SECTION V. METALLURGY

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Losses of copper and precious metals with slag in mine smelting of copper-, lead containing raw materials

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Abstract

The article studies the losses of copper, lead and precious metals with slag during joint mine reduction smelting of copper and lead containing sulfide intermediates and oxidized materials.

The distribution coefficients of copper, lead and precious metals between matte and slag are calculated and the laws of their change depending on the composition of the matte are established.

Quantitative ratios of oxide and sulfide losses of copper in slags are determined. It was found that the loss of copper with slag is mainly characterized by the oxide form of losses, the proportion of which is ~ 75% of the total copper content in the slag. The presence of copper losses in sulfide form (mechanical losses) correlates with gold losses with slag. It is shown that the loss of gold in the slag is contained in the mechanical suspension of matte. To increase the extraction of gold into matte, it is necessary to reduce the mechanical loss of copper with slag. An increase in the extraction of silver in matte is directly related to a decrease in the content of lead in slag.

Keywords: copper, lead, arsenic, antimony, gold, silver, loss of metals with slag, forms of occurrence.

Introduction

Autogenous copper smelting processes using oxygen or oxygen-enriched air to oxidize iron sulfide have a number of characteristic advantages: increased production, reduced energy consumption and the production of high-quality SO₂ gas for sulfuric acid production. On the other hand, the disadvantage of these processes is that volatile and harmful elements, such as lead, arsenic, antimony when using oxygen-enriched blast, tend to reduce their fractional distribution in the gas phase due to a decrease in the volume of gas. In addition, the autogenous processes of copper and lead production are accompanied by large losses of metals with slag. The envisaged measures to reduce the loss of metals with slag using additional equipment (electrically heated sedimentation tanks) or by flotation do not provide the proper effect of increasing the extraction of metals. The loss of non-ferrous metals with slag is a global problem that every enterprise tries to solve with the help of locally available resources and technical means [1-3].

The issue of copper losses with slag is sufficiently fully and thoroughly studied in relation to various modern processes of copper production. At the same time, electrochemical losses are 65-80%, and mechanical losses are 20-35% of the total copper content in the slag [4]. With regard to lead smelting, it is not possible to transfer this approach to estimate lead losses with slag due to the complex mechanism of lead distribution between smelting products [5-8]. Even within the widespread classical scheme of lead production: agglomeration – mine reduction melting – refining, for the technology of mine reduction melting of agglomerate this issue requires further research in terms of assessing the impact of the composition of the resulting matte and slag on the loss of copper and lead with slag. The

study of losses of copper and lead with slag is of particular relevance for the process of mine contractile melting of semi-products and circulating materials of lead production, in relation to their separate processing in the mine furnace.

In the literature there is no consensus on the forms of lead in the slag. The results of studies on this issue are fragmentary and are not systematized in the framework of the experimental conditions. In [4, 7] two forms of lead in slag are established: dissolved (Pb^{2+}) and mechanical (PbS). According to [8], the forms of lead in matte and slag are more complex: along with the forms of losses described above, it is necessary to additionally take into account the form of lead in matte and slag in the form of dissolved metal (Pb_{metal}). At the same time, as the results of [9, 10] show, the complex nature of the forms of copper and lead in the products of mine contractile melting and strong metallization of matte have a significant impact on the redistribution of Cu, Pb, As, Sb and noble metals between the melting products. This clarification is fundamental to practice. This issue is particularly relevant for technologies of separate processing of semi-products and circulating materials of lead production.

The aim of this work is to study the losses of copper, lead and precious metals with slag during joint mine reduction smelting of copper, lead containing sulfide intermediates and oxidized materials.

Research methods

The work used the results of industrial compositions of matte and slag obtained in the processing of copper, lead containing intermediate products and working materials of lead production in the conditions of mine contractile melting. The analysis of the results of the composition of paired samples of matte and slag from factory practice was carried out on the basis of a study of the phase and elemental composition, mineralogical studies of samples of matte and slag, and the mathematical processing of the obtained data. The atypical results of matte and slag compositions, which clearly differ from the total sample, were discarded and were not processed. The amount of initial data was 85 paired samples of the compositions of slags and mattes, which were sufficient for mathematical processing in order to identify significant dependencies and build quantitative mathematical models.

Elemental and phase analysis of matte and slag samples was performed using the mass spectrometer Agilent 7700 Series ICP-MS with inductively coupled plasma.

Mineralogical studies of the surface structure of solid air-hardened samples of matte and slag were carried out using a microscope Neofot (Carl Zeiss AG, Germany). Micro- and morphological analysis of the surface of individual slag samples was carried out using electronic scanning microscope JEOL EDS System (USA).

Results and discussion

Forms of copper, lead, arsenic and antimony in the matte and slag mine contractile melting.

To analyze the forms of copper and precious metals in matte and slag, a sample array presented in Table 1.

Comprehensive studies of the elemental and phase composition of solid samples of matte and slag showed that in all samples of matte copper, mainly ~80%, found in the form of sulfide (Cu_2S). About 15% of copper from its total content was found in the form of intermetallic compounds – Cu_3As , Cu_3Sb . The remaining amount of copper (~5%) are presented in the form of ferrite (CuFeO_2). Established in matte minor compounds of arsenic and antimony with iron. Lead in matte is detected in sulfide (PbS) and dissolved form. The dissolved part of the lead presented in the form of PbO , related to the silicate ($\text{PbO} \cdot \text{SiO}_2$), and dissolved metal (Pb_{Me}). The proportion of dissolved and sulfide forms of lead in the matte are approximately equal.

Zinc in matte is represented mainly in the form of sulfide, which accounts for 65 % of its total content in matte. In significant amounts of zinc in the matte found in the form of

oxide, its share in the matte reaches 25 %. The remaining part of zinc in matte (~10%) is presented in the form of zinc ferrites.

Iron in matte, in its bulk, is presented in the form of sulfide. The proportion of the sulfide of part is at the level of 80% from its total content in the matte. Up to 8% of iron was found in the form of ferrous iron (Fe^{2+}). The proportion of trivalent iron (Fe^{3+}) in matte is 11%. The remaining fraction of iron (~1.0%) in matte is found in metallic form and is associated with antimony and arsenic.

Copper in slag is mainly presented in oxide form. The proportion of copper sulphide varies from 30% to 38%. Lead in slag was found in oxide (PbO), metal (Pb_{Me}) and sulfide (PbS) forms, which is in good agreement with the data of the work [8].

Table 1

The results of the compositions of the matte and slag of the mine contractile melting

№ nm.	Composition of matte, % mass									Composition of slag, % mass									
	[Cu]	[Pb]	[Zn]	[Fe]	[S]	[As]	[Sb]	[Au]*	[Ag]*	(Cu)	(Pb)	(ZnO)	(SiO ₂)	(Fe _{total})	(CaO)	(As)	(Sb)	(Au)*	(Ag)*
1	38.6	26.33	4.2	7.63	11.43	4.38	1.98	16.3	1375	0.5	1.08	11.54	24.2	20.7	20.7	0.19	0.14	0.073	4.2
2	32.55	29.34	4.24	8.94	10.17	4.77	1.62	14.47	1530	0.47	1.24	11.72	26.49	21.18	19.7	0.17	0.14	0.068	4.9
3	40.25	24.36	4.73	9.49	11.9	4.39	2.36	16.9	1203	0.52	0.89	10.7	25.67	19.72	21.47	0.16	0.15	0.075	3.6
4	36.19	26.16	4.33	8.29	9.82	4.19	1.85	15.3	1463	0.49	1.45	11.64	25.31	20.5	18.69	0.23	0.14	0.073	6.0
5	38.54	28.74	3.24	5.96	10.6	4.98	2.28	16.37	1548	0.52	1.45	10.42	24.69	21.5	19.85	0.25	0.13	0.07	4.6
6	40.41	29.66	2.96	5.62	12.07	5.94	2.62	16.8	1570	0.53	1.38	11.52	25.78	20.9	18.08	0.23	0.12	0.074	5.2
7	42.97	26.42	4.13	8.88	10.4	3.91	1.54	17.07	1430	0.54	1.26	17.3	21.83	22.2	18.91	0.1	0.14	0.076	4.4
8	29.95	25.11	4.76	12.93	12.9	3.29	1.44	13.43	1330	0.5	1.3	9.94	25.15	24.25	15.0	0.15	0.16	0.073	4.8
9	39.51	25.47	5.25	13.17	11.3	2.88	1.35	15.6	1373	0.53	0.63	8.54	25.51	22.22	21.02	0.16	0.17	0.07	3.3
10	34.3	23.29	6.07	12.43	10.2	3.06	1.13	14.7	1200	0.45	0.84	7.92	26.74	21.2	19.92	0.13	0.15	0.067	4.1
11	36.93	24.09	4.95	9.96	9.87	3.22	1.93	15.8	1245	0.51	0.98	6.87	23.85	22.73	16.87	0.11	0.14	0.073	4.1
12	35.8	28.76	4.24	7.87	10.84	4.02	1.75	18.0	1513	0.52	1.67	7.35	25.6	22.47	16.61	0.24	0.13	0.072	5.9
13	33.55	25.9	4.12	9.05	11.27	3.94	1.68	16.1	1287	0.46	1.12	9.21	27.08	21.36	18.54	0.15	0.15	0.068	3.7
14	23.8	19.42	6.75	13.71	6.07	3.02	1.06	12.2	997	0.34	0.7	10.02	27.77	20.7	17.48	0.12	0.17	0.053	3.2
15	24.19	19.76	6.84	12.8	7.5	2.8	1.02	12.7	1037	0.35	0.67	11.42	26.19	20.93	19.17	0.21	0.16	0.054	3.7
16	32.59	26.36	5.07	10.78	12.4	3.35	1.45	14.7	1330	0.45	0.99	10.44	24.57	23.12	17.83	0.12	0.13	0.068	3.7
17	36.3	23.18	5.13	11.58	11.2	2.8	2.04	15.3	1123	0.57	0.84	9.97	26.53	22.41	18.22	0.11	0.14	0.08	3.2
18	34.55	22.74	5.23	12.24	9.31	2.83	1.62	13.6	1163	0.47	0.81	10.76	26.0	23.05	17.51	0.09	0.15	0.07	3.6

It was found that the proportion of sulfide and oxide component of lead in the slag is approximately equal. This indicates that in the mine contractile melting redistribution of forms of lead between the matte and slag does not occur. Therefore, to minimize the content of lead in slag during mine contractile smelting, it is necessary to provide for measures aimed at reducing both dissolved (PbO , Pb_{Me}) and mechanical losses of lead (PbS) in them.

Zinc in the slag is found in the form of oxide, ferrites and sulfide. The proportion of zinc in the form of oxide is about 80%. Up to 16% of zinc in slag is found in the form of zinc ferrites. The remaining zinc in the slag is present as sulfide.

Iron in the slag is found in the form of sulfide (FeS), ferrous and ferric trivalent, as well as in small amounts in metallic form in the form of iron arsenide and antimonide.

Minor elements - arsenic and antimony in slags, for the most part, are presented in the oxide form. Antimony is also found in metallic form (Sb^0). The results obtained are consistent with the data of [11-13].

As the results of mineralogical studies show, in conditions of strong metallization of matte, resulting from a lack of sulfur to bind non-ferrous metals and iron in sulfide form, and increased arsenic and antimony in matte, the proportion of copper and iron intermetallic compounds increases. The distribution of copper and iron intermetallic compounds between matte and slag, as well as black lead during smelting leads to the redistribution of non-ferrous metals between them in the direction of deterioration. As a result, the quality of the resulting matte and rough lead is reduced, which leads to increased losses of copper with black lead and slag.

The results obtained by the modes of occurrence of copper, lead, arsenic and antimony make it possible to describe the total movement of metals between the condensed phases of the mine contractile melting in the form of the model, which is shown in Figure 1.

Figure 1. Model of distribution of Cu, Pb, As, Sb between products of mine contractile melting

It is easy to see that in mine contractile smelting, the distribution of copper and lead between matte and slag is determined by the presence and movement of various forms of copper and lead, and has a complex mechanism. This is essential for practice. The presence of mechanical sulphide suspensions and dissolved losses of copper and lead in slag will determine not only their total losses with slag, but also, of course, determine the final content (loss) of precious metals with slag. At the same time, in the case of estimating the losses of noble metals with slag, the unambiguous approach associated with their correlation with the lead content in the slag is not entirely correct and requires clarification.

Distribution of gold and silver between matte and slag.

Established as a result of mineralogical studies of hardened slag samples identity compositions of copper sulphide inclusions in them with the composition of the final copper-lead matte suggests that copper sulfide inclusions in the slag are mechanical inclusions of matte, not separated from the slag. Therefore, by determining the volume fraction of copper sulphide inclusions in each of the hardened samples, it is possible to determine the copper content in them. According to calculations, mechanical inclusions of copper sulphides in the slag leave 30-38% of copper from its total amount.

According to A.V. Vanyukov, noble metals practically do not dissolve in slag and their losses with slag are mainly due to small mechanical inclusions of matte [14]. In this case, we consider low concentrations of gold in the slag on the one hand, the identity of the compositions of mechanical sulfide inclusions of copper in the slag with the compositions of the resulting matte on the other, as well as the fulfillment of the condition $L_{Au} \geq L_{Cu}$, given in Table 2, fully confirm this position. The dependence of the copper (L_{Cu}) and gold (L_{Au}) distribution coefficient between matte and slag on the copper content in matte is shown in Figure 2.

Calculations to determine the proportion of mechanical ($d_{mechanical}$) and dissolved ($d_{dissolved}$) copper losses in the slag were carried out on the assumption that all the gold in the slag is in a mechanical suspension of matte. The proportion of mechanical losses of copper was determined from the expression:

$$d_{mechanical} = 1 - d_{dissolved} = L_{Cu} / L_{Au} \quad (1)$$

The results of calculations are summarized in Table 2. It is easy to see that the absolute values of dissolved copper losses in the slag vary slightly from 0.23 to 0.38% (weight) and their share is up to 70% of the total copper content in the slag. Mechanical losses of copper vary within 30 - 38% of the total copper content in the slag and are consistent with the data obtained as a result of mineralogical studies. A small spread shows the practical constancy of the values of dissolved copper losses in the slag, which indicates the high accuracy of the results.

Table 2

Calculated values of distribution coefficients Cu, Au, Ag between matte and slag

№	Composition of matte, % mass			Composition of slag, % mass.			L_{Me}			$d_{Cu0.5}$	(Cu) ^{dissolved} , %
	[Cu]	[Au]*	[Ag]*	(Cu) _{total}	(Au)*	(Ag)*	L_{Cu}	L_{Au}	L_{Ag}		
1.	38.6	16.3	1375	0.5	0.073	4.2	77.2	223	325	0.65	0.33
2.	32.55	14.47	1530	0.47	0.068	4.9	69	213	306	0.68	0.317
3.	40.25	16.9	1203	0.52	0.075	3.6	77.4	225	331	0.66	0.341
4.	36.19	15.3	1463	0.49	0.073	6.0	73.9	210	244	0.65	0.317
5.	38.54	16.37	1548	0.52	0.07	4.6	74	234	336	0.68	0.355
6.	40.41	16.8	1570	0.53	0.074	5.2	76.2	227	302	0.66	0.352
7.	42.97	17.07	1430	0.54	0.076	4.4	79.6	233	325	0.66	0.355
8.	29.95	13.43	1330	0.5	0.073	4.8	60	204	277	0.67	0.337
9.	39.51	15.6	1373	0.53	0.07	3.3	74.5	223	410	0.66	0.353
10.	34.3	14.7	1200	0.45	0.067	4.1	76.2	219	289	0.65	0.293
11.	36.93	15.8	1245	0.51	0.073	4.1	72.4	216	304	0.66	0.339
12.	35.8	18.0	1513	0.52	0.072	5.9	68.8	222	256	0.72	0.377
13.	33.55	16.1	1287	0.46	0.068	3.7	72.9	209	343	0.69	0.318
14.	23.8	12.2	997	0.34	0.053	3.2	70	198	307	0.69	0.236
15.	24.19	12.7	1037	0.35	0.054	3.7	69	202	280	0.71	0.247
16.	32.59	14.7	1330	0.45	0.068	3.7	72.4	216	355	0.66	0.3
17.	36.3	15.3	1123	0.57	0.08	3.2	63.7	191	350	0.67	0.38
18.	34.55	13.6	1163	0.47	0.07	3.6	73.5	212	320	0.62	0.29

□ the contents of Au and Ag, g/t

The established regularities are confirmed by statistical analysis of the results of industrial melting. Gold concentrated in the matte phase is mainly closely related to the copper content in the matte:

$$[Au] = 6.205 + 0.259 [Cu], r = 0.92. \quad (2)$$

The weak dependence of the gold content on the lead content in matte is taken into account by the equation:

$$[Au] = 4.146 + 0.204 [Cu] + 0.157 [Pb], r = 0.922. \quad (3)$$

Figure 2. Dependence of the distribution coefficient of copper (L_{Cu}), gold (L_{Au}) between matte and slag from copper content in matte

Based on the above, the gold content in the slag phase should have a close relationship with the copper content in it. This assumption is confirmed by the equation of pair correlation with high correlation coefficient: $r = 0.96$.

$$(Au) = 0.017 + 0.107 (Cu). \quad (4)$$

The correlation between the gold content and the copper content in the slag phase (Figure 3) shows almost a direct correlation between the desired values.

Interpolation direct to zero gold content determines the value of the dissolved copper loss in the slag equal to 0.31-0.34%, which confirms the above assumption about the almost complete presence of gold in the slag in the form of a mechanical suspension of matte.

Set the ratio of the total (Cu_{total}) dissolved ($Cu_{dissolved}$) and mechanical $[(Cu_{total}) - (Cu_{dissolved})]$ the losses of copper in the slag and their dependence on the copper content in the matte are shown in Figure 4.

Figure 3. Dependence of gold content in slag from the copper content in it

Figure 4. Dependence of mechanical losses of copper with slag from the copper content in the matte

Increase of copper content in matte by 5.0% increases the mechanical loss in the slag is 10%. The insignificant dispersion of values of mechanical losses of copper in slags and their practical coincidence with results of mineralogical researches testifies to sufficient accuracy of the carried-out calculations. In terms of the process of mine contractile melting to increase the extraction of gold in the matte, it is necessary to provide for the reduction of mechanical losses of copper with slag.

In the conditions of the reducing atmosphere the reverse picture should be expected – subordination of the values of dissolved copper losses in relation to mechanical losses. This phenomenon can be interpreted on the basis of the following considerations. A significant amount of "solid" oxygen in the composition of Converter slag is loaded from the initial charge of the mine contractile melting. The high content of Fe_3O_4 (up to 25%) during melting shifts the equilibrium of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ towards the formation of trivalent iron and has a significant effect on the growth of mechanical and dissolved losses of copper and lead with slag [4]. At the same time, the growth of dissolved copper and lead losses, along with the main sulfide oxidation reactions, occurs due to the reaction:

The content of silver in matte is closely related to the content of lead in it and their relationship is described by the equation:

$$[\text{Ag}] = 57.492[\text{Pb}] - 135.97, \quad r = 0.96. \quad (6)$$

A closer relationship has been established between the lead content and the silver concentration present in the slag phase. The equation of pair correlation has the form:

$$(\text{Ag}) = 0.31 + 3.789 (\text{Pb}), \quad r = 0.97. \quad (7)$$

The transition of silver to slag is mainly determined by the mechanism of dissolution of lead in slag. It can be argued that the total loss of silver is directly related to the loss of lead with slag and depends on its distribution between the matte and slag.

The distribution coefficient of silver between matte and slag is described by the equation:

$$L_{\text{Ag}} = 221.86 + 2.27[\text{Pb}], \quad r = 0.93. \quad (8)$$

Equations (6) – (8) allow to predict the quantitative loss of silver from the slag in the conditions of the mine contractile melting.

Conclusion

1. It is established that industrial matte is highly metallized. The formation of copper and iron intermetallic compounds with arsenic and antimony has a

significant impact on the redistribution of copper, lead, arsenic and antimony between smelting products in the direction of deterioration.

2. Quantitative ratios of copper oxide and sulphide losses in slags were determined. It is established that the losses of copper with slag are mainly characterized by the oxide form of losses, the share of which is ~75% of the total copper content in the slag. The presence of copper losses in sulfide form (mechanical losses) indicates insufficient separation of smelting products – matte and slag.
3. It is shown that all the gold in the slags is contained in the mechanical suspension of matte. To increase the extraction of gold in the matte, it is necessary to reduce the mechanical losses of copper with slag. The increase in silver recovery in matte is directly related to the decrease in lead content in slag.

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