EQUILIBRIUM MODELS AND PARAMETERS OPTIMIZATION

FOR EXTRACTION PROCESS OF BISMUTH

AND ANTIMONY WITH N1923[1]

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ABSTRACT

The solvent extraction process for removal of bismuth and antimony from copper electrolyte by primary amine N1923 — additive(iso-octanol) — kerosene has been studied. The extraction e-quilibrium models are created on the basis of experimental equilibrium data. An objective function for optimization is created which can satisfy different demands. A variety of optimized technological parameters combination of the process are determined and one of them was veified with laboratory extraction cascade experiments. It indicates that the experimental values are nearly consistent with the calculated values.

Key words: solvent extraction   N1923   bismuth and antimony   copper electrolyte   equilibrium model   parameters optimization

1   INTRODUCTION

The solvent extraction method is obviously superior to those current processes, which have been used to remove bismuth and antimony from copper electrolyte[1]. The primary amine N1923 extraction system was used to remove bismuth and antimony from copper electrolyte in this study. Because of the complexity of the treated system and a lot of influence factors of extraction and removal, a great many of experimental work is needed to provide a group of satisfying technological parameters of the process and control factors. However, it could not even be known whether those parameters are the best ones.

By creating the extraction equilibrium models, simulating the cascade extraction processes and optimizing the technological method, the authors had successfully studied the extraction techniques[2,3]; and computer was used to treat some necessary experimental values gained during test to make them linear regression while mathematical model was obtained, and then the optimum calculation was carried out.
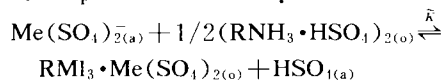
2   EXTRACTION EQUILIBRIUM AND DISTRIBUTION MODEL

2.1   *Extraction Equilibrium*

The N1923-iso-octanol-kerosene/bismuth-antimony-copper electrolyte system combines with complex aqueous phase and organic phase. In the aqueous phase, there are HSO_4, SO_4^2, H^+, OH, Cl, metal-ions(Cu^2, Bi^3, Sb^3) and complexions which formed with metal-ions (Bi, Sb) and SO_4^2.

Their equilibrium relations are very complex because the concentrations of different constituents can restrict and influence to each other and the concentrations of HSO_4, SO_4^2, metal-ions and complexions could affect the N1923 extracting metal

directly[4]. In the organic phase, N1923 treated to pre-equilibrium by 2 mol/L H_2SO_4, has three impossible existences such as: $RNH_2 \cdot RNH_3 HSO_4$ and $(RNH_3 \cdot HSO_4)_2$. During the concentration range of N1923 in this study, N1923 exists mainly as the form of a dipolymer[5]. It is well known that the extraction of N1923 to metal-ion belongs to the ion associated extraction. The extraction reaction could be expressed as follows:

$$Me(SO_4)_{2(a)}^{-} + 1/2(RNH_3 \cdot HSO_4)_{2(o)} \overset{\widetilde{K}}{\rightleftharpoons}$$

$$RMI_3 \cdot Me(SO_4)_{2(o)} + HSO_{4(a)}$$

Its apparent equilibrium constant is

$$\widetilde{K} = \frac{[RNH_3 \cdot Me(SO_4)_{2(o)}] \cdot [HSO_{4(a)}^{-}]}{[Me(SO_4)_{2(a)}^{-}] \cdot [(RNH_3 \cdot HSO_4)_{2(o)}]^{1/2}} \quad (1)$$

The distribution coefficient of metal ion is

$$D = \frac{\widetilde{K}[RNH_3 \cdot HSO_4)_{2(o)}]^{1/2}}{[HSO_{4(a)}^{-}]} \quad (2)$$

Because $\widetilde{K} = e^{(-\Delta H^\circ/RT + c)}$ (3)

where H is the normal enthalpy of extraction reaction.

Because there is a little of Bi and Sb in the copper electrolyte and $y_{Me} \ll RCON$, there is

$$[(RNH_3 \cdot HSO_4)_{2(o)}] = RCON - y_{Me}$$
$$\approx RCON \quad (4)$$

where $RCON$ is the initial concentration of N1923, y_{Me} is the metal — ionconcentration in organic phase

Due to the fact that y_{Me} is small, HSO_4^{-} in organic phase is very little replaced by metal ions and $[HSO_4^{-}]$ in aqueous phase closes to a constant.

Substituting equations (3) and (4) into (2), then there is

$$D = a_1 e^{(-(a_2/RT) + a_3)} RCON^{a_4} \quad (5)$$

where a_1, a_2, a_3 and a_4 are model parameters

As shown in equation (5), the distribution coefficient corresponds with extracting temperature and $RCON$ of N1923 in the organic phase.

2.2 Agents, Method of Extraction Equilibrium Experiment and Equilibrium Parameters for Extracting Bismuth and Antimony

The primary amine N1923 is chemically pure, which has been transmitted into $(RNH_3 H_2SO_4)_2$ by 2mol/L H_2SO_4 in advance to keep the acidity of copper electrolyte stable during extraction process. Sulfonated kerosene is used as a dilu-

ent and 5% of iso-octanol is added into the organic phase to improve the effect of extraction.

The extraction experiment carried out in a thermostat, temperature was controlled in a range of ± 1 C to the assigned temperature. The 20 mL centrifugal tubes were used when the 10 min oscillating was last on an oscillating agitator.

After phases were separated by oscillating, the metal ion concentrations in aqueous phase could be measured directly with flame atom absorption method, and the contents of organic phase could be counted from mass balance.

In this study, the extraction equilibrium distribution coefficients of bismuth and antimony had been measured under the conditions of extraction temperature $301 \sim 328$ K and concentrations of extractant in a range of $5\% \sim 20\%$ (Table 1).

Table 1　Extraction equilibrium distribution coefficients

Temperature / K	Concentration of extractant (%)	Distribution coefficient	
		Bi	Sb
301	5	3.205	0.3084
301	10	5.624	0.3883
301	15	7.775	0.4704
301	20	10.30	0.5075
308	5	2.867	0.2418
308	10	5.077	0.3876
308	15	7.068	0.4285
308	20	9.642	0.5015
318	5	2.448	0.2108
318	10	4.399	0.3428
318	15	6.356	0.4085
318	20	7.094	0.4438
328	5	2.359	0.1609
328	10	3.939	0.2211
328	15	5.894	0.2771
328	20	6.659	0.4096

Organic phase: N1923— 5% iso-octanol-kerosene

Aqueous phase: copper electrolyte, O/A = 1

2.3 Extraction Equilibrium Distribution Model of Bi and Sb

It is very necessary to create the extraction equilibrium model of Bi and Sb so that the relation

between the distribution coefficients and the control facts could be defined accurately. According to the experimental data, the model should reflect the quantitative relations among distributing coefficients, concentrations of N1923 in organic phase and extraction temperatures.

On the basis of experiments and use of Marquardt method[6] regression with the help of computer the distribution model of Bi and Sb was caught out as follows:

$$D_{Bi} = 0.4\,032e^{(-0.2578+1449/T)}$$
$$\times RCON^{0.8255} \qquad (6)$$

Average relative error 3.3%

$$D_{Sb} = 0.07\,408e^{(-1.632+1345/T)}$$
$$\times RCON^{0.5179} \qquad (7)$$

Average relative error 9.5%

The errors of the two models, which were smaller than 10%, could reflect the results of the experiment accurately and satisfy the needs of process study. The error of Bi was smaller and the one of Sb was relatively bigger, which is due to the more complex state of Sb in aqueous phase.

3　OPTIMIZATION PARAMETERS OF EXTRACTION PROCESS FOR REMOVAL OF Bi AND Sb

3.1　*Process Analysis*

The central task of extraction process research is to look for the quantitative relations among the purity of products, recoveries and process parameters, and determine the process conditions for treating concrete subject.

A process flow should be generally economic, practical and safe. The characteristic of the subject system, the needs of products and the limits of operation sequences should be thoroughly analysed when the flow was combined. During the extract circulation, the consumption and grades of extraction agent reflected economic parameter, and temperature and relative flow rate were limited by the chemical characteristics of elements, needs of product and operation sequences.

Based on those motioned above, the extract temperature was elected to be 55 C so that the presented processing could treat the fact copper elec-

trolyte directly. The multistage counter-current extraction method was used to remove bismuth and antimony in this study.

3.2　*Optimization of Process Parameters*

During optimization counting, the consumption of organic phase (It is indicated by $RCON$ and ROA: the former is the concentration of N1923 and the later is the flow ratio of two phases) and N (extraction stage) are mainly considered to be as small as possible, and $y_{Bi(1)}$ (export concentration of Bi in organic phase) to be as high as possible. Under the condition that $X_{Bi(N)}$ (export concentration of Bi in aqueous phase) was sure to be lower than 0.01 g/L, the object function was created as

$$min.J = (RCON \cdot ROA)^p \cdot N^q / y_{Bi(1)}^r \qquad (8)$$

where $RCON$, ROA and N need to be optimizing parameters and $p + q + r = 1$, $p, q, r \in [0,1]$.

The objective function has a special form when $p = r = 0$ and $q = 1$, that is

$$min.J = ABS(0.01 - x_{Bi(N)}) \cdot N \qquad (9)$$

Besides extraction stages, the equation considered that $x_{Bi}(N)$ should be close to 0.01 g/L as possible, so the percentage extraction of Bi can be sure and $x_{Bi(N)}$ will not be too small in order to save extraction agent.

A complex method was used in numerical optimization, and the counted results was shown in Table 2.

Table 2　Different Optimization Results

p	q	r	ROA	$RCON$ (%)	N	$y_{Bi(N)}$ /g·L^{-1}
1/3	1/3	1/3	0.205	20	9	3.317
1	0	0	0.205	18.9	10	3.320
0	1	0	0.738	13.8	3	0.922
0	0	1	0.198	20	10	3.434
0.5	0	0.5	0.197	20	10	3.448
0.5	0.5	0	0.723	5	6	0.941
0	0.5	0.5	0.300	20	5	2.267

Organic phase: N1923—5% iso—octanol—kerosene;

Aqueous phase: copper electrolyte;

Temperature: 55 C

Weighting factor values of p, q and r were changing with the different considerable focal

points of the objective function. When decreasing organic phase consumption and operating costs are mainly considered, a bigger p value may be allowed; when decreasing extraction stages and cost of equipment are mainly considered, a bigger q value may be allowed. When retrieving metal bismuth is mainly considered, bigger r value may be allowed. Under the different conditions with different weighting factors, there are different combinations of optimized parameters(Table 2).

3.3 *Cascade Experiment*

In order to provided the process parameters, which were according to the distribution equilibrium model, simulated with the cascade process and decided by optimization counting, one combination of optimization parameters ($p = r = 0$, $q = 1$) selected from Table 2 was used to do an extraction cascade simulation experiment at the laboratory condition. The results of cascade experiment and counting at the same condition are shown in Table 3 together. It could be seen from Table 3 that three stages counter-current extraction could remove Bi completely and Sb partly. The concentration of Bi in extraction raffinate was only 0. 00 535 g/L, which had satisfied the needs of recovery ratio of 99%.

Comparing experimental values and calculative values of concentrations of every constituent, it could be found that higher concentrations led to the experimental ones agree with the calculative ones; on a contrary, lower concentrations led to some errors between the experimental ones and calculative ones. However, the orders of magnitude of the concentrations were the same.

The errors had two sources : one takes place in the operating process, which was due to the two phases mixing with each other; the other one comes from the distribution model itself.

Table 3　Cascade Experimental Results

($p = r = 0$, $q = 1$)

extraction stages	1 st stage		2nd stage		3rd stage	
	A	O	A	O	A	O
Bi /g·L⁻¹	0. 174 (0. 164)	0. 888 (0. 885)	0. 053 (0. 039)	0. 288 (0. 211)	0. 0054 (0. 0079)	0. 064 (0. 042)
Sb /g·L⁻¹	0. 400 (0. 401)	0. 137 (0. 130)	0. 362 (0. 383)	0. 130 (0. 124)	0. 304 (0. 309)	0. 078 (0. 100)

Organic phase: 13. 8%N1923－5%iso-octanol-kerosene;
Aqueous phase: copper electrolyte; O/A＝0. 74, T ＝55 C;
Values between parenthesis are calculative values

4　CONCLUSIONS

This study has created a distribution model of extraction removal of Bi and Sb by using N1923-5%iso-octanol-kerosene from copper electrolyte, which can be expressed as follows:

$$D_{Bi} = 0. 1032e^{(-0.2578 + 1119/T)} \cdot RCON^{0. 8255}$$
$$D_{Sb} = 0. 07408e^{(1. 632 - 1315/T)} \cdot RCON^{0. 5179}$$

Based on the above equations, the optimization calculations for extraction removal of bismuth and antimony were carried out on computer, and several combinations of process parameters with a wide range to apply had been created up; then one of them was verified with laboratory extraction cascade experiments. The results were essentially consistent with the calculative ones.

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