Behavior of Cu, Zn, Pb, As compounds during copper-zinc concentrate and matte comelting in converters

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The practicability of improving the existing technology of converting copper mattes by comelting with the difficult-to-process high-sulfur copper-zinc concentrate. The basis for research in the behavior of non-ferrous metals, arsenic and antimony is thermodynamic analysis of the reactions of matte components, converter slag and copper-zinc concentrate interaction in the temperature range 1073–1573 K. The behaviour mechanism of copper, zinc, lead, arsenic, and antimony compounds during co-processing of copper-zinc concentrate with matte is established. High values of the Gibbs free energy of reactions of interaction between oxides of lead and zinc with elemental sulfur, sulfides of non-ferrous metals and iron show the feasibility of the highest possible extraction of lead and zinc into dust in the form of their volatile compounds: sulfides, as well as oxides of lead and zinc in the metallic state in the form of gas. There is shown the possibility of the highest possible extraction of arsenic and antimony into dust by means of converting their non-volatile pentavalent oxides (As_2O_5, Sb_2O_5) into volatile trivalent oxides (As_2O_3, Sb_2O_3) and non-toxic sulfides (As_2S_3, Sb_2S_3) by the converter slag sulfidizing with the components of copper–zinc concentrate: elemental sulfur and iron sulfide.

Direct processing of copper-zinc concentrate in converter allows selective extracting copper into matte as well as lead and zinc into a rich semiproduct suitable for their extraction by existing technologies. It is shown that a significant quality improvement of the resulting converter slag and blister copper is achieved by the high sublimation of arsenic and antimony into dust under conditions of converting copper-lead mattes together with a high-sulfur concentrate.

Key words: copper matte, conversion, copper-zinc concentrate, copper, lead, zinc, arsenic, antimony, Gibbs free energy, comelting, sulfidizing, thermodynamic analysis.

DOI: 10.17580/nfm.2020.02.02

Introduction

The world practice of processing copper concentrates in converters together with matte demonstrates considerable opportunity for using converter as a melting facility [1–3]. Thus, the BOR plant (Yugoslavia) receives 94 tons of copper from a 3.96×9.14 m converter as a result of concentrate and matte comelting. At that, 66.3 tons are obtained due to processing in converter of 650 kg of charge per 1 ton of matte containing 20% copper and cold additions. The Copperhill plant (USA) processes copper sulphide concentrate with a copper content of 17.13% concurrently with matte containing 13.7% copper in air-blast converters. The concentrate consumption is 750 kg per 1 ton of matte [2]. In Chile (Caletonos plant), copper matte (46% Cu) is comelted with copper sulphide concentrate that contains up to 40% copper. The plant simultaneously processes more than 1 ton of concentrate per 1 ton of matte without reducing the amount of processed matte. In [3], it is shown that when converting matte (32% Cu) on air blast, it is possible to process 0.157 t of concentrate per 1 t of hot matte.

In spite of the accomplished positive results, the developed technologies have a number of serious shortcomings. In particular, feeding the concentrate into converter requires its special preparation (drying, grinding, use of complex installation of charging). Low dust entrainment cannot be achieved. The resulting converter slags are characterized by an increased content of copper and concomitant metal impurities: lead, arsenic and antimony. In this case, the converting process is accompanied by low extraction of copper into blister copper. The authors did not consider the possibility of simultaneous use of high-sulfur concentrate components (pyrite, chalcopyrite, etc.) as a sulfidizing agent to improve the quality of the resulting products: converter slag and blister copper.

It is difficult to apply the experience of foreign plants directly to the sulphide concentrates of Kazakhstan in view of their polymetallic nature, low copper content and higher content of impurities (Pb, As, Sb). Nevertheless, the development of technologies, for example, for co-processing of difficult-to-process copper-zinc and copper-lead-zinc concentrates with matte in converters could be a significant breakthrough and a reserve for improving general production indicators of metallurgical enterprises.

A number of papers have been devoted to the problem of processing the copper-zinc semiproducts [4–6].

Some of the proposed technologies have been tested in a pilot scale, but they have not been applied into commercial production for various reasons [6]. The investigations on the interaction between the non-stoichiometric sulphides (chalcopyrite concentrate) and melted slag may be reffered to the system studies [7–9]. The authors have found that the excess sulfur of higher sulphides interacts with slag and is spent either on magnetite recovery or slag sulfidizing. The similar conclusions are reported in [10]. Based on the study of the interactions of individual oxides and sulphides of non-ferrous metals with iron compounds (sulphide, oxide), the mechanism of magnetite recovery and sulfidizing of non-ferrous metal oxides is established by differential thermal analysis. The potentiality of the high-sulfur copper concentrate usage as a sulfidizing agent for depleting converter slags has been studied in these probably isolated investigations.

When processing high-sulfur polymetallic concentrates in converters, it is necessary to take into account the specifics of raw materials, in which the mutual influence of sulphide components in the concentrate composition determine largely the distribution of metals between the smelting products. This problem is topical, first, for studying the interaction between the components of copper-zinc concentrate and converter slag obtained during converting of copper-lead mattes.

It seems appropriate to treat $Cu - Fe - S - O - SiO_2$ system with a sulfidizing agent before and after the converter slag formation. In this case, it is necessary to decide: how, at what time and in what quantity one should supply sulfidizing agents in order to achieve a synergetic effect? These questions are of fundamental importance and take on special significance.

Processing concentrates together with matte in converters should pursue a **complex goal**:

a) to obtain additional products (copper, precious metals),

b) improve the quality of converter slag and blister copper,

c) ensure high recovery of lead and zinc into dust to obtain a semiproduct suitable for the extraction of lead and zinc by the existing methods.

In this article, the ways to achieve this goal are shown based on thermodynamic analysis of reactions of interaction between the copper-zinc concentrate components and converter slag.

Research technique

Thermodynamic esimation of the interaction reactions between the components of converter slag and copper sulphide and copper-zinc concentrate was performed based on thermodynamic calculations that were brought to determining the dependence of the Gibbs free energy on temperature. Data on the free energies of source materials and reaction products, as well as their entropies and heat capacities, are borrowed from [11, 12]. Pure liquid supercooled oxide (MeO_l) and sulphide (MeS_l) has been taken as the standard state of oxides and sulphides of non-ferrous metals, iron, arsenic and antimony. The exceptions are arsenic and antimony sulphides, the standard state of which has been taken as As_2S_3, Sb_2S_3 – gas. Only those reactions that were characterized by high values of the Gibbs free energy decline (ΔG) were accepted for analysis. Thermodynamic calculations of a multicomponent $Cu - Me - Fe - S - O - SiO_2$ (Me – Pb, Zn, As, Sb) system were carried out taking into account the results of *X*-ray phase analysis of converter slag, copper-zinc concentrate, as well as mineralogical studies on the forms of metals' presence in converter slags.

Studies of the form of metals' presence in solid samples of industrial matte and converter slags were carried out using *X*-ray phase analysis and mineralogical research. Slowly cooled matte melts and "hardened" in water samples of converter slags were studied.

Elemental analysis of the studied assays was performed on an Agilent 7700 Series ICP-MS inductively coupled plasma mass spectrometer (USA).

The study of the forms of metal presence was carried out using a DRON-3 automated *X*-ray diffractometer with $Cu_{K\alpha}$ radiation, a β-filter. Conditions for shooting diffractograms: $U = 35$ kV; $I = 20$ mA; shooting θ-2θ; detector 2 deg/min. *X*-ray phase analysis on a semiquantitative basis was carried out by diffractograms of powder samples of slags and mattes using the method of equal sample charges and artificial mixtures. Quantitative ratios of crystal phases were determined. Interpretation of the diffractograms was performed using the ICDD data file: the PDF2 (Powder Diffraction File) powder diffractometric database and diffractograms of pure minerals. Content calculation was fulfilled for the main phases.

For the purpose of reproducibility of the obtained results, separate paired powder samples of slags and mattes were subjected to additional processing on a Bruker D8 Advance *X*-ray diffractometer with α-Cu radiation at a tube voltage of 40/40. Handling of the obtained diffractogram data and calculation of interplane distances were performed using EVA software. Sample identification and phase search were carried out by the Search/match program using the ASTM card database.

Mineralogical investigations were performed using a Carl Ziss Jena Neophot microscope (Germany). Microanalysis and morphological study of the surface of individual slag samples were conducted with the use of a JEOL EDS System electron scanning microscope (USA).

Examined were 36 paired samples of solid mattes and converter slags. It was found that the structure of all solid samples of slags and mattes under study remained constant with the exception of minor quantitative changes in the phase associations (under changes of the iron content in the matte) that make up their basis.

Results and discussion

1. Characteristics of raw materials

Averaged chemical compositions of the source copper-lead matte and converting products from Kazzinc LLC that were used for the analysis are shown in Table. 1.

The results of complex investigations (chemical, phase analysis, mineralogical studies) of the forms of metal presence in matte have showed that they are basically represented by a solid pyrrhotite solution, monosulfide solid solutions of lead and zinc.

In all the matte samples subjected to mineralogical studies (Fig.1), copper is mainly found as sulphide (Cu_2S).

Compounds of copper with arsenic (Cu_3As) and small amounts of compounds of copper with antimony (Cu_3Sb) with distinct countours were found. Small copper inclusions are presented in the form of ferrites. Iron in mattes, along with sulphide, is found to a very slight degree as arsenic and antimony intermetallides (Fe_xAs_y, Fe_xSb_y), which can be ignored. Individual magnetite grains were found. Large and small inclusions of copper metal were determined. Clean plattnerite (PbO_2) is found in a thin chip [13].

The mattes contain the phases dispersed into each other: very large inclusions of the slag composition containing delafossite ($CuFeO_2$), magnetite (Fe_3O_4), fayalite (Fe_2SiO_4) and lead metal. This evidences that the same structural components may have different origins: they can crystallize from a melt, or they can represent a result of transformations in the solid state. Therefore, to determine the final volume ratios and quantitative composition of the mattes one should proceed not only from the melt composition, but also should take into account the phase crystallization conditions. The existense of various forms of metal presence can be seen on the converter slag microsection fragments, shown in Fig. 2.

Copper sulphides and oxides were found, as well as a small amount of copper intermetallic compounds with arsenic and antimony. The proportion of the copper sulphide form represented as mechanical losses is ~38%.

Arsenic and antimony are also detected in the pentavalent form of As^{5+}, Sb^{5+} (As_2O_5 and Sb_2O_5), which is supported by the research in [14, 15].

Lead in slag is presented as sulphide, oxide and lead metal. The share of lead in the form of oxide (~60%) bound with silica is approximately three times more than that of the sulphide component.

2. Thermodynamics of $Cu - Me - Fe - S - O - SiO_2$ (Me – Zn, Pb, As, Sb) system

The development of a new method for processing high-sulfur copper-zinc concentrate together with matte is based on thermodynamic estimation of reactions involving ZnS and ZnO, in which zinc in a gaseous state is obtained as one of the melting products. The reactions describing physical and chemical interaction processes between the converter slag components and copper-zinc concentrate can be divided into three groups:

1st group – the reactions of non-ferrous metal and iron sulphides oxidation with oxygen;

Table 1

Averaged compositions of the source matte and converter slag

Product	Metal content, % mass.				
	Cu	Pb	Zn	As	Sb
Copper-lead matte	35.3	25.9	3.4	3.8	0.7
Blister copper	94.8	1.1	–	0.9	0.6
Converter slag	3.83	33.5	4.54	2.3	0.94
Converter dust	8.3	54	3.5	13.5	1.3

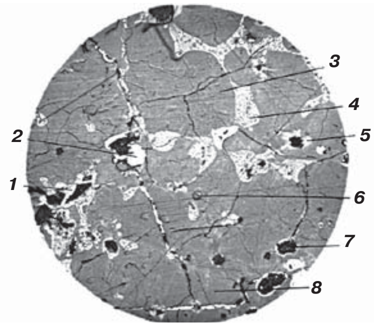

Fig. 1. Microstructure of copper-lead matte (magnification — ×500): *1* — copper intermetallides (Cu_xAs_y, Cu_xSb_y); *2* — metallic copper; *3* — bornite Cu_5FeS_4; *4* – galena PbS; *5* — troilite FeS; *6* — magnetite Fe_3O_4; *7* — lead metal PbMe; *8* – sphalerite ZnS

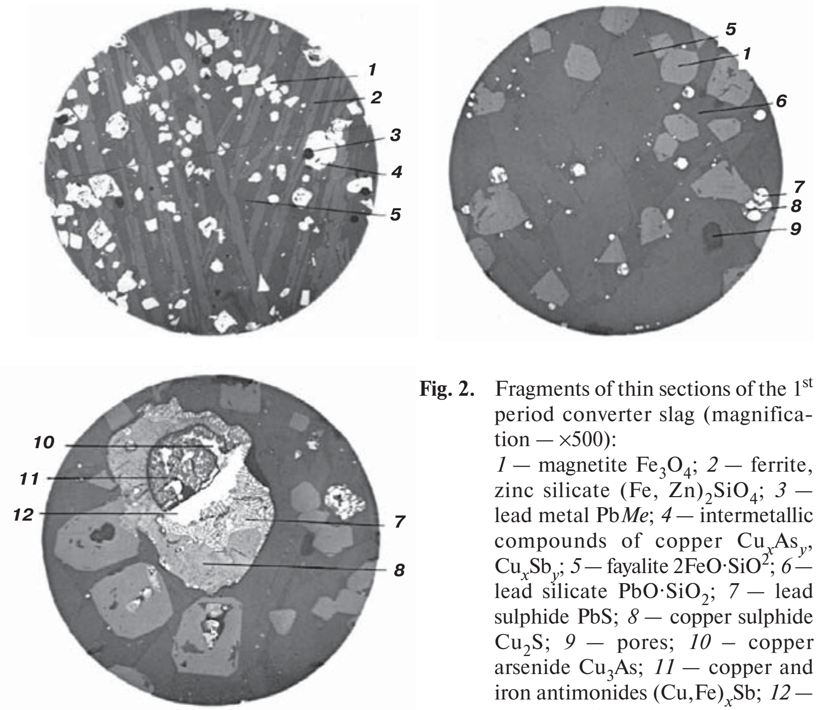

Fig. 2. Fragments of thin sections of the 1st period converter slag (magnification — ×500):
1 — magnetite Fe_3O_4; *2* — ferrite, zinc silicate $(Fe, Zn)_2SiO_4$; *3* — lead metal Pb*Me*; *4* — intermetallic compounds of copper Cu_xAs_y, Cu_xSb_y; *5* — fayalite $2FeO·SiO^2$; *6* — lead silicate $PbO·SiO_2$; *7* — lead sulphide PbS; *8* — copper sulphide Cu_2S; *9* — pores; *10* — copper arsenide Cu_3As; *11* — copper and iron antimonides $(Cu,Fe)_xSb$; *12* — iron arsenide, FeAs

2nd group — higher sulfide dissociation reactions and reactions of interaction of non-ferrous metal and iron oxides with the higher sulfide decomposition products;

3rd group — exchange reactions of interaction between oxides and sulphides of non-ferrous metals and iron.

This division does not mean a strict sequence of reactions according to the specified scheme and is “conditional”. When charging the concentrate into converter, the above-mentioned reactions proceed at a high rate, so it is not possible to quantify the behavior of metals. This is evidenced by calculations of the melting time of single sulphide particles carried out in [16], where it is shown that the period of its oxidation at a slag temperature of 1300 °C can be 15—17 seconds for a particle 6 μm in diameter. However, the chosen approach allows conducting a qualitative assessment of metal behavior and argue the physical and chemical transformations of components under the conditions of the copper matte converting together with copper-zinc concentrate from the point of view of thermodynamic analysis.

The mechanism of oxidation of non-ferrous metal and iron sulphides, representing the 1st group, is considered in detail in [13].

For the intended purpose, the phase transformations and interaction of the components that make up the fundamentals of the 2nd and 3rd groups, represent the conversion of lead, zinc to dust, and copper sulphide into matte with the formation and separation of the matte and slag phases.

The mechanism of the processes in progress can be described by a system of reactions as follows:

$$2CuFeS_2 = Cu_2S + 2FeS + 0.5S_2$$
$$\Delta G_T^0 = 138.9 - 0.353T,\ \text{kJ/mol}, \qquad (1)$$

$$FeS_2 = FeS + 0.5S_2$$
$$\Delta G_T^0 = 170.75 - 0.167T,\ \text{kJ/mol}, \qquad (2)$$

$$2FeO + 1.5S_2 = 2FeS + SO_2$$
$$\Delta G_T^0 = -175.66 + 0.074T,\ \text{kJ/mol}, \qquad (3)$$

Table 2
Calculated values of the Gibbs free energy (ΔG_T^0, kJ/mol·K) for reactions (1) – (8) in the temperature range 1073–1573 K

No.	Reaction	ΔG_T^0, kJ/mol·K			
		Temperature, K			
		1073	1273	1473	1573
1	$2CuFeS_2 = Cu_2S + 2FeS + 0.5S_2$	–22.07	–82.97	–147.15	–180.25
2	$FeS_2 = FeS + 0.5S_2$	–9.37	–41.83	–74.76	–91.37
3	$2FeO + 1.5S_2 = 2FeS + SO_2$	–96.75	–81.27	–66.73	–59.78
4	$4Fe_3O_4 + S_2 = 12FeO + 2SO_2$	259.00	132.95	6.10	–57.72
5	$3Fe_3O_4 + FeS + 5SiO_2 = 5(2FeO{\cdot}SiO_2) + SO_2$	–74.54	–77.97	–79.40	–92.20
6	$4Cu_2O + 3S_2 = 4Cu_2S + 2SO_2$	–579.15	–589.06	–599.04	–594.07
7	$Cu_2O + FeS = Cu_2S + FeO$	–96.41	–106.63	–116.39	–118.63
8	$Cu_2O + PbS = Cu_2S + PbO$	–46.01	–56.27	–66.44	–67.43

$$4Fe_3O_4 + S_2 = 12FeO + 2SO_2$$
$$\Delta G_T^0 = 938.95 - 0.633T,\ \text{kJ/mol}, \qquad (4)$$

$$3Fe_3O_4 + FeS + 5SiO_2 = 5(2FeO{\cdot}SiO_2) + SO_2$$
$$\Delta G_T^0 = -50.695 - 0.021T,\ \text{kJ/mol}, \qquad (5)$$

$$4Cu_2O + 3S_2 = 4Cu_2S + 2SO_2$$
$$\Delta G_T^0 = -542.84 + 0.036T,\ \text{kJ/mol}, \qquad (6)$$

$$Cu_2O + FeS = Cu_2S + FeO$$
$$\Delta G_T^0 = -47.88 - 0.046T,\ \text{kJ/mol}, \qquad (7)$$

$$Cu_2O + PbS = Cu_2S + PbO$$
$$\Delta G_T^0 = 3.207 - 0.046T,\ \text{kJ/mol}. \qquad (8)$$

The calculated values of the Gibbs free energy decline for reactions (1) – (8) in the temperature range from 1073 to 1573 K are shown in Table. 2.

We notice that in the conditions of converting copper mattes jointly with copper and/or copper-zinc concentrate (1573 K) the calculated values of the Gibbs free energy of reactions (1) – (8) are quite high, except that for the reaction (4), which becomes active at a temperature above 1473 K.

High thermodynamic probability of reactions (6) – (8) proves the potentiality of copper oxide sulfidizing with higher sulfide decomposition products and sulfides of non-ferrous metals and iron introduced with copper-zinc concentrate. The course of reactions (6) – (8) is strongly biased towards Cu_2S formation because of high affinity between copper and sulfur, and that of iron and lead with oxygen. This ensures the formation of a matte phase with high copper content.

When feeding copper-zinc concentrate, iron sulphide reacts with magnetite by reaction (5). Thermodynamic probability of magnetite recovery is quite high: $\Delta G_{1573K} = -92.20$ kJ/mol. The course of reaction (5) creates conditions for reducing the solubility of non-ferrous metals in slag.

It is particulary remarkable that existing technology of converting copper mattes provides concentrating a major portion of lead and zinc in the slag (20 and ~40%, respectively). Such a distribution reduces their extraction into dust and assistes with their accumulation during the converter slag processing in the «melting – converting» chain. One should expect a redistribution of lead and zinc between the converting products when coprocessing copper-zinc concentrate. The set of processes that take place involving PbS and PbO can be described by the reactions of interaction between lead oxide and the higher sulphide dissociation products (S_2, FeS):

$$2PbO + 1{,}5S_2 = 2PbS + SO_2$$
$$\Delta G_T^0 = -277.84 + 0.075T\text{, kJ/mol,} \quad (9)$$

$$PbO + FeS = PbS + FeO$$
$$\Delta G_T^0 = -51.089 + 0.001T\text{, kJ/mol,} \quad (10)$$

$$PbO + ZnS = PbS + ZnO$$
$$\Delta G_T^0 = -40.46 + 0.006T\text{, kJ/mol,} \quad (11)$$

$$2PbO{\cdot}SiO_2 + 2FeS = 2PbS + 2FeO{\cdot}SiO_2$$
$$\Delta G_T^0 = -182.86 + 0.1T\text{, kJ/mol,} \quad (12)$$

$$2PbO{\cdot}SiO_2 + 2ZnS = 2PbS + 2ZnO{\cdot}SiO_2$$
$$\Delta G_T^0 = -88.356 + 0.034T\text{, kJ/mol,} \quad (13)$$

$$PbS + 2PbO = 3Pb + SO_2$$
$$\Delta G_T^0 = -88.356 + 0.034T\text{, kJ/mol.} \quad (14)$$

The results of thermodynamic calculations of the Gibbs free energy for reactions (9) – (14) in the temperature range from 1073 to 1573 K are shown in Table. 3

The completeness of the course of reaction (14) is determined by the direction of reactions (8) and (9) – (13). Thermodynamic probability of reactions (9) – (13) is ensured over the entire temperature range. The highest value of the Gibbs free energy lessening is distinctive for the reaction (9), $\Delta G_{1573K} = -162.18$ kJ/mol. In the presence of copper oxide in the slag, passing of reaction (6) seems to be the most preferable due to stronger affinity of copper to sulfur than that to oxygen, as is evidenced by high calculated value of the Gibbs free energy ($\Delta G_{1573K} = -594.07$ kJ/mol).

Comparative analysis of the absolute values of the Gibbs free energy of reaction (10) $\Delta G_{1573K} = -51.19$ kJ/mol with the values of ΔG for reactions (7) and (5) equal to $\Delta G_{1573K} = -118.63$ kJ/mol and $\Delta G_{1573K} = -92.20$ kJ/mol, respectively, demonstrates some slowing down of reaction (10). However, when loading a fresh batch of concentrate, one can expect a shift in the equilibrium of reaction (10) towards the lead sulphide formation, owing to an increase in the FeS mass fraction in iron and stronger affinity with oxygen than that of lead. This will create a positive effect for more complete lead sublimation into dust in the form of its sulphide.

The interaction of zinc sulphide with lead oxide and lead silicate by reactions (11) and (13) is technologically significant. The course of these reactions ensures lead converting to readily volatile sulphde and decreasing its content in the slag. The value of the Gibbs free energy decline for reaction (13) decreases from $\Delta G_{1073K} = -54.22$ kJ/mol to $\Delta G_{1573K} = -38.19$ kJ/mol as the temperature rises from 1073 K to 1573 K (Table 3). Therefore, the highest activity of reaction (13) should be expected at the initial stage of the concentrate loading into converter. To increase sublimation of lead and zinc into dust, it is necessary to correct the silica content in the slag towards reduction.

The behavior of zinc during processing of copper-zinc concentrate in converters together with matte seems to be somewhat complicated. The mechanism of the zinc sulphide behavior under converting conditions can be represented by the following reactions:

$$ZnS + O_2 = Zn\ (g) + SO_2$$
$$\Delta G_T^0 = 23.61 - 0.124T\text{, kJ/mol,} \quad (15)$$

$$ZnS + 1/2O_2 = ZnO + S_2$$
$$\Delta G_T^0 = -164.66 + 0.009T\text{, kJ/mol,} \quad (16)$$

$$ZnS + 2/3O_2 = ZnO + SO_2$$
$$\Delta G_T^0 = -887.82 + 0.156T\text{, kJ/mol,} \quad (17)$$

$$3ZnS + 2Cu_2O = 3Zn\ (g) + 2Cu_2S + SO_2$$
$$\Delta G_T^0 = 884.14 - 0.608T\text{, kJ/mol,} \quad (18)$$

$$ZnS + 2Cu_2O = Zn\ (g) + 4Cu + SO_2$$
$$\Delta G_T^0 = 349.13 - 0.258T\text{, kJ/mol,} \quad (19)$$

$$ZnS + Cu_2O = Cu_2S + ZnO$$
$$G_T^0 = -49.25 - 0.033T\text{, kJ/mol.} \quad (20)$$

Fig. 3 illustrates the dependence of the change in the Gibbs free energy decline on temperature.

It is not difficult to see that the greatest probability of zinc sulphide oxidation in the entire temperature range under investigation from 1073 to1573 K runs by reaction (17). Thermodynamic probabilities of reactions (15) and (16) are equivalent to each other, but much lower than that of reaction (17). This indicates that zinc is mainly distributed between converter slag and dust under converting conditions.

Zinc sulphide has a favorable effect on the copper transfer from slag to matte due to reactions (18) – (20).

Table 3

Calculated values of the Gibbs free energy (ΔG_T^0, kJ/mol·K) for reactions (9) – (14) in the temperature range 1073–1573 K

No.	Reaction	ΔG_T^0, kJ/mol·K Temperature, K 1073	 1273	 1473	 1573
9	$2PbO + 1.5S_2 = 2PbS + SO_2$	–197.55	–181.99	–166.65	–162.18
10	$PbO + FeS = PbS + FeO$	–50.40	–50.35	–49.96	–51.19
11	$PbO + ZnS = PbS + ZnO$	–34.37	–33.01	–31.68	–32.57
12	$2PbO{\cdot}SiO_2 + 2FeS = 2PbS + 2FeO{\cdot}SiO_2$	–78.46	–54.09	–33.39	–31.15
13	$2PbO{\cdot}SiO_2 + 2ZnS = 2PbS + 2ZnO{\cdot}SiO_2$	–54.22	–43.58	–37.72	–38.19
14	$PbS + 2PbO = 3Pb + SO_2$	9.41	–25.41	–52.36	–63.70

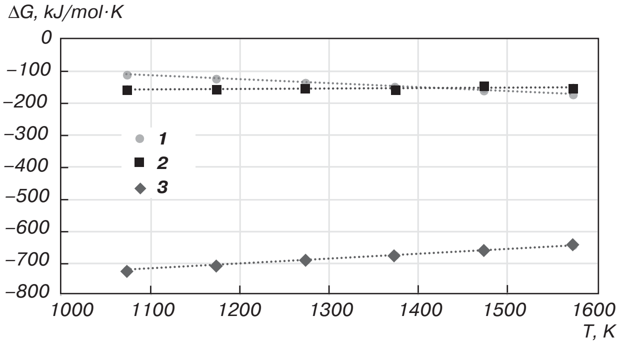

Fig. 3. Dependence of the Gibbs free energy (ΔG_T^0) of reactions (15) – (17) on temperature:
1 — $ZnS + O_2 = Zn(g) + SO_2$; *2* — $ZnS + 1/2O_2 = ZnO + S_2$; *3* – $ZnS + 2/3O_2 = ZnO + S_2$

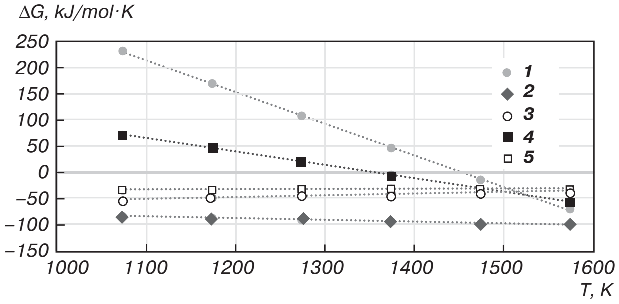

Fig. 4. Dependence of the Gibbs free energy (ΔG_T^0) of reactions (18) – (21) on temperature:
1 — $3ZnS + 2Cu_2O = 3Zn(g) + 2Cu_2S + SO_2$; *2* — $ZnS + Cu_2O = Cu_2S + ZnO$; *3* – $2ZnS + 2PbO{\cdot}SiO_2 = 2PbS + 2ZnO{\cdot}SiO_2$; *4* — $ZnS + 2Cu_2O = Zn(g) + 4Cu + SO_2$; *5* — $ZnS + PbO = PbS + ZnO$

Stronger affinity of copper to sulfur than that of zinc accents the equilibrium of reactions towards the formation of copper sulphide, which forms the matte phase. This is also proved by the values of the Gibbs free energy of reactions (18) – (20), which at the converting process temperature (1523 K) are negative (Fig. 4).

High value of the Gibbs free energy of reaction (20), $\Delta G_{1573K} = -100.0$ kJ/mol, and equivalent values of the Gibbs free energy of reactions (18), (19) point out their greater contribution and priority interaction of copper oxide with zinc sulphide rather than with lead sulphide according to reaction (8). In converting conditions, passing of reactions (18), (19) are favourable for transfering zinc to a gas phase.

Fig. 4 gives the values of the Gibbs free energy changes for reactions (11) and (13). It is not difficult to see the practicability of interaction between zinc sulphide and zinc oxide by reaction (11) as well as between zinc sulphide and lead silicate by reaction (21). The course of these two equivalent reactions promotes the highest possible lead transfer to dust in the form of its readily volatile sulphide. At high temperatures, lead sulphide and lead oxide are quite volatile compounds: the steam pressure of PbS at 1100 °C is 13.9 kPa [17], and that of PbO is 2.0 kPa [18].

Zinc oxide, formed by reactions (11), (13), (16), (17) and (20), will be converted into sulphide by interaction with an additional amount of FeS introduced with copper-zinc concentrate, and volatize with dust. This reaction is strongly biased towards the zinc sulphide formation because iron possesses greater affinity for oxygen than zinc does.

The increase in the zinc mass fraction in the melt owing to the copper-zinc concentrate loading and high temperature of the converting process (1573 K) creates auspicious conditions for segregating lead and zinc into a gas phase. These accords well with the literature data [19–20]. A gain of the zinc content in the melt increases sublimation of zinc approximately by a factor of five: the pressure of zinc sulphide vapor at 1100 °C is 0.28 kPa, that of pure zinc is 101.3 kPa, but at already 906 °C [20].

The greatest interest from a technological and environmental point of view represents a study of reactions that describe the behavior of arsenic and antimony. The purpose of this group of reactions is to ensure the highest possible removal of arsenic and antimony from the converting process by means of their deep sublimation into dust by transferring them to readily volatile oxides (As^{3+}, Sb^{3+}) and non-toxic volatile sulphides (As_2S_3, Sb_2S_3).

As the results of mineralogical studies have shown, arsenic and antimony are present as copper intermetallides (Cu_3As, Cu_3Sb) in mattes, and in the form of non-volatile oxides As_2O_5 and Sb_2O_5 — in converter slags. Taking into account the established forms of presence, the mechanism of interaction of arsenic and antimony compounds in the conditions of converting copper matte jointly with copper-zinc concentrate can be represented by the following reactions:

$$2Cu_3As + 3O_2 = 3Cu_2O + As_2O_3\,(g)$$
$$\Delta G_T^0 = -1354.147 + 0.342T,\ \text{kJ/mol}, \qquad (21)$$

$$2Cu_3As + 4O_2 = 3Cu_2O + As_2O_5\,(l)$$
$$\Delta G_T^0 = -1663.422 + 0.641T,\ \text{kJ/mol}, \qquad (22)$$

$$2Cu_3Sb + 3O_2 = 3Cu_2O + Sb_2O_3\,(g)$$
$$\Delta G_T^0 = -1173.967 + 0.509T,\ \text{kJ/mol}, \qquad (23)$$

$$2Cu_3Sb + 4O_2 = 3Cu_2O + Sb_2O_5\,(l)$$
$$\Delta G_T^0 = -1430.959 + 0.697T,\ \text{kJ/mol}, \qquad (24)$$

$$2Cu_3As + 3S_2 = 3Cu_2S + As_2S_3\,(g)$$
$$\Delta G_T^0 = -610.905 + 0.003T,\ \text{kJ/mol}, \qquad (25)$$

$$2Cu_3Sb + 3S_2 = 3Cu_2S + Sb_2S_3\,(g)$$
$$\Delta G_T^0 = -508.484 + 0.207T,\ \text{kJ/mol}, \qquad (26)$$

$$2As_2O_5 + 5{,}5S_2 = 2As_2S_3 + 5SO_2$$
$$\Delta G_T^0 = -73.48\text{-}0.082T,\ \text{kJ/mol}, \qquad (27)$$

$$2Sb_2O_5 + 5{,}5S_2 = 2Sb_2S_3 + 5SO_2$$
$$\Delta G_T^0 = -62.61 - 0.084T,\ \text{kJ/mol}, \qquad (28)$$

$$3As_2O_5 + 5FeS = 6As + 5FeO + 5SO_2$$
$$\Delta G_T^0 = 1979.63 - 1.657T,\ \text{kJ/mol}, \qquad (29)$$

$$3Sb_2O_5+5FeS = 6Sb+5FeO+5SO_2$$
$$\Delta G_T^0 = 1891.599 - 1.442T, \text{ kJ/mol}. \quad (30)$$

The calculated values of the Gibbs free energy (ΔG_T^0) for reactions (21) – (30) and their dependences on temperature are shown in Table 4.

Table 4
Calculated values of the Gibbs free energy (ΔG_T^0, kJ/mol·K) for reactions (21) – (30) in the temperature range 1073–1573 K

No.	Reaction	ΔG_T^0, kJ/mol·K			
		Temperature, K			
		1073	1273	1473	1573
21	$2Cu_3As + 3O_2 = 3Cu_2O + As_2O_3$ (*g*)	–908.87	–891.67	–876.59	–878.02
22	$2Cu_3As + 4O_2 = 3Cu_2O + As_2O_5$ (*l*)	–899.04	–820.26	–744.66	–716.3
23	$2Cu_2Sb + 2{,}5O_2 = 2Cu_2O + Sb_2O_3$ (*g*)	–574.21	–506.86	–441.24	–413.89
24	$2Cu_2Sb + 3{,}5O_2 = 2Cu_2O + Sb_2O_5$ (*l*)	–639.31	–527.51	–422.02	–376.55
25	$2Cu_3As + 3S_2 = 3Cu_2S + As_2S_3$ (*g*)	–622.27	–612.9	–606.15	–606.14
26	$2Cu_3Sb + 3S_2 = 3Cu_2S + Sb_2S_3$ (*g*)	–297.23	–248.95	–203.77	–183.23
27	$2As_2O_5 + 5{,}5S_2 = 2As_2S_3 + 5SO_2$	–821.16	–840.88	–856.28	–862.41
28	$2Sb_2O_5 + 5{,}5S_2 = 2Sb_2S_3 + 5SO_2$	–704.38	–727.57	–741.34	–746.4
29	$3As_2O_5 + 5FeS = 6As + 5FeO + 5SO_2$	–642.59	–817.78	–986.2	–1059.08
30	$3Sb_2O_5 + 5FeS = 6Sb + 5FeO + 5SO_2$	–363.31	–538.78	–694.82	–756.4

Thermodynamic calculations have determined the peak values of the Gibbs free energy decline (in absolute magnitude) for reactions (21) – (30) within the entire examined temperature range from 1073 to 1573 K.

High thermodynamic possibility of reactions (21), (23) promotes the formation of readily volatile trivalent oxides of arsenic and antimony as well as the growth of their sublimation with gases, which will positively affect their elimination from the technological scheme. Under conditions of the increased air consumption, the formation of non-volatile pentavalent oxides of arsenic and antimony by reactions (22) and (24) is highly probable, which will lead to the opposite effect – to the growth of their concentration in converter slag and accumulation in the general technological scheme.

When loading a fresh portion of copper-zinc concentrate into converter, the excess sulfur, formed by reaction (1) and (2) can interact with copper intermetallides (Cu_3As, Cu_3Sb) and non-volatile pentavalent oxides of arsenic and antimony according to the reactions (27) and (28).

A deeper sublimation of As, Sb into dust is to be expected owing to the interaction between iron sulphide, that is additionally introduced with a concentrate, and non-volatile oxides As_2O_5 and Sb_2O_5 by reactions (29), (30) as evidenced by their high values of the Gibbs free energy at 1523 K (Table 4). Under oxidative conditions of converting, the resulting elemental arsenic and antimony will be oxidized to their volatile oxides and sublimated with dust, which agree with the results of [14, 15].

The progress of reactions (27) – (30) under converting conditions (1523 K) contributes to the highest possible removal of arsenic and antimony from technological scheme in the metallic state and in the form of non-toxic volatile sulfides As_2S_3 and Sb_2S_3. This will cause the reduction of their accumulation in the primary copper production and significantly improve the quality of converter slag and blister copper. The most elimination of arsenic and antimony from converter slag and blister copper will significantly reduce material expenses of the following processing operations.

Thus, the results of thermodynamic analysis show the feasibility of direct melting of difficult-to-process copper-zinc concentrate in converters together with matte. Preliminary calculations of the material and heat balance of the copper-lead matte converting together with copper-zinc concentrate has showed the possibility of direct melting of up to 25% of the concentrate by the matte weight. The calculation results will be covered in the following publications, which will also show in detail a highly efficient method for loading fine concentrate with the use of the ejection feeder that ensures minimal dust entrainment of the material when it is loaded into converter. The use of the device does not require special preparation of the concentrate and is easily integrated into the current converting technology without any material expenses.

Conclusions

– Based on thermodynamic analysis, the practicability of using high-sulfur copper-zinc concentrate as a sulfidizing agent to improve the quality of converter slag and blister copper is shown.

– It is shown that the interaction of the converter slag components with copper-zinc concentrate provides a high probability of reducing copper losses with slag. The mechanism of the copper oxide interaction with excess sulfur and iron sulphide, which are the products of dissotiating the concentrate higher sulphides, is established.

– High values of the Gibbs free energy for reactions of interaction between oxides of lead and zinc with elemental sulfur, sulphides of non-ferrous metals and iron sulphides demonstrates the peak recovery of lead and zinc into dust as their volatile compounds: sulphides, lead oxide, and zinc metal in the form of gas.

– There is shown the possibility of the highest possible extraction of arsenic and antimony into dust by converting their non-volatile pentavalent oxides (As_2O_5, Sb_2O_5) into volatile trivalent oxides (As_2O_3, Sb_2O_3) and non-toxic sulfides As_2S_3 and Sb_2S_3 by the converter slag sulfidizing with copper-zinc concentrate.

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