THE SEPARATION OF Pb–Sb ALLOYS BY VACUUM DISTILLATION①

Dai Yongnian② Zhang Guoj ing③
Kunming Institute of Technology, Kunming 650093, China

ABSTRACT

This paper summarizes the research results of vacuum distillation of Pb–Sb alloy and crude antimony. In our study, we have found the basic law which states that in Pb–Sb phase diagrams, the part which is rich in lead can be used to guide the purification of lead by distillation, while the part rich in antimony can be used to guide the purification of Sb, where the compositional point C is the azeotropic mixture. The technical experimental results at temperatures between 700–850℃ are coincident with those of theorical study. The expanding experiment at the 100kg scale produced satisfactory results.

Key words: Pb–Sb alloy, vacuum distillation, separation coefficient

1 INTRODUCTION

Crude antimony always contains a certain amount of lead which comes from the ore. If the ore is Jamesonite ($Pb_4FeSb_6S_{14}$, Pb:Sb = 1.134), only Pb–Sb alloy is available and the lead must be separate from alloy in order to obtain pure antimony. This separation is difficult by fire refinement[1], but feasibility by hydroelectrolysis though high in cost, complicated in technique, long in its flow sheet and low in metal recovery.

The separation of lead by vacuum distillation is non-economical[1], but our previous work[2–5] has shown that the method is good for the separation of fine antimony with a small amount of Pb– Sb (<50Sb) alloy. This method needs no reagent but electricity only, and is simple, reasonable and economic.

2 CHARACTER OF DISTILLATING Sb–Pb ALLOY

In distillation, the volatilization of elements in alloys depends on the actual vapor pressure P_i, which relates to the vapor pressure P_i^o of the pure element. The separation coefficient (β_i), is used to determine the possibility and extent of separation of these two elements when distillating.

$$\beta_i = \gamma_1 P_1^o / \gamma_2 P_2^o \tag{1}$$

Where γ_1, γ_2 are the activity coefficient of elements 1, 2.

$$\rho_1 / \rho_2 = \beta_1 a_1 / a_2 \tag{2}$$

Where, ρ_1, ρ_2 are vapor density of elements 1, 2 in gas (g / cm^3) and their contents in liquid are a_1 and a_2(g) respectively.

The relation between vapor pressure and temperature of pure lead and pure antimony is

①Manuscript received November 2, 1990
②Professor; ③Lecturer

shown in Fig.1. It demonstrates that there is an obvious change at 630.5℃ when solid antimony and lead turn to liquid and P^o_{Sb}/P^o_{Pb} varies greatly with the rising of temperature (see Fig.2). It's maximum value is about 140 at the melting point of antimony (630. 5℃), but it is only about 10 at the corresponding point of lead (1100℃).

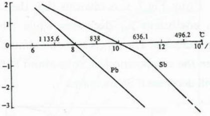

Fig.1 $\lg P^o_i$–1 / T of lead and antimony.

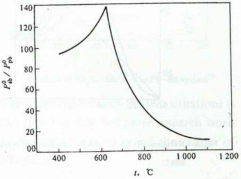

Fig.2 Relation of P^o_{Sb}/P^o_{Pb}–t in Pb–Sb systems

The thermodynamics property of Pb–Sb is shown in Fig.3, from which we can find both a_{Pb} and a_{Sb} have a small negative deviation from the diagonal and the values of γ_{Sb}/γ_{Pb} are around 0. 779～1. 284 at the temperature of 632℃, $\beta_{Sb\cdot 800℃}$ varies with N_{Pb} and is always larger than 1. (table 1)

From equation (2), the content of antimony in gas is proven to be higher than that in liquid, namely

$$(\rho_{Sb}\rho_{Pb})/(a_{Sb}a_{Pb})=\beta_{Sb}>1$$

The percentage of antimony in gas (Sb_g%) is:

$$[\rho_{Sb}/(\rho_{Sb}+\rho_{Pb})]\times 100=Sb_g\%.$$

or $$[1/(1+\rho_{Pb}/\rho_{Sb})]\times 100=Sb_g\% \quad (3)$$

An equilibrium figure as shown in Fig. 4 can be obtained through calculation. It shows that the vapor containing higher antimony can be obtained by distilling Pb–Sb alloys of any composition.

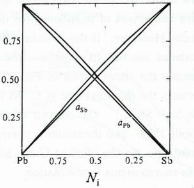

Fig.3 Relations of a_i—N_i in Sb–Pb system(632℃)[5]

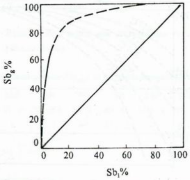

Fig. 4 Relation of Sb_g% –Sb_l% in Pb–Sb systems at 800℃.

Table 1 Values of N_{Pb}–γ_{Sb}/γ_{Pb}–$\beta_{Sb\cdot 800℃}$ in Pb–Sb system.

N_{Sb}	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
γ_{Sb}/γ_{pb}	0.779	0.813	0.861	0.905	0.851	1.000	1.051	1.105	1.162	1.222	1.284
$\beta_{Sb800℃}$	29.6	31	32.7	34.4	36.1	38	38.9	42	44.2	46.4	48.8

Fig.4 shows the change of equilibrium composition of gas and liquid at different temperature. It can explain the relation among materials, conditions of operation and quality of product. So the structure in equipment, and style of operation can be defined. For example, when distillating crude antimony with 1% Pb at 827℃, a condensate of 10^{-1}—10^{-2}% Pb is obtained; while the temperature is 927℃, the content of lead in the condensate is up to 10^{-1}—10^{0}%. Besides, the lead content in the condensate will increase if it is higher in raw materials. So we can choose the temperature and stages of distillation for desired products. However, if the content of lead in raw material reaches 10^{1}—10^{2}%, the result will assume the curve shown in Fig. 6, which intersects the diagonal line at C. At this point $Sb_g\% = Sb_l\%$, the content of antimony is about 22%, and the resulting compound is an azeotrope. So the alloy at C can not separate into two elements by distillation.

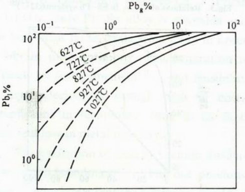

Fig.5 Equilibrium relation of $Pb_g\%$–$Pb_l\%$ in Pb–Sb system.

At the right of C, the alloy is rich in antimony, so $Sb_g\% > Sb_l\%$, and antimony is concentrated in vapor. Therefore crude antimony and the Pb–Sb alloy can be refined by distillation. The products are pure antimony and an alloy with a composition close to point C.

At the left of C, lead is rich and the curve is under the diagonal line, so

$$Sb_g\% < Sb_l\%$$

Upon distillation, lead is concentrated and refined in vapor. and the products are pure lead and concentrated antimony in residual.

From Fig.7, it is obvious that the separation coefficient β_{Sb} decreases while temperature increases. The β_{Sb} is at its maximum value when the composition of Sb is about 80% and it will decrease if Sb increases.

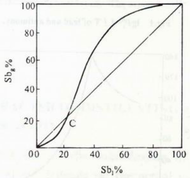

Fig. 6 Relation of $Sb_g\%$ –$Sb_l\%$ in Pb–Sb system at 800℃

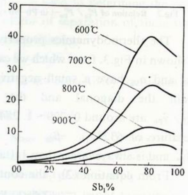

Fig.7 Relation of β_{Sb}–$Sb_l\%$–t in Pb–Sb systems[5]

Fig.8 shows the relation of $Sb_g\%$– $Sb_l\%$ –t. When β_{Sb} changes and the temperature increases, point C moves towards the direction where Sb% is higer and the separation of the Pb–Sb alloy breaks down. When temperature decreases, point C moves towards the direction where Sb_l% is lower, the separation of Pb–Sb alloy improves and the content of antimony in azeotrope decreases.

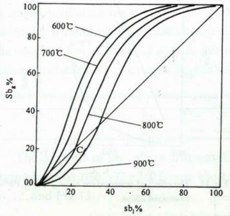

Fig.8 Relation of Sb_g%–Sb_l%–t in Pb–Sb system[5]

The diversity between the two situations is obvious (See Fig. 8), but more research work should be carried out to reveal the reason of the difference.

2 EXPERIMENTAL RESULTS

We have studied the volatility of pure antimony, technology of continuous and discontinous operation and its equipments.

2.1 *Volatilization of Pure Antimony*

The vapor pressure of pure antimony and temperature are measured and listed in Table 2.

At the pressure of 66.7 Pa, the volatilization rates at different temperature are measured and listed in Table 3 [7].

Fig. 9 shows that the volatilization rate is influenced by pressure, and the critical pressure at different temperature are listed in Table 4. At the critical pressure, the volatilization rate(ω) will not change with the decrease of residual pressure which is of great help for the selection of optimal pressure, vacuum degree and equipment.

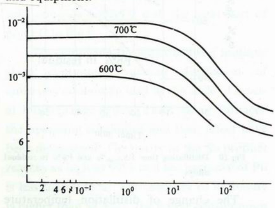

Fig. 9 Relation of pressure and volatilization rate ω of pure antimony

Table 4 Critical pressure (p_{crit}) at different temperatures[7]

℃	600	650	700	720	750	800
P^0_{Sb}(Pa)	11.3	26.604	65.2	69.31	138.4	275.26
P_{crit}(Pa)	–	26.6	–	45.32	–	–61.32

Table 2 Vapor pressure of Sb at different temperatures

t (℃)	650	700	750	800	850	900	950
P^*_{Sb} (p_a)	28.4	65.2	138.4	273.3	509	890.1	1 513.6

Table 3 Volatilization rate(ω) at different temperatures

t (℃)	650	713	740	780	814	873	915
ω_{sb} (g / cm^2 min)	2.12×10^{-3}	4.83×10^{-3}	9.83×10^{-2}	1.25×10^{-2}	1.47×10^{-2}	1.76×10^{-2}	1.88×10^{-2}

2.2 *Discontinuous Distillation of Crude Antimony.*

Crude antimony with 10% Pb is distillated at the pressure of 40 Pa and at the temperature of 800℃. The content of lead increases from 0.32% to 2.91% in condensed alloys, and from 31.67 to 71.37% in residual alloys.

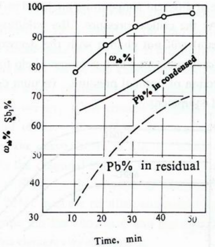

Fig.10 Distillating time $VS.\omega_{Sb}\%$ **and Pb% in residual alloys**

The change of distillation temperature will influence the rate of volatilization and the content of lead in antimony. If temperature increases from 700℃ to 800℃, the amount of volatilization of antimony will increases about 40%. Meanwhile, the content of lead in antimony increases from 0.3% to 1%. Volatilization of antimony increases from 80% to 92% if temperature ranges about 800℃ to 900℃, but the content of lead increases from 1% to 4%, only if the change coincide with the previous analysis. If distillation temperature is at 800℃, more volatilization of antimony and antimony containing less lead can be obtained.

Crude antimony can be changed into fine antimony through four stages of discontinous vacuum distillation. The compositon of crude and refined antimony is listed in Table 5.

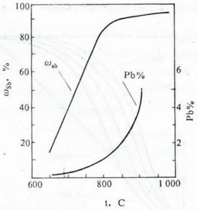

Fig. 11 The effect of temperature on $\omega_{Sb}\%$ **and Pb% in condensed alloys**

From Table 5, we can find that separating lead from crude antimony is inreasonable without the use of multiple stages vacuum distillation.

2.3 *Vacuum Distillation of* Pb–Sb*Alloys*

An alloy of definite composition is made of pure lead and pure antimony. The scale is 70g, volatilization lasts for 1 h at 40Pa and at 800℃. The comparative composition of alloy and condensate is listed in Table 6.

Fig.6 is based on the data of Table 6. The line at the left of point C is refer to antimony separated from crude lead by vacuum refining, while the line at the right of point C represents the law governing the refining and separating of lead from crude antimony.

Table 5 Composition of crude and refined antimony

composition	Sb	As	S	Pb	Fe	Cu	total of impurity
crude antimony%	81–94	0.2–9.6	0.96–0.48	0.02–0.3	3–7.1	–	6–19
refined antimony%	>99	0.08–0.17	0.12–0.31	0.026–0.18	0.003	0. 003	0.23–0.67

Table 6 Comparison between Pb–Sb alloy and condensate

Sb% in alloy	0	4.91	11.30	19.8	24.66	40.36	53.91	69.98	74.68	76.53	83.73	89.78	100
Sb% in condensate	0	2.44	7.13	19.26	22.09	63.33	83.89	93.53	96.06	97.70	99.44	99.64	100
Volatilization rate of antimony g/cm^2 min	0	0.002679	0.00404	0.0206	0.04491	0.2440	0.5270	0.8535	1.5270	2.3296	4.1960	6.5678	10.11
Volatilization rate of lead g/cm^2 min	0.1936	0.1093	0.0859	0.0863	0.1584	0.1378	0.1075	0.0458	0.06144	0.04029	0.02701	0.01582	0

The content of lead in the condensate decreases about ten times of that in raw material by single distillation (as in Table 6), which is reasonable if multiple stage distillation is used. The composition of material used in our multiple stage distillation experiment is as follows:

Table 7 The composition of exeperimental material (%)

Sb	Pb	As	Cu	Ag	Bi	Fe	Zn	S
90.84	8.05	0.75	0.034	0.014	0.1	0.011	0.01	<0.03

The contents of Sb, Pb in different distillation stages at 650 ℃ –750℃ are shown in Fig.12. and Fig.13.

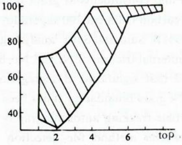

Fig.12 Sb content in different distillation stages

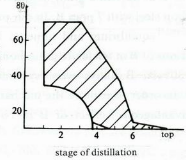

Fig.13 Pb content in different dislillation stages

It shows that antimony is concentrated on the top of column above the sixth vacuum distillating stage at 650–750℃. The content of antimony produced can reach as high as 99% and the content of lead decreases to less than 1%. But at the bottom of column the content of antimony decreases to about 30% and the content of lead increases to 30–60%. The results coincide perfectly with the right part of point C in Fig 6.

We completed the experiment of multiple stage continuous vacuum distillation of antimony containing lead at the scale of several hundred kgs a day. The type of furnace, the operating conditions and their effect have been determined. The purity of the Sb product reaches as high as 99% and the impurity of Pb is less than 0.16%. The recovery of antimony is higher than 91.8%, the power consumption is about 2.7kWh / kg, the operating temperature is below 750℃ and the vacuum is about 99Pa.

3 CONCLUSIONS

Through the study, we have now made clear the law of vacuum distillation of Pb–Sb alloys and crude antimony as well as its degree and limit of separation. This law has been proved in small (dozen gram), medium (kilogram) and large scale (hundred kilograms) experiments. The possibility of separating small amounts of lead (less than few percent) from crude antimony by vacuum distillation is thus made certain. (to be continued on page 60)