BEHAVIORS OF ACCESSORY ELEMENTS IN COPPER PYROMETALLURGY①

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ABSTRACT By a mathematical model of distribution behaviors of Ni, Co, Sn, Pb, Zn, As, Sb, Bi, Au and Ag in copper smelting process, accessory-element behavior was studied for two types of slag, fayalite and ferrite, and two levels of oxidation. The model can predict any set of controllable process parameters, such as feed composition, smelting temperature, degree of oxygen enrichment and volume of oxygen enriched air, in copper flash smelting, Mitsubishi and Noranda processes. The predictions by the present computer model were compared with the known commercial data from Guixi Smelter in China, Horne Smelter in Canada and Naoshima Smelter in Japan. The agreement between the computer predictions and the commercial data was excellent, therefore the present computer model can be used to monitor and optimize the actual industrial operations of copper smelting. The effects of oxygen enrichment, matte grade, smelting temperature and types of slag, on accessory-element behavior were elucidated.

Key words mathematical model copper smelting accessory element distribution behavior

1 INTRODUCTION

During the smelting of copper concentrates, it is important to eliminate deleterious minor elements such as As, Sb and Bi, while recover valuable elements such as Au and Ag to copper. Basic studies on the behaviors of As, Sb and Bi in the Noranda process, Pierce-Smith converting and flash smelting process have been reported. Itagaki[1] evaluated the behaviors of the fifth group elements in copper smelting process. Chaubal[2] developed a model describing minor-element (As, Sb and Bi) behavior during oxidation of chalcopyrite concentrate or copper matte in flash smelting furnace and flash converting furnace.

2 COMPUTER MODEL

The authors have already developed a computer model of the distribution behaviors of accessory elements in the copper smelting process[3, 4]. 21 elements and 74 compounds were considered in the model.

The 53 reactions can be represented in terms of matrices as

$$(V_{j,i})(A_{i,k}) = (B_{j,k})$$

$$(i = 1 \text{ to } 21,\ j = 1 \text{ to } 53,\ k = 1 \text{ to } 21) \quad (1)$$

The matrix $(V_{j,i})$ can be obtained from the following calculation:

$$(V_{j,i}) = (U_{k,i})(B_{j,k}) \quad (2)$$

where $(U_{k,i})$ denotes the invert matrix of $(A_{i,k})$ which has to be calculable.

The equilibrium constants, k_j, of the reactions that produce dependent components from independent components are given as

$$k_j = \exp[-(\Delta G_j^{\ominus} - \sum_i V_{ji} \cdot \Delta G_i^{\ominus})/RT] \quad (3)$$

The molar amounts of independent and dependent components in equilibrium state are related to each other by Eqn. (4)

$$k_j = (X_j \cdot \gamma_j / Z_{m(j)}) \prod_i (\gamma_i \cdot X_i / Z_{m(i)})^{V_{ji}} \quad (4)$$

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If ideality is assumed for the gas phase, the value of the total pressure in the system can be used for the values of γ_i and γ_j of the components which belong to the gas phase. The total molar amount of the mth phase is denoted by Z_m, and $Z_{m(i)}$ and $Z_{m(j)}$ denote the molar amounts of the phases containing the ith independent and the jth dependent components, respectively.

As a closed system is considered, then

$$Q_k = \sum_i A_{i,k} \cdot X_i + \sum_j B_{j,k} \cdot X_j \qquad (5)$$

Z_m is expressed in terms of X_i and Y_j as

$$Z_m = \sum_{i(m)} X_i + \sum_{j(m)} X_j \qquad (6)$$

In Eqn. (6), $i(m)$ means that the summation must be performed only when the ith independent component belongs to the mth phase, and similarly, $j(m)$ means that the summation must be performed only when the jth dependent component belongs to the mth phase.

By solving these equations, the molar amount of each component in the equilibrium state can be obtained. This calculation is carried out using the Newton-Raphson method to solve a set of 74 simultaneous equations.

For the matte-making process, the general equations[5] related to the data for suspension-free phases which have entrainment of one phase in another are

$$[M]^{Ap}_{Mt} = \{[M]_{Mt} \cdot (100 - S^{Mt}_{Sl}) + [M]_{Sl} \cdot S^{Mt}_{Sl}\}/100 \qquad (7)$$

$$[M]^{Ap}_{Sl} = \{[M]_{Sl} \cdot (100 - S^{SL}_{Mt}) + [M]_{Mt} \cdot S^{Sl}_{Mt}\}/100 \qquad (8)$$

Using these suspension indices, the apparent composition of each melting phase can be calculated from the thermodynamically calculated composition for suspension-free phases.

The model can not only predict the effects of process factors such as composition of charges, volume of oxygen-enriched air, smelting temperature, volume fraction of O_2 in oxygen-enriched air, Fe/SiO_2 and matte grade upon the distribution behaviors of accessory elements (Ni, Co, Sn, Pb, Zn, As, Sb, Bi, Au, Ag) in copper smelting, but also simulate the following copper smelting process: copper flash process, Noranda matte-making process, Noranda copper-making process, Mitsubishi continuous process etc. By using this model, the distribution behaviors of accessory element were studied for two types of slag, fayalite and ferrite, and the directive function of thermodynamic analysis in the actual industrial operation was discussed.

3 COMPUTER PREDICTION AND COMMERCIAL DATA

Comparison of the prediction with the commercial data of flash smelting process at Guixi Smelter[4] is listed in Table 1. Calculated and observed[5] distribution coefficients for Noranda matte-making process and Noranda copper-making process are listed in Table 2. The Mitsubishi process produces copper continuously in three interconnected furnaces. Smelting and slag cleaning furnaces are simulated, respectively. Comparison of the prediction with the commercial data[6] of Mitsubishi process is listed in Table 3. The above tables show that the agreement between the computer predictions and the commercial data is excellent, therefore the present computer model can be used to monitor and optimize the practical operations of copper smelting.

Table 1 Comparison of prediction with commercial data of flash smelting process at Guixi Smelter

Composition/%	Cu	S	Fe	SiO_2	Pb	Zn	As	Bi	Sb	Co	Au*	Ag*
Charge	21.22	29.11	26.34	12.24	0.13	0.33	0.12	0.041	0.092	0.01	6.59	77
Industrial matte	51.94	22.63	–	0.24	0.24	0.35	0.10	0.061	0.083	0.016	17.1	182
Predicted matte	51.47	20.97	22.65	0.64	0.23	0.36	0.06	0.014	0.086	0.013	17.3	190
Industrial slag	1.13	0.57	39.08	32.94	0.037	0.46	0.12	< 0.005	0.11	0.003	0.22	8.3
Predicted slag	0.90	0.40	45.15	31.43	0.027	0.41	0.09	< 0.005	0.12	0.003	0.17	1.9

Note: * —Au, Ag 10^{-6}kg/kg

Table 2 Calculated and observed distribution coefficients for Noranda process at Horne Smelter

	Ag	As	Au	Bi	Ni	Pb	Sb	Zn	Sn
Noranda copper-making process									
Observed $L_{Cu/Sl}$	30	30	250	2	1.4	0.11	15	0.01	1.8
Calculated $L_{Cu/Sl}$	25	32	246	9	1.7	0.10	11	0.01	2.8
Observed $L_{Cu/Mt}$	2.4	5.7	171	4	1.5	1.4	15	0.11	10
Calculated $L_{Cu/Mt}$	2.4	5.0	152	5	1.1	2.0	12	0.31	15
Noranda matte-making process									
Observed $L_{Mt/Sl}$	16.0	1.8	16.0	5.3	1.3	0.7	0.9	0.13	
Calculated $L_{Mt/Sl}$	16.0	2.0	22.0	1.4	1.0	0.5	0.9	0.17	

Table 3 Comparison of prediction with commercial data of Mitsubishi process at Naoshima Smelter

Composition/ %	Cu	S	Fe	SiO_2	Pb	Zn	As	Sb	Al_2O_3
Industrial matte (In S-Furnace)	66.5	21.7	9.89	–	0.14	0.21	0.034	0.013	–
Predicted matte (In S-Furnace)	66.4	21.9	10.4	–	0.22	0.29	0.038	0.013	–
Industrial slag (In C-Furnace)	0.62	0.56	42.1	30.0	0.033	0.55	0.069	0.061	5.26
Predicted slag (In C-Furnace)	0.33	0.10	42.1	32.7	0.047	0.59	0.030	0.017	4.87

4 DISTRIBUTION BEHAVIORS OF ACCESSORY ELEMENTS DURING FAYALITE-SLAG-MAKING IN COPPER SMELTING

The industrial operation conditions and compositions of charge at Guixi Smelter are the basis of simulation. The simulated results are shown in Fig. 1, 2 and 3. $(M)_g$, $\langle M\rangle_{Sl}$ and $\{M\}_{Mt}$ (M = As, Sb, Bi, Ni, Co, Sn, Pb, Zn) in the Figs above denote the distributions of accessory elements in gaseous phase, slag and matte, respectively.

4.1 Distributions and smelting temperature

Effect of smelting temperature on the distributions was simulated, and is shown in Fig. 1. $(M)_g$ (M = As, Sb, Bi, Sn, Pb, Zn) increases with increasing smelting temperature. $\{As\}_{Mt}$, $\{Sb\}_{Mt}$, $\{Bi\}_{Mt}$, $\{Ni\}_{Mt}$ and $\{Co\}_{Mt}$ do not become too large, but $\{Sn\}_{Mt}$, $\{Pb\}_{Mt}$ and $\{Zn\}_{Mt}$ decrease significantly.

4.2 Distributions and oxygen-enrichment

Effect of oxygen-enrichment in blowing gas on the distributions at 51% Cu grade was simulated, and is shown in Fig. 2. $(M)_g$ (M = As, Sb, Bi, Sn, Pb, Zn) decreases and $\{M\}_{Mt}$ (M = As, Bi, Sn, Pb, Zn) increases with increasing oxygen content. They suggest that the use of oxygen causes difficulty in eliminating accessory elements though it has a great advantage of saving energy. The distributions of Ni and Co in matte and slag do not change too much with increasing oxygen content.

4.3 Distributions and matte grade

Fig. 3 shows the effects of matte grade on the distributions of accessory elements during copper smelting. $\{As\}_{Mt}$ increases with increasing matte grade, while $\{Sn\}_{Mt}$, $\{Pb\}_{Mt}$, $\{Zn\}_{Mt}$, $\{Ni\}_{Mt}$ and $\{Co\}_{Mt}$ decrease, only $\{Sb\}_{Mt}$ and $\{Bi\}_{Mt}$ do not have a remarkable change. $\langle M\rangle_{Sl}$ (M = As, Sb, Bi, Sn, Ni, Co, Pb, Zn) increases with increasing matte grade, especially, $\langle Pb\rangle_{Sl}$, $\langle Zn\rangle_{Sl}$, $\langle Ni\rangle_{Sl}$ and $\langle Co\rangle_{Sl}$ change significantly.

5 DISTRIBUTION BEHAVIORS OF ACCESSORY ELEMENTS DURING FERRITE-SLAG-MAKING IN COPPER SMELTING

The conventional copper smelting process is

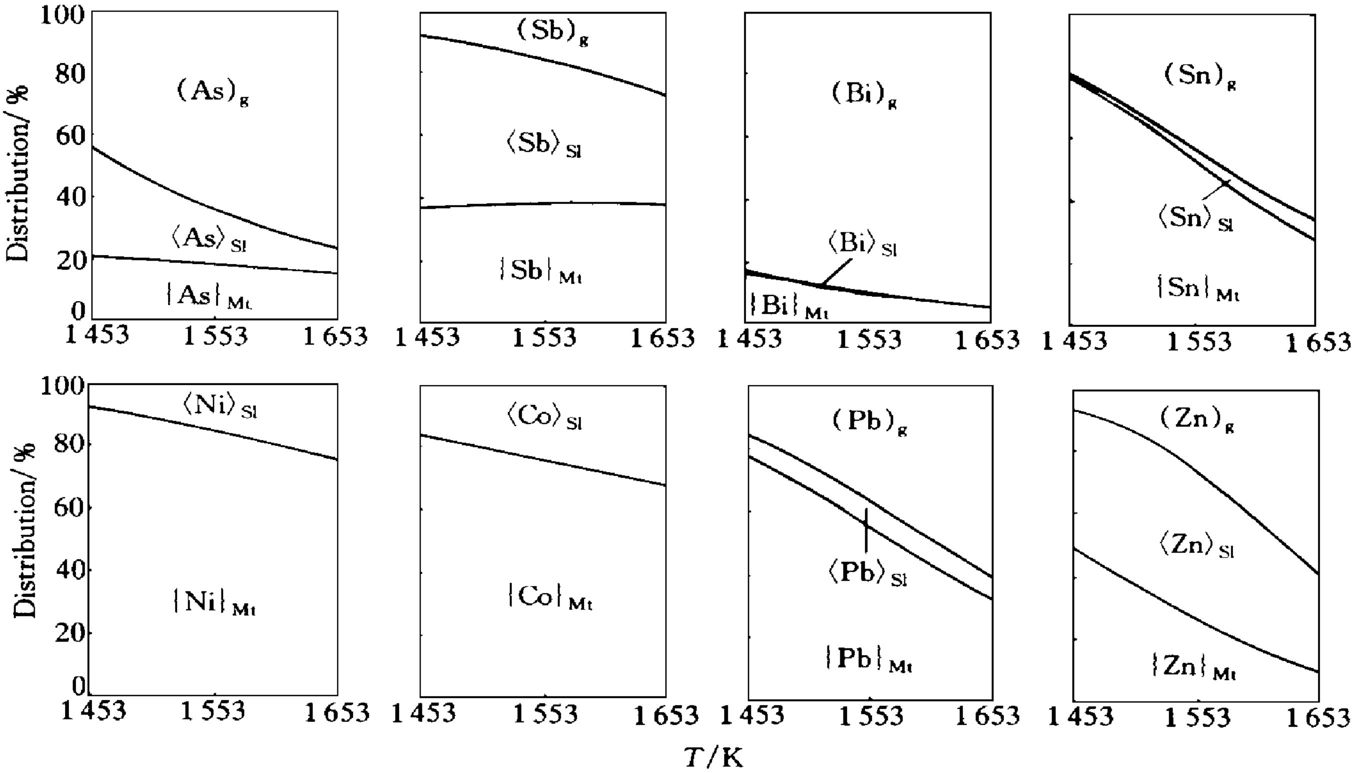

Fig. 1 Effects of smelting temperature on distributions of accessory elements during fayalite-slag-making in copper smelting

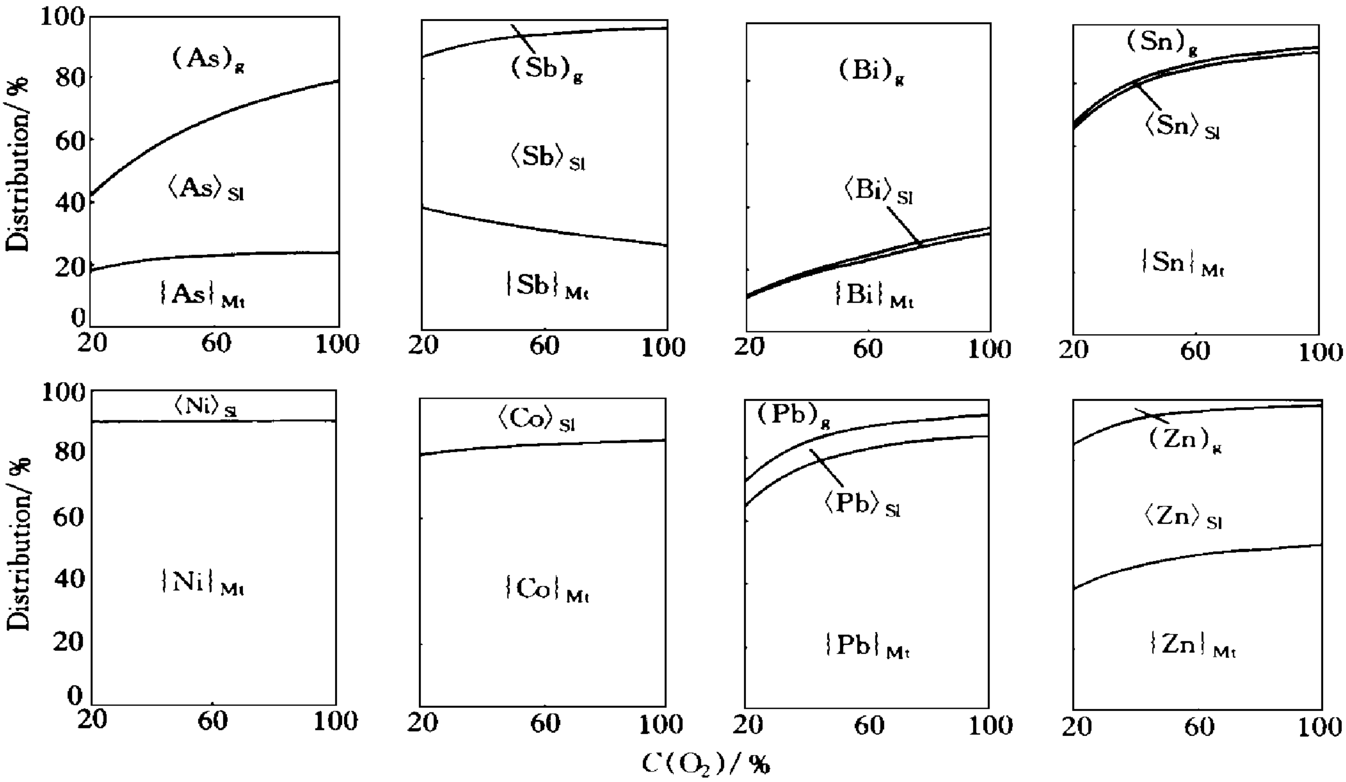

Fig. 2 Effects of oxygen-enrichment in blowing gas on distributions of accessory elements during fayalite-slag-making in copper smelting

essentially based on the quinary Cu-Fe-S-O-SiO_2 system. However, in the case of ferrite slag, SiO_2 is replaced by CaO. The mutual solubility of ferrite slag and matte is much higher than that of silicate slag and matte[7]. Test results from pilot plant studies of flash converting with ferrite slag have been reported by Asteljoki[8].

Fig. 4 shows the effects of matte grade on the distributions of accessory elements among ferrite slag, matte and gaseous phase. Comparing Fig. 4 with Fig. 3, we can see that ferrite slag is more effective than fayalite slag in removing As, Sb, Sn and Co from matte, while fayalite slag is more effective than ferrite slag in

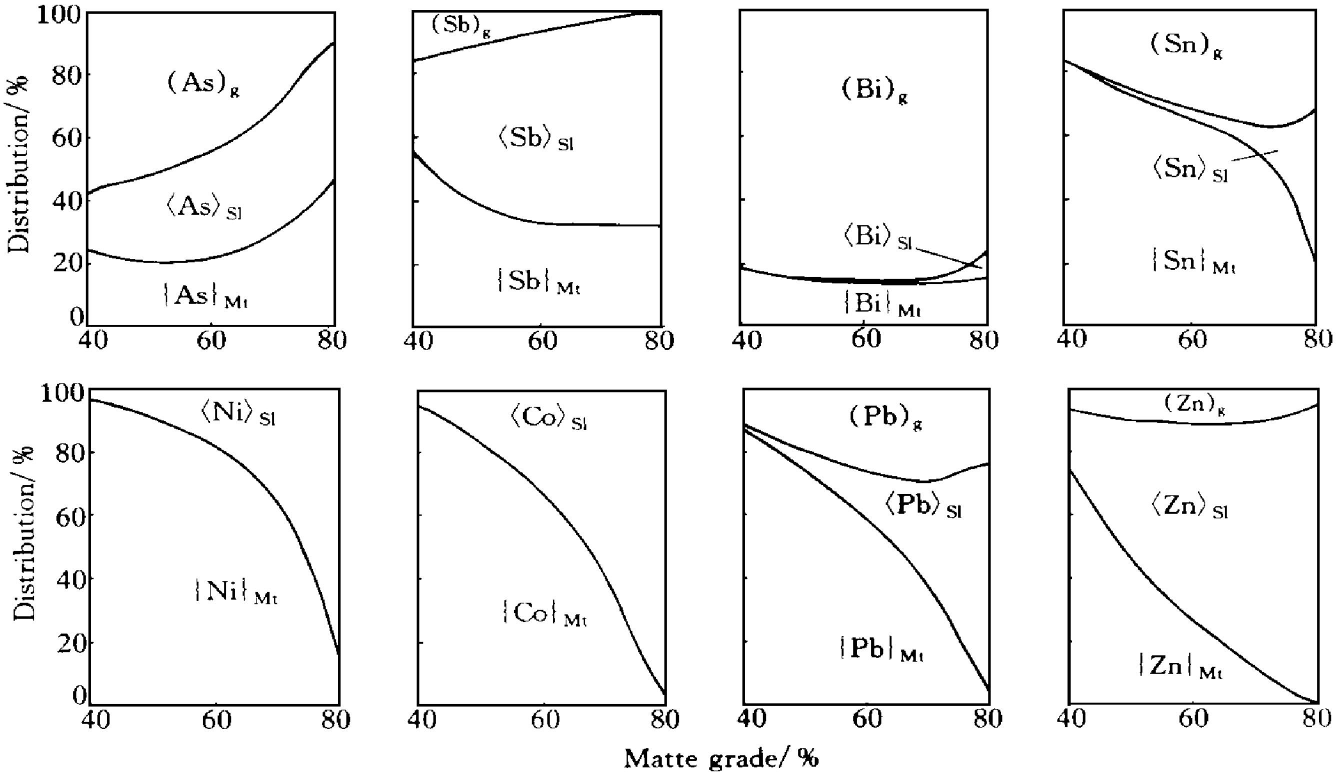

Fig. 3 Effects of matte grade on distributions of accessory elements during fayalite-slag-making in copper smelting

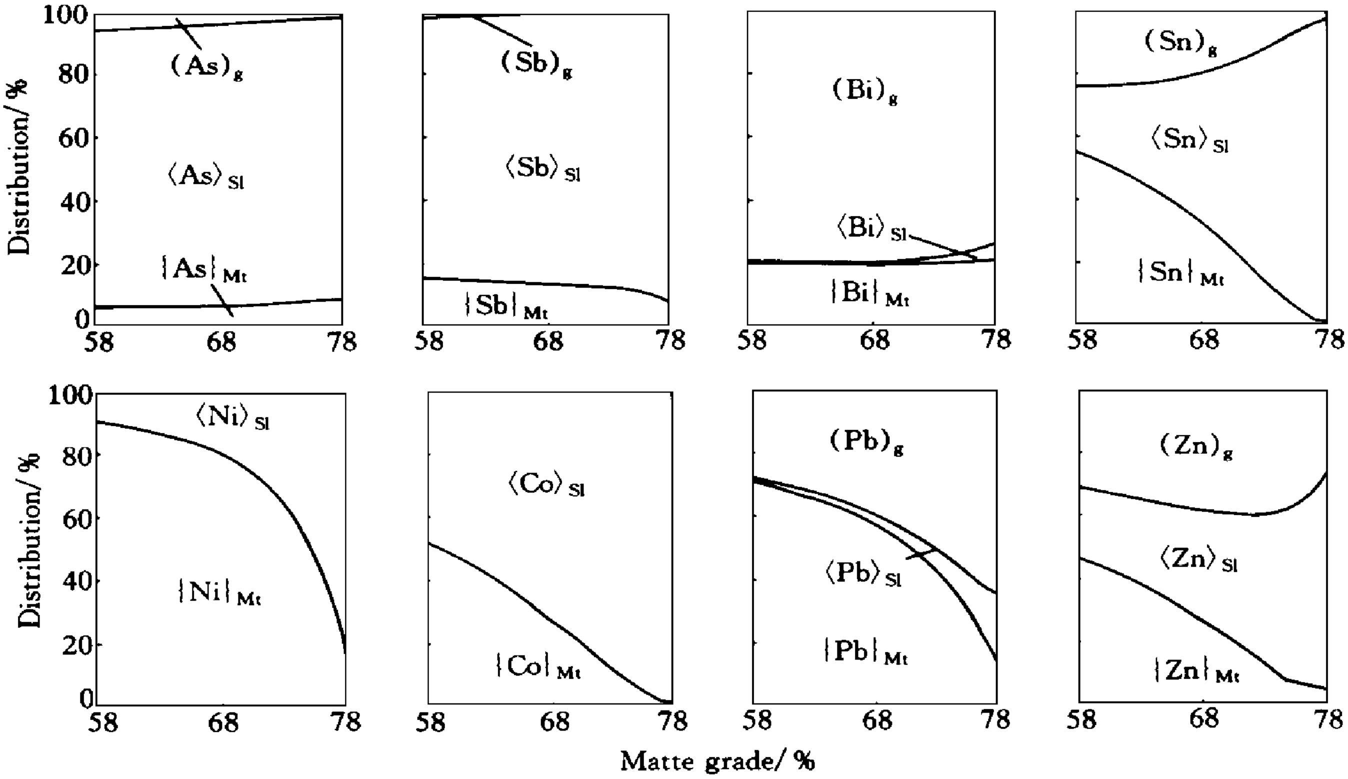

Fig. 4 Effects of matte grade on distributions of accessory elements during ferrite-slag-making in copper smelting

removing Pb and Zn from matte. The distributions of Ni and Bi in fayalite slag system and ferrite slag system are similar.

6 CONCLUSION

By the developed computer model, flash smelting process, Noranda process and Mitsubishi process were simulated. The distribution behaviors of Ni, Co, Sn, Pb, Zn, As, Sb, Bi, Au and Ag in copper smelting process were described.

LIST OF SYMBOLS

$A_{i,k}$, $B_{j,k}$ —number of the kth constituent element in the ith independent component or in the jth dependent component;

$\Delta G_i^{\ominus}$, $\Delta G_j^{\ominus}$ —the standard Gibbs energy of the ith independent component and the jth dependent component, respectively;

k_j —equilibrium constant for the formation reaction of the jth dependent component from the set of independent components;

$L_{Cu/Sl}$ —distribution coefficient,

$$L_{Cu/Sl} = [x]_{Cu}/[x]_{Sl}.$$

$L_{Mt/Sl}$ —distribution coefficient,

$$L_{Mt/Sl} = [x]_{Mt}/[x]_{Sl};$$

$[M]$ —mass fraction of M;

Q_k —total molar amount of the kth element in the system;

R —gas constant;

$m(i)$, $m(j)$ —phase number to which the ith independent component and the jth dependent component belong, respectively;

N —molar fraction;

S_i^j —mass fraction of suspended phase i in bulk phase j;

T —smelting temperature;

$V_{j,i}$ —coefficient of independent reactions;

X_i, X_j —molar amount of the ith independent component and the jth dependent component, respectively;

Z_m —total molar amount of the compounds in the mth phase;

γ_i, γ_j —Raoultion activity coefficient of the ith independent component and the jth dependent component, respectively;

g, Mt, Sl —gaseous, matte or slag phases;

Ap —apparent.

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