The solubility of Cu, Pb, As, Sb of copper-lead matte in the slag

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Abstract. An installation was developed and studies were carried out to determine the oxide solubility of copper, lead, arsenic, and antimony from copper-lead matte to slag under conditions of controlled values of $P_{\text{O}_2}=2.74 \times 10^{-4}$ Pa and $P_{\text{S}_2}=1.45 \times 10^{2}$ Pa, applicable to smelting reduction processes of copper-, lead-containing raw materials. It was found that the oxide solubility of copper from matte to slag increases monotonously with an increase of copper content in the matte. The presence of lead in the matte does not significantly affect the final solubility of copper in the slag. In a reducing atmosphere, the solubility of copper in slag is $0.28-0.35\%$, at the range of copper content of $30-45\%$ in the matte, which is typical for industrial practice. The solubility of lead from copper-lead matte to slag has higher values and increases to $1\%$. According to the results of mineralogical studies, there is no metallic form of arsenic in slags. Arsenic in slags was found in the form of oxide ($\text{As}_2\text{O}_5$) bound to silicate. Antimony in slag was found in oxide and metallic form. Moreover, the proportion of the last form in the slag prevails. It is shown that under reduction conditions the sublimation of arsenic and antimony from copper-lead matte is difficult. Equilibrium concentrations of As, Sb in the slag ($0.17\%$) are achieved with their optimum content in the matte which is about $0.63\%$. Obtained results can be used to predict the loss of oxide solubility of copper and to develop optimal solutions to reduce the total loss of copper with slag during the reduction processes of separate processing of copper-, lead-containing raw materials.

Keywords: copper, lead, arsenic, antimony, matte, slag, solubility, partial pressure of oxygen and sulfur, losses with slag.

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Introduction

Almost all smelting processes of sulphide copper and lead concentrates are followed by the stages of melting and formation of two-phase system (slag, matte), wherein after phase break and slag removal, matte is further processed. In this case, most of the gangue components are removed from the system as part of the slag phase. Depending on the selected process, the copper content in the slag can vary in the range of 0.5 to 2%. High copper content slags obtained by autogenous smelting processes are usually further processed by flotation or other known methods [1, 2].

The issues of copper loss with smelting slag are widely discussed in the technical literature [1–7], while data on the solubility of lead in slag, even within the widespread practice of classical mine reduction smelting technology, remain debatable [8, 9, 10]. There is a particular interest of the study of copper and lead losses with slags obtained during separate mine contractile smelting of intermediate products and recycled materials of lead production. Although this technology does not allow achieving high technological indicators: copper extraction into matte is $\sim 83\%$, lead into lead bullion barely reaches $60\%$ [11], this application is an industrial necessity caused by significant increase of processed products and lack of efficient technology for their processing. Solution of the problem requires a detailed study of the equilibrium of the copper-lead matte-slag-gas phase system in order to establish thermodynamic
solubility limit of copper and lead in slags and to determine the quantitative ratios of the form of losses (mechanical and dissolved). This will allow choosing optimal solutions to reduce not only the loss of non-ferrous metals with slag, but also to determine the equilibrium distribution of impurity metals between matte and slag.

The purpose of the work is to study the solubility of copper, lead and associated metals from copper-lead matte to slag in relation to conditions of mine contractile smelting of intermediate products and recycled materials of lead production.

**Research methods**

To study the solubility of lead, copper, arsenic and antimony, the results of phase, elemental composition and mineralogical studies of samples of industrial mattes and slags obtained during the processing of copper, lead containing intermediate products and recycled materials of lead production were used under conditions of mine contractile smelting [12]. Modern approaches of mathematical processing methods are widely used in the work.

Elemental and phase analysis of matte and slag samples was performed by using Helling mass spectrometer and Agilent 7700 Series ICP-MS at room temperature.

Mineralogical studies of the surface structure of solid air-hardened slag samples were conducted on MS-46 CAMECA electron microprobe and Neofot microscope (Carl Zeiss AG, Germany).

To study the equilibrium of the copper-lead matte-slag-gas phase system, the method of dynamic flow of gas mixture CO-CO$_2$-SO$_2$ was used which allows setting of required partial pressure of oxygen (P$_{O_2}$) and sulfur (P$_{S_2}$) in the system.

**Results and discussion**

To analyze the industrial data of smelting products of mine contractile smelting, selective array of matte and slag was used, compositions are shown in Table 1.

The results of [12], obtained on the basis of detailed complex mineralogical studies of industrial samples of slags and mattes, showed that the iron in the slags is present in the form of sulfide (FeS), ferrous and trivalent iron, also insignificant amounts in the metallic form as arsenide and antimonide of iron.

In order to clarify the quantitative ratios of ferrous and ferric iron in slags, additional studies were carried out, the essence of which was as follows. From the slag samples previously taken from the furnace, the sulfide part was separated by known methods. Obtained slag was subjected to a comprehensive study by the methods of chemical and NGR analysis as well as mineralogical studies. The chemical method of analysis was used to determine total (Fe$_{\text{total}}$) and divalent (Fe$^{2+}$) iron content in the slag. According to the results of the obtained data, the content of ferric iron (Fe$^{3+}$) was calculated based on the difference: Fe$^{3+}$ = Fe$_{\text{total}}$ - Fe$^{2+}$.

**Table 1** – chemical composition of paired samples of matte and slag

| №  | [Cu]   | [Pb]   | [Zn]  | [Fe]  | [S]  | [As] | [Sb] | [Au]* | [Ag]* |
|----|--------|--------|-------|-------|------|------|------|-------|-------|
| 1  | 38.6   | 26.33  | 4.2   | 7.63  | 11.43| 4.38 | 1.98 | 16.3  | 1375  |
| 2  | 32.55  | 29.34  | 4.24  | 8.94  | 10.17| 4.77 | 1.62 | 14.47 | 1530  |
| 3  | 40.25  | 24.36  | 4.73  | 9.49  | 11.9 | 4.39 | 2.36 | 16.9  | 1203  |
| 4  | 36.19  | 26.16  | 4.33  | 8.29  | 9.82 | 4.19 | 1.85 | 15.3  | 1463  |
| 5  | 38.54  | 28.74  | 3.24  | 5.96  | 10.6 | 4.98 | 2.28 | 16.37 | 1548  |
| 6  | 40.41  | 29.66  | 2.96  | 5.62  | 12.07| 5.94 | 2.62 | 16.8  | 1570  |
| 7  | 42.97  | 26.42  | 4.13  | 8.88  | 10.4 | 3.91 | 1.54 | 17.07 | 1430  |
| 8  | 29.95  | 25.11  | 4.76  | 12.93 | 12.9 | 3.29 | 1.44 | 13.43 | 1330  |
| 9  | 39.51  | 25.47  | 5.25  | 13.17 | 11.3 | 2.88 | 1.35 | 15.6  | 1373  |
| 10 | 34.3   | 23.29  | 6.07  | 12.43 | 10.2 | 3.06 | 1.13 | 14.7  | 1200  |
| 11 | 36.93  | 24.09  | 4.95  | 9.96  | 9.87 | 3.22 | 1.93 | 15.8  | 1245  |
| 12 | 35.8   | 28.76  | 4.24  | 7.87  | 10.84| 4.02 | 1.75 | 18.0  | 1513  |
| 13 | 33.55  | 25.9   | 4.12  | 9.05  | 11.27| 3.94 | 1.68 | 16.1  | 1287  |
| 14 | 23.8   | 19.42  | 6.75  | 13.71 | 6.07 | 3.02 | 1.06 | 12.2  | 997   |
| 15 | 24.19  | 19.76  | 6.84  | 12.8  | 7.5  | 2.8  | 1.02 | 12.7  | 1037  |
| 16 | 32.59  | 26.36  | 5.07  | 10.78 | 12.4 | 3.35 | 1.45 | 14.7  | 1330  |
| 17 | 36.3   | 23.18  | 5.13  | 11.58 | 11.2 | 2.8  | 2.04 | 15.3  | 1123  |
| 18 | 34.55  | 22.74  | 5.23  | 12.24 | 9.31 | 2.83 | 1.62 | 13.6  | 1163  |
### Table 1: Composition of slag, wt.%

| (Cu) | (Pb) | (ZnO) | (SiO$_2$) | (Fe$_{total}$) | (CaO) | (As) | (Sb) | (Au)* | (Ag)* |
|------|------|-------|-----------|---------------|-------|------|------|-------|-------|
| 0.5  | 1.08 | 11.54 | 24.2      | 20.7          | 20.7  | 0.19 | 0.14 | 0.073 | 4.2   |
| 0.47 | 1.24 | 11.72 | 26.49     | 21.18         | 19.7  | 0.17 | 0.14 | 0.068 | 4.9   |
| 0.52 | 0.89 | 10.7  | 25.67     | 19.72         | 21.47 | 0.16 | 0.15 | 0.075 | 3.6   |
| 0.49 | 1.45 | 11.64 | 25.31     | 20.5          | 18.69 | 0.23 | 0.14 | 0.073 | 6.0   |
| 0.52 | 1.45 | 10.42 | 24.69     | 21.5          | 19.85 | 0.25 | 0.13 | 0.07  | 4.6   |
| 0.53 | 1.38 | 11.52 | 25.78     | 20.9          | 18.08 | 0.23 | 0.12 | 0.074 | 5.2   |
| 0.54 | 1.26 | 17.3  | 21.83     | 22.2          | 18.91 | 0.1  | 0.14 | 0.076 | 4.4   |
| 0.5  | 1.3  | 9.94  | 25.15     | 24.25         | 15.0  | 0.15 | 0.16 | 0.073 | 4.8   |
| 0.53 | 0.63 | 8.54  | 25.51     | 22.22         | 21.02 | 0.16 | 0.17 | 0.07  | 3.3   |
| 0.45 | 0.84 | 7.92  | 26.74     | 21.2          | 19.92 | 0.13 | 0.15 | 0.067 | 4.1   |
| 0.51 | 0.98 | 6.87  | 23.85     | 22.73         | 16.87 | 0.11 | 0.14 | 0.073 | 4.1   |
| 0.52 | 1.67 | 7.35  | 25.6      | 22.47         | 16.61 | 0.24 | 0.13 | 0.072 | 5.9   |
| 0.46 | 1.12 | 9.21  | 27.08     | 21.36         | 18.54 | 0.15 | 0.15 | 0.068 | 3.7   |
| 0.34 | 0.7  | 10.02 | 27.77     | 20.7          | 17.48 | 0.12 | 0.17 | 0.053 | 3.2   |
| 0.35 | 0.67 | 11.42 | 26.19     | 20.93         | 19.17 | 0.21 | 0.16 | 0.054 | 3.7   |
| 0.45 | 0.99 | 10.44 | 24.57     | 23.12         | 17.83 | 0.12 | 0.13 | 0.068 | 3.7   |
| 0.57 | 0.84 | 9.97  | 26.53     | 22.41         | 18.22 | 0.11 | 0.14 | 0.08  | 3.2   |
| 0.47 | 0.81 | 10.76 | 26.0      | 23.05         | 17.51 | 0.09 | 0.15 | 0.07  | 3.6   |

Results of the NGR analysis and mineralogical studies of powder and solid slag samples showed good convergence by forms of presence of iron as well as with data obtained by the chemical analysis method. In all studied slag samples, the part of ferrous iron was 74-78% and the part of ferric iron was around 15% of the total iron content in the slag.

Total iron content (Fe$_{total}$) in all slag samples varied within 20-24 wt.%. The change in the content of Fe$^{2+}$ in the slag was 15-18 wt.%. The content of Fe$^{3+}$ in the slag varied within 3-4 wt.%. Slight fluctuations in the content of Fe$^{2+}$ and Fe$^{3+}$ in the slags allow to argue that technological parameters affecting the distribution of metals between the smelting products were constant under the conditions of the mine contractile smelting process.

Using the results obtained by the equation $\text{lg}(\text{Fe}^{3+}/\text{Fe}^{2+})=0.196^*\text{lgP_{O2}}+0.722$ [13], the partial pressure of oxygen was calculated, which showed a slight change: from $\text{lgP_{O2}}=-9.2$ до $\text{lgP_{O2}}=-9.9$ (P$_{O2}$, atm.), which is associated with fluctuations of iron content in the matte. Established level of oxygen partial pressure was chosen for laboratory experiments to study the equilibrium of the matte-slag-gas phase system.

The minor elements - arsenic and antimony in the slag, are mostly represented in oxide form. Antimony has also been found in metallic form (Sb°). Obtained results are consistent with the data in studies [14–16].

Installation to study equilibrium of the system of copper-lead matte-slag-gas phase is shown in Fig. 1.

![Figure 1](image-url)

Figure 1 General scheme of dynamic gas flow method to study the equilibrium of the matte–slag–gas phase system
Methodology of the experiments was as follows. Samples of copper matte and iron-silicate slag are placed in a boat crucible, which is placed on a special stand J2 made of foam material. In order to avoid mechanical losses of copper with slag, the stand is made so that when a boat crucible is installed on it, it is slightly inclined (~5°) to the horizontal axis of the quartz reactor.

Slag and matte in the boat crucible are located opposite to each other so that once slag melts, it flows to the liquid matte. Up to five boat crucibles with an initial test portion are simultaneously loaded into the working zone of quartz reactor.

The temperature difference along the entire length of the working zone is minimal and in the range of ±10°C from the set point. Temperature measurement is done by PT-1 thermocouple.

After loading the boat crucibles, the quartz reactor 9 is closed by branch pipe equipped with two holes - for the entrance and exit of the CO–СО₂ gas mixture, the composition of which sets the required value of P⁰₂ = 2.74·10⁻⁴ Pa and P⁰₃₂ = 1.45·10⁻¹⁰ Pa. Maintaining a constant level of P⁰₂ and P₃₂ during the experiment is achieved by collecting gas mixture prepared in advance with the following composition, vol. %: 17 SO₂, 71 CO₂ and 12 CO [17] in the gas tank 6 and its further supply to the reaction zone. The consumption of the gas mixture is 1 L/h. Throughout the experiment, the composition of the gas mixture was continuously monitored at the inlet and outlet of the reactor by chromatograph. Constant composition of the gas mixture at the inlet and outlet of the reactor indicated achievement of the equilibrium in the system.

Once experiment is done, stand with boat crucibles were removed from the furnace. Smelting products (slag, matte) after their separation were subjected to the elemental analysis.

Experiments were performed with copper-lead matte, which was prepared by mixing pure sulfides of copper, lead and iron, based on the calculation of the sum of copper and lead contents of 30, 40, 50, 60, 70, and 80 wt.% at the ratio of copper to lead equal to 1:0, 2:0 and 3:0. Selected initial matte compositions completely cover the range of matte compositions obtained in practice.

Composition of iron-silicate slag in the experiments was constant and contained, wt. %: 65.46 FeO; 30.8 SiO₂; 3.74 Fe₂O₃.

The test portion of matte and slag in all experiments was constant and amounted to 3 and 6 g, respectively. Metallic arsenic and antimony equal to 2% of the weight of the original matte were added to all samples of mattes. The temperature of the experiments is 1523 K.

The test conditions and study results are given in Table 2.

The dependence of the content of copper in slag on its content in matte, shown in Fig. 2, shows an increase in the content of copper in slag with increasing its content in the matte. It is interesting that the data of the solubility of copper in slag, regardless of the change in the ratio of copper to lead in the original matte, lies on the same line. The established consistent pattern can be explained by general positions of the theory and practice of metallurgical processes.

Table 2 Results of the study of the equilibrium of the system of copper-lead matte - slag - gas phase at controlled values P⁰₂=2.74·10⁻⁴ Pa and P⁰₃₂=1.45·10⁻¹⁰ Pa

| #  | Composition of initial matte, wt.% | Composition of Me in the final matte, wt.% | Composition of final slag, wt.% |
|----|-----------------------------------|------------------------------------------|--------------------------------|
|    | [Cu]    [Pb] | [Cu]    [Pb] | [Fe] | [As] | [Sb] | [Cu] | [Pb] | [As] | [Sb] | [FeO] | [SiO₂] |
| 1  | 5 25 | 4.37 | 23.08 | 42.57 | 0.21 | 1.01 | 0.13 | 0.37 | 0.13 | 0.28 | 58.93 | 28.43 |
| 2  | 10 20 | 11.2 | 19.4 | 39.75 | 0.22 | 0.89 | 0.14 | 0.34 | 0.13 | 0.24 | 64.03 | 28.31 |
| 3  | 15 15 | 16.3 | 13.72 | 39.70 | 0.36 | 1.00 | 0.16 | 0.28 | 0.14 | 0.28 | 59.23 | 27.84 |
| 4  | 20 10 | 19.04 | 9.5 | 40.55 | 0.35 | 1.01 | 0.15 | 0.35 | 0.14 | 0.28 | 63.16 | 28.29 |
| 5  | 20 20 | 22.71 | 18.31 | 31.27 | 0.51 | 0.62 | 0.17 | 0.39 | 0.16 | 0.17 | 63.33 | 27.74 |
| 6  | 25 15 | 24.9 | 13.85 | 32.66 | 0.53 | 0.62 | 0.16 | 0.41 | 0.14 | 0.18 | 64.2 | 27.89 |
| 7  | 30 10 | 31.62 | 8.67 | 31.05 | 0.41 | 0.63 | 0.16 | 0.37 | 0.15 | 0.17 | 59.87 | 29.1 |
| 8  | 25 25 | 26.32 | 23.45 | 24.67 | 0.61 | 0.48 | 0.18 | 0.61 | 0.18 | 0.15 | 65.36 | 28.7 |
| 9  | 30 20 | 28.4 | 19.21 | 26.02 | 0.58 | 0.49 | 0.18 | 0.47 | 0.18 | 0.14 | 64.29 | 27.4 |
| 10 | 30 30 | 29.87 | 28.63 | 18.08 | 0.73 | 0.42 | 0.22 | 0.69 | 0.19 | 0.12 | 63.83 | 28.05 |
| 11 | 35 25 | 36.42 | 23.17 | 16.75 | 0.86 | 0.4 | 0.23 | 0.58 | 0.21 | 0.13 | 64.02 | 27.97 |
| 12 | 40 20 | 39.07 | 19.42 | 17.31 | 0.9 | 0.37 | 0.21 | 0.62 | 0.21 | 0.13 | 60.73 | 29.54 |
| 13 | 35 35 | 34.8 | 32.86 | 11.08 | 1.01 | 0.34 | 0.24 | 0.93 | 0.23 | 0.1 | 57.9 | 28.78 |
| 14 | 40 30 | 38.1 | 28.57 | 11.37 | 1.1 | 0.34 | 0.27 | 0.9 | 0.24 | 0.11 | 62.87 | 27.97 |
| 15 | 45 25 | 44.8 | 23.18 | 9.92 | 1.18 | 0.39 | 0.28 | 0.87 | 0.25 | 0.11 | 59.74 | 29.45 |
| 16 | 50 25 | 48.74 | 22.8 | 7.1 | 1.16 | 0.35 | 0.3 | 0.98 | 0.26 | 0.1 | 61.83 | 28.64 |
| 17 | 55 20 | 56.09 | 18.62 | 4.16 | 1.37 | 0.38 | 0.32 | 1.18 | 0.29 | 0.11 | 65.73 | 27.13 |
The solubility of copper from matte to slag occurs because of the oxidation of copper sulfide:

$$\text{Cu}_2\text{S} + 1,5 \text{ O}_2 = 2\text{CuO}_{0.5} + \text{SO}_2.$$  \hspace{1cm} (1)

The constant of reaction (1) is determined by the expression:

$$K_{(1)} = a^{2}\text{CuO}_{0.5} \cdot P_{\text{SO}_2} / a_{\text{Cu}_2\text{S}} \cdot P^{1.5}_{\text{O}_2}.$$ \hspace{1cm} (2)

where:  
- $a_{\text{Cu}_2\text{O}_{0.5}}$ – activity of copper oxide in the slag;
- $a_{\text{Cu}_2\text{S}}$ – activity of copper sulfide in the matte;
- $P_{\text{SO}_2}$, $P_{\text{O}_2}$ – partial pressure of $\text{SO}_2$ and oxygen.

By solving (2) with respect to $a_{\text{Cu}_2\text{O}_{0.5}}$, we obtain:

$$a^{2}\text{CuO}_{0.5} = a_{\text{Cu}_2\text{S}} \cdot K_{(1)} \cdot P^{1.5}_{\text{O}_2} / P_{\text{SO}_2}.$$ \hspace{1cm} (3)

Under equilibrium of the system, the values as $K_{(1)}$, $P_{\text{O}_2}$, and $P_{\text{SO}_2}$ are constant; therefore, activity of copper oxide in the slag is determined by the change in the activity of copper sulfide ($a_{\text{Cu}_2\text{S}}$). Consequently, the presence of lead in the matte will have only weak effect on the solubility of copper in the slag.

Significant excess of the copper content in the slag of industrial data compared with experimental results seems quite natural. Figure 2 shows the total copper content for industrial slags (the sum of mechanical and dissolved copper losses), while the results of experimental studies consider only content of copper oxide solubility in the slag. The increase in the total losses of copper with slag is accompanied by the influence of a higher temperature of the mine contractile smelting process (1573 K) than the temperature of laboratory experiments (1523 K).

The results of experimental studies are in good agreement with the data given in study [18], where the solubility of copper in iron-silicate slag from copper matte was studied, at all other equal conditions of conducting experiments. The identical nature of the established patterns indicates that the mechanism of oxide solubility of copper in slag, both from copper and copper-lead mattes, is uniform. Since oxide solubility of copper is determined mainly by the value of $a_{\text{Cu}_2\text{S}}$ (3), obtained dependency indicates that $a_{\text{Cu}_2\text{S}}$ in the $\text{Cu}_2\text{S}$–$\text{FeS}$–$\text{FeO}$ and $(\text{Cu}_2\text{S} + \text{PbS})$–$\text{FeS}$–$\text{FeO}$ systems are close to each other.

Traditional dependency of the content of lead in the slag from its content in the matte remains for the lead as well, as can be seen from Fig. 3.
A comparative analysis of industrial data with experimental data shows that the plant results, as for copper, exceed the experimental ones, which is explained by the elevated temperature of mine contractile smelting. On the other hand, in the case with plant practice, the results for total lead content in slags are given (Table 1), but not its oxide solubility. It should be noted that the lead is more soluble in slag than copper. When the lead content in matte is 20-25%, typical for industrial practice, dissolved form of lead in slag rises to 1%, which leads to increase in its total losses with slag.

Figure 3 Dependence of lead content in slag from its content in the matte

Under the conditions of the experiments, the thermodynamic probability of oxidation of lead sulfide can be described by the following reactions:

\[
PbS + 1.5O_2 = PbO + SO_2, \quad (4)
\]

\[
PbS + FeO = PbO + FeS. \quad (5)
\]

The reaction (4) is preferable \( \Delta G^{°}_{1523K} = -290552,2 \text{ J/mol} \) than reaction (5): \( \Delta G^{°}_{1523K} = -85372 \text{ J/mol} \).

When the system is in equilibrium, constants of reactions (4) and (5) are equal \( K_{(4)} = K_{(5)} \), therefore, we can write:

\[
a_{PbO} \cdot a_{SO_2}^{1.5} = a_{PbS} \cdot a_{FeS}/a_{PbS} \cdot a_{FeO}. \quad (6)
\]

Considering that under the experimental conditions, the values of \( P_{O_2} \) and \( P_{SO_2} \) are fixed, by solving the left side of expression (6) with respect to \( a_{PbO} \), we obtain:

\[
N_{PbO} = A_1 \cdot N_{PbS}, \quad (7)
\]

where activities are replaced by the product, \( a = N \cdot \gamma \); \( A_1 \) is constant, \( A_1 = K_{(4)} \cdot P_{O_2} \cdot \gamma_{PbS}/P_{SO_2} \cdot \gamma_{PbO} \).

On the other hand, solution of the right-hand side of expression (6) with respect to \( a_{PbO} \) allows us to write:

\[
N_{PbO} = A_2 \cdot N_{PbS}/N_{FeS}, \quad (8)
\]

where activities are replaced by the product, \( a = N \cdot \gamma \);

\[
A_2 = K_{(5)} \cdot \gamma_{PbS} \cdot N_{FeO}/\gamma_{FeS} \cdot \gamma_{PbO}.
\]

From the expression (7) it is seen that the solubility of lead in the slag increases with increasing the lead content in the matte. Expression (8) indicates that an increase in the Cu/Pb ratio in the matte by decreasing the lead content in it rises the iron content in the matte. In this case, the equilibrium of reaction (5) is shifted towards the formation of lead sulfide, which leads to decrease in the lead content in the slag. The established pattern is not difficult to see from the results given in Table 2.

Dependence of the content of arsenic and antimony in the slag on their content in the matte is shown in Fig. 4.
Equilibrium concentrations of arsenic and antimony in slags, equal to 0.17 wt.%, are achieved when their total content in the original matte is around 0.63 wt.%. Experimental data for both arsenic and antimony practically lies on a straight line. Moreover, the curve for arsenic is more gentle than for antimony. In the latter case, desired dependence is more pronounced.

The results of mineralogical analysis of slag samples obtained after the experiment showed that there is no metal form of arsenic in slags. Arsenic in slags was found in the form of oxide (As$_2$O$_5$) bound to silicate. Antimony in slag was found in oxide and metal form. Moreover, the proportion of the last form in the slag prevails.

This indicates that under reduction conditions the sublimation of antimony to the gas phase is difficult, therefore, its main part is concentrated in the slag as a metallic form (Sb°). This position is consistent with the results of [14]. Under the conditions of the experiments, the main part of antimony passes from matte to the slag directly, without undergoing any physicochemical changes. As a result, its final content in the slag, with some deviation (its minimal oxidation), is determined by its initial content in matte, which is observed in Fig. 4. In this case, tangible separation of antimony between matte and slag should not be expected.

Conclusions

1. The installation was developed and studies were carried out to determine the oxide solubility of copper, lead, arsenic, and antimony from copper-lead matte to the slag under conditions of controlled values of $P_{O_2} = 2.74 \times 10^{-4}$ Pa and $P_{S_2} = 1.45 \times 10^{2}$ Pa, applicable to smelting reduction processes of copper-, lead-containing raw materials.

2. It was found that the oxide solubility of copper from matte to slag increases monotonously with an increase of copper content in the matte. The presence of lead in the matte does not significantly affect the final solubility of copper in the slag. In a reducing atmosphere, the solubility of copper in slag is 0.28-0.35%, at the range of copper content of 30-45% in the matte, which is typical for industrial practice.

3. It was shown that the solubility of lead from copper-lead matte to slag has higher values than for the copper. Increase in the solubility of lead in slag rises with an increase in its content in matte. When the lead content in the matte is 20-25%, which is typical for industrial practice, its solubility in the slag increases to 1%.

4. It is established that under reduction conditions the sublimation of arsenic and antimony from copper-lead matte is difficult. Equilibrium concentrations of these metals in the slag (0.17%) are achieved with their optimum content in the matte at about 0.63%.

5. Obtained results can be used to predict the loss of oxide solubility of copper and to develop optimal solutions to reduce the total loss of copper with slag during the reduction processes of separate processing of copper-, lead containing raw materials.

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Figure 4 The dependence of the content of As, Sb in the slag from their content in matte
Мысты-қорғасынды штейннен Cu, Pb, As, Sb шлакқа еріштірі

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Түйіндеме. Бұл жұмыста қондырғы жасақталды және мыс-, қорғасын құрамды шикізатты тотықсыздандырп балқыту процесіне колданбалы РО2=2,74·10-4 Па және РS2=1,45·10² Па тұрақты мәндері жағдайында мысты-қорғасынды штейндерден мыстың, қорғасының, мышьяктың, сурьманың шлакқа еріштігін анықтау бойынша зерттеулер жүргізілді. Мыс тотығының штейннен шлакқа еріштігі 0,2-0,3% кезінде және оның шлактағы ерігіштігі 1% дейін артады. Минералогиялық зерттеулер нәтижелерінен шлакта мышьяктың металдық формасының жоқтығы орнатылды. Мыс-қорғасынды штейннен шлакқа еріштігі штейндегі мыстың мөлшері артқан сайын тұрақты өсетіні анықталды. Өндірістік тәжірибенің мыс-қорғасынды штейннен шлакқа еріштігі штейндегі мыстың мөлшері 30-45% кезінде тотықсыздандыру атмосферасы жағдайында мыстың шлакқа еріштігі 0,2-0,3% құрайтыны көрсетілген.

Қорғасынның мысты-қорғасынды штейннен шлакқа еріштігі едәуір жоғары екені орнатылды және оның шлактағы ерігіштігі 1% дейін артады. Минералогиялық зерттеулер нәтижелерінен шлакта мышьяктың металдық формасының жоқтығы орнатылды. Шлакта мышьяк силикатпен байланысқан тотық түрінде (As₂O₅) табылды.

Сурьма шлакта тотық және металдық түрінде табылды. Айта кететіні шлакта соңғы түрінің үлесі басым.

Тотықсыздандыру жағдайында мышьяк пен сурьма мыс-қорғасынды штейннен сублимациясы затруднена. Показано, что равновесные концентрации As, Sb в шлаке (0,17%) достигаются при их оптимальном содержании в штейне, которое составляет ~0,63%, в штейне ~0,63%. Полученные результаты могут использоваться для прогнозирования потерь оксидной растворимости меди и выработки оптимальных решений по снижению общих потерь меди со шлаком при организации восстановительных процессов раздельной переработки медь-, мышьяк содержащего сырья.

Растворимость Cu, Pb, As, Sb из медно-свинцовых штейнов в шлак

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Аннотация. В настоящей работе разработана установка и проведены исследования по определению оксидной растворимости меди, свинца, мышьяка и сурьмы из медно-свинцовых штейнов в шлак в условиях контролируемых значений РО2=2,74·10-4 Па и РS2=1,45·10² Па, применительно к восстановительным процессам плавки медь-, сурьма содержащего сырья. Установлено, что растворимость оксида меди из штейна в шлак монотонно возрастает с увеличением содержания меди в штейне. Показано, что в условиях восстановительной атмосферы растворимость меди в шлак, в пределах содержания меди в штейне 30-45%, характерных для заводской практики, составляет 0,2-0,3%. Растворимость свинца из медно-свинцового штейна в шлак имеется более высокое значения и возрастает до 1%. По результатам минералогических исследований установлено, что металлическая форма мышьяка в шлаках отсутствует. Мышьяк в шлаках обнаружен в виде оксида (As₂O₃), связанного с силикатом. Сурьма в шлаке обнаружена в оксидной и металлической форме. Причем доля последней формы в шлаке превалирует. Показано, что в условиях восстановления сублимация мышьяка и свинца из медно-свинцового штейна затруднена. Равновесные концентрации As, Sb в шлаке (0,17%) достигаются при их оптимальном содержании в штейне, которое составляет ~0,63%. Полученные результаты могут использоваться для прогнозирования потерь оксидной растворимости меди и выработки оптимальных решений по снижению общих потерь меди со шлаком при организации восстановительных процессов раздельной переработки медь-, свинц содержащего сырья.

Ключевые слова: медь, свинец, мышьяк, сурьма, штейн, шлак, растворимость, парциальное давление кислорода и серы, потери со шлаком.

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