GAS-LIQUID EQUILIBRIUM OF Pb-Cd-Zn SYSTEM UNDER VACUUM①

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ABSTRACT

The gas-liquid equilibrium of Pb-Cd-Zn system under vacuum was calculated and analysed. For the alloy containing (wt.-%) Pb 1.5 Cd 0.3 Zn 98.2, the content ratio of gas to liquid $N_{Pb,g}/N_{Pb,l}$ and $N_{Cd,g}/N_{Cd,l}$ was 1.1460×10^{-2}, 11.62 when distillation temperature was 1 180K and 3.308×10^{-3}, 45.04 when distillation temperature was 773 K respectively. The molecular distillation of Pb-Cd-Zn alloy at batch process was simulated. The results showed that vacuum distillation had lower operating temperature, better separation efficiency and lower energy consumption than distillation under atomosphere pressure.

Key Words: Pb-Cd-Zn system vacuum distillation gas liquid equilibrium

1 INTRODUCTION

The main impurities in crude zinc are lead, cadmium, copper, iron and tin. Because the boiling points of iron, copper and tin are very high, we can consider that only lead, cadmium and zinc take part in the processes during distillation of crude zinc. The study of gas-liquid equilibrum of lead-cadmium-zinc system under vacuum has practical significance for the vacuum distillation of crude zinc. The gas-liquid equilibrium of Pb-Cd-Zn system under vacuum is calculated and analysed. For the alloy containing Pb 1.5wt.-% Cd 0.3wt.-% Zn 98.2wt.-%, the molecular distillation at batch process is simulated. The results show that vacuum distillation has lower operating temperature, better separation efficiency and lower energy consumption than distillation under atmosphere pressure.

2 CALCULATION BASEMENTS

The vapor pressure of each species in Pb-Cd-Zn alloy,

$$P_i = \gamma_i N_{i,l} P_i^o \quad (1)$$

where γ_i is the Raoultian activity coefficient of species i; $N_{i,l}$ is mole fraction of species i in liquid phase; P_i^o is vapor pressure of pure species i, Pa; P_i is pressure of species i in gas phase, Pa.

The vapor pressure of pure lead, cadmium and zinc[1]:

$$\lg P_{Pb}^o = -10\,130/T - 0.985\lg T + 13.285 \quad (600 \leqslant T \leqslant 2013) \quad (2)$$

$$\lg P_{Cd}^o = -5\,819/T - 1.257\lg T + 14.412 \quad (973 \leqslant T \leqslant 1\,313) \quad (3)$$

$$\lg P_{Zn}^o = -6\,620/T - 1.255\lg T + 14.465 \quad (699 \leqslant T \leqslant 1\,323) \quad (4)$$

where T is the temperature of liquid alloy, K.
For liquid Pb-Cd-Zn alloy, Kozuka[2] got the activity coefficient of each species:

$$\lg\gamma_{Pb} = 10\,470/T^{1.5}\{-(1-N_{Cd,l})^{0.41}N_{Pb,l}N_{Cd,l} + [1-(1-N_{Cd,l})^{0.59}]/0.59\} + 9\,550 \div T^{1.35}\{-(1-N_{Zn,l})^{0.52}N_{Pb,l}N_{Zn,l} + [1-(1-(N_{Zn,l})^{0.48}]/0.48\} + 372/T$$

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$$\times[-(1-N_{Zn,l})^{-0.30}N_{Cd,l}N_{Zn,l}] \quad (5)$$

$$\lg\gamma_{Cb}=10\,470/T^{1.5}\{-(1-N_{Cd,l})^{0.41}N_{Pb,l}N_{Cd,l}+[1-(1-N_{Cd,l})^{0.41}]N_{Pb,l}\}+9\,550\div T^{1.35}\{-(1-N_{Zn,l})^{-0.52}N_{Pb,l}N_{Zn,l}+372/T\times[-(1-N_{Zn,l})^{-0.30}N_{Cd,l}N_{Zn,l}]+[1-(1-N_{Zn,l})^{0.70}]/0.70\} \quad (6)$$

$$\lg\gamma_{Zn}=10\,470/T^{1.5}[-(1-N_{Cd,l})^{0.41}N_{Pb,l}N_{Cd,l}+9\,550/T^{1.35}[-(1-N_{Zn,l})^{-0.52}N_{Pb,l}N_{Zn,l}+(1-N_{Zn,l})^{0.3}+372/T\times[-(1-N_{Zn,l})^{-0.30}N_{Cd,l}N_{Zn,l}+(1-N_{Zn,l})^{0.30}N_{Pb,l}] \quad (7)$$

The total vapor pressure of gas phase

$$P=P_{Pb}+P_{Cd}+P_{Zn} \quad (8)$$

where P is total vapor pressure of gas phase, Pa.

Consuming that metal vapor is monoatomic gas[3,4,5] and is ideal gas[6], the mole fraction of species i in gas phase $N_{i,g}$ can be expressed as:

$$N_{i,g}=\frac{P_i}{P} \quad (9)$$

yielding mass fraction $X_{i,g}$

$$X_{i,g}=\frac{M_iN_{i,g}}{\sum M_iN_{i,g}} \quad (10)$$

Separation coefficient[7]:

for Cd and Zn $$\beta_{CZ}=\frac{\gamma_{Cd}P^{o}_{Cd}}{\gamma_{Zn}P^{o}_{Zn}} \quad (11)$$

for Zn and Pb $$\beta_{ZP}=\frac{\gamma_{Zn}P^{o}_{Zn}}{\gamma_{Pb}P^{o}_{Pb}} \quad (12)$$

3 RESULTS AND ANALYSES

A computer program is written in FORTRAN and compiled and executed on an IBM system SOLAR computer. The results of gas liquid equilibrium of Pb-Cd-Zn alloy under different pressure are shown in Table 1. When the total pressure becomes lower, the boiling temperature T_b (K) lower, $N_{Pb,g}$ lower and $N_{Cd,g}$ higher. consequently, it benefits the separation of Pb-Cd-Zn alloy.

Table 1 Gas liquid equilibrium of Pb-Cd-Zn alloy under different pressure

No	$N_{Pb,l}$	$N_{Cd,l}$	$N_{Zn,l}$	$P=13.33$ Pa				$P=133.3$ Pa			
				T_b	$N_{Pb,g}$	$N_{Cd,g}$	$N_{Zn,g}$	T_b	$N_{Pb,g}$	$N_{Cd,g}$	$N_{Zn,g}$
1	0.077	0.698	0.231	600	1.812×10^{-6}	0.9597	0.0403	674	8.565×10^{-6}	0.9492	0.0508
2	0.143	0.429	0.429	608	5.895×10^{-6}	0.9161	0.0839	686	2.821×10^{-5}	0.8925	0.1075
3	0.200	0.200	0.600	625	2.672×10^{-5}	0.8069	0.1931	706	$1.183\times\ ^{4}$	0.7595	0.2405
4	0.200	0.600	0.200	602	3.105×10^{-6}	0.9531	0.0469	678	1.659×10^{-5}	0.9420	0.0580
5	0.333	0.333	0.333	614	8.242×10^{-7}	0.8703	0.1297	693	4.549×10^{-5}	0.8449	0.1551
6	0.429	0.143	0.429	631	2.539×10^{-6}	0.6657	0.3343	714	1.350×10^{-5}	0.6241	0.3759
7	0.231	0.639	0.077	600	2.408×10^{-6}	0.9803	0.0197	673	1.285×10^{-5}	0.9761	0.2391
8	0.429	0.429	0.143	604	3.806×10^{-7}	0.9349	0.0651	683	2.448×10^{-5}	0.9234	0.0766
9	0.600	0.200	0.200	616	8.456×10^{-6}	0.7934	0.2066	699	5.870×10^{-5}	0.7705	0.2295
10	0.0048	0.0018	0.9934	671	4.544×10^{-4}	0.1020	0.8980	756	7.555×10^{-4}	0.0661	0.9339

Continued

$P=1333.2$ Pa				$P=13332.2$ Pa				$P=101325$ Pa			
T_b	$N_{Pb,g}$	$N_{Cd,g}$	$N_{Zn,g}$	T_b	$N_{Pb,g}$	$N_{Cd,g}$	$N_{Zn,g}$	T_b	$N_{Pb,g}$	$N_{Cd,g}$	$N_{Zn,g}$
770	4.133×10^{-5}	0.9362	0.0638	899	2.063×10^{-4}	0.9199	0.0801	1056	8.828×10^{-4}	0.9023	0.0977
785	1.344×10^{-4}	0.8634	0.1366	918	6.565×10^{-4}	0.8274	0.1276	1081	2.731×10^{-3}	0.7890	0.2110
810	5.166×10^{-4}	0.7048	0.2952	950	2.283×10^{-3}	0.6420	0.3580	1121	8.599×10^{-3}	0.5807	0.4192
775	8.819×10^{-5}	0.9287	0.0713	906	4.826×10^{-4}	0.9123	0.0877	1067	2.231×10^{-3}	0.8947	0.1052
794	2.478×10^{-4}	0.8153	0.1847	932	1.375×10^{-3}	0.7806	0.2194	1 101	6.381×10^{-3}	0.7450	0.2549
820	7.037×10^{-4}	0.5795	0.4205	964	3.707×10^{-3}	0.5314	0.4686	1 143	1.630×10^{-2}	0.4862	0.5137
770	7.229×10^{-5}	0.9708	0.0292	900	4.188×10^{-4}	0.9644	0.0356	1 059	2.040×10^{-3}	0.9576	0.0424
783	1.550×10^{-4}	0.9100	0.0900	919	1.001×10^{-3}	0.8941	0.0106	1 088	5.320×10^{-3}	0.8774	0.1225
805	3.969×10^{-4}	0.7450	0.2550	951	2.711×10^{-3}	0.7159	0.2840	1 134	1.501×10^{-2}	0.6868	0.3131
863	1.283×10^{-3}	0.0425	0.9575	1006	2.271×10^{-3}	0.0270	0.9730	1 180	3.391×10^{-2}	0.0179	0.9821

The calculation results of gas liquid equilibrium of alloy containing Pb 1. 5 wt. -%、Cd 0. 3 wt. -%、Zn 98. 2 wt. -% under different temperatures are shown in Table 2. It can be seen that when evaporation temperature decreases, β_{CZ} and $N_{Cd,g}/N_{Cd,l}$ decrease while β_{ZP} *and* $N_{Pb,g}/N_{Pb,l}$ increase. Therefore, the reflux ratio of lead column and evaporative duty of cadmium column decreased in the vacuum rectification of crude zinc. At the same time, β_{CZ} is 11 times larger than β_{ZP} under atomosphere pressure. In the vertical refining process developed by New Jersey Zinc Co. , the boiler tray and reflux tray numbers of lead column should be different from those of cadmium column.

4 MOLECULAR DISTILLATION SIMULATION OF Pb- Cd- Zn ALLOY AT BATCH PROCESS

Under molecular distillation, if the evaporation surface is very clear, the concentration of the species at evaporation surface is the same as that in solution and there is no resistance between evaporation surface and condenser surface, the evaporation rate of each species can be calculated by Langmiur model:

$$\omega_i = 4.37 \times 10^{-4} \alpha_i \gamma_{i,l} P_i^{\circ} \sqrt{Mi/T} \qquad (14)$$

Here α represents accommodation coefficient (surface evaporation coefficient), considering the fact that some of molecules reached condenser surface do not condense and return the evaportion surface, thus, generally speaking α is less than one unity. Langmiur proved that α can be taken as a unity for most liquid metals. In our calculation, α_i is considered to be unity.

The weight of starting material is 50 g per patch in distillation experiment, which contains Pb 1. 5 wt. -%, Cd 0. 3 wt. -%, Zn 98. 2 wt. -%. The evaporation area is 8. 042 cm^2. The calculated results are shown in Fig. 1～3.

It can be seen from Fig. 1 that evaporation temperature determines evaporation rate. When

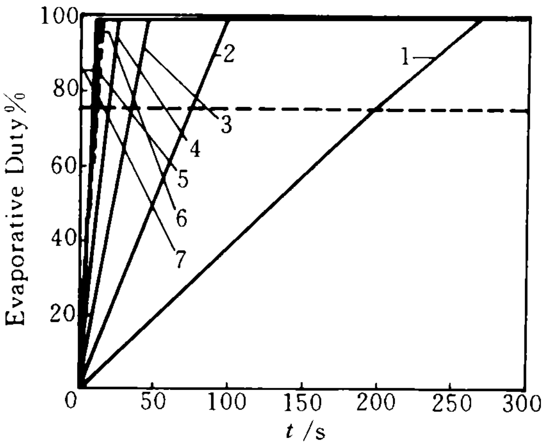

Fig. 1 The evaporation rate of alloy *vs* time at different temperature evaporation temperature

1—773 K; 2—823 K; 3—873 K; 4—923 K; 5—973 K; 6—1 073 K; 7—1 180 K

Table 2 Gas liquid equilibrium of alloy containing Pb 1. 5 wt. -%, Cd 0. 3 wt. -%, Zn 98. 2 wt. -% under different temperature

T	P	β_{ZP}	β_{CZ}	$N_{Pb,g}$	$N_{Cd,g}$	$N_{Zn,g}$	$N_{Pb,g}/N_{Pb,l}$	$N_{Cd,g}/N_{Cd,l}$
773	200	546	36. 7	8.285×10^{-6}	0. 06116	0. 9388	3.308×10^{-3}	45. 04
823	606	429	29. 3	1.066×10^{-5}	0. 04951	0. 9505	4.013×10^{-3}	35. 48
873	1 612	344	24. 0	1.343×10^{-5}	0. 04097	0. 9590	4.806×10^{-3}	28. 72
923	3 844	281	20. 1	1.658×10^{-5}	0. 03455	0. 9654	5.688×10^{-3}	23. 78
973	8 362	232	17. 2	2.015×10^{-5}	0. 02962	0. 9704	6.660×10^{-3}	20. 08
1 023	16 822	195	14. 9	2.412×10^{-5}	0. 02576	0. 9742	7.722×10^{-3}	17. 23
1 073	31 619	165	13. 1	2.851×10^{-5}	0. 02269	0. 9773	8.873×10^{-3}	15. 00
1 123	56 066	142	11. 6	3.332×10^{-5}	0. 02019	0. 9798	1.011×10^{-2}	13. 22
1 173	94 483	122	10. 4	3.854×10^{-5}	0. 01815	0. 9818	1.144×10^{-2}	11. 77
1 180	101 325	121	10. 3	3.931×10^{-5}	0. 01789	0. 9821	1.160×10^{-2}	11. 62

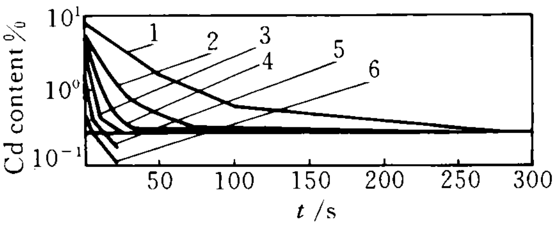

Fig. 2 Cadmium content in condensator alloy *vs* time at different evaporation temperature
1—773K; 2—823K; 3—873K; 4—923K; 5—973K; 6—1 073K; 7—1 180K

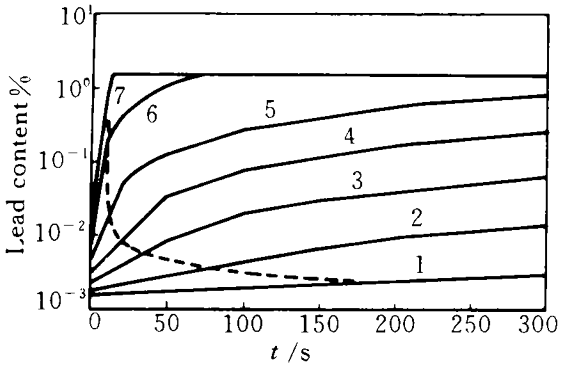

Fig. 3 Lead content in condensator alloy *vs* time at different evaporation temperature
1—773K; 2—823K; 3—873K; 4—923K; 5—973K; 6—1 073K; 7—1 180K

evaporation temperature increases, evaporation rate increases evidently. From Fig. 2, The cadmium content in condensate decreases with the increasement of time. The evaporation of cadmium can be seen to complete quickly. Therefore, there is the separation of lead and zinc in lead column and the separation of zinc and cadmium in cadmium column during the rectification of crude zinc.

As shown in Fig. 3, when the evaporative duty is equal to 75% (expressed in dashed line), the lead content in evaporating alloy increases quickly with the increasement of temperature. When evaporation temperature is 773 K and 1 180 K, the lead content of condensate is 0. 002 3%, 0. 008 1% and 0. 012% respectively. At 773 K, the composition of lead in condensate in up to the composition standard of special number 1 refined zinc. At this time, the evaporating alloy can directly enter cadmium column without refluxing in lead column. If the evaporation rate of zinc is equal to 100%, the content of lead in condensate is only 0. 00275%, which is still up to the composition standard of special number 1 refined zinc. Therfore, vacuum refining under low temperature befits in improving product quality, decreasing reflux ratio and energy consumption.

5 SUMMARY

The gas-liquid equilibrium of Pb-Cd-Zn system under vacuum is calculated and analysed. For the alloy containing Pb 1. 5wt.-% Cd 0. 3wt.-% Zn 98. 2wt.-%, the content ratio of gas phase to liquid phase $X_{Pb,g}/X_{Pb,l}$ and $X_{Cd,g}/X_{Cd,l}$ are 1.160×10^{-2}, 11. 62 when distillation temperature is 1 180 K and 3.308×10^{-3}, 45. 04 when distillation temperature 773K respectively. The molecular distillation of Pb-Cd-Zn alloy at batch process is simulated. The results show that vacuum distillation has lower operating temperature, better separation efficiency and lower energy consumption than distillation under atmosphere pressure.

REFERENCES

1 Kubaschewski, O; Alcock, C B. Metallurgical Theremochemistry, 1979.
2 Kozuka, Z; Moriyama, J. J Min Metall, Inst Japan, 1962, 80, 916, 887—892.
3 Nesmeyanov, A N. Vapour Pressure of the Chemical Elements. Elsevier Publishing Company. 1963.
4 Wu P C S, Metall Trans., 1980 11A, 123—126.
5 Zhang, Shulin. Physical Fundamental of Vacuum Technology. Shenyang: Press of Northeastern University, 1988.
6 Dai, Yongnian. Separation of Various Elements in Crude Metal of Alloy During Vacuum Distillation. In: Sohn H Y, eds, Metallurgical Processes for the Year 2000 and Beyond, 335—346, Las Vegas, Nevada, February 27—March 3, 1989.
7 Knacke, O; Stranski, I N. Prog Met Phys, 1956, 6: 181—235.