DEARSENICATION FROM COBALT-ARSENIC CONCENTRATE BY VACUUM DISTILLATION①

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ABSTRACT

The feasibility and regularity of dearsenication from cobalt-arsenic under vacuum have been investigated on the self-made vacuum furnace. The influences of temperature, time, residual pressure, and pellet size on the envaporation ratio of arsenic have been tested with the fixed furnace configuration. The experimental results show that the process of dearsenication from cobalt-arsenic concentrate by vacuum distillation is effective. Under proper conditions, the envaporation ratio of arsenic comes up to 89%～95%. When the condensate experiences redistillation under vacuum, refined arsenic can be obtained which contains 99.7% arsenic.

Key words: vacuum distillation cobalt-arsenic concentrate condensate residue redistillation

1 INTRODUCTION

Processes comercially used in the world to extract cobalt from cobalt- arsenic concentrate are classfied as two types: a hydro-metallurgical process and a pyro-hyro-metallurgial one. Because all soluble arsenides are poisonous, so the hyro-metallurgical process is a threat to the work condition and environment. In the pyro-hydro-metallurgical process, which is used in a smeltery in Jiangxi Province, the smelting-roasting technique is adopted to remove the major part of arsenic in the form of As_2O_3, then a hydrometallurgy process is followed to remove impurities and extract cobalt. At its pyrometallurgical stage, large amount of poisonous burnergas full of As203 is produced both in electric arc smelting and in fluidization roasting process. The As203 burnergas is so harmful that after dedusting purification, it still brings vicious circus of arsenic and pollutes the environment.

Therefore, in this paper we concentrate on the possibility of process, where vacuum distillation is adopted as an alternative to improve the pyrometallurgical process. By using this method we can eliminate environmental pollution, save the cost of dedusting, and obtain refined arsenic as a by-product. Therefore it is economical and competitive.

2 THEORETICAL ANALYSIS

The chemical composition of cobalt- arsenic concentrate is shown in Table 1. The X- ray spectro-chemical analysis indicates that the main species are the arsenides of cobalt, iron, and nickel The rational analysis of the constituents shows 96%of arsenic is combined in the arsenides of cobalt, iron, and nickel. Therefore, the main task is to break down the arsenides of cobalt, iron, and nickel. by vacuum distillation and capture elemental arsenic.

According to literature [1], we can determine whether a binary alloy system A-B can be separated or not by the value of seperation factor β. The

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Table 1 The chemical composition of cobalt-arsenic concentrate

elements	C	As	Fe	Ni	S
%	9.96	56.91	7.24	2.10	0.99
elements	Ca	Mg	SiO_2	Au	Ag
%	2.20	0.73	5.90	13g/T	88g/T

value of β is defined by the following formula:

$$\beta = \frac{\gamma_A \cdot P^\circ_A}{\gamma_B \cdot P^\circ_B}$$

where γ_A and γ_B refer to activity coefficient of constituent A and B respectively. P°_A and P°_B refer to the vapor pressure of pure A and B respectively.

According to the activity coefficents of binary systems As-Fe and As-Ni at 1 150 ℃ given by literatutre[2], we can calculate the two seperation factors of binary systems As-Fe and As-Ni. Because the two values of $\beta_{As\text{-}Fe}$ and $\beta_{As\text{-}Ni}$ are both far too less than 1, then we draw a conclusion that the As-Fe system and the As-Ni system can be separated by vacuum distillation. Although we are short of the activity coefficents of As-Co system, we still deduce that the As-Co system can also be seperated under vacuum because of the similar properties of cobalt and nickel.

The decomposition reactions of high arsenic compounds of cobalt, iron, and nickel[3] indicates that when the arsenides are heated, they break down and seperated out arsenic.

3 EXPERIMENTAL APPARATUS AND PROCEDURES

The experiment is carried out on the self-made small vacuum furnace. The dimension of furnace boby is d175 mm × 275 mm, the power is 3 kW. Graphite crucibles are adopted. The evaperation of graphite at the experimental temperature can be ignored, so the crucible will not influence the compositions of condensate and residue. The inside diameter of crucible is 3.2 cm, and every charge is 20 g. A platinum-rhodium thermocouple is placed outside of the bottom of crucible. A 2X-4 type mechanical pump is taken as the vacuum-pumping equipment and a Meleod vacuum gage, a U-pressure gage as the vacuum-measuring equipments.

4 RESULTS AND DISCUSSION

4.1 *Influence of Temperature*

The experimental conditions are as follows:
Residual pressure: 6.67～9.93 Pa
Pellet size: 0.45～0.90 mm
Time: 20 mn.
Charge: 20 g

Fig. 1 shows the evaporation ratio of arsenic increases with increasing temperature, especially rapid below 950 ℃. So the temperature above 950 ℃ is necessary for effective dearsenication. But there is a limitation. Because the aim of this research is not to keep arsenic to a minimum but to improve the present dearsenication process, then we should consider the proper content of arsenic in roasted mass demanded by the leaching stage. To the advantage of leaching efficiency, the roasted mass need containing 6%—8% arsenic, so the distillation temperature shoud be lower than 1 200 ℃.

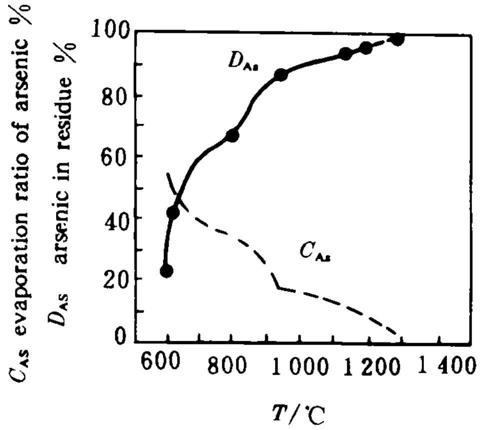

Fig. 1 Effect of temperature(T) on evaporation ratio of As(D_{As})
residual Pressure: 6.67～9.93 Pa; pellet size: 0.45～0.90 mm; time: 20 min; charge: 20 g

Also we observed that below 1 100 ℃ the residue remains bulk solid, above 1 100 ℃ molten state appeared, at 1 200 ℃ the residue is wholly melted into alloy and slag, two phases are separated. By this we shall later have a discussion on the discharging mode and the corresponding technological process.

4. 2 *Influence of Residual Pressure*

The experimental conditions are as follows:
Temperature: 1 100 ℃;
Time: 40 min;
Pellet size: 2. 0～2. 5 mm;
Charge: 20 g.

Fig. 2 shows the evaporation ratio of arsenic increases with the decreasing of residual pressure in vacuum furnace. When the pressure reduces to 6. 67 Pa, the curve trends to horizontal line, which means the evaporation ratio does not vary any more according to the decreasing of pressure. In this case the evaporation rate becomes independent of pressure and reaches maximum. Therefore, the residual pressure is not necessarily less than 6. 67 Pa when we distill the cobalt-arsenic concentrate. Too low pressure does not contribute to dearsenication, on the contrary it will put on the cost of equipment and running.

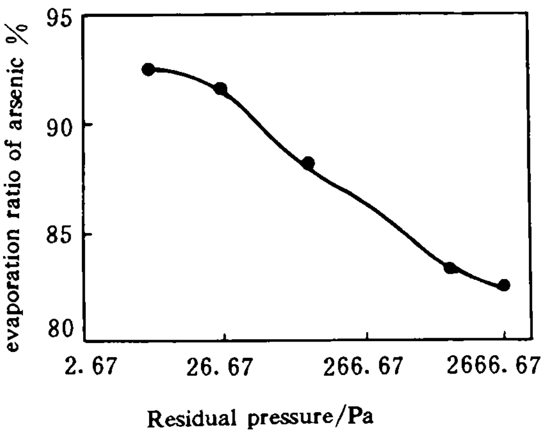

Fig. 2 Effect of residual pressure on evaporation ratio of arsenic(D_{As})

temperature: 1 100 ℃; time: 40 min; pellet size: 2. 0～2. 5 mm; charge: 20 g

4. 3 *Influce of Time*

The experimental conditions are as follows :
Temperature : 1 100 ℃;
Pellet size: 2. 0～2. 5 mm;
Charge : 20 g.
Ressidual Pressure: 6. 67～9. 33 Pa

Fig. 3 shows the evaporation ratio of arsenic increases slightly with increasing time indicating that the influence of time is not as significant as that of temperature and pressure . After 40 min, the curve trends to horizontal line. In this case, it is difficult to increase evaporation ratio any more by lasting time, too long time will reduce the evaporation rate, thus decrease the plant productivity and put on energy consumption.

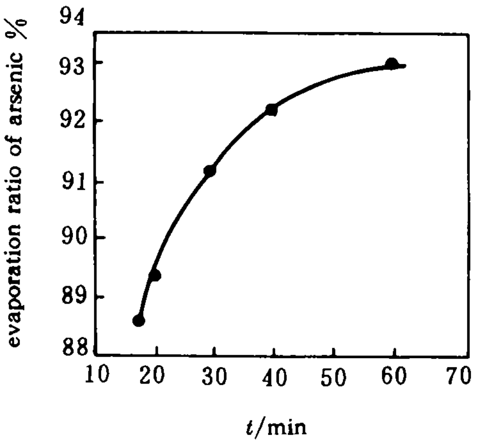

Fig. 3 Effect of time on evaporation ratio of arsenic(D_{As})

temperature: 1 100 ℃; pellet size: 2. 0～2. 5 mm; charge: 20 g; residuel pressure: 6. 67～9. 33 Pa

4. 4 *Influence of Pellet Size*

The experimental conditions are:
Temperature: 1 100 ℃;
Residual Pressure: 6. 67～9. 33 Pa;
Time: 20 min;
Charge: 20 g.

Fig. 4 shows the evaporation ratio of arsenic decrease with the decreasing mean diameter of powder, more significantly when the size is bigger than 1. 5 mm. So it is necessary to keep the pellet size less than 1. 5 mm to the advantage of dearsenication. Nevertheless the pellet size can not be smaller than 0. 5 mm. Otherwise too small interparticle porosity and light weight may cause splashing while the heated arsenides break down and give off large quantity of arsenic vapour. The material spits out of the crucible, thus incurs unexpected error, even makes it unable to continue the experiment. The suitable pellet size is more or less 1. 0 mm. Besides in a large scale equipment the big evaporating pan will take the place of small crucible thus eliminating material splashing.

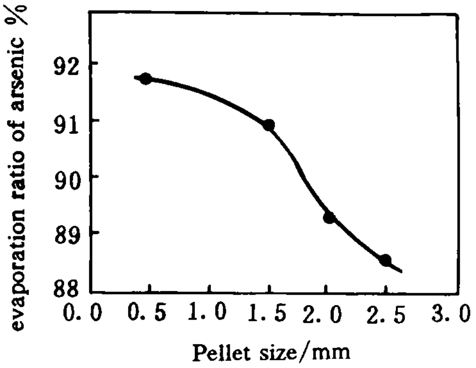

Fig. 4 Effect of pellet size on evaporation ratio of arsenic

temperature: 1 100 ℃; residual pressare: 6.67～9.33 Pa; time: 20 min; charge: 20 g

To sum up, with the present furnace configuration, the optimum small-scale labolatory experimental conditions of dearsenication are as follows:

Temperature: 950～1 200 ℃;
Time: 40 min;
Residual Pressure: 6.67～26.67 Pa;
Pellet size: 0.5～1.5 mm.

As a result, the evaporation ratio of arsenic is 89%～95%, arsenic content in residue is 9.90% ～18%, arsenic in condensate is 76%～97%, recovery ratio of arsenic in condensate is 70% ～ 80%.

4.5 3 kg-*Scale Experiment*

3 kg-scale experiment is carried out in the self-made tens kg scale vacuum furnace. The experimental conditions are as follows:

Charge: 3 kg;
Temperature : 1 100;
Residual Pressure: 666.7—1 333 Pa;
Time: 4 h.

The results obtained are arsenic condensate 84.44% and recovery ratio of arsenic 74.2%. The residue is composed of two phases. They are slag and alloy. The slag contains arsenic less than 1% and cobalt 0.54%, which is mixed incidently. So the slag can be stored up and later treated. Alloy is melt of metals and their arsenides. It concentrates cobalt and noble metals such as silver, gold. It will be treated in the next technological process. Both small-scale and 3 kg-scale experiments verify the feasibility of dearsenication of cobat-arsenic concentration under vacuum.

4.6 *Vacuum Redistillation*

The primary condensate generally contains 85% arsenic after a primary vacuum distillation. Redistillation is needed to obtain refined arsenic suitable for sell, and to recover metals spiting into the condensate.

Vacuum redistillation is carried out in the same furnace under the conditions of temperature: 550 ℃; residual pressure: 5.53-6.67 Pa.

The result obtained shows the secondary condensate contains 99.7% As, recovery ratio of As is 76.5%. It is evident that refined As can be obtained by redistillation.

5 COMPARISION OF DISCHARGING MODE AND CORRESOPONDING TECHNOLOGICAL PROCESS

Fig. 5 and Fig. 6 give two technological processes which can be used to improve the present electric arc smelting-fluidzation roasting process. Two processes are optional and can be selected on the basis of concrete conditions.

As mentioned above, at different temperatures, the residue presents bulk solid or molten state, in corresponding with two discharging modes and technological processes. Besides, after vacuum distillation, the residue is composed of metals and their arsenics, yet at the leaching stage of cobalt metallurgy, it is demanded that the metal element be in the form of metallic oxides such as CoO, Fe_3O_4 etc., which can be dissolved easily by acid. For this reason, the residue should experience roasting in air after vacuum distillation.

The proper temperature is determined to be 950～1 200 ℃. At 950～1 100 ℃ bulk solid residue is discharged. Because slag and arsenides are mixed in the bulk solid residue, mineral concentratie is needed to remove slag and obtain cobalt matte, only cobalt matte is roasted in air. On the

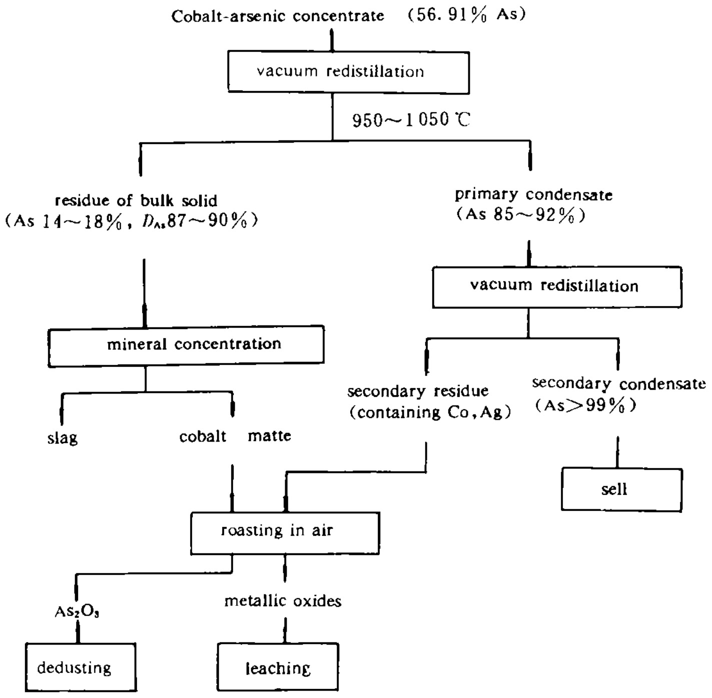

Fig. 5 Advisable flow sheet of discharging bulk solid

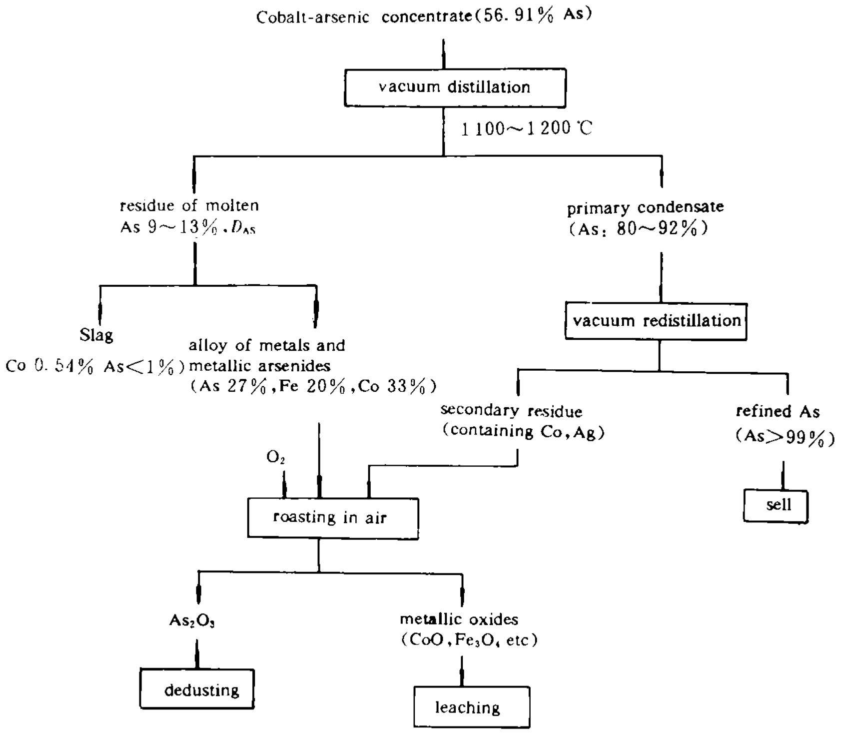

Fig. 6 Advisable flow sheet of discharging molten

other hand, if vacuum distillation proceeds at 1 100 — 1 200 ℃, molten residue is discharged. Slag in this molten residue is separated from alloy. We may take off the slag, roast the alloy in air.

6 CONCLUSIONS

Dearsenication from cobalt- arsenic concentrate by vacuum disrtillation is feasible to improve the previous pyrometallurgical process. At 950～1 050 ℃, bulk solid residue is discharged while at 1 100～1 200 ℃ molten residue is discharged. Refined arsenic can be obtained after vacuum redistillation which contains 99. 7% arsenic.

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4 CONCLUSIONS

(1) The phase diagram of the ternary system $CeCl_3$-$BaCl_2$-LiCl was determined. There were 5 liquidus surfaces corresponding to $CeCl_3$, α-$BaCl_2$ (α type of $BaCl_2$), β-$BaCl_2$ (β type of $BaCl_2$), LiCl and Ba_3CeCl_9 respectively and 6 univariants curves corresponding to the secondary crystallization. Two ternary reactions occur in the system:

$$L + \beta\text{-}BaCl_2 \rightleftharpoons Ba_3CeCl_9 + LiCl$$

P(50. 0 wt. -% $CeCl_3$, 22. 8 wt. -% $BaCl_2$, 27. 2 wt. -% LiCl; 480 ℃)

$$L \rightleftharpoons CeCl_3 + Ba_3CeCl_9 + LiCl$$

E(65. 8 wt. -% $CeCl_3$, 2. 5 wt. -% $BaCl_2$, 32. 2 wt. -% LiCl; 452 ℃)

(2) According to the results of DTA and X-ray diffraction Analysis (XRD), it was found that an unstable compound was formed in solid state and decomposed at 410 ℃.

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