THERMODYNAMICS OF As, Sb AND Bi DISTRIBUTION DURING REVERB FURNACE SMELTING

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Abstract

The results of thermodynamic analysis of arsenic, antimony and bismuth distribution between copper matte and discard slag in reverberatory smelting at 1573 K are shown in this paper. On the basis of chemical analysis of the melt samples taken during stable operation of the reverb furnace No.2 in the Copper Smelter and Refinery, RTB Bor (Yugoslavia), the distribution coefficients of As, Sb, and Bi between copper matte and slag are calculated. The influence of the matte grade on the minor element distribution coefficients between copper matte and slag is also analyzed, as well as arsenic, antimony and bismuth distribution in slag.

1. Introduction

Sulfide copper ores contain minor elements such as Au, Ag (noble metals); Co, Ni, Pt, Pd (Group VIII); Zn, Cd, Hg (Group II-B); Sn, Pb (Group IV-A); Mo (Group VI-B); Bi, Sb, As (Group V-A); Se, Te (chalcogens); and Cl (halogen).

It is very important to determine the behavior of minor elements in regard to their effects on the quality of the copper produced as well as their impact on economical and environmental factors. Minor elements transition from copper matte into slag can be consider as impurity elimination or valuable component losses into slag [1].

Arsenic forms Cu_3As particles in annealed copper and can reduce the electrical conductivity of the metal by 23% at arsenic content of only 0.1 wt.%. Bismuth in copper at a concentration of 0.001 wt.% renders the host metal brittle, and both antimony and arsenic raise the recrystallization temperature of copper. So, their concentration must be limited in the final product to ensure its commercial viability. Because of that, it is essential to elucidate the thermodynamic nature of As, Sb, and Bi in order to establish effective ways of eliminating these impurities during smelting.

2. Industrial Investigation

The industrial investigation of arsenic, antimony and bismuth distribution between copper matte and slag along the furnace length is done by deep sonding of the melt from the reverberatory furnace No.2 sealing in the Copper Smelter and Refinery, RTB BOR (Yugoslavia) [2,3].

3. Results and Discussion

3.1. Minor Element Distribution between Copper Matte and Slag

In times past all metals present in fayalite slag are consider to be in oxidic form, because slag is mixture of oxides simply presented by FeO-Fe_2O_3-SiO_2 system [4]. But this stands only for Co, Ni, Pb, Sn, Zn. Investigations [5,6] showed that behavior of other elements in slag is different. Depending on nature of the element and operating conditions, the following mechanisms of chemical dissolution elements in fayalite slag can be considered [1]:

- Oxidic dissolution: Co, Cu, Ni, Pb, Zn;

- Sulfidic dissolution: Co, Cu, Ni, Pb;
- Monoatomic dissolution: Ag, As, Au, Bi, Sb, Se, Te;
- Molecular dissolution: S, Se, Te;
- Halidic dissolution: Ag, Au, Cu, Pt.

The first three dissolution mechanisms can be confirmed by analysis of sulfur and oxygen partial pressures diagram at 1573K which presents the stability of metal, sulfide and oxide of each element, with presumption that $a_{Me} = a_{MeS} = a_{MeO}$, Fig. (1).
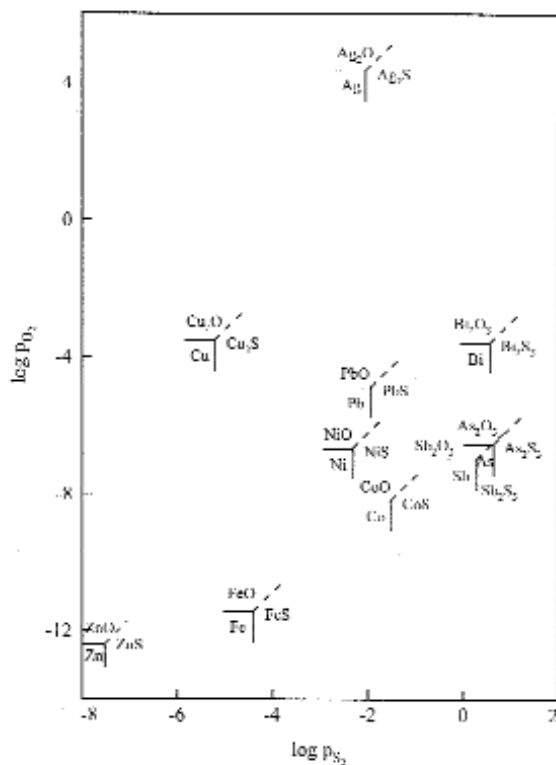

Figure 1. Sulfur-oxygen potential for metal-sulfur-oxygen systems at 1573K

Sulfides and oxides of zinc, cobalt, nickel, lead and copper are stable in smelting conditions, so these elements are present in melt in both forms. On the other side, antimony, arsenic, bismuth and silver are stable in metallic form.

Calculated distribution coefficients of arsenic, antimony and bismuth are shown in Fig. (2).

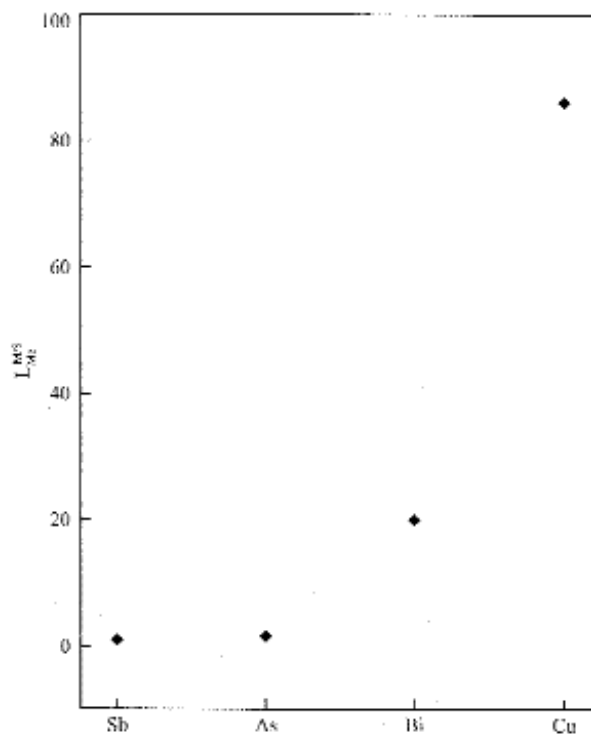Copper has the highest distribution coefficient, whose concentration in the

Figure 2. Minor element distribution coefficients

copper matte is 86 times higher than in the slag. The transition of bismuth into the matte is almost complete ($L \gg 1$). Arsenic has distribution coefficient a little above one; its concentration is higher in copper matte. But, because of the fact that the slag mass is around 70% of total furnace melt mass, bigger amount of arsenic is in the slag. And finally, distribution coefficient of

antimony is less than one, so it is concentrating in the slag. This confirms one of the most important technological functions of discard slag - refining, for it dissolves unwanted elements from copper matte.

3.2. Thermodynamic Consideration

Thermodynamically, the distribution of a metal Me between matte and slag can be analyzed on the base of its affinity to sulfur and oxygen:

$$MeS + FeO = MeO + FeS \tag{1}$$

$$K_1 = \frac{a_{MeO}}{a_{MeS}} \cdot \frac{a_{FeS}}{a_{FeO}} \tag{2}$$

Activities of FeS and FeO in the copper matte with average copper content equal 0.4 [1], thus:

$$K_1 = \frac{a_{MeO}}{a_{MeS}} = \frac{N_{MeO}}{N_{MeS}} \cdot \frac{\gamma_{MeO}}{\gamma_{MeS}} \tag{3}$$

where are:

N_{MeO} - mole fraction of MeO in slag;

N_{MeS} - mole fraction of MeS in copper matte;

γ - activity coefficient of MeO or MeS.

Therefore, the distribution of a metal can be considered as ratio of mole fraction of oxide in slag and sulfide in copper matte. The thermodynamic values for arsenic, antimony and bismuth distribution between slag and matte at 1573K is given in Table 1.

Calculated values for N_{MeO} / N_{MeS} show that almost all amount of bismuth and copper are transferred into copper matte, while almost all amounts of arsenic and antimony are transferred into slag.

On the basis of Gibbs free energy values at 1573K (Table 1) it can be concluded that the most stable oxides have arsenic and antimony; this means that during the smelting process arsenic and antimony are oxidized and

Table 1:   Thermodynamic values for minor element distribution between slag and matte at 1573K

ELEMENT	ΔG^{o}_{1573} (kJ)	K	$\gamma_{MeO} / \gamma_{MeS}$	N_{MeO} / N_{MeS}
As	- 14.2	3.0	≈ 0.20	15.00
Bi	125.6	$6.7 \cdot 10^{-5}$	≈ 0.20	$3.4 \cdot 10^{-4}$
Cu	129.7	$4.9 \cdot 10^{-5}$	1.00	$4.9 \cdot 10^{-5}$
Sb	- 15.4	3.3	≈ 0.20	16.50

transferred to slag phase. This mechanism of transition into slag is directed by thermodynamic (melting point, boiling point, chemical equilibrium, distribution coefficient, activity, activity coefficient, influence of partial pressure of oxygen and sulfur), kinetic (density, viscosity, gas and liquid flow, diffusion coefficient) and process (temperature, slag composition, furnace construction) parameters [7].

On the other side, sulfides of arsenic, antimony and bismuth have high vapor pressure ($>>1,5 \cdot 10^{-5}$ and $9 \cdot 10^{-2}$ atm, respectively). It is very hard to remove them by oxidation ($\Delta G^{o}_{1573} > 0$) and introduce them into the slag, so they evaporate in sulfidic form [8].

Besides, the direct reduction of sulfide to metal vapor is characteristic for antimony and bismuth. The mechanism of evaporation depends on similar parameters as mechanism of transition into the slag [7].

3.3. Matte Composition Influence on Minor Element Distribution

The influence of copper content in the matte on arsenic, antimony and bismuth distribution coefficients is shown in Fig.(3). The increasing of copper concentration in the matte decrease the values of distribution coefficients of all analyzed minor elements.

3.4. Minor Element Distribution in Slag

The results of investigation of minor element distribution in the slag phase along the slag melt depth and the furnace length are shown in Table 2 and Figure 4. The concentration of arsenic, antimony and bismuth decrease from SL3 to SL6. As mentioned before, sulfides of these elements, as well as
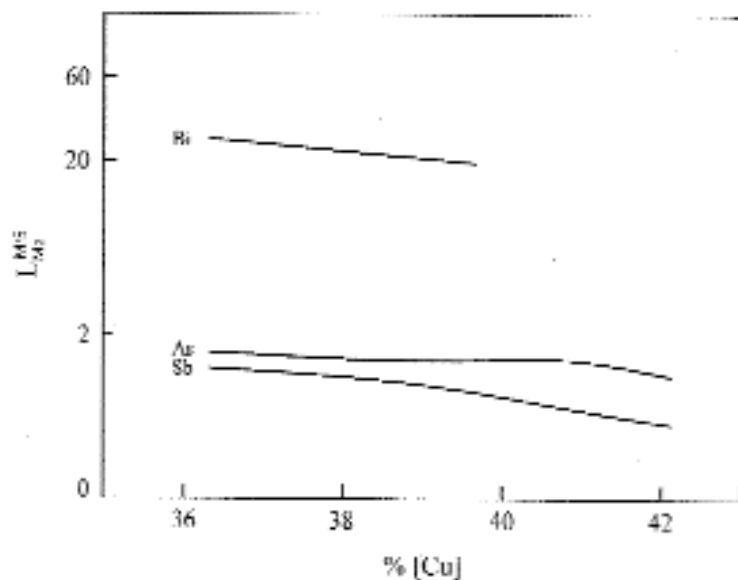

Figure 3. Minor element distribution coefficients vs. copper matte composition

metallic antimony and bismuth, have high vapor pressures, so they traverse to gas phase which lowers their concentration in the slag.

4. Conclusion

On the basis of chemical analysis of the samples taken during stable operation of the reverb furnace No.2 in Copper Smelter and Refinery, RTB Bor (Yugoslavia), the distribution coefficients of arsenic, antimony and

Table 2. Minor element content in slag along slag depth and furnace length

SAMPLE		ELEMENT		
		As	Bi	Sb
SL3	I	0.04	0.0007	0.003
	II	0.05	0.0008	0.004
	III	0.05	0.0010	0.006
	IV	0.06	0.0020	0.008
SL4	I	0.02	0.0005	0.002
	II	0.03	0.0006	0.003
	III	0.03	0.0007	0.004
	IV	0.04	0.0015	0.007
SL5	I	0.01	0.0003	0.001
	II	0.02	0.0005	0.002
	III	0.02	0.0006	0.003
	IV	0.03	0.0010	0.006
SL6	I	0.01	0.0001	0.001
	II	0.01	0.0003	0.001
	III	0.02	0.0005	0.002
	IV	0.02	0.0010	0.004

bismuth between copper matte and slag are determined. The transition of bismuth into the matte is almost complete (L>>1). Arsenic has distribution coefficient a little above one. And finally, a distribution coefficient of antimony is less than one, so it is concentrating in the slag.
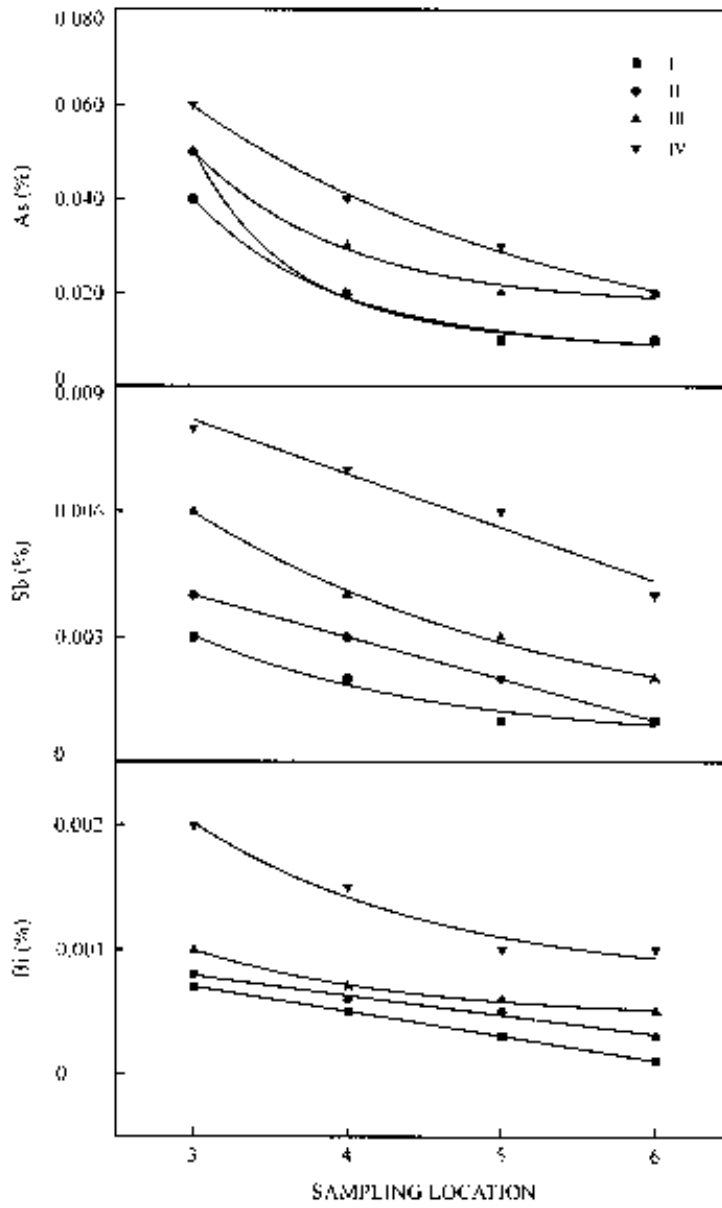
Figure 4. Minor element distribution in the slag phase

The influence of the matte grade on the minor element distribution coefficients is also analyzed. The increasing of copper concentration in the matte decrease the values of distribution coefficients of all analyzed minor elements.

The distribution of these elements in the slag phase is determined, too. The concentration of arsenic, antimony and bismuth decrease from SL3 to SL6. Their sulfides, as well as metallic antimony and bismuth have high vapor pressures, so they traverse to gas phase, which lowers their concentration in the slag.

Acknowledgements

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