substance flow *R*:

$$R=\sum_{i=1}^{m}\sum_{j=1}^{m}R_{i,j} \tag{3}$$

(3) Stock substance flow *S*:

$$S=\sum_{j=1}^{m}S_j \tag{4}$$

(4) Emission substance flow *E*:

$$E=\sum_{j=1}^{m}E_j \tag{5}$$

(5) Output substance flow *P*, where P_j is the product of each process.

2.3 Mass balance calculation

Two parts of the data are required to analyze the substance flow of a specific element. One part is the flow rate, M_i, t/d, which is the amount of each material containing an objective element in the production system. This part of the data is collected and converted from enterprise production report. The other part is the concentration of an objective element in each material, C_i, wt.%, which is obtained by sampling and analyzing each material. Taking Sb as an example, the concentration of antimony in each substance flow, m_i, can be obtained by

$$m_i=M_i\cdot C_i,\ i=1,\ 2,\ \cdots,\ m \tag{6}$$

In this study, the mass balance calculation of unit processes and the whole system was based on 1 t of antimony output from the production system. We expressed this as flow ratio, the mass of Substance *i* for each tonne of antimony produced within the balance area. The flow ratio of substance flow *i*, f_i, is calculated as

$$f_i=m_i/m_{\mathrm{m}} \tag{7}$$

where m_{m} is the quantity of the objective element in the final product output from the production system, t(Sb)/d.

2.4 Unsuspected losses

Balancing mass flow is a difficult task for substance flow analysis. Even if the mass-balance principle is applied to each unit process in the production system, 100% mass balance cannot always be accurately obtained. Usually, when the output material of a process is less than the input material, some material loss occurs in the process. In most metallurgical enterprises, the general measurement unit of raw materials and products is tonne. Still, some pollutant emissions, such as tail gas, need to be accurate to kilogram or even gram. Therefore, measurement error is one of the main reasons for the failure of mass balance. In addition, fugitive emission–pollutant generated in the production process that cannot be effectively collected is also an important influencing factor. For example, in the process of volatilization smelting, feeding, slag discharge, and other operations can cause some dust to be discharged into the environment, resulting in mass balance failure.

To obtain 100% mass balance of each process and the whole system, the unsuspected losses caused by (1) measurement errors and (2) fugitive emissions are regarded as a virtual substance flow in this study. Considering that this part of mass loss does not enter any product in the system, the unsuspected loss is regarded as an exceptional emission substance flow [26]. The input and output of each unit process have been measured and calculated. Taking antimony as an example, the failure degree of mass balance (γ) is calculated by the following formula:

$$\gamma=\frac{I_{\text{antimony}}-O_{\text{antimony}}}{I_{\text{antimony}}}\times 100\% \tag{8}$$

where I is input and O is output.

Previous studies have shown that 10% balance difference between input and output is acceptable and insignificant for conclusions [31,32].

2.5 Evaluation indicators of SFA

To explain the relationship between different substance flows and their resource efficiency and environmental load, three indicators are proposed in this study as follows.

(1) Direct recovery of the primary processes, α, the proportion of objective element in qualified products to the total output flows of the process, %. For the Process j, α_j is calculated as

$$\alpha_j=[P_j/(P_j+R_j+S_j+E_j)]\times 100\% \tag{9}$$

(2) Waste recovery of the process, ω, the proportion of recycle substance flow in all the substance flows not included in the final product, %:

$$\omega=[R/(R+S+E)]\times 100\% \tag{10}$$

(3) Resource efficiency, ε, the proportion of objective element in the final product to the total input flows, %:

$$\varepsilon=(A-S-E)/A=(P/A)\times 100\% \tag{11}$$

3 System definition and data collecting

This study takes a pyrometallurgical process for producing antimony ingot from antimony−gold concentrate as the system boundary. The process includes primary processes of volatilization smelting, reduction smelting, refining, and assistant processes for slags, flue dust, and tail gas treatment. The process is developed and operated by an antimony production enterprise with an annual output of 20000 t of antimony ingot in Hunan Province, China. Many domestic enterprises adopt this representative treatment technology. The simplified flow of the target process is shown in Fig. 2.

The antimony−gold concentrate is granulated with approximately 10% lime to obtain granular ore with appropriate particle size. Granular ore with an antimony grade of 40%−50% is sent into the blast furnace with the recycled material, fuel, and fluxing agent of the system. Smelting slag, antimony matte, and crude antimony are obtained from the melt produced in the volatilization smelting process through forehearth treatment. The crude antimony is then treated in a cupellation furnace to produces Sb−Au alloy, antimony oxide, and ash slag. The Sb−Au alloy is sent to the gold production system. Antimony oxide is used as the raw material for the production of antimony. At the same time, the dust collecting system treats the antimony-containing dust produced in the volatilization smelting process.

The antimony oxide produced in the above process is used as the raw material for reduction smelting, combined with an appropriate amount of reduction coal, so that the antimony oxide is reduced to antimony. The produced slag contains high antimony and returns to the blast furnace; crude antimony contains arsenic, lead, copper, iron, and other impurity elements, which need to be further refined. In the process of refining, through the application of arsenic removal agent (sodium carbonate) and lead removal agent (phosphoric acid), the impurity elements, arsenic and lead, in crude antimony are reduced to national standard. Arsenic and lead are enriched in arsenic−alkali residue and lead slag, respectively. The refined antimony is then cast to obtain antimony ingot.

In this study, antimony and arsenic were selected as target elements to study their flow and distribution in the above production systems. The input, recycle, emission, stock, and output data of each substance flow in the system were obtained from the production report of the enterprise. To determine the content of antimony and arsenic in each logistics, all materials in the system were sampled and analyzed on the stable production day. The sampling period was three consecutive days. The antimony and arsenic contents of samples were averaged and compared with the production data of the enterprise. The mass balance was calculated in combination with the production flow data.

The collected solid samples were dried in an

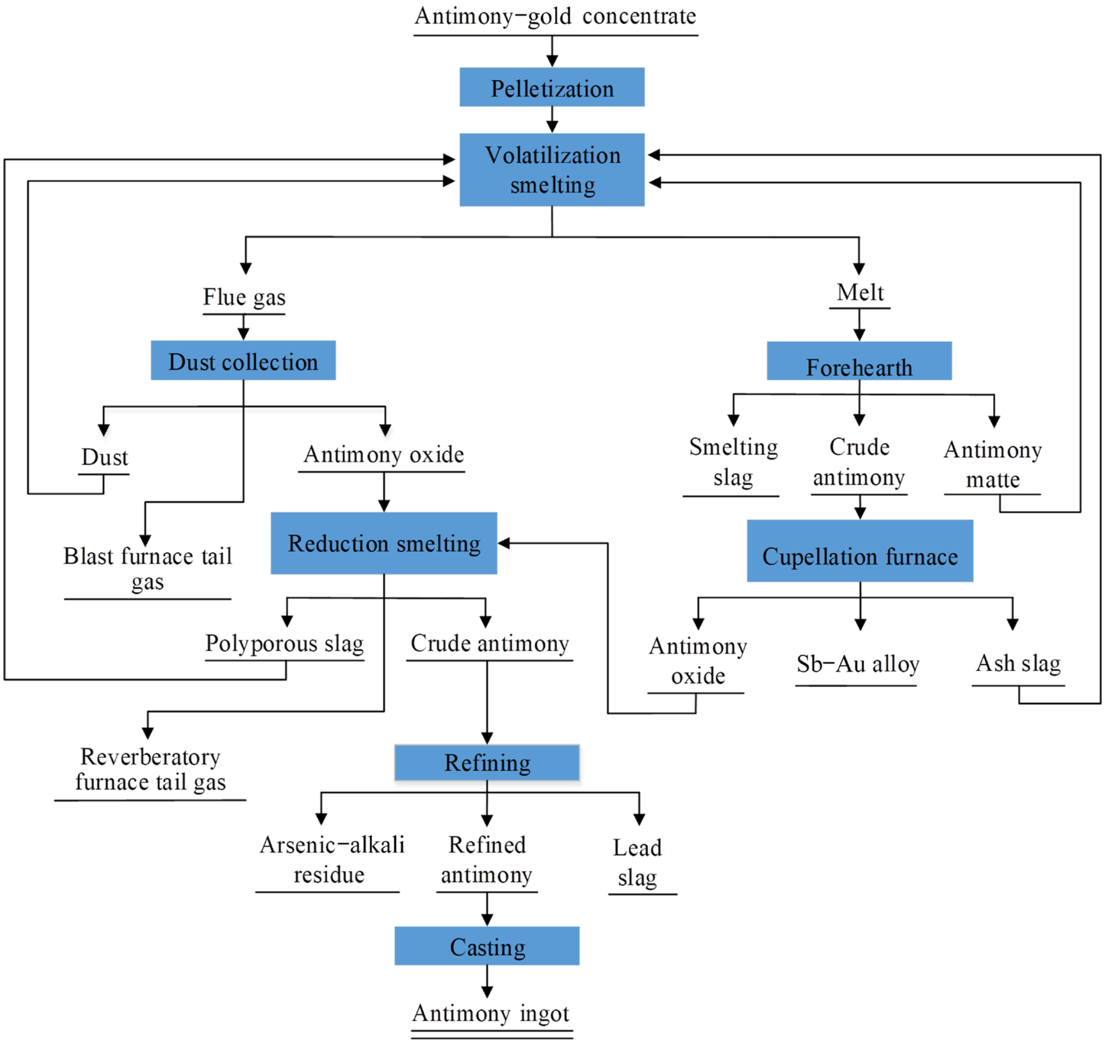


Fig. 2 Simplified flowsheet of pyrometallurgical process for antimony production

oven at 60 °C for 24 h. The concentration of the main elements in the sample was determined by using an ICP−OES (Optima 7300 V, Perkin Elmer, USA). An XRD analyzer (D8 Discover 2500) using a PANalytical X'Pert X-ray diffractometer (Cu K_α radiation) and a scanning electron microscope (SEM, JSMIT500LV, JEOL, Japan) equipped with energy dispersive spectrometer (EDS) were used to determine the phase composition of some solid samples. Before scanning electron microscope (SEM) analysis, antimony−gold concentrate particles were dispersed in epoxy resin, then polished with fine diamond spray, and the sample was sputtered with gold (10−20 nm gold film). HSC chemistry 6.0 was a thermochemical software often used for chemical reaction and equilibrium calculation [33,34]. The reaction equation module in the software was used to calculate the Gibbs free energy of reactions.

4 Results and discussion

4.1 Substance flow analysis of antimony

4.1.1 Mass balance calculation

Based on the enterprise production data and analysis of all materials streams, the antimony mass balance for producing 1 t antimony-containing products was established according to the method in Section 2.3. The antimony flow of input, recycle, emission, stock, and output in each unit process is listed in Table 1.

4.1.2 Substance flow chart of antimony

Figure 3 shows the substance flow chart of antimony. The whole system includes 27 substance flows of five types: input, recycle, stock, emission, and output. Each substance flow is identified with both name and flow code, as shown in Table 1.

Table 1 Input and output flow ratios of antimony in each substance flow of production system (t/t(Sb))

No.	Process unit	Input		Output	
		Substance flow	Flow ratio, f_i	Substance flow	Flow ratio, f_i
1	Pelletization	Antimony−gold concentrate, A_1	1.121	Granular ore, P_1	1.121
		Total input	1.121	Total output	1.121
2	Volatilization smelting	Granular ore, P_1	1.121	Melt, $P_{2,3}$	0.189
		Antimony matte, $R_{3,2}$	0.071	Flue gas, $P_{2,5}$	1.15
		Ash slag, $R_{4,2}$	0.01	Loss from volatilization smelting, E_2	0.028
		Dust, $R_{5,2}$	0.064		
		Polyporous slag, $R_{6,2}$	0.101		
		Total input	1.367	Total output	1.367
3	Forehearth	Melt, $P_{2,3}$	0.189	Crude antimony, P_3	0.097
				Antimony matte, $R_{3,2}$	0.071
				Smelting slag, $E_{3\text{-}1}$	0.018
				Loss from forehearth, $E_{3\text{-}2}$	0.003
		Total input	0.189	Total output	0.189
4	Cupellation furnace	Crude antimony, P_3	0.097	Sb−Au alloy, $E_{4\text{-}1}$	0.004
				Antimony oxide, P_4	0.082
				Ash slag, $R_{4,2}$	0.01
				Loss from cupellation furnace, $E_{4\text{-}2}$	0.001
		Total input	0.097	Total output	0.097
5	Dust collection	Flue gas, $P_{2,5}$	1.15	Dust, $R_{5,2}$	0.064
				Antimony oxide, P_5	1.062
				Antimony oxide, S_5	0.015
				Blast furnace tail gas, $E_{5\text{-}1}$	0.0005*
				Loss from dust collection, $E_{5\text{-}2}$	0.009
		Total input	1.15	Total output	1.15
6	Reduction smelting	Antimony oxide, P_4	0.082	Crude antimony, P_6	1.041
		Antimony oxide, P_5	1.062	Polyporous slag, $R_{6,2}$	0.101
				Reverberatory furnace tail gas, $E_{6\text{-}1}$	0.0003*
				Loss from reduction smelting, $E_{6\text{-}2}$	0.002
		Total input	1.144	Total output	1.144
7	Refining	Crude antimony, P_6	1.041	Refined antimony, P_7	1
				Arsenic-alkali residue, $E_{7\text{-}1}$	0.022
				Lead slag, $E_{7\text{-}2}$	0.016
				Loss from refining, $E_{7\text{-}3}$	0.003
		Total input	1.041	Total output	1.041
8	Casting	Refined antimony, P_7	1	Antimony ingot, P_8	1
		Total input	1	Total output	1

* The unit is kg/t(Sb)

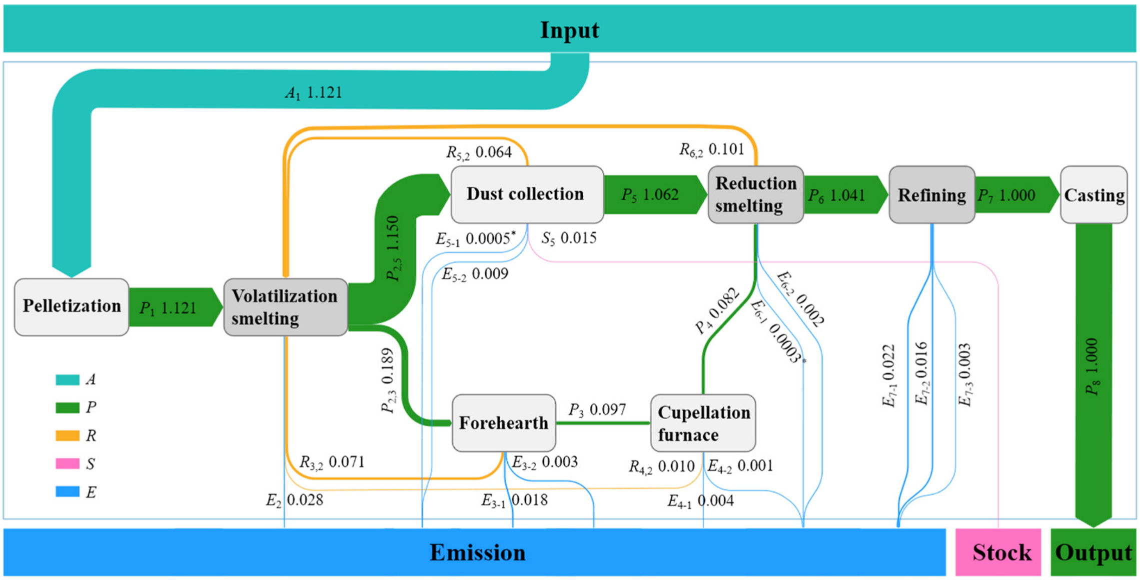


Fig. 3 Antimony substance flow chart of antimony pyrometallurgical production system (t/t(Sb))

4.1.3 Evaluation of antimony production process

Table 2 gives the evaluation results based on the defined indicators. The antimony recovery rates of volatilization smelting, reduction smelting, and refining processes are 78.79%, 91.00%, and 96.06%, respectively. The resource efficiency of antimony production process reaches 89.21%. The reason for this high resource efficiency is a high waste recycling rate, 67.03%, which means that 67.03% of antimony "lost" in the production process is returned to the production system.

Table 2 Results of evaluation indicators for antimony production process

Evaluation indicator	Value
Input raw substance flow, $A/[\mathrm{t\cdot t(Sb)^{-1}}]$	1.121
Recycle substance flow, $R/[\mathrm{t\cdot t(Sb)^{-1}}]$	0.246
Stock substance flow, $S/[\mathrm{t\cdot t(Sb)^{-1}}]$	0.015
Emission substance flow, $E/[\mathrm{t\cdot t(Sb)^{-1}}]$	0.106
Direct recovery of volatilization smelting, $\alpha_2/\%$	78.79
Direct recovery of reduction smelting, $\alpha_6/\%$	91.00
Direct recovery of refining, $\alpha_7/\%$	96.06
Waste recovery rate of process, $\omega/\%$	67.03
Resource efficiency, $\varepsilon/\%$	89.21

(1) Input raw material flow of antimony, *A*

As shown in Table 2, the total input antimony substance flow of the production system is 1.121. For 1 t of antimony produced, the antimony−gold concentrate having 1.121 t antimony is consumed.

(2) Recycle substance flow of antimony, *R*

As shown in Fig. 3, the system includes four recycle substance flows: antimony matte $R_{3,2}$ (0.071), ash slag $R_{4,2}$ (0.01), dust $R_{5,2}$ (0.064), and polyporous slag $R_{6,2}$ (0.101). The total recycle substance flow of the system is 0.246 t. In the total recycle substance flow, the polyporous slag produced in the reduction smelting process accounts for the largest part, 41.06%; the antimony matte produced in the forehearth process, the dust produced in the dust collection process, and the ash slag produced in the cupellation furnace process account for 28.86%, 26.02%, and 4.06%, respectively. Blast furnace has the characteristics of handling complex materials: it reuses the recycled materials of the system and improves the resource efficiency of the system.

(3) Stock substance flow of antimony, *S*

One stock substance flow in the production process is S_5, antimony oxide (0.015). The antimony oxide obtained from the flue gas produced in the volatilization smelting after condensation and separation is the raw material for the subsequent reduction smelting process. The antimony oxide is stored in the tank through the conveying device. According to production plan, the enterprise allocates the corresponding mass of antimony oxide to the reduction smelting process. In this production period, the antimony oxide required for the reduction smelting process is less than that produced by the volatilization smelting process, so part of the antimony oxide is stored in the tank.

(4) Emission substance flow of antimony, *E*

There are 12 emission substance flows in the system, which can be divided into four categories: 1) by-product: Sb−Au alloy $E_{4\text{-}1}$ (0.004), 2) solid waste: smelting slag $E_{3\text{-}1}$ (0.018), arsenic−alkali residue $E_{7\text{-}1}$ (0.022), lead slag $E_{7\text{-}2}$ (0.016), 3) tail gas: blast furnace tail gas E_5 (0.0005*), reverberatory furnace tail gas E_6 (0.0003*), and 4) unsuspected losses. The total emission substance flow of the system is 0.106 t. The gold resources in the antimony−gold concentrate processed in the production system are mainly enriched in the by-product: the antimony in Sb−Au alloy can be recycled in the gold production system. Arsenic−alkali residue and lead slag produced in the refining process account for 20.75% and 15.09% of the emission substance flow, respectively. Blast furnace tail gas and reverberatory furnace tail gas are purified by a gas collection device (including a surface cooler, bag dust collection chamber, etc.).

Unsuspected losses caused by measurement errors mainly exist in the following unit processes: 1) volatilization smelting (E_2): the blast furnace used in this process consumes about 150 t antimonial materials per day, and the weighing system in the factory cannot accurately measure the quality of each material; 2) dust collection ($E_{5\text{-}2}$): part of antimony oxide remains in the conveying equipment and pipelines, and the factory cannot clean it every day, resulting in inaccurate measurements of the mass of antimony oxide; 3) reduction smelting and refining ($E_{6\text{-}2}$ and $E_{7\text{-}3}$): the two processes are carried out in the same reverberatory furnace, and the mass of crude antimony cannot be measured, but is indirectly obtained through the calculation and measurement of other input and output materials in the two processes. Fugitive emissions mainly exist in the following unit processes: volatilization smelting (E_2), forehearth ($E_{3\text{-}2}$), cupellation furnace ($E_{4\text{-}2}$), and reduction smelting ($E_{6\text{-}2}$). The equipment used in the above processes is not fully enclosed, and some dust escaped during feeding, slag discharge, and other operations, resulting in unsuspected losses.

Therefore, the unsuspected losses are caused by measurement errors and fugitive emissions, but the contribution of the two factors to each lost substance flow is different. The balance difference of antimony in the production process is calculated using the criteria in Section 2.4, and the results are acceptable, as shown in Table 3.

Table 3 Ratio of antimony loss from each process

No.	Process	Antimony loss ratio/%
1	Pelletization	<0.01
2	Volatilization smelting	2.05
3	Forehearth	1.59
4	Cupellation furnace	1.03
5	Dust collection	0.78
6	Reduction smelting	0.17
7	Refining	0.29
8	Casting	<0.01

According to the mass-balance principle, the total input of the system is equal to the total output, and the corresponding total output substance flow includes emission, stock, and output substance flow, as shown in Fig. 3. The output substance flow accounts for 89.21%, which is the system antimony resource efficiency. The proportion of other substance flows is shown in Fig. 4.

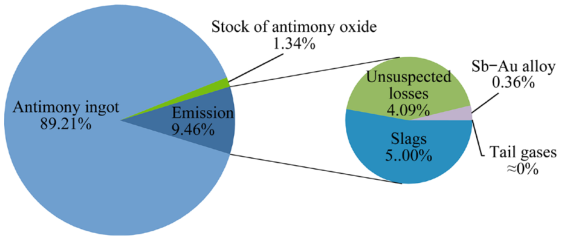


Fig. 4 Distribution of antimony in total output substance flows

4.2 Substance flow analysis of arsenic

Arsenic is an associated impurity element of antimony−gold concentrate and is a harmful component that is difficult to remove during antimony production. Therefore, relevant evaluation based on the definition in Section 2.5 is not conducted. The distribution behavior of arsenic in the primary process of antimony smelting is clarified through the substance flow analysis of arsenic and the phase analysis of related products.

4.2.1 Mass balance calculation

The mass balance of arsenic based on the qualified products containing 1 t antimony produced by the system is established. The substance flow ratio of arsenic in each unit process is given in Table 4.

4.2.2 Substance flow chart of arsenic

Based on the production process and arsenic substance flow data, a substance flow chart of arsenic is established. Each arsenic substance flow corresponds to the antimony substance flow in Fig. 5. The total amount of each type of arsenic substance flow in the system is given in Table 5. The arsenic concentration in some products in the antimony smelting process is given in Table 6.

Table 4 Input and output flow ratios of arsenic in each substance flow of production system (kg/t)

No.	Process unit	Input		Output	
		Substance flow	Flow ratio, f_i	Substance flow	Flow ratio, f_i
1	Pelletization	Antimony−gold concentrate, A_1	11.94	Granular ore, P_1	11.94
		Total input	11.94	Total output	11.94
2	Volatilization smelting	Granular ore, P_1	11.94	Melt, $P_{2,3}$	0.97
		Antimony matte, $R_{3,2}$	0.09	Flue gas, $P_{2,5}$	13.80
		Ash slag, $R_{4,2}$	0.08	Loss from volatilization smelting, E_2	0.05
		Dust, $R_{5,2}$	0.45		
		Polyporous slag, $R_{6,2}$	2.26		
		Total input	14.82	Total output	14.82
3	Forehearth	Melt, $P_{2,3}$	0.97	Crude antimony, P_3	0.79
				Antimony matte, $R_{3,2}$	0.09
				Smelting slag, $E_{3\text{-}1}$	0.09
		Total input	0.97	Total output	0.97
4	Cupellation furnace	Crude antimony, P_3	0.79	Sb−Au alloy, $E_{4\text{-}1}$	0.01
				Antimony oxide, P_4	0.69
				Ash slag, $R_{4,2}$	0.08
				Loss from cupellation furnace, $E_{4\text{-}2}$	0.01
		Total input	0.79	Total output	0.79
5	Dust collection	Flue gas, $P_{2,5}$	13.80	Dust, $R_{5,2}$	0.45
				Antimony oxide, P_5	13.11
				Antimony oxide, S_5	0.19
				Blast furnace tail gas, $E_{5\text{-}1}$	0.0004
				Loss from dust collection, $E_{5\text{-}2}$	0.05
		Total input	13.80	Total output	13.80
6	Reduction smelting	Antimony oxide, P_4	0.69	Crude antimony, P_6	11.48
		Antimony oxide, P_5	13.11	Polyporous slag, $R_{6,2}$	2.26
				Reverberatory furnace tail gas, $E_{6\text{-}1}$	0.0003
				Loss from reduction smelting, $E_{6\text{-}2}$	0.06
		Total input	13.80	Total output	13.80
7	Refining	Crude antimony, P_6	11.48	Refined antimony, P_7	0.31
				Arsenic-alkali residue, $E_{7\text{-}1}$	10.84
				Lead slag, $E_{7\text{-}2}$	0.26
				Loss from refining, $E_{7\text{-}3}$	0.07
		Total input	11.48	Total output	11.48
8	Casting	Refined antimony, P_7	0.31	Antimony ingot, P_8	0.31
		Total input	0.31	Total output	0.31

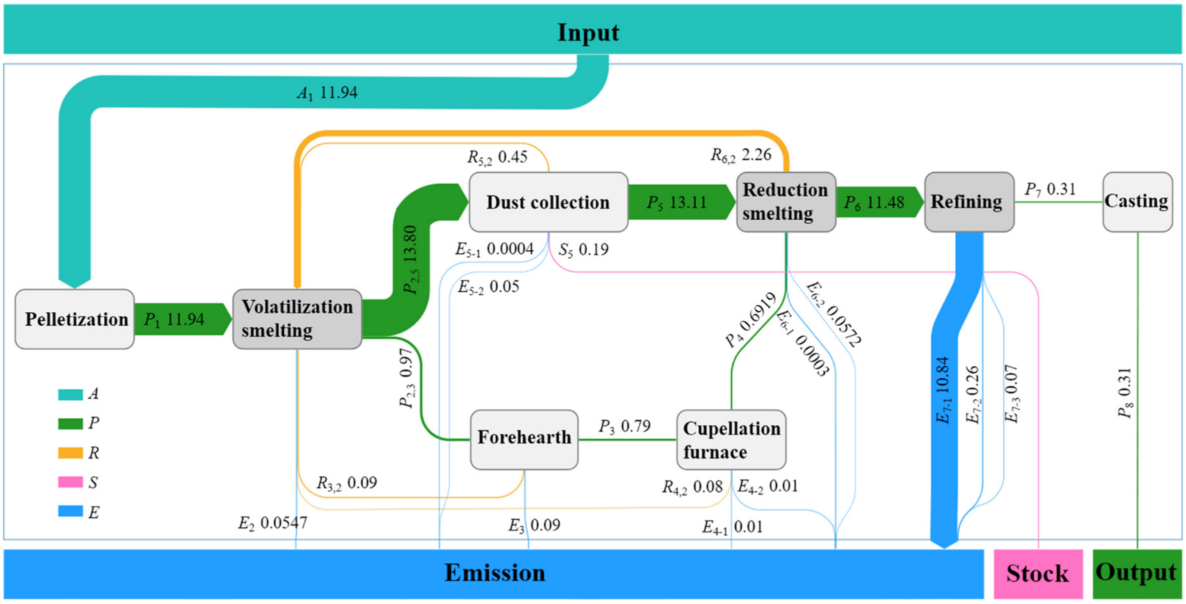


Fig. 5 Arsenic substance flow chart of antimony pyrometallurgical production system (kg/t)

Table 5 Total quantity of arsenic in each substance flow of production system (kg/t)

Evaluation indicator	Value
Input raw material flow, *A*	11.94
Recycle substance flow, *R*	2.88
Stock substance flow, *S*	0.19
Emission substance flow, *E*	11.44

(1) Input substance flow of arsenic

The total input substance flow ratio of arsenic is 11.94 kg/t, indicating that 11.94 kg of arsenic enters the production system for 1 t of antimony produced. The antimony−gold concentrate is the only input source in the system, with an arsenic concentration of 0.513%. It is complex antimony−gold resource with a high arsenic concentration. Therefore, clarifying the distribution behavior of arsenic in the smelting process plays a vital role in controlling the emission of arsenic-containing pollutants.

(2) Recycle substance flow of arsenic

Part of the arsenic circulates in the system with four recycle substance flows. The total recycle flow ratio of arsenic is 2.88 kg/t. Among them, polyporous slag $R_{6,2}$ (2.26) and dust $R_{5,2}$ (0.45) account for 78.47% and 15.63%, respectively. Some of the intermediate products are reused to obtain a high recovery of antimony in production system. However, the arsenic in the intermediate products re-enters the system, resulting in the continuous potential accumulation of arsenic in the system. Therefore, improving the reduction smelting process and reducing the output of polyporous slag is beneficial to both improving direct antimony recovery and reducing the risk of arsenic accumulation in the system.

(3) Stock substance flow of arsenic

The system has only one stock substance flow of antimony oxide, S_5. The total flow ratio of stock is 0.19 kg/t. The arsenic content of antimony oxide is 0.924%. When the antimony oxide required for reduction smelting is greater than the output of volatilization smelting in a subsequent production cycle, the stock of antimony oxide can be used.

(4) Emission substance flow of arsenic

The total arsenic emission substance flow ratio of the system is 11.44 kg/t. The emission substance flow consists of 11 streams: smelting slag E_3 (0.09), arsenic−alkali residue $E_{7\text{-}1}$ (10.84), lead slag $E_{7\text{-}2}$ (0.26), blast furnace tail gas $E_{5\text{-}1}$ (0.0004), reverberatory furnace tail gas $E_{6\text{-}1}$ (0.0003), and Sb−Au alloy $E_{4\text{-}1}$ (0.01). Arsenic entering Sb−Au alloy can be further treated in the gold production system. The arsenic content in the two tail gases is very low, which can be treated later by desulfurization. The total unsuspected loss of arsenic (0.24) accounts for 2.10% of the total emission substance flow of arsenic. Using the criterion in Section 2.4, the calculation results of arsenic balance difference are acceptable, as given in Table 7.

Table 6 Arsenic content in some products (wt.%)

Product	Antimony−gold concentrate	Antimony matte	Smelting slag	Dust	Antimony oxide
Arsenic concentration	0.513	0.009	0.007	0.327	0.924

Product	Crude antimony (for refining)	Polyporous slag	Arsenic−alkali residue	Lead slag	Antimony ingot
Arsenic concentration	1.46	1.261	15.693	0.040	0.031

Table 7 Ratio of arsenic loss from each process

No.	Process	Arsenic loss ratio/%
1	Pelletization	<0.01
2	Volatilization smelting	0.34
3	Forehearth	<0.01
4	Cupellation furnace	1.27
5	Dust collection	0.36
6	Reduction smelting	0.43
7	Refining	0.61
8	Casting	<0.01

Among these emissions, arsenic−alkali residue accounts for 94.76%, and arsenic concentration is 15.693%, which is a hazardous waste. The high arsenic content makes this solid waste need to be stored in a special warehouse. After decades of production, the stockpile of arsenic−alkali residue has been massive. Some enterprises return the arsenic−alkali residue to the smelting system for antimony recovery treatment, resulting in secondary arsenic−alkali residue with low antimony content. Past nonstandard treatment and long-term storage have caused severe harm to the environment [35]. Therefore, it is necessary to safely and adequately deal with these solid wastes.

4.3 Distribution behavior of arsenic

Arsenic associated with antimony−gold concentrate is a harmful element in the smelting process. It brings technological challenges to the antimony smelting and purification process. Moreover, the generation of arsenic-containing pollutants in this process is a major environmental problem. Therefore, it is essential to clarify the distribution behavior of arsenic in the smelting process to realize the clean production of antimony.

(1) Volatilization smelting

Table 8 gives the distribution of arsenic in the main process. In the process of volatilization smelting, 93.12% of raw arsenic enters the flue gas, and 6.55% of arsenic enters the melt due to the volatile characteristics of arsenic compounds. The flue gas is treated by the dust collection system, 3.28% of arsenic enters the dust, and 96.38% of arsenic enters antimony oxide, which is the input source of arsenic in subsequent smelting process. The melt is separated in forehearth. A total of 9.28% arsenic enters the smelting slag, 9.28% arsenic enters the antimony matte and 81.44% arsenic enters the crude antimony.

Table 8 Distribution of arsenic in primary production processes of system

Unit process	Intermediate product	Flow ratio/ $(\mathrm{kg \cdot t^{-1}})$	Distribution ratio/%
Volatilization smelting	Melt	0.97	6.55
	Flue gas	13.80	93.12
	Unsuspected loss	0.05	0.37
Forehearth	Smelting slag	0.09	9.28
	Antimony matte	0.09	9.28
	Crude antimony	0.79	81.44
Dust collection	Dust	0.45	3.28
	Antimony oxide	13.30	96.38
	Tail gas	0.0004	~0
	Unsuspected loss	0.05	0.36
Reduction smelting	Crude antimony	11.48	83.19
	Polyporous slag	2.26	16.38
	Tail gas	0.0003	~0
	Unsuspected loss	0.06	0.43
Refining	Refined antimony	0.31	2.70
	Arsenic−alkali residue	10.84	94.43
	Lead slag	0.26	2.26
	Unsuspected loss	0.07	0.61

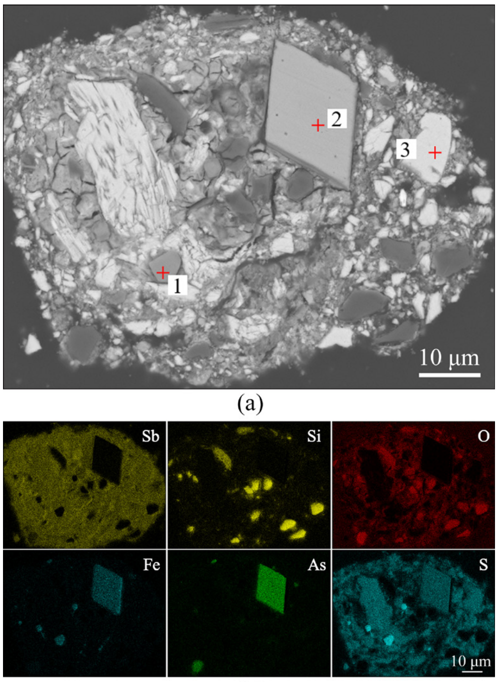
According to results of SEM−EDS analysis, arsenic in antimony−gold concentrate mainly exists in the form of arsenopyrite (FeAsS), as shown in Fig. 6 and Table 9. In the blast furnace, arsenopyrite decomposes into AsS(g), As_2(g), AsO(g) [36]. Part of arsenic is further oxidized to As_2O_3 and collected into flue gas. Reaction between arsenopyrite and sulfur dioxide is expressed as Reaction (14) [37]. The form of arsenic in the antimony oxide is shown in Fig. 7(b).

$$FeAsS+FeS_2=2FeS(l)+AsS(g) \tag{12}$$

$$FeAsS+FeS(l)+0.5As_2(g) \tag{13}$$

$$As_2(g)+O_2(g)=2AsO(g) \tag{14}$$

$$FeAsS+3/4SO_2(g)=FeS(l)+1/4As_4O_6(g)+3/8S_2(g) \tag{15}$$



(a)

(b)

Fig. 6 SEM image of antimony−gold concentrate (a) and EDS mappings of antimony−gold concentrate (b)

Table 9 Analytical results of antimony−gold concentrate (at.%)

Point in Fig. 7(a)	Sb	S	As	Fe	Si
1	−	67.6	−	32.4	−
2	−	35.9	33.6	30.5	−
3	41.4	57.7	−	−	0.9

(2) Reduction smelting and refining

In the process of reduction smelting, 83.19% arsenic enters crude antimony, and remaining 16.38% arsenic enters polyporous slag. As_2O_3 in antimony oxide undergoes the following reduction reaction, and the generated As(l) enters crude antimony.

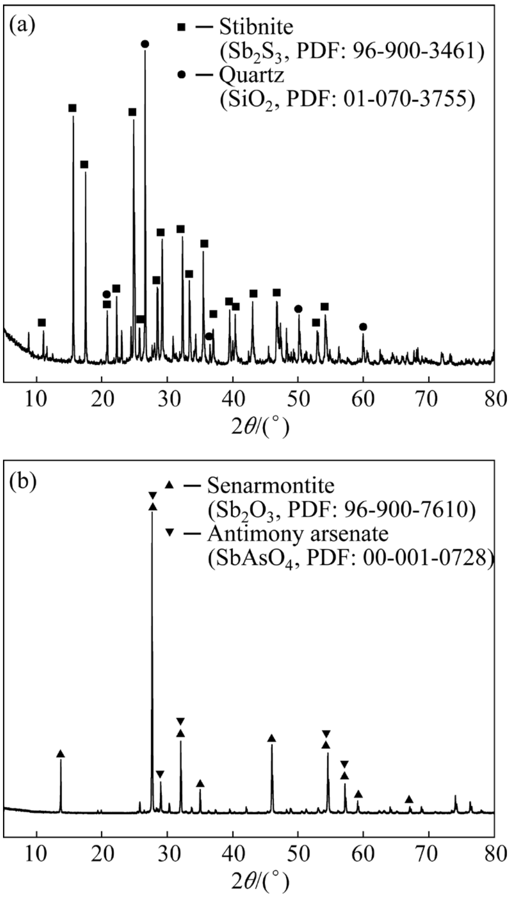


Fig. 7 XRD pattern of antimony−gold concentrate (a) and antimony oxide (b)

$$As_2O_3(l)+3C=2As(l)+3CO(g) \tag{16}$$

$$As_2O_3(l)+3CO(g)=2As(l)+3CO_2(g) \tag{17}$$

$$As_2O_3(l)+3/2C=2As(l)+3/2CO_2(g) \tag{18}$$

$$As_2O_3(l)+2Sb(l)=2As(l)+Sb_2O_3(l) \tag{19}$$

In refining, 94.43% arsenic enters the arsenic−alkali residue, the remaining 2.70% and 2.26% arsenic enter the refined antimony and lead slag, respectively. Through the oxygen blowing operation and using the arsenic removing agent (sodium carbonate), the elemental arsenic is oxidized to arsenic trioxide. It then reacts with sodium carbonate to form sodium arsenate and sodium arsenite into arsenic−alkali residue [38].

$$4/5As(l)+O_2(g)+6/5Na_2CO_3= 4/5Na_3AsO_4+6/5CO_2(g) \tag{20}$$

$$4/3As(l)+O_2(g)+2/3Na_2CO_3= 4/3NaAsO_2+2/3CO_2(g) \tag{21}$$

The curves of the above reaction standard Gibbs free energy change with temperature are drawn, as shown in Fig. 9. In the production process, the following complex reactions of arsenic-containing compounds occur during volatilization smelting, reduction smelting, and refining, which can be carried out spontaneously under normal production conditions.

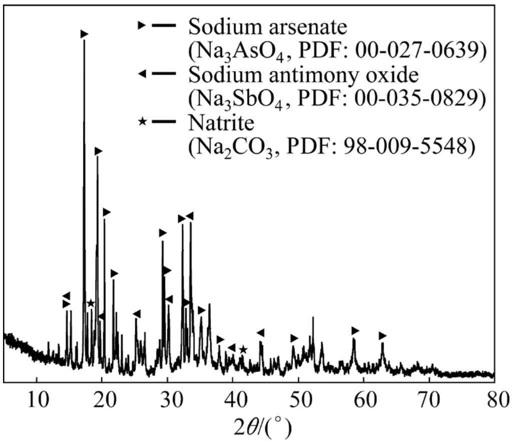


Fig. 8 XRD pattern of arsenic−alkali residue

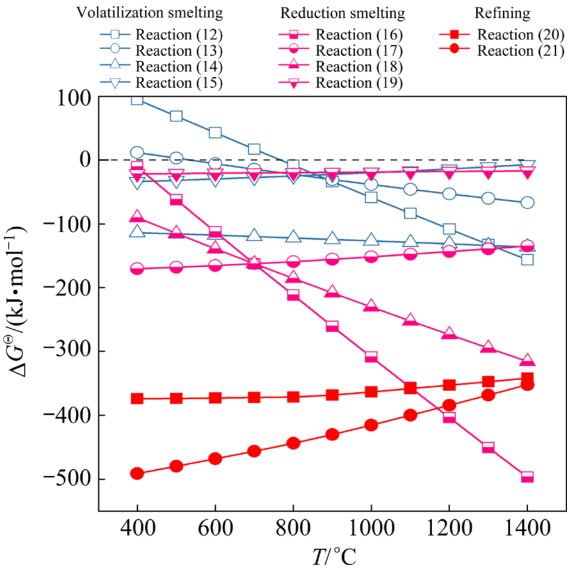


Fig. 9 Relationship between standard free energy change and temperature of multiphase arsenic reaction in antimony smelting process (Data source: HSC Chemistry 6.0)

Based on the systematic substance flow analysis, the following improvement measures are proposed: In the volatilization smelting process, due to the relatively high vapour pressures of Sb_2O_3 and As_2O_3, antimony and arsenic are enriched in the flue gas, which brings certain difficulties to the subsequent separation of antimony and arsenic. Therefore, if the controllable separation of antimony and arsenic is achieved in the dust collection stage of the flue gas to obtain relatively pure antimony oxide, the output of arsenic−alkali residue in the refining process can be reduced correspondingly, and the goal of reducing the source of solid waste can be achieved. The waste recycling rate of the whole system reaches 67.03%, which makes the resource efficiency of antimony reach 89.21%. Still, this also causes the circulation and accumulation of arsenic in the system, which has potential environmental risks. Using natural gas as a heat source in the reduction smelting stage can correspondingly reduce the output of polyporous slag and SO_2, reduce the antimony arsenic cycle rate, and improve the clean production level of the enterprise.

5 Conclusions

(1) The antimony resource efficiency of the smelting system is 89.19%, and the antimony direct recovery of volatilization smelting, reduction smelting, and refining processes are 78.78%, 91.00%, and 96.03%, respectively. The antimony loss caused by measurement error and fugitive emission is collectively referred to as unsuspected loss. The difference in mass balance in each unit process is within 5%.

(2) For the arsenic substance flow in the smelting process, 11.94 kg of arsenic is carried into the system with antimony−gold concentrate for 1 t of antimony produced. In the process of volatilization smelting, 6.55% and 93.12% of arsenic are fed into melt and flue gas, respectively. In the process of reduction smelting, the distribution ratios of arsenic in crude antimony and slag are 83.19% and 16.38%, respectively. In the process of refining, 94.43% arsenic enters the arsenic−alkali residue, and the remaining 2.70% and 2.26% arsenic enters the refined antimony and lead slag, respectively.

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锑火法冶炼过程锑、砷物质流分析

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摘　要：应用物质流分析于锑火法冶炼系统。以锑、砷为目标元素，建立基于生产系统的物质平衡表和物质流图，构建有关系统直接回收率、废物回收率、资源效率的评价指标体系。结果表明：锑的资源效率为 89.21%，挥发熔炼、还原熔炼和除杂精炼过程锑的直收率分别为 78.79%、91.00%和 96.06%。同时，每产出 1 t 金属锑，会有 11.94 kg 的砷进入到冶炼系统中。砷为冶炼过程主要杂质元素。重点分析砷在主要单元过程中的分布转化行为。基于物质流分析提出提高锑资源利用效率和清洁生产的建议。

关键词：锑冶金；物质流分析；锑资源效率；砷分布行为

(Edited by Bing YANG)