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Copper and arsenic substance flow analysis of pyrometallurgical process for copper production

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Abstract: The metabolism of copper and arsenic in a copper pyrometallurgy process was studied through substance flow analysis method. The mass balance accounts and substance flow charts of copper and arsenic were established, indicators including direct recovery, waste recycle ratio, and resource efficiency were used to evaluate the metabolism efficiency of the system. The results showed that, the resource efficiency of copper was 97.58%, the direct recovery of copper in smelting, converting, and refining processes was 91.96%, 97.13% and 99.47%, respectively. Meanwhile, for producing 1 t of copper, 10 kg of arsenic was carried into the system, with the generation of 1.07 kg of arsenic in flotation tailing, 8.50 kg of arsenic in arsenic waste residue, and 0.05 kg of arsenic in waste water. The distribution and transformation behaviors of arsenic in the smelting, converting, and refining processes were also analyzed, and some recommendations for improving copper resource efficiency and pollution control were proposed based on substance flow analysis.

Key words: copper smelting; substance flow analysis; copper; arsenic; distribution behavior

1 Introduction

Copper industry is a crucial industry in the global economy as copper is widely used in many fields and it is irreplaceable in some industries [1]. Currently, copper is mainly extracted from sulfide minerals and pyrometallurgical process is the most dominant technology for copper production [2−4]. However, the pyrometallurgical process for copper production is facing the challenge of pollution control, as copper resources become more and more complex. For example, arsenic commonly occurs in copper concentrates, and the emission of arsenic into atmosphere during the pyrometallurgical production causes a serious environmental issue [5,6]. At present, many studies about improving production efficiency or reducing pollutants discharge have been conducted, but few of them have focused on the metabolism of copper or other detrimental elements flow in production process. Substance metabolism affects both energy and resource consumption of a factory, taking a deep insight into the metabolism of copper and other key elements is the foundation for process improvement.

Substance flow analysis (SFA) is an analytical tool that could be applied to investigating the metabolism of a specific substance flow in a given system and providing insight into the effects of the substance metabolism on economy and environment [7,8]. In the past decades, SFA has experienced a growing tendency in many fields [9]. Specially, it is extensively used to analyze the stock and flows of metals (lead, zinc, copper, etc) and other substances in local region [10], country [11−14], or global level [15,16]. Moreover, SFA was exploited as a supported tool in mineral

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resources management [17,18], industry chain evaluation [19], waste management [20], environmental risk assessment and pollution control during industrial production [21,22]. However, most previous studies that analyzed a specified substance flow just concentrated on the stock and potential waste generation in a national or regional scope [10−16].

Applying SFA to trace the substances quantities and migration in a production process could determine the metabolism efficiency of the process and reveal the pathways through which pollutants are generated, which is beneficial to the resource management and pollution control of a factory. YOSHIDA et al [23] studied the fate of total organic carbon, 32 elements and 4 groups of organic pollutants in a conventional wastewater treatment plant through SFA, and then an assessment on the treatment efficiency and potential environmental impact of the plant was given out. BAI et al [8] applied SFA to calculating lead substance balance in a lead smelting process and evaluating the metabolism efficiency of the system, through which some recommendations on improving emission control and pollution prevention for the smelting factory were also proposed. WANG et al [24] emphasized copper stocks and flows variation in production stage in the USA from 1974 to 2012, which was a meaningful reference for copper production industry of newly industrialized countries.

Most previous studies on copper metabolism were conducted at the state level, focusing mainly on the manufacturing and consumption stages, and there is rare report of SFA on the metallurgical processes of copper [25−28]. Especially, as an important associated element in copper concentrate, arsenic receives little attention in industrial metabolism analysis [29]. SFA of copper and arsenic in copper metallurgical process helps to find the measures for improving the utilization efficiency of copper concentrate and reveal the generation of arsenic-containing contaminant flows. In this study, SFA was used as an analytical tool to study the metabolism of a pyrometallurgical process for copper production. The mass balance accounts and substance flow charts of copper and arsenic in the production system were established. The metabolism efficiency of the system was evaluated, and the distribution and transformation behaviors of arsenic were analyzed. This study focused on the element metabolism efficiency with a microcosmic perspective, providing a reference for the process improvement.

2 Methodology

Compared to applying SFA to a large system with the scope of global or regional scale, applying SFA to a production process is more microcosmic and more specific. The SFA model of a production process generally includes the substance flow of a single process and the whole production system composed of several single processes [8].

2.1 Definition of substance flows in single process

If a single process in the production system is defined as process j, the substance flows input to and output from process j include the following stages.

(1) Input raw material flow, A_j.

(2) Input upstream product substance flow, $P_{m,j}$.

(3) Recycle substance flow from downstream process i, $R_{i,j}$. The substance flow which is recycled to upstream process k from process j is called $R_{j,k}$.

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

(5) Emission substance flow, E_j. This flow includes the by-products and pollutants which are discharged outside of the objective system from process j.

(6) Output product substance flow, P_j. The substance flow which is the by-product of process j and is transported to process k for further treating is called $P_{j,k}$.

According to the conservation of mass, for the single process j, it can be expressed as

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

2.2 Substance flows of whole system

The combination of all the single processes makes up the whole system, and the substance flows of the whole system are the sums of corresponding flows in all single processes, which are described as follows.

(1) Input raw material flow A

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

(2) Recycle substance flow R

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

(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 product substance flow P

$$P=\sum_{j=1}^{m} P_j \tag{6}$$

2.3 Mass balance calculation

To analyze the substance flow of a specific element, two parts of data are required. One part is the flow quantity M_j, which is the amount of each material that contains the objective element, and this part of data is collected from the daily production reports. The other part is the content C_j of an objective element in each material, and it is obtained by sampling and analyzing for each material. Then, the flow quantity of the objective element is calculated by Eq. (7):

$$m_j=M_j \times C_j \tag{7}$$

where m_j is the quantity of the objective element in the substance flow j.

In this study, the mass balance calculation of all single processes and the whole system is based on 1 t copper output from the production system, the flow ratio of objective element in each substance is expressed as f_j:

$$f_j=m_j/m_m \tag{8}$$

where m_m is the quantity of the objective element in the final product output from the production system.

2.4 Evaluation indicators of SFA

In order to evaluate the production efficiency of a process and its influence on environment, three indicators are proposed in this study as follows.

(1) Direct recovery of the primary single processes, D, the proportion of objective element in qualified products to the total output flows of a single process, %. For a single process j, D_j is calculated by Eq. (9):

$$D_j=P_j/(P_j+S_j+R_{j,k}+P_{j,k}+E_j)\times 100\% \tag{9}$$

A high direct recovery of a process means low resource consumption for per ton of qualified product from the process.

(2) Waste recycle ratio of the process, α, the proportion of recycle substance flow in all the substance flows which are not included in the final product, %:

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

Increasing the waste recycle ratio helps to reduce the environmental load caused by discharging of rejected substance flows and to improve resource efficiency.

(3) Resource efficiency, ε, the proportion of objective element in final product to the total input flows, including both natural and secondary resources, %:

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

3 System boundary description and data collecting

In this study, a pyrometallurgical process of copper production, including the primary processes of smelting, converting, refining, and the assistant processes for slags, flue dust, and tail gas treatment, is chosen as system boundary. The process is exploited by a copper production enterprise in Shandong Province, China, which produces copper of 3×10^5 t/a. And this kind of process is with great development potential. The simplified flowsheet of the objective process is shown in Fig. 1.

The oxygen-enriched smelting is conducted in a bottom blown furnace, in which the oxidation reactions occur. Copper concentrate with a grade of 20%−25% and some recycled products are fed into the bottom blown furnace along with fuel and flux. Copper matte with a grade of 65%−75% and some stock matte as a by-product in reserve are produced from smelting. The copper matte is converted into crude copper with a grade of 98.5%−99% by converting in a PS converter, and some waste copper is also put into the converting process. The crude copper is upgraded to about 99.5% through refining to meet the impurity content standard of subsequent electrolysis process. During the

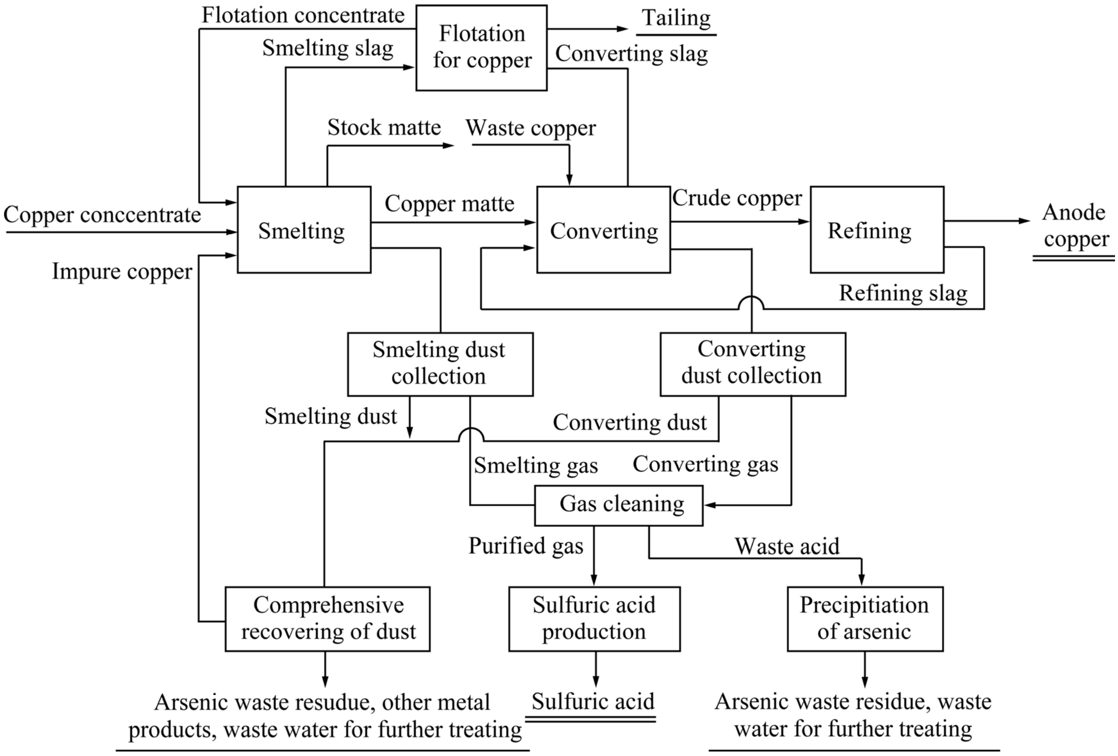

Fig. 1 Simplified flowsheet of pyrometallurgical process for copper production

production process, some slags and flue dust are also generated. The smelting slag and converting slag are cooled slowly and then transported to a flotation system for recovering residual copper. Then, the flotation concentrate is recycled to smelting process, and the refining slag is recycled to converting process. For the purposes of reducing arsenic accumulation and maximizing economic profit, the flue dust from smelting and converting is gathered to remove arsenic and recover copper after separating from tail gas, and the impure copper product from dust treatment is recycled to smelting process. The tail gas from smelting and converting, which contains a large amount of sulfur dioxide, is gathered for sulfuric acid production after cleaning. Arsenic precipitation is carried out for the waste acid produced from the gas cleaning process. The arsenic waste and waste water generated from flue dust and tail gas treating systems are considered as emission substance flows and then discharged outside the production system for further treatment. The by-product sulfuric acid is also considered as emission substance flow.

The quantities of input and output material flows were measured for the time scale of 30 d, and the data were collected from the production reports of objective plant. In order to determine the copper and arsenic contents in each material flow, all the flows were sampled and analyzed each production day. The sampling period was 30 d corresponding to the production reports, and the copper and arsenic contents of samples were averaged for mass balance calculation.

Some solid samples were dried at 50 °C in a vacuum oven for 12 h, and then characterized through X-ray diffraction (XRD, TTR III, with Cu K_α radiation, Rigaku, Japan) for phase composition analysis by slow scanning, at the 2θ range from 10° to 80°, a step size of 0.02° and a scanning speed of 2 (°)/min.

4 Results and discussion

4.1 Substance flow analysis of copper

4.1.1 Mass balance calculation

Based on the production data, the mass balance account of copper in all single processes of the system was built upon 1 t of copper output from the system. The flow ratio of copper in each substance flow is shown in Table 1.

4.1.2 Substance flow chart of copper

Figure 2 shows the substance flow chart of copper. There are 26 strands of substance flows within the whole system, and each of them has been

Table 1 Input and output flow ratios of copper in each substance flow of production system

No.	Process unit	Input		Output	
		Substance flow	Flow ratio, f_j	Substance flow	Flow ratio, f_j
1	Smelting	Copper concentrate (A_1)	1.0201	Copper matte (P_1)	1.0253
		Flotation concentrate ($R_{3,1}$)	0.0833	Stock matte (S_1)	0.0172
		Impure copper ($R_{6,1}$)	0.0116	Smelting slag ($P_{1,3}$)	0.0657
				Smelting dust and gas ($P_{1,4}$)	0.0068
		Total input	1.115	Total output	1.115
2	Converting	Copper matte (P_1)	1.0253	Crude copper (P_2)	1.0053
		Waste copper (A_2)	0.0047	Converting slag ($P_{2,3}$)	0.025
		Refining slag ($R_{10,2}$)	0.0053	Converting dust and gas ($P_{2,5}$)	0.005
		Total input	1.0353	Total output	1.0353
3	Flotation system	Smelting slag ($P_{1,3}$)	0.0657	Flotation concentrate ($R_{3,1}$)	0.0833
		Converting slag ($P_{2,3}$)	0.025	Tailing (E_3)	0.0074
		Total input	0.0907	Total output	0.0907
4	Smelting dust collection	Smelting dust and gas ($P_{1,4}$)	0.0068	Smelting dust ($P_{4,6}$)	0.0068
				Smelting gas ($P_{4,7}$)	0
		Total input	0.0068	Total output	0.0068
5	Converting dust collection	Converting dust and gas ($P_{2,5}$)	0.005	Converting dust ($P_{5,6}$)	0.005
				Converting gas ($P_{5,7}$)	0
		Total input	0.005	Total output	0.005
6	Comprehensive Recovering of dust	Smelting dust ($P_{4,6}$)	0.0068	Impure copper ($R_{6,1}$)	0.0116
		Converting dust ($P_{5,6}$)	0.005	Other metal products ($E_{6\text{-}1}$)	0
				Arsenic waste residue ($E_{6\text{-}2}$)	0
				Waste water ($E_{6\text{-}3}$)	0.0002
		Total input	0.0118	Total output	0.0118
7	Gas cleaning	Smelting gas ($P_{4,7}$)	0	Purified gas ($P_{7,8}$)	0
		Converting gas ($P_{5,7}$)	0	Waste acid ($P_{7,9}$)	0
		Total input	0	Total output	0
8	Sulfuric acid production	Purified gas ($P_{7,8}$)	0	Sulfuric acid (E_8)	0
		Total input	0	Total output	0
9	Precipitation of arsenic	Waste acid ($P_{7,9}$)	0	Arsenic waste residue ($E_{9\text{-}1}$)	0
				Waste water ($E_{9\text{-}2}$)	0
		Total input	0	Total output	0
10	Refining	Crude copper (P_2)	1.0053	Anode copper (P_{10})	1
				Refining slag ($R_{10,2}$)	0.0053
		Total input	1.0053	Total output	1.0053

identified with name and flow code, as shown in Table 1.

4.1.3 Evaluation of copper production process

Table 2 shows the evaluation results based on the defined indicators. As can be seen, the direct recovery of copper in smelting, converting, and refining processes is 91.96%, 97.13%, and 99.47%, respectively. According to the definition of direct

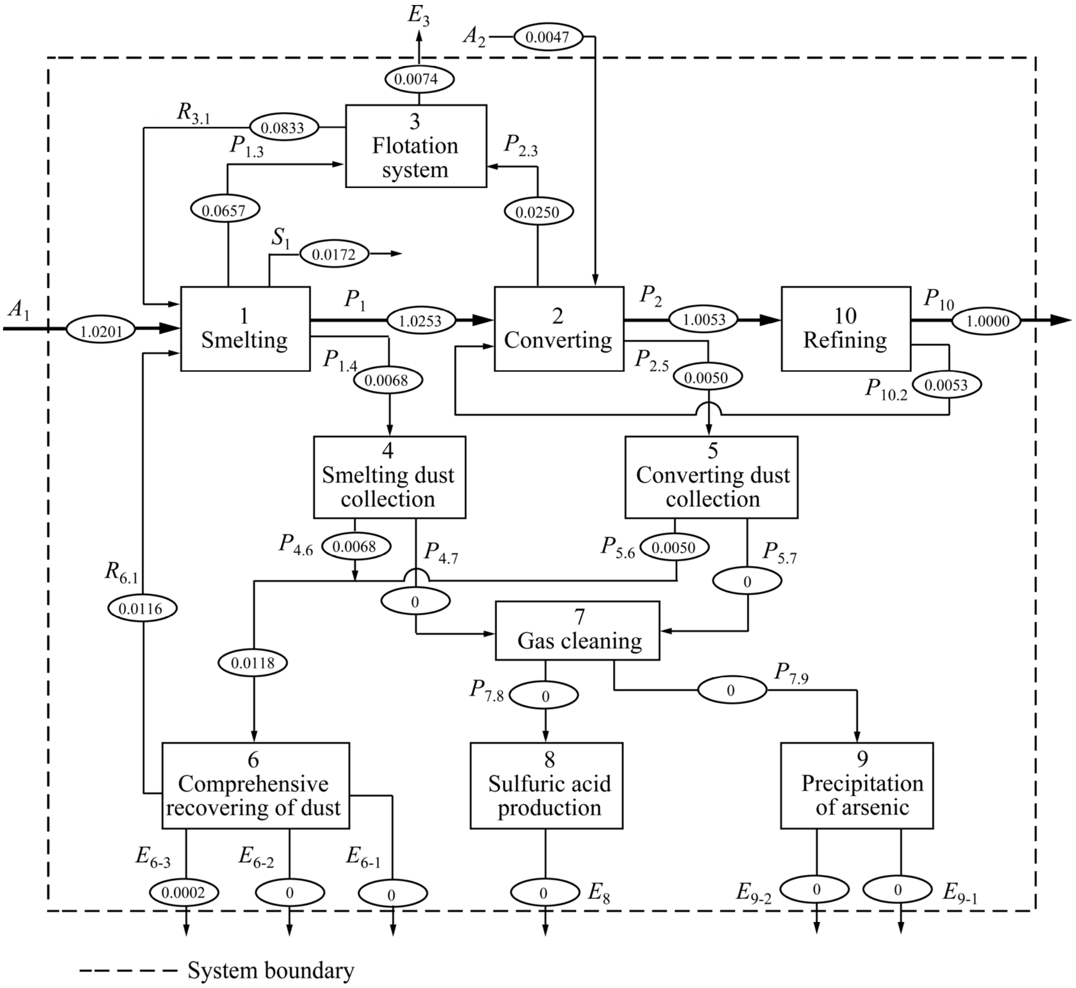

Fig. 2 Copper substance flow chart of investigated production system

Table 2 Results of evaluation indicators for copper production system

Evaluation indicator	Value
Input raw material flow, *A*	1.0248
Recycle substance flow, *R*	0.1002
Stock substance flow, *S*	0.0172
Emission substance flow, *E*	0.0076
Output product substance flow, *P*	1.0000
Direct recovery of melting process, D_1/%	91.96
Direct recovery of converting process, D_2/%	97.13
Direct recovery of refining process, D_8/%	99.47
Waste recycle ratio of production system, α/%	80.16
Resource efficiency, ε/%	97.58

recovery, the proportion of by-product (for example, stock matte) is not included in direct recovery. The waste recycle ratio of the production system is 80.16%, which means that 80.16% of the rejected products produced during production are recycled to the system for further copper recovering. Thus, a high resource efficiency of the whole system, 97.58%, is observed due to such a high waste recycle ratio. The details of the defined substance flows of the whole production system are discussed in the following sections.

(1) Input substance flow of copper *A*

As is shown in Table 2, the total input substance flow is 1.0248. This result indicates that, to produce 1 t of copper into the final product (anode copper), 1.0248 t of pure copper contained in copper concentrate or waste copper is consumed. The input substance consists of two flows: A_1, copper concentrate 1.0201; A_2, waste copper, 0.0047. Suppose the copper content of copper concentrate and waste copper is 23% and 96%, respectively. Then, 4.4352 t of copper concentrate and 0.0050 t of waste copper are put into this production system to produce 1 t of copper in anode copper.

(2) Recycle substance flow of copper *R*

There are three recycle substance flows in the production: $R_{3,1}$, flotation concentrate; $R_{6,1}$, impure copper; $R_{10,2}$, refining slag.

Among the recycle substance flows, flotation concentrate accounts for the largest portion, 83.13%. The flotation recovery of copper is up to 91.84%. The slag generated in refining process is recycled to converting process directly, and this strand accounts for a small portion of all the recycle substance flows, 5.29%.

As a whole, the recycle substance flow is 0.1002, accounts for 80.16% of the rejected products (including recycle substance flow of 0.1002, stock substance flow of 0.0172, and emission substance flow of 0.0076), that is the guarantee of high resource efficiency.

(3) Emission substance flow of copper *E*

The emission substance flows consist of the flotation tailing, arsenic waste and waste water from comprehensive recovering of dust, sulfuric acid, arsenic waste and waste water during tail gas treatment. In fact, almost no copper is carried in the tail gas from the separation of flue dust for the low volatility of copper. As we can see, no copper is discharged outside the system with sulfuric acid, arsenate waste and waste water generated from tail gas treatment processes. The flotation tailing, 0.0074, accounts for 97.37% of emission substance flows, and the copper content in tailing is 0.3%. Thus, improving flotation efficiency may contribute to a higher resource efficiency. Another emission substance flow is the waste water from dust treating process, 0.0002, which contains a certain amount of copper (about 500 mg/L), accounting for 2.63% of emission substance flows. Before the waste water is discharged into environment, further copper removal should be carried out.

(4) Stock substance flow of copper *S*

Only one stock substance flow is generated during stable production. The main portion of stock substance flow is the extra copper matte from smelting process. When the production quantity of smelting process is larger than that of converting process, the product is not digested completely. Thus, some of the copper matte is stocked in the warehouse. The other source of stock substance flow is the low-grade matte produced from the settling of slags. Usually, the stock substance flow is relatively unstable compared to other substance flows, as it depends on the production quantity of smelting and converting to a large extent. The stock substance flow will be put into the production process when the production capacity is sufficient.

4.2 Substance flow analysis of arsenic

As arsenic is a hazardous element that flows into the system associated with copper rather than valuable element, the evaluation defined in Section 2.4 is not conducted for arsenic substance flow. However, for the purpose of giving an insight into the arsenic migration and translation in the production process, the distribution and transformation behaviors of arsenic in the primary single processes (smelting, converting, and refining) were analyzed based on arsenic substance flow analysis and phase analysis of some products.

4.2.1 Mass balance calculation

The mass balance account of arsenic in all single processes of the system was also built upon producing 1 t of copper output from the system, the results are shown in Table 3.

4.2.2 Substance flow chart of arsenic

Figure 3 shows the substance flow chart of arsenic. All the arsenic substance flows are corresponding to the copper substance flows in Fig. 2. The total quantity of arsenic in each kind of substance flow is shown in Table 4. The details of each substance flow are discussed in the following sections.

(1) Input substance flow of arsenic

The total input substance flow of arsenic is 0.01000, which indicates that to produce 1 t of copper into the final product (anode copper), 10 kg of arsenic is carried into the system. All the input arsenic is carried by copper concentrate, and the arsenic content of copper concentrate is 0.23%, which belongs to the kind of high arsenic copper concentrate. This result also reveals that, with the copper resources being complex globally, the amount of arsenic input to copper production system increases. It is necessary to clarify the transformation behavior of arsenic in the copper production process. Another input substance flow of copper, i.e. waste copper, does not carry arsenic into the system, as the arsenic content of copper products conforms to quality standard.

Table 3 Input and output flow ratios of arsenic in each substance flow of production system

No.	Process unit	Input		Output	
		Substance flow	Flow ratio, f_j	Substance flow	Flow ratio, f_j
1	Smelting	Copper concentrate, A_1	0.01000	Copper matte, P_1	0.0034
		Flotation concentrate, $R_{3,1}$	0.00120	Stock matte, S_1	0.00007
		Impure copper, $R_{6,1}$	0	Smelting slag, $P_{1,3}$	0.00183
				Smelting dust and gas, $P_{1,4}$	0.0059
		Total input	0.0112	Total output	0.0112
2	Converting	Copper matte, P_1	0.0034	Crude copper, P_2	0.00032
		Waste copper, A_2	0	Converting slag, $P_{2,3}$	0.00044
		Refining slag, $R_{10,2}$	0.00001	Converting dust and gas, $\mathrm{P}_{2,5}$	0.00265
		Total input	0.00341	Total output	0.00341
3	Flotation system	Smelting slag, $P_{1,3}$	0.00183	Flotation concentrate, $R_{3,1}$	0.0012
		Converting slag, $P_{2,3}$	0.00044	Tailing, E_3	0.00107
		Total input	0.00227	Total output	0.00227
4	Smelting dust collection	Smelting dust and gas, $P_{1,4}$	0.0059	Smelting dust, $P_{4,6}$	0.00432
				Smelting gas, $P_{4,7}$	0.00158
		Total input	0.0059	Total output	0.0059
5	Converting dust collection	Converting dust and gas, $P_{2,5}$	0.00265	Converting dust, $P_{5,6}$	0.00194
				Converting gas, $P_{5,7}$	0.00071
		Total input	0.00265	Total output	0.00265
6	Comprehensive recovering of dust	Smelting dust, $P_{4,6}$	0.00432	Impure copper, $R_{6,1}$	0
		Converting dust, $P_{5,6}$	0.00194	Arsenic waste residue, $E_{6\text{-}1}$	0.00622
				Other metal products, $E_{6\text{-}2}$	0
				Waste water, $E_{6\text{-}3}$	0.00004
		Total input	0.00626	Total output	0.00626
7	Gas cleaning	Smelting gas, $P_{4,7}$	0.00158	Purified gas, $P_{7,8}$	0
		Converting gas, $P_{5,7}$	0.00071	Waste acid, $P_{7,9}$	0.00229
		Total input	0.00229	Total output	0.00229
8	Sulfuric acid production	Purified gas, $P_{7,8}$	0	Sulfuric acid, E_8	0
		Total input	0	Total output	0
9	Precipitation of arsenic	Waste acid, $P_{7,9}$	0.00229	Arsenic waste residue, $E_{9\text{-}1}$	0.00228
				Waste water, $E_{9\text{-}2}$	0.00001
		Total input	0.00229	Total output	0.00229
10	Refining	Crude copper, P_2	0.00032	Anode copper, P_{10}	0.00031
				Refining slag, $R_{10,2}$	0.00001
		Total input	0.00032	Total output	0.00032

(2) Recycle substance flow of arsenic

Arsenic is recycled to the system with two flows: $R_{3,1}$, flotation concentrate; $R_{10,2}$, refining slag. The total recycled arsenic substance flow is 0.00121, accounting for 11.10% of the arsenic distributed in rejected products. Almost all of the arsenic distributed in dust and tail gas is removed in the separated treating process and is not cycled to

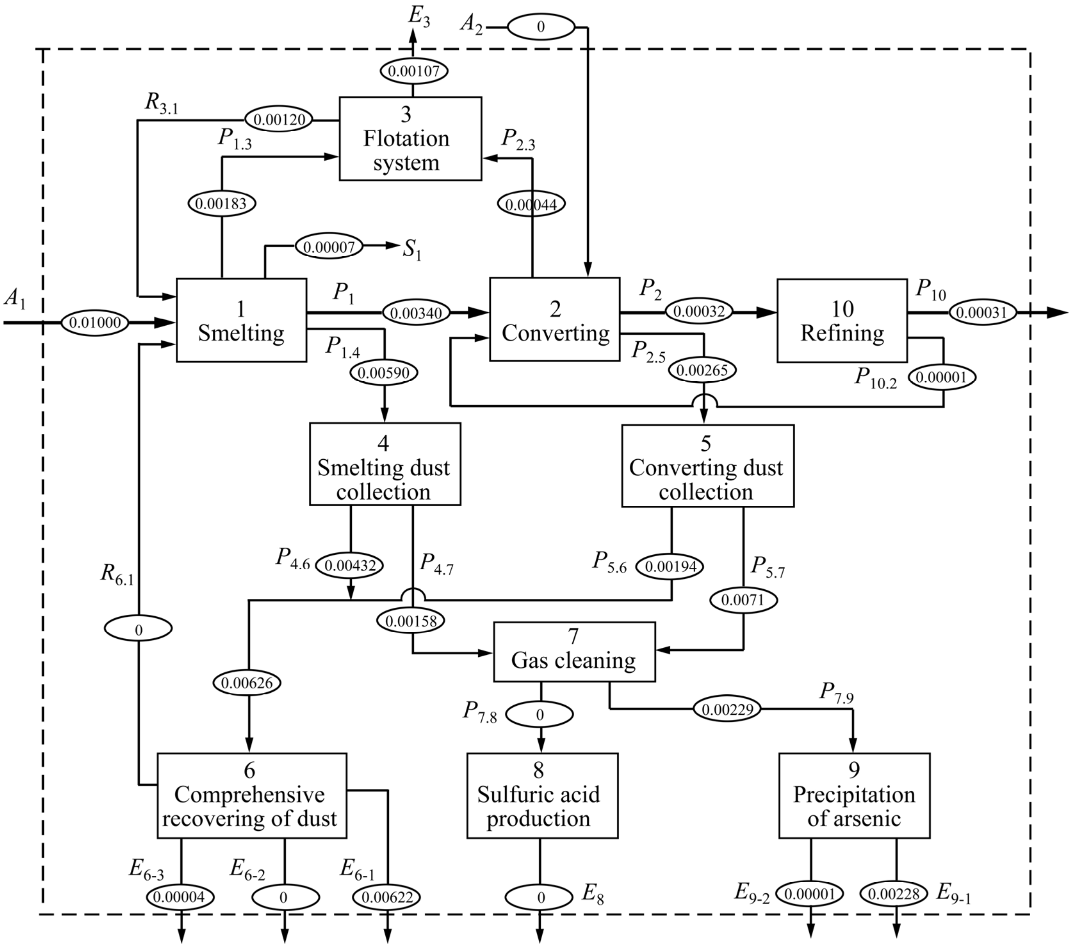

Fig. 3 Arsenic substance flow chart of investigated production system

Table 4 Flow ratio of arsenic in each substance flow of production system

Evaluation indicator	Value
Input raw material flow, *A*	0.01000
Stock substance flow, *S*	0.00007
Cycle substance flow, *R*	0.00121
Emission substance flow, *E*	0.00962

the production system, which helps to avoid arsenic accumulation in production system.

The flotation concentrate ($R_{3,1}$=0.00120) accounts for most of the recycled arsenic substance flows (R=0.00121), 99.17%, which means that improving the selective depressing of arsenic in flotation process could contribute to a smaller amount of recycled arsenic. And for this purpose, it is necessary to do sufficient liberation of arsenic minerals before floatation.

(3) Emission substance flow of arsenic

Some arsenic is discharged outside the production system in the form of flotation tailing E_3 (0.00107), arsenic waste residue $E_{6\text{-}1}$ (0.00622) and waste water $E_{6\text{-}3}$ (0.00004) from comprehensive recovering of dust, arsenic waste residue $E_{9\text{-}1}$ (0.00228) and waste water $E_{9\text{-}2}$ (0.00001) from tail gas treating. In summary, to produce 1 t of copper, 1.07 kg of arsenic in flotation tailing, 8.50 kg of arsenic in arsenic waste residue (the sum of $E_{6\text{-}1}$ and $E_{9\text{-}1}$), and 0.05 kg of arsenic in waste water (the sum of $E_{6\text{-}3}$ and $E_{9\text{-}2}$) is generated. The other metal products from comprehensive recovering of dust and sulfuric acid do not carry arsenic out of the system.

Among these emissions, arsenic waste residue from dust and tail gas treatment accounts for 88.36%, and is considered as hazardous waste, thus the stabilization level of arsenic in waste residue should be assessed for the purpose of minimizing environmental pollution risk. And the waste water should be treated further before discharging into the natural environment, as the arsenic content of waste water (1.4 mg/L) exceeds emission standard in China (Emission standard of pollutants for copper, nickel, cobalt industry, GB 25467—2010). Reusing the waste water to the gas cleaning process is a reasonable way.

(4) Stock substance flow of arsenic

The amount of arsenic in stock flow, 0.00007, is very small compared to the other substance flows. And this substance flow will be put into the production process along with copper.

4.2.3 Distribution and transformation behaviors of arsenic

With the copper resources being complex globally, the amount of arsenic entering copper production system increases. It is necessary to clarify the evolution behaviors of arsenic during copper production. The content of arsenic in copper concentrate and some products from the production system is shown in Table 5. The distribution and transformation behaviors of arsenic are analyzed in detail in the following sections.

Table 5 Contents of arsenic in copper concentrate and some products (wt.%)

Copper concentrate	Copper matte	Smelting dust	Smelting slag	Crude copper
0.23	0.22	7.01	0.10	0.04

Converting dust	Converting slag	Anode copper	Refining slag
5.93	0.08	0.03	0.04

(1) Smelting process

Table 6 shows the distribution of arsenic in the primary single processes. The results indicate that, in smelting process, a large portion of arsenic flows with flue gas (including 38.56% in smelting dust, and 14.11% in tail gas) for its low volatile point. Then, most of the volatile arsenic is collected in smelting dust by dust collection process, which results in the high arsenic content of smelting dust, 7.01%. Besides, there are still large portion of arsenic (30.36%) distributed in copper matte followed by 16.34% in smelting slag and 0.63% in stock matte.

The main occurring forms of arsenic in raw material (copper concentrate) are Cu_3AsS_4 and CuAsS (shown in Fig. 4(a)), and these complex compounds are decomposed rapidly into As_2S_3 at high temperatures. During copper smelting, arsenic sulfides are oxidized and decomposed as follows:

Table 6 Distribution of arsenic in primary production processes of system

Process unit	Product	Flow ratio, f_j	Distribution rate/%
Smelting	Copper matte	0.00340	30.36
	Stock matte	0.00007	0.63
	Smelting slag	0.00183	16.34
	Smelting dust	0.00432	38.56
	Smelting gas	0.00158	14.11
Converting	Crude copper	0.00032	9.38
	Converting slag	0.00044	12.91
	Converting dust	0.00194	56.89
	Converting gas	0.00071	20.82
Refining	Anode copper	0.00031	96.88
	Refining slag	0.00001	3.12

$$As_2S_3+O_2(g)=2AsS(g)+SO_2(g) \tag{12}$$

$$2AsS+2O_2(g)=As_2(g)+2SO_2(g) \tag{13}$$

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

$$2As_2S_3=4AsS(g)+S_2(g) \tag{15}$$

$$2AsS=As_2(g)+S_2(g) \tag{16}$$

Therefore, arsenic flows into flue gas in the forms of $As_2(g)$, AsS(g), and AsO(g), some arsenic is further oxidized to As_2O_3 during flowing, and part of it is collected into dust. The form of arsenic in smelting dust is shown in Fig. 4(c).

Some arsenic is also oxidized in the molten bath and enters smelting slag in the form of As_2O_3 which is detected by slow scanning XRD, as shown in Fig. 4(d), and the following reactions occur:

$$4AsO(g)+O_2(g)=2As_2O_3(l) \tag{17}$$

$$As_2(g)+1.5O_2(g)=As_2O_3(l) \tag{18}$$

$FeAsO_4$ is also detected as shown in Fig. 4(d). This result indicates that in the slag, $As_2O_3(l)$ further reacts with iron oxides to form iron arsenate.

During the flowing of the melt, As_2O_3 is reduced to As(l) that is the existing form in copper matte (shown in Fig. 4(b)) by FeS as follows:

$$As_2O_3(l)+FeS(l)=2As(l)+FeO(l)+SO_2(g) \tag{19}$$

Meanwhile, a part of As(l) in copper matte can also be oxidized to $As_2O_3(l)$ by Cu_2O and then enters the smelting slag:

$$2As(l)+2Cu_2O(l)+2FeS(l)+1.5O_2(g)=As_2O_3(l)+2FeO+2Cu_2S(l) \quad (20)$$

$$2As(l)+1.5O_2(g)=As_2O_3(l) \quad (21)$$

Besides, a part of As_2O_3 is also reduced to $As_2(g)$, and flows back into flue dust:

$$As_2O_3(l)+FeS(l)=As_2(g)+FeO(l)+SO_2(g) \quad (22)$$

In fact, all of the above reactions form a balanced cycle in the smelting process.

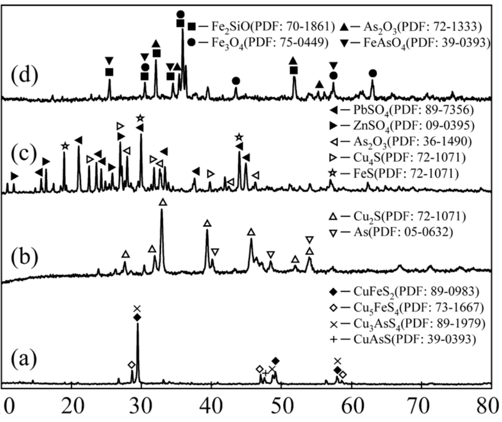

Fig. 4 Slow scanning XRD patterns of copper concentrate (a), copper matte (b), smelting dust (c), and smelting slag (d)

(2) Converting process

As shown in Table 6, in converting process, the arsenic collected in converting dust accounts for the largest portion, 56.89%, resulting in high arsenic content of the dust, 5.93%. 20.82% of arsenic flows into converting gas, 12.91% of arsenic is distributed in converting slag, and 9.38% of arsenic is distributed in crude copper.

During this process in PS converter, the arsenic in copper smelt is oxidized to As_2O_3 by O_2, and Eqs. (20) and (21) occur. A large amount of As_2O_3 flows into flue gas and part of it is collected into dust (shown in Fig. 5(a)) in converting dust collection process. A part of As_2O_3 enters converting slag and can be detected by XRD as shown in Fig. 5(b). Similar to the smelting process, some As_2O_3 further reacts with iron oxides to form iron arsenate, and $FeAsO_4$ can be detected (shown in Fig. 5(b)). A small amount of arsenic in copper matte is not oxidized and stays in crude copper.

(3) Refining process

In refining process, 96.88% of arsenic stays in anode copper and the rest in slag is recycled to converting process. During this process, the arsenic in crude copper is difficult to be oxidized due to its low content (0.04%). Thus, most of arsenic is distributed in anode copper in the form of As(l), and a small part of arsenic is oxidized to As_2O_3 (shown in Fig. 6) and enters refining slag. Besides, some As_2O_3 also reacts with iron oxides, and thus iron arsenate $FeAsO_4$ is formed as shown in Fig. 6.

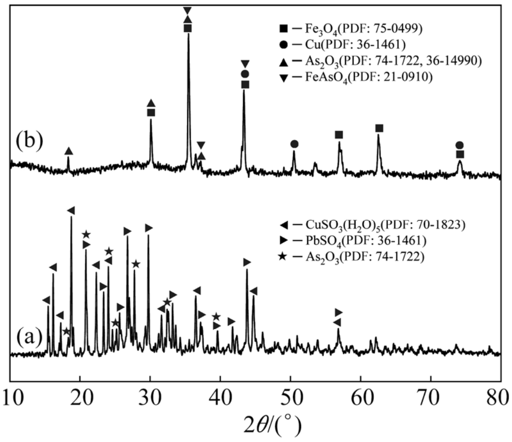

Fig. 5 Slow scanning XRD patterns of converting dust (a) and converting slag (b)

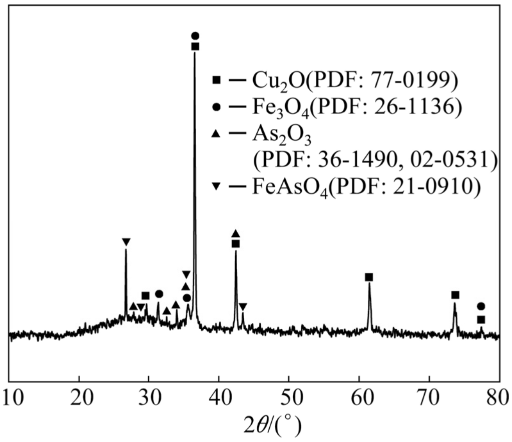

Fig. 6 Slow scanning XRD pattern of refining slag

It is worth noting that, in consideration of the high arsenic content in dust from smelting and converting, centralized treatment of the two dusts is a reasonable way to avoid arsenic accumulation in the production system instead of recycling it to smelting and converting processes directly.

5 Conclusions and recommendations

(1) For the copper substance flows, the resource efficiency of copper for the production process is 97.58%. The direct recovery of copper in smelting, converting, and refining processes is 91.96%, 97.13%, and 99.47%, respectively.

(2) For the arsenic substance flows, to produce 1 t of copper, 10 kg of arsenic is carried into the system, with the generation of 1.07 kg of arsenic in flotation tailing, 8.50 kg of arsenic in arsenic waste residue, and 0.05 kg of arsenic in waste water. In smelting process, the distribution rate of arsenic in smelting dust, tail gas, copper matte, smelting slag, and stock matte is 38.56%, 14.11%, 30.36%, 16.34%, and 0.63%, respectively. In converting process, the distribution rate of arsenic in converting dust, tail gas, crude copper, and converting slag is 56.89%, 20.82%, 9.38%, and 12.91%, respectively. In refining process, the distribution ratio of arsenic in anode copper and slag is 96.88% and 3.12%, respectively. For the transformation behaviors, arsenic occurs in dust from smelting and converting as As_2O_3, in slag from smelting, converting and refining as As_2O_3 and arsenate, in copper matte, crude copper and anode copper as As.

(3) Some recommendations for improving copper resource efficiency and pollution control were proposed based on substance flow analysis: The centralized treatment of dust from smelting and converting with high arsenic content is a reasonable way for avoiding arsenic accumulation in the production system. The selective depressing of arsenic in flotation process should be improved for a smaller amount of recycled arsenic. Meanwhile, improving flotation efficiency may contribute to a higher copper resource efficiency. The stabilization level of arsenic in waste residue should be assessed to minimize the risk of environmental pollution. The waste water from dust and tail gas treatment should be treated further before discharging into natural environment. Since the arsenic content is high, it is with good environmental and economic benefits to reuse the waste water to the gas cleaning process.

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铜火法冶炼过程中铜和砷物质流分析

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摘　要：采用物质流分析方法对铜火法冶炼过程铜和砷的代谢进行分析，建立铜和砷的物质平衡表及物质流图。采用直接回收率、废物循环率和资源效率等指标评价流程代谢效率。结果表明，该流程铜资源效率为97.58%，在熔炼、吹炼和精炼单元过程铜的直接回收率分别为91.96%、97.13%和99.47%。同时，生产1 t金属铜有10 kg砷进入系统。其中，1.07 kg砷进入浮选尾矿，8.50 kg砷进入除砷废渣，0.05 kg砷进入生产废水。此外，分析生产过程中砷在熔炼、吹炼和精炼单元中的分配和转化行为，并在物质流分析基础上，提出提高铜资源效率及控制污染的建议。

关键词：铜冶炼；物质流分析；铜；砷；分配行为

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