

Computer Simulation of the Distribution Behavior of Minor Elements in the Copper Smelting Process

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Abstract

Computer simulation was used for thermodynamic evaluation of the distribution behavior of minor elements in group VA of the periodic table (As, Sb and Bi) in the smelting stage of the copper smelting process based on thermodynamic data and operating data of the Mitsubishi process.

The fractional distributions between the gas, slag and matte phases considered as the degree of vapor saturation are as follows: 53.8, 27.2 and 19% for As, 23.6, 56.6 and 19.8% for Sb, and 91.3, 1.1 and 7.6% for Bi, respectively. Arsenic is mostly distributed to the gas and slag phases. It is effectively eliminated by volatilizing and slagging. Antimony is mainly in the slag phase, which is suitably removed by slagging. Bismuth is easily vaporized to the gas phase. The degree of vapor saturation has a large effect on the distribution behaviors of the three elements between the three phases. The amount of a minor element in the charge has an effect on the distribution of As but no effect on the distributions of Sb and Bi. Increasing matte grade and temperature results in significant change of distributions for As and Sb. The change in the distribution ratio between slag and matte phases also considerably affects the distributions of As and Sb. The distribution behavior of Bi is not significantly changed by the change in matte grade, temperature and distribution ratio.

Keywords: distribution behavior, copper smelting, arsenic, antimony, bismuth, slag, matte.

1. Introduction

The elimination of some minor elements in group VA of the periodic table (As, Sb and Bi) in the smelting stage of the copper smelting process are of importance before transferring to converting and electro-refining processes because of the strong affinity of these minor elements with crude copper, which causes difficulty in refining in the converting stage. Ajima, et al.⁽¹⁾ reported the difficulties in the elimination of the impurities at the copper smelter and refinery and suggested that it should be necessary to investigate the most favorable operation for the elimination of the impurities from the system. The distribution behaviors of these elements in the gas, slag and matte phases have to be clarified in order to attain the optimum condition during the copper smelting

process for their elimination. In this study, the fractional distribution behavior of these elements in the gas, slag and matte phases was evaluated based on thermodynamic data and operating data of the Mitsubishi process, and varying the amount of a minor element in the charge, matte grade and temperature.

2. Procedure for Evaluation

2.1. Methodology

The method for thermodynamic evaluation of the fractional distributions of minor elements for the copper smelting process proposed by Itagaki and Yazawa was used in this calculation. The weight balance of a minor element at any step of calculation is shown in Eq. (1). The details are explained in a separate paper⁽²⁾.

$$\begin{aligned}
W_1 &= (X)_1 + (A_0 L_X^{s/m} + B_0) (\{ \% \}_1 - \{ \% \}_0) / 100 + \{ \% \}_1 (\Delta A L_X^{s/m} + \Delta B) / 100 \\
W_2 &= (X)_2 + (A_0 L_X^{s/m} + B_0) (\{ \% \}_2 - \{ \% \}_1) / 100 + \{ \% \}_2 (\Delta A L_X^{s/m} + \Delta B) / 100 \\
&\vdots \\
W_n &= (X)_n + (A_0 L_X^{s/m} + B_0) (\{ \% \}_n - \{ \% \}_{n-1}) / 100 + \{ \% \}_n (\Delta A L_X^{s/m} + \Delta B) / 100
\end{aligned} \quad (1)$$

Here W_n is the weight of X in the charge at the n^{th} step. $\{ \% \}_n$ is the content of X in the matte bath. $(X)_n$ is the weight of X discharged from the furnace during the n^{th} part that can be calculated by the use of Eq. (2), which was derived on the basis of the law for the ideal gas and of the assumption that $X_\alpha(g)$, $XS(g)$ and $XO(g)$ are

predominant among the gas species of X and its compounds. A_0 and B_0 are the amounts of charges injected into the slag and matte phases, respectively. The discharged slag and matte from the furnace in a given period are designated by ΔA and ΔB .

$$(X)_i = SV_i \{ \alpha M_X K_1 a_{X,i}^\alpha + M_X a_{X,i} (K_2 p_{S_2}^{1/2} + K_3 p_{O_2}^{1/2}) \} / RT \quad (2)$$

Here V_i is the amount of gas, R the gas constant, M_X molar quantity of X. K_1 , K_2 and K_3 are the equilibrium constants for the reactions of $\alpha X(l) = X_\alpha(g)$, $X(l) + \frac{1}{2} S_2(g) = XS(g)$ and $X(l) + \frac{1}{2} O_2(g) = XO(g)$, respectively. $a_{X,i}$ is the activity of X in the matte. p_{S_2} and p_{O_2} are the sulfur and oxygen potentials, respectively. S denotes the degree of vapor saturation with X, being intimately dependent on the state of the contact between the gas and matte phases, as well as the vaporization velocity of X in the matte phase.

Thermodynamic quantities of equilibrium constants of the reactions, the activity coefficients of minor elements and the activities of the components in matte and slag phases are necessary in this calculation. The free energies of formation of X and gaseous compounds are listed in Table 1. The activity coefficients of minor elements determined by Itagaki and Yazawa⁽²⁾, and the activities of various components determined by Yazawa⁽³⁾ at 1573 K, $p_{SO_2} = 0.1$ atm are shown in Fig. 1 and Fig. 2, respectively. These data were used in this evaluation.

2.2. Thermodynamic data

Table 1. Free energies of formation and gaseous compounds

Reaction	$\Delta G^\circ_T / \text{cal.mol}^{-1}$	References
As(s) = As(g)	71830 - 32.30 T	3
As(s) = 1/2 As ₂ (g)	22310 - 18.82 T	3
As(s) = 1/4 As ₄ (g)	8990 - 10.18 T	3
As(s) = As(l)	5650 - 5.19 T	4
Sb(l) = Sb(g)	56820 - 24.56 T	3
Sb(l) = 1/2 Sb ₂ (g)	20750 - 11.20 T	3
Bi(l) = Bi(g)	45860 - 23.86 T	3
Bi(l) = 1/2 Bi ₂ (g)	21670 - 11.17 T	3
1/2 As ₂ (g) + 1/2 S ₂ (g) = AsS(g)	8730 - 1.95 T	1
1/2 Sb ₂ (g) + 1/2 S ₂ (g) = SbS(g)	3310 - 1.46 T	1
1/2 Bi ₂ (g) + 1/2 S ₂ (g) = BiS(g)	-1090 - 1.75 T	1
1/2 As ₂ (g) + 1/2 O ₂ (g) = AsO(g)	-6990 - 3.19 T	1
1/2 Sb ₂ (g) + 1/2 O ₂ (g) = SbO(g)	19710 - 2.37 T	1
1/2 Bi ₂ (g) + 1/2 O ₂ (g) = BiO(g)	1830 - 1.87 T	1

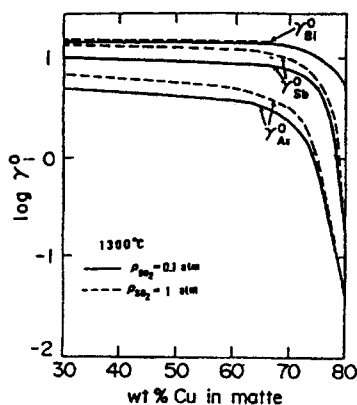


Fig. 1 Relation between matte grade and Raoultian activity coefficients of arsenic, antimony and bismuth in

the matte phase at 1573 K⁽²⁾.

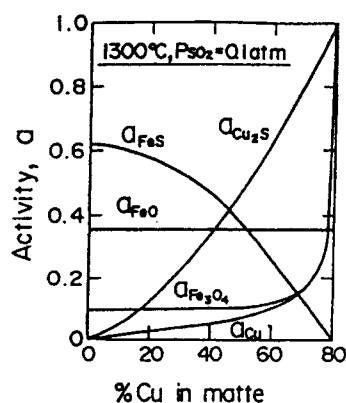


Fig. 2 Relation between matte grade and activities of various components at 1573 K and $p_{SO_2} = 0.1 \text{ atm}$ ⁽³⁾.

2.3. Operating data

The compositions of concentrate, matte, Cl slag and C slag^(6, 7) are shown in Table 2. The operating data of the smelting furnace of the Mitsubishi process^(6, 7) are given in Table 3. In this evaluation, the degree of vapor

saturation in the Mitsubishi process is expected at 1 and the partial pressure of SO_2 at 0.2. The distribution ratio of As, Sb and Bi between slag and matte phases is 1, 2 and 0.1, respectively. The temperature in the smelting furnace of the Mitsubishi process is 1503 K.

Table 2. Analytical compositions of charge and products in the Mitsubishi process.

	%Cu	%Fe	%S	%SiO ₂	%CaO	%Al ₂ O ₃
Concentrate	32.32	22.81	28.00	7.50	0.83	1.68
Matte	68.13	7.97	22.11			
Cl slag	0.67	39.88	0.41	37.33	5.43	5.09
C slag	14.02	40.57	0.21	0.27	17.70	0.21

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Table 3. Operating data of the smelting furnace of the Mitsubishi process.

Input (t / hr)

Concentrate	97.9
Scrap	4.4
Silica sand	14.1
C slag	10.6

Output (t / hr)

Matte	50.6
Slag	61.3
Lance Air (Nm ³ / hr)	
Air	13,062
O ₂ -enriched Air	20,637 (80%O ₂)

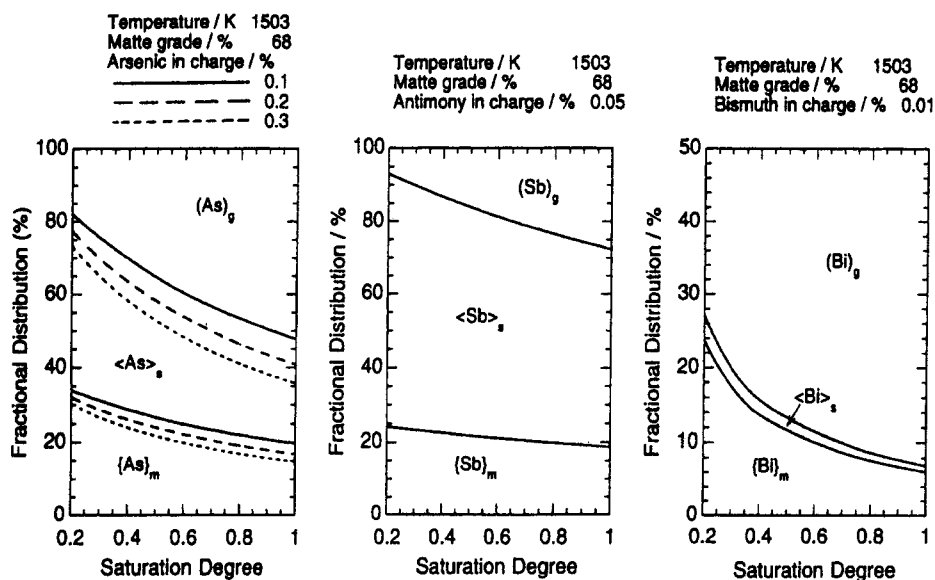


Fig. 3 Distributions of As, Sb and Bi in the smelting stage and degree of vapor saturation at $p_{\text{SO}_2} = 0.2 \text{ atm.}$, temperature = 1503 K.

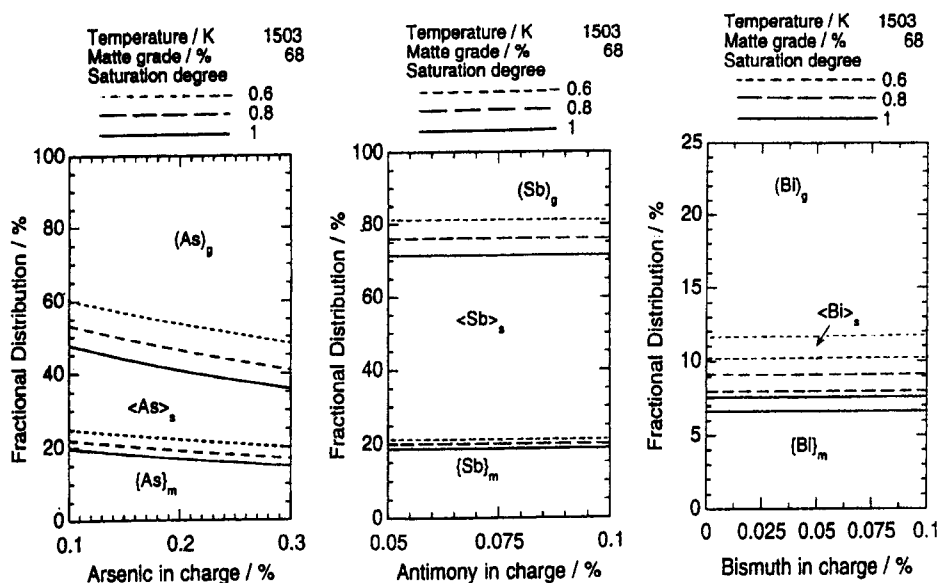


Fig. 4 Distributions of As, Sb and Bi in the smelting stage and the amount of a minor element in the charge at $p_{\text{SO}_2} = 0.2 \text{ atm.}$, temperature = 1503 K.

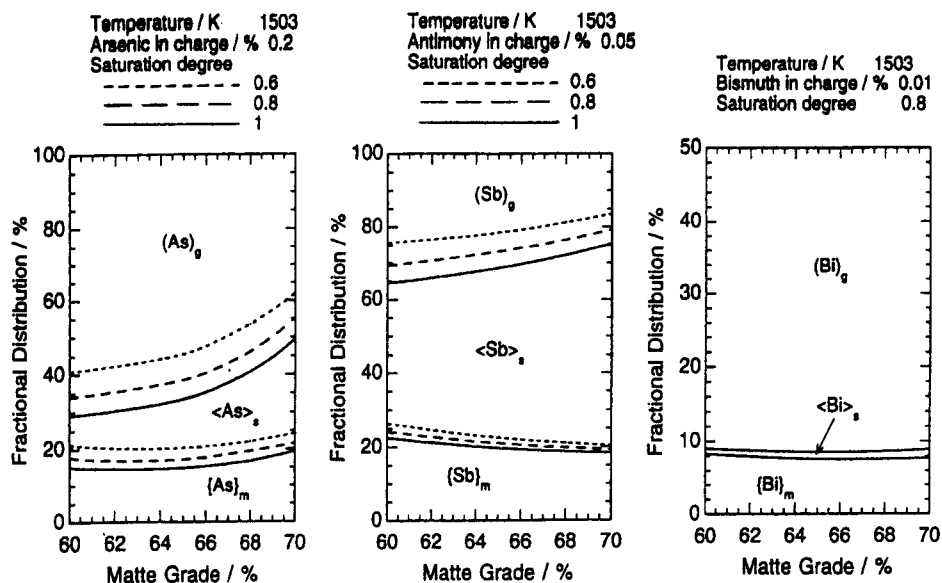


Fig. 5 Distributions of As, Sb and Bi in the smelting stage and matte grade at $p_{\text{SO}_2} = 0.2$ atm., temperature = 1503 K.

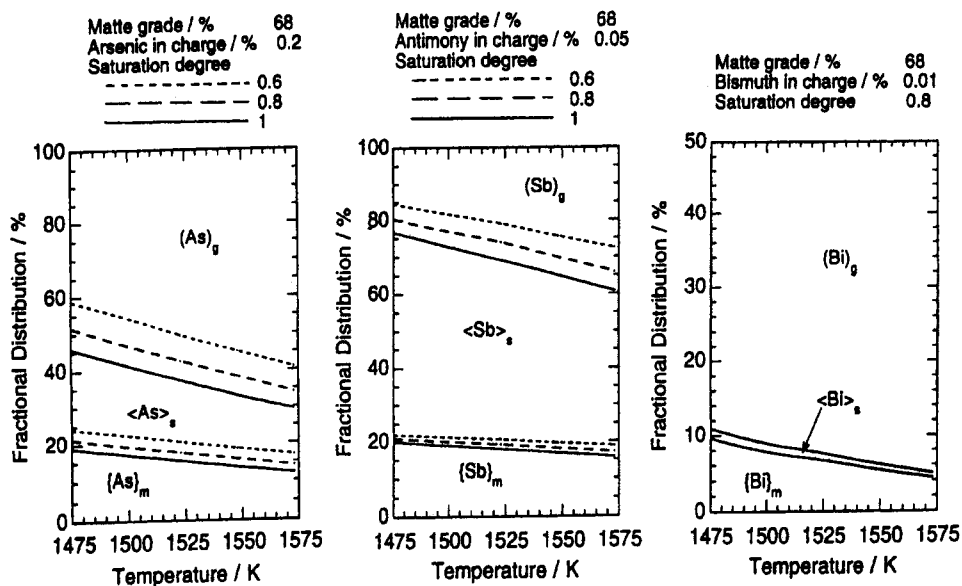


Fig. 6 Distributions of As, Sb and Bi in the smelting stage and temperature at $p_{\text{SO}_2} = 0.2$ atm.

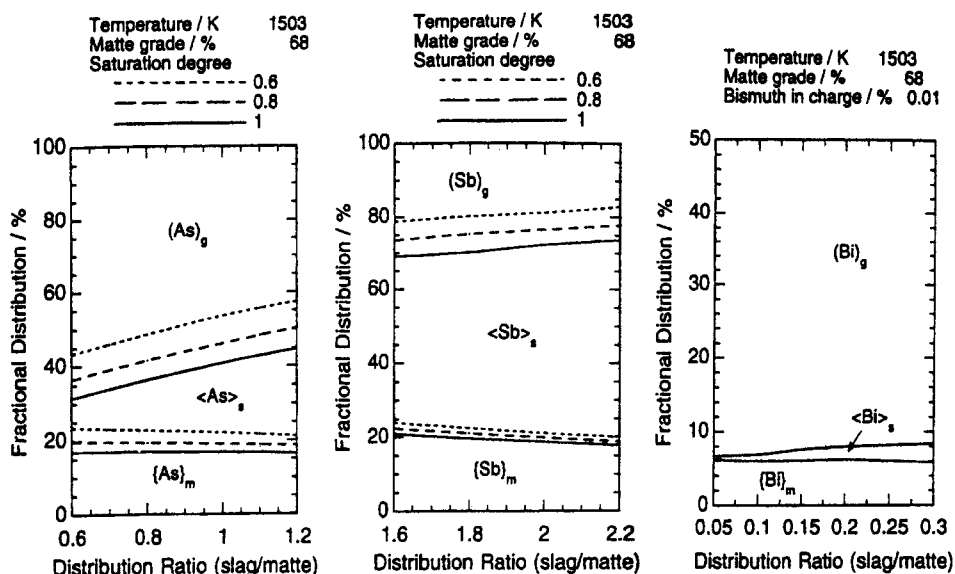


Fig. 7 Distributions of As, Sb and Bi in the smelting stage and the distribution ratio of a minor element between slag and matte phases at $p_{\text{SO}_2} = 0.2 \text{ atm.}$, temperature = 1503 K.

4. Conclusions

The fractional distributions of VA elements (As, Sb and Bi) between gas, slag and matte phases in the smelting stage of the copper smelting process were evaluated based on thermodynamic data and operating data of the Mitsubishi process using the method proposed by Itagaki and Yazawa.

The fractional distribution of As between the gas, slag and matte phases is about 53.8, 27.2 and 19%, respectively at the degree of vapor saturation of 1.0. It is effective to eliminate it by volatilizing and slagging. An increase in the matte grade results in a great decrease in the gas phase but comparative increase in the slag phase. Temperature has a large effect on an increase in gas phase and a decrease in slag phase, but it has small effect on a decrease in matte phase. $L_{\text{As}}^{s/m}$ results mostly in the distribution in the gas and slag phases.

Antimony is mostly distributed to slag phase. At 1.0 degree of vapor saturation the fractional distribution between the gas, slag and matte phases is 23.6, 56.6 and 19.8%, respectively. An increase in the amount of Sb in the charge has no effect on the fractional

distribution. An increase in the matte grade results in a significant decrease in the gas phase and an increase in the slag phase but a slight decrease in the matte phase. Increasing temperature causes mostly Sb from the slag phase to volatilize to the gas phase, but Sb in matte phase to very slightly decrease. The change in $L_X^{s/m}$ results in the significant change in the distribution between the gas and slag phases for As and Sb.

Bismuth is mostly vaporized to gas phase due to the high activity coefficient in matte phase and the low distribution ratio between slag and matte phases. The fractional distributions in the gas, slag and matte phases at the vapor saturation degree of 1.0 are about 91.3, 1.1 and 7.6%, respectively. Increasing the amount of Bi in the charge has no effect on the fractional distribution which is the same as that of As. The amount of Bi in the slag phase is very low and almost constant even though matte grade or temperature is increased. The results of increasing matte grade and temperature are not significant. $L_X^{s/m}$ has a small effect on the distribution between the gas and slag phases.

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6. References

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