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BEHAVIOR OF COPPER AND SULFUR DURING HIGH-TEMPERATURE SULFURIZATION OF COPPER-SMELTING SLAGS WITH ELEMENTAL SULFUR

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The article presents the results of experimental sulfidization of smelt and converter slags of copper smelting production using granular elemental sulfur at a temperature of 1300°C in an inert atmosphere without hydrocarbon or metal reducing agents. The distribution of sulfur over products and the behavior of copper are considered. It is shown that feeding elemental sulfur to the slag recovers magnetite and sulfidizes iron, forming a sulfide phase whose yield increases with the consumption of elemental sulfur. An increase in the sulfur consumption leads to a decrease in the concentration of copper in the matte and slag. In the range of sulfur consumption considered, the copper content decreases to less than ~0.1% in smelt slag and to ~0.2% in converter slag. The concentration of sulfur in the gas is high. The maximum uptake of sulfur by the melt does not exceed ~49%. The results obtained indicate the possibility of using elemental sulfur without additional reducing agents to sulfidize copper-smelting slags, either rich or poor in copper, to a high degree of copper recovery.

Keywords: copper smelting, slag cleaning, sulfidization, elemental sulfur, matte, slag.

Introduction

Sulfidization (formation of sulfides of metals in a reaction between metals or oxides with sulfur-containing reagents) occurs and is used in various metallurgical processes. Oxidized nickel ores are processed through the solid-phase (at a temperature of about 700°C) sulfidization of lateritic ores with melted sulfur in a tube furnace [1, 2], the sulfidization of ferronickel melt with elemental sulfur at a temperature of 1500°C [3], and the sulfidization of oxides with pyrite during matte smelting of oxidized nickel ores in shaft furnaces and in a Vanyukov pilot furnace [4, 5]. The capabilities of the sulfidization of melts of oxidized nickel ores with elemental sulfur and calcium sulfide were studied. For example, matte formation during sulfidization of melt of oxidized nickel ores with gaseous and lump elemental sulfur in the conditions of liquid-phase smelting in a Vanyukov furnace at temperatures of 1300 and 1350°C was studied in [6]. Feeding lump sulfur onto the melt surface did not lead to the formation of the sulfide phase. Blowing sulfur vapor in an amount of up to 20% of the mass of starting ore through the melt resulted in a sulfide-phase yield of no higher than 3% of the mass of starting ore, which corresponds to no more than 4% sulfur utilization for the formation of matte. The sulfidization of oxidized nickel ores with calcium sulfide was compared with sulfidization with pyrite in blast melting in [7]. It was established that using calcium sulfide decreases the loss of nickel with slag and increases the nickel content in matte. However, charcoal as a reducer was added during the experiments, which does not allow us to conclude on the effectiveness of the sulfidizing agent in this process.

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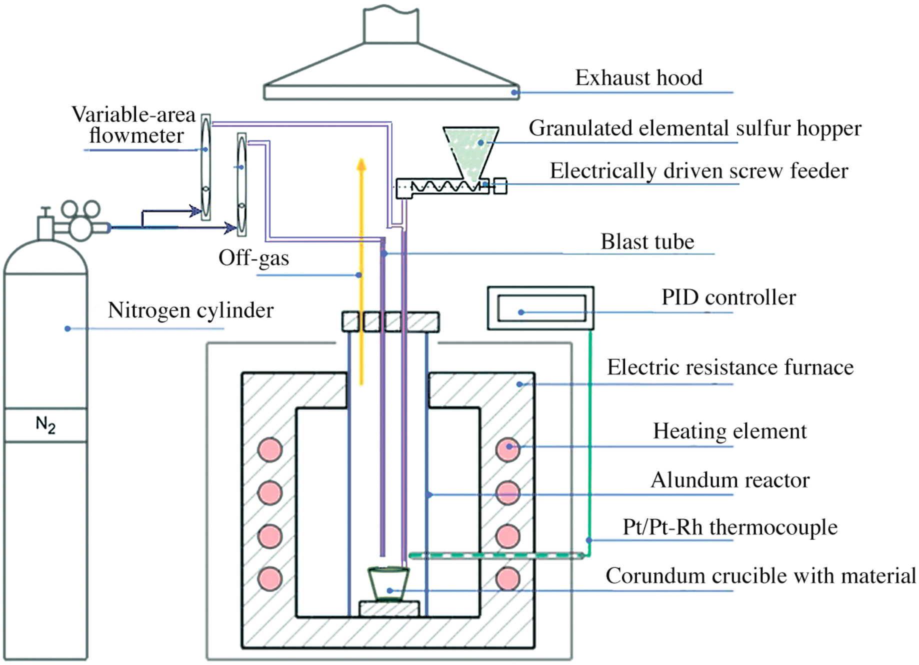


Fig. 1. Schematic of experimental setup.

During processing sulfide copper and nickel–copper ores and concentrates, sulfidization is used in the stage of slag cleaning. Pyrite, low-grade sulfide ores, and concentrates are used as sulfidizers. As a rule, sulfidization is combined with reduction [8–12].

The use of copper-poor high-ferrous sulfide materials allows, if the necessary conditions are created, effective cleaning of copper and copper–nickel smelting slags. However, this method increases the volume of slag and power consumption (needed for heating and melting of the sulfidizer) and increases the costs of processing of the resulting poor matte.

In this respect, the use of elemental sulfur as a sulfidizer in cleaning copper-smelting slags appears preferable.

Here we discuss the results of laboratory experiments on the sulfidization of copper-smelting slags with granulated elemental sulfur which were intended:

- to establish the possibility of cleaning of slag by sulfidizing it with elemental sulfur without carbon-bearing reducers and recovery of matte containing non-ferrous metals (this was not achieved in [6]);
- to determine the distribution of sulfur and its evaporation because this influences possible process solutions;
- to determine the consumption of elemental sulfur necessary for effective cleaning of slags and the composition and amount of the resulting sulfide phase.

Experimental Procedure

The experimental setup is schematized in Fig. 1. All the experiments were conducted in a alundum reactor placed in a resistance furnace. The power supplied to the furnace was controlled with a proportional–integral–differential (PID) controller. The temperature was controlled with a Pt/Pt-13% Rh thermocouple connected to

Table 1
Composition of Starting Slag, wt.%

Slag type	Cu, %	S, %	$Fe_{(tot)}$, %	Fe^{2+}, %	Fe_3O_4, %	SiO_2, %
VF smelt slag	1.05	1.84	42.41	31.26	15.41	28.41
Converter slag	6.56	1.21	49.10	35.10	19.35	21.94

a temperature controller. High-purity nitrogen (99.998 N_2) was used to create an inert atmosphere in the reactor and to feed ultrahigh-purity granulated elemental sulfur (99.999 S) to the melt. Elemental sulfur was continuously fed with an electrically driven sealed screw feeder. The starting material was smelt slag of a Vanyukov furnace (VF) and converter slag of the Balkhash Copper-Smelting Combine (see Table 1 for their compositions).

The content of elements in the starting materials and products of the experiments was determined by the following methods: Cu, $Fe_{(tot)}$, SiO_2 by the ICP-AES method, S by the gravimetric method according to the NSAM 3-X procedure, Fe^{2+} by the titration method, and Fe_3O_4 by formula (1):

$$(Fe_3O_4)\% = \left((Fe_{tot})\% - \left(Fe^{2+}\right)\%\right)\cdot\frac{Mr\left(Fe_3O_4\right)}{Mr(Fe)\cdot 3}, \tag{1}$$

where $Mr(Fe_3O_4)$ is the molar mass of magnetite, g/mol; Mr(Fe) is the atomic mass of iron, g/mol.

To minimize the influence of the entrainment of elemental sulfur that has not reacted with the melt on the degree of its uptake by the melt, the feed rate and grain size of sulfur were chosen 0.005 g/sec and 1 + 0.5 mm, respectively, based on preliminary experiments.

The main series of experiments were conducted as follows. The corundum crucible was filled with 25–50 g of slag and placed at the bottom of the reactor, which was then filled and washed with nitrogen to maintain an inert atmosphere. The temperature in the reactor was 1300 °C in all the experiments. There was a blast tube over the crucible to feed nitrogen. The reactor was sealed with a chamotte plug. The slag in the crucible completely melted in 15 min. After melting of the slag, the second blast tube was inserted into the melt to inject granulated sulfur with nitrogen at a rate of about 0.005 g/sec maintained constant with the screw feeder. The flow rate of nitrogen for feeding the sulfur and sparging the melt was about 4 ml/sec. The total amount of sulfur loaded into the melt was determined by the rate and time of feeding it into the slag. After the completion of the sulfur feed, the blast tube was removed from the melt, which then settled for 15 min. After that, the crucible was removed from the reactor and quenched in water, and the products were then separated and analyzed. The experiment conditions are described in Table 2.

Discussion of the Results

The main experimental results are presented in Table 3 and Figs. 2–7. The amount of sulfur in the gas was determined from the difference between its total amount loaded (taking into account the sulfur in the starting slag) and the amount of sulfur in the condensed products.

The reaction of sulfides with iron-silicate slags was considered in [13, 14]. For example, in [13] the kinetics and mechanism of reaction of sulfides of copper, iron, and sulfur with slag was studied from the release rate of

Table 2
Main Experimental Conditions

Starting material	Experiment number	Mass of starting slag, g	Mass of fed sulfur, g	Mass fraction of sulfur in slag, %	Blasting time, min
VF smelt slag	1	50	1.50	3.00	5
	2	50	3.00	6.00	10
	3	50	4.50	9.00	15
	4	50	6.00	12.00	20
	5	50	7.50	15.00	25
	6	50	8.88	17.76	30
	7	50	9.86	19.72	33
Converter slag	8	25	0.75	3.00	3
	9	25	1.50	6.00	5
	10	25	2.36	9.44	8
	11	25	3.01	12.04	10
	12	25	3.74	14.96	12
	13	25	4.45	17.80	15
	14	25	5.16	20.64	17

Table 3
Experimental Results

Starting material	Experiment number	Matte mass, g	Matte yield as percentage of slag mass, %	Composition of matte, %			Mass of slag, g	Composition of slag, %						Degree of uptake of sulfur by melt, %
				Cu	Fe	S		Cu	S	Fe_{tot}	Fe^{2+}	Fe_3O_4	SiO_2	
VF smelt slag	1	0.46	0.92	19.41	44.63	19.40	50.69	0.73	2.49	41.36	33.91	10.29	–	29.16
	2	3.15	6.30	8.45	54.91	19.90	46.81	0.39	2.57	41.09	32.51	11.86	26.17	30.33
	3	8.23	16.46	4.15	55.31	18.90	41.99	0.30	2.48	35.57	33.72	2.55	24.58	37.26
	4	11.55	23.10	3.54	57.80	22.80	39.33	0.13	1.91	36.87	28.28	11.87	–	41.08
	5	13.29	26.58	2.76	58.54	21.20	32.74	0.09	1.86	32.34	27.90	6.14	31.70	35.19
	6	17.26	34.52	2.70	58.21	25.90	35.56	0.08	1.70	30.07	25.47	6.36	–	46.79
	7	15.92	31.84	2.86	61.07	25.00	34.08	0.06	1.55	31.03	27.40	5.01	–	36.39

Table 3 (continued)

Starting material	Experiment number	Matte mass, g	Matte yield as percentage of slag mass, %	Composition of matte, %			Mass of slag, g	Composition of slag, %						Degree of uptake of sulfur by melt, %
				Cu	Fe	S		Cu	S	Fe_{tot}	Fe^{2+}	Fe_3O_4	SiO_2	
Converter slag	8	1.09	4.36	67.48	6.46	20.40	23.91	1.39	0.79	47.65	36.94	18.72	–	14.81
	9	1.32	5.28	42.59	23.04	20.10	23.68	1.33	2.08	47.80	34.10	9.12	–	31.25
	10	2.72	10.88	19.65	43.00	19.70	22.28	0.76	2.39	43.86	36.36	10.37	–	33.43
	11	4.37	17.48	22.83	41.04	20.90	20.63	0.91	2.8	45.38	35.06	1.66	–	40.78
	12	7.63	30.52	13.84	48.72	20.60	17.37	0.78	2.78	40.87	28.55	8.03	–	48.30
	13	7.84	31.36	10.94	54.39	23.20	17.16	0.26	1.2	34.81	26.63	8.66	–	39.22
	14	8.48	33.92	10.55	54.19	24.50	16.52	0.21	1.29	31.72	27.40	7.04	–	39.08

SO_2 after one-time loading of sulfide samples into the slag melt. It is noted that the main cause of the formation of SO_2 (sulfur in gas in this form) is the reaction of sulfides and sulfur with slag magnetite.

As applied to the experimental conditions, the mechanism of reaction of sulfur with slag can most generally be described as follows. After being added to slag, sulfur is rapidly heated and evaporated. The sulfur vapor primarily reacts with slag magnetite releasing SO_2 according to the reaction

$$S_2(g) + 4(Fe_3O_4) = 12(FeO) + 2SO_2(g). \tag{2}$$

If the pressure of sulfur vapor is high, the FeO of slag is sulfidized, accompanied by release of gaseous SO_2 and formation of FeS dissolved in slag in the first stage:

$$3S_2(g) + 4(FeO) = 4(FeS) + 2SO_2(g). \tag{3}$$

If the concentration of magnetite decreases, slag can sulfidize without the formation of SO_2 according to the following reaction [13]:

$$S_2(g) + 8(FeO) = 2(FeS) + 2(Fe_3O_4). \tag{4}$$

As the sulfidization reaction develops, the amount and activity of the iron sulfide dissolved in the slag increase. As the concentration of FeS in the slag exceeds its limiting solubility, the necessary thermodynamic conditions are created and it precipitates into a separate sulfide phase.

The sulfide phase also includes a portion of the copper contained by the slag. The mechanism of this process can generally be described as follows. Copper is known to be present in slag as a mechanical suspension of matte drops and as dissolved Cu_2S and Cu_2O. As FeS precipitates as the sulfide phase, matte drops suspended

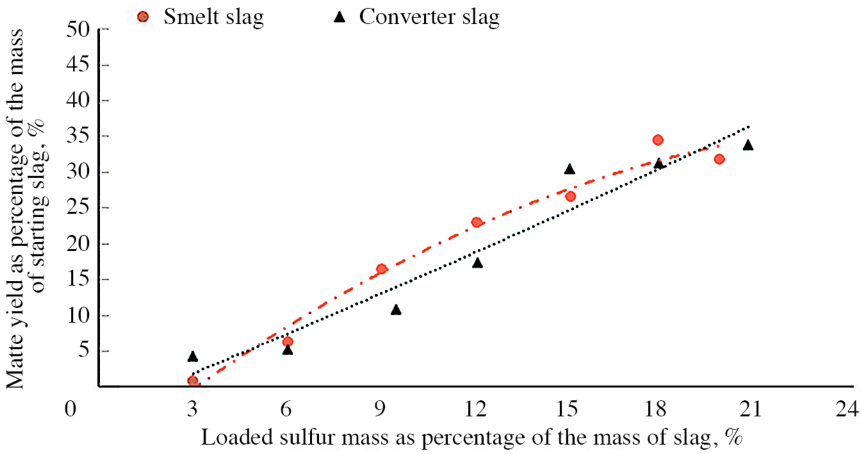


Fig. 2. Influence of the amount of loaded elemental sulfur on the amount of produced matte.

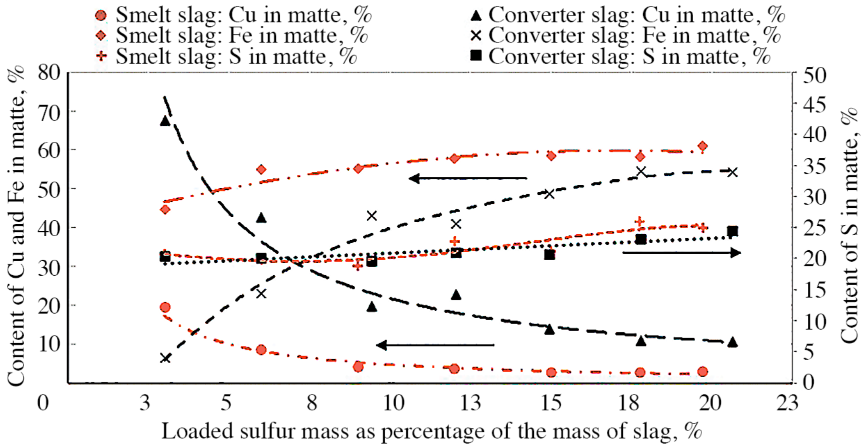


Fig. 3. Influence of the amount of loaded elemental sulfur on the composition of matte.

in the slag are diluted, which decreases the mechanical losses of copper provided that the number of these drops in slag remains the same. With decrease in the concentration of copper in the matte phase and in its activity in the system, the copper sulfide dissolved in the slag is redistributed in favor of matte, reducing the concentration of the dissolved Cu_2S in the slag. The content of dissolved copper in oxide form also decreases due to the decrease in the oxidation potential of the system during reduction.

The mechanism of reaction of sulfur with copper-smelting slag described in a very simple way essentially (qualitatively) agrees with the main results presented in Table 3: much sulfur in gas, increase in the amount of matte phase with increase in the sulfur consumption, decrease in the concentration of copper in matte and slag with increase in the sulfur consumption. Quantitative effects and patterns are important for developing specific process solutions. Let us consider the most important of them.

Behavior of Sulfur. Figures 2 and 3 shows the dependence of the amount and composition of matte (percentage of the mass of the starting slag) on the consumption of elemental sulfur (percentage of the mass of the starting slag).

It can be seen that the amount of matte (Fig. 2) and the content of iron increase and, as a result, the content of copper in matte decreases (Fig. 3) with increasing sulfur consumption. The matte produced by sulfidizing

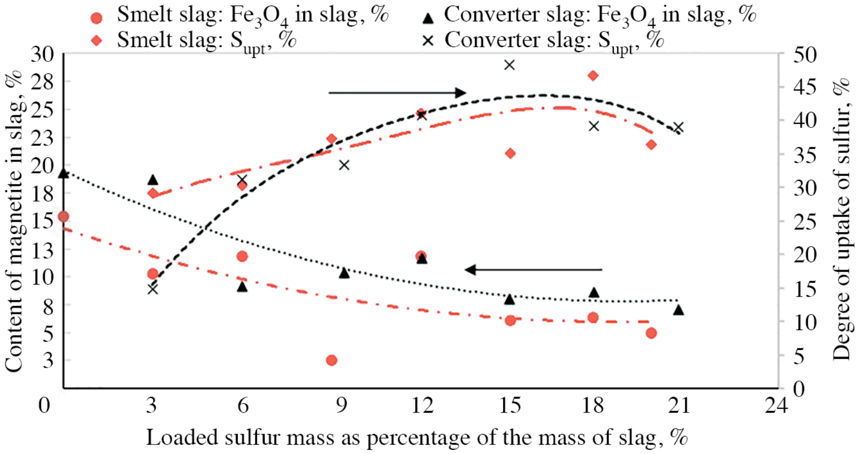


Fig. 4. Influence of the amount of loaded elemental sulfur on the content of magnetite in slag and the degree of uptake of sulfur by the melt.

converter slag is naturally richer than that produced by sulfidizing smelt slag because converter slag initially contains more matte and copper [15]. The amount of sulfide phase after loading of the first 3% of sulfur is slightly lower (especially for smelt slag) than the rate of its increase with further loading of sulfur, which can be due to the higher consumption of sulfur in the initial stages for increasing the concentration of iron sulfide in the slag and more sulfur in gas because of the higher concentration of magnetite. If the consumption of sulfur is higher than 15% of the mass of slag, the increase in the amount of matte per unit mass of loaded sulfur decreases a little. This can be due to the redistribution of sulfur after the change of the composition of slag and matte. For example, the content of iron decreases by ~10% in smelt slag and by ~15% in converter slag, while the content of magnetite in slag decreases by ~5–8%. The content of copper in matte decreases to ~3–10%. The content of sulfur in poor matte increases by 2–3% after the maximum amount of sulfur is loaded. How natural is the decrease in the gain of the matte mass with increase (more than 15% of the slag mass) in sulfur consumption and how this is related to the change in the composition of the condensed products can be concluded after conducting experiments with a sulfur consumption of higher than 20–30% of the slag mass. However, this was not our task here because such sulfur consumptions are not of applied interest.

During sulfidization of slag, its magnetite content decreases and the distribution of sulfur changes. Figure 4 shows the dependence of the magnetite content in slag and the degree of uptake of sulfur on the amount of elemental sulfur fed to the melt. The degree of uptake of sulfur by the melt is calculated by the formula

$$S_{\text{upt}} = \frac{\left(M_{\text{mt}} \cdot \frac{(S_{\text{mt}})}{100} + M_{\text{sl}} \cdot \frac{(S_{\text{sl}})}{100} - M_{\text{st.sl}} \cdot \frac{(S_{\text{st.sl}})}{100}\right) \cdot 100}{M_{\text{S}}}, \qquad (5)$$

where S_{upt} is the degree of uptake of elemental sulfur by the melt, %; M_{mt}, M_{sl}, $M_{\text{st.sl}}$ are the masses of the produced matte and slag and the mass of the starting slag, respectively; (S_{mt}), (S_{sl}), $(S_{\text{st.sl}})$ are the contents of sulfur in the produced matte and slag and in the starting slag, respectively, %; M_{S} is the mass of the loaded elemental sulfur.

Figure 4 shows that with increase in the sulfur consumption, the degree of uptake of elemental sulfur by the melt increases by ~15% (for converter slag) and ~29% (for smelt slag) at the minimum sulfur consumption (3% of the slag mass) or by 40 ± 5% at higher sulfur consumption. In this case, the content of magnetite in slag

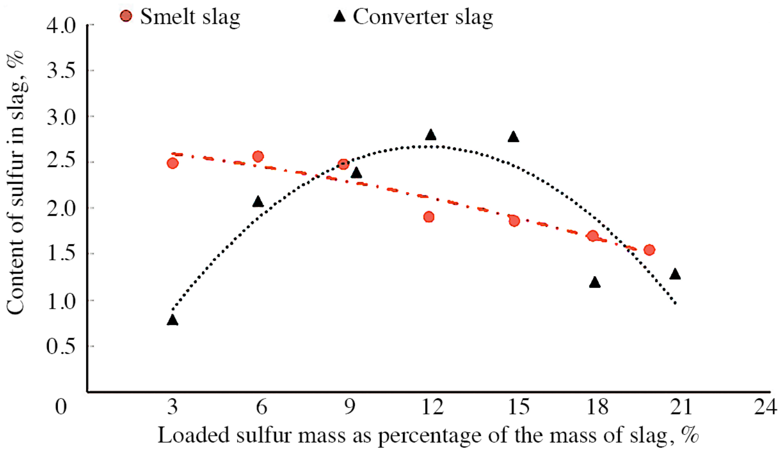


Fig. 5. Dependence of the content of sulfur in slag on the consumption of elemental sulfur.

naturally decreases, stabilizing at a level of ~5–6% for smelt slag and ~7–8% for converter slag. The weak effect of the increase in the amount of fed sulfur on the content of magnetite in slag naturally results in the weak effect on the degree of its uptake by the melt at high sulfur consumptions because the reaction of sulfur with magnetite with release of SO_2 is the major contribution to the amount of sulfur in gas. Certainly, sulfur appears in gas not only as SO_2, but also as S_2 vapor. For better understanding of the distribution of sulfur and the factors affecting it, a thermodynamic analysis of the sulfidizatin of slag is necessary. Figure 5 shows the dependence of the content of sulfur in slag on the consumption of elemental sulfur.

It can be seen that the content of sulfur in smelt slag decreases almost monotonically with the maximum being 2.5% at lower sulfur consumption. It is obvious that this value is closest to the limiting solubility of sulfur in starting slag at which iron sulfide and associated poor matte start to form. The decrease of the concentration of sulfur in smelt slag with further increase in its consumption can be due to the change in the composition of slag because of the precipitation of sulfidized iron, the increased dissolution of the crucible material, and longer time of sparging of slag. An increase in the amount of SiO_2, Al_2O_3, and CaO in slag is known to worsen the solubility of sulfur in slag [15]. For converter slag, this dependence is not so explicit. If the consumption of elemental sulfur is minimum, so is its content in slag (0.79%). However, the resulting matte is rich and its composition is close to that of the matte drops in converter slag [16]. It is most likely that this matte results from the deposition of matte drops suspended in converter slag, rather than from the sulfidization of slag iron. Since the concentration of magnetite in the starting converter slag is high, the lead elemental sulfur mainly goes to reduce the magnetite rather than to sulfidize the slag iron. At large amounts of sulfur fed, the sulfidization of iron of converter slag abruptly intensifies, which leads to an increase in the content of sulfur in slag to 2.4–2.8% and to the formation of poorer matte. At maximum loading of sulfur, its concentration in slag, as well as in smelt slag decreases.

Behavior of Copper. According to Figs. 2 and 3, the yield of matte increases with the consumption of elemental sulfur. The content of iron in matte increases, and it becomes poorer in copper. When sulfidizing smelt slag, the copper content of matte varies in the range ~3–20%, and the content of converter slag varies in the range ~10.5–67.5%. Richer mattes result from the sulfidization of converter slag because of the greater amount of copper in the starting slag.

Since during the sulfidization of slag with elemental sulfur, additional copper does not enter the system, and only copper from the starting slag passes into the matte, the copper concentration in slag decreasing. Figure 6 shows the influence of the amount of sulfur fed to slag on the content of residual copper in slag. It can be seen

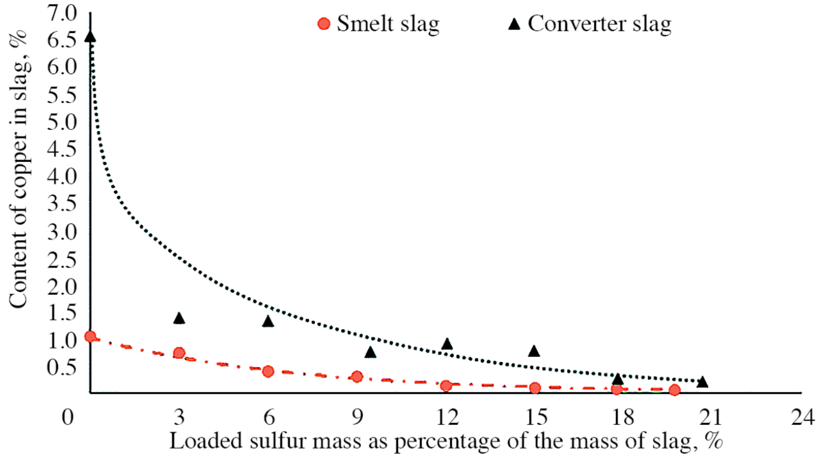


Fig. 6. Dependence of the content of copper in slag on the consumption of elemental sulfur.

from Fig. 6 (and Table 1) that the copper content in slag decreases with increase in the consumption of elemental sulfur, reaching less than 0.1% for smelt slag and ~0.2% for converter slag.

Besides the state variables and slag composition, the distribution of copper between matte and slag is substantially dependent on the copper content of matte. Figure 7 compares the dependences of the copper content in slag on its content in matte obtained here and by other researchers.

It can be seen that our results for poor mattes with ~20% copper content are in good agreement with the data by other authors, considering the differences in the experimental conditions. For richer mattes (40–70% Cu), the copper content of slag we obtained in sulfidizing converter slag is slightly higher than those reported by other authors. This may be due to the high content of suspended matte and the thermodynamic conditions of sulfidization of converter slag and the composition of the products.

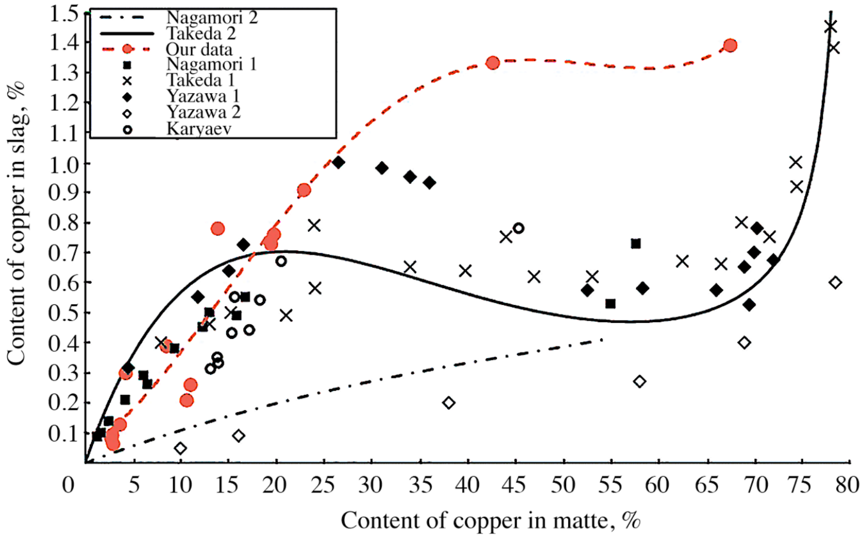
Noteworthy is the high recovery of copper from both smelt and converter slags of copper smelting production sulfidized using elemental sulfur, even without the use of hydrocarbon or other reducers. The residual content of copper in slags can be reduced to lower than ~0.2%.

CONCLUSIONS

Our research has demonstrated that feeding elemental sulfur into slag melt leads to the sulfidization of slag iron accompanied by the formation of the sulfide phase. Besides iron, copper is effectively recovered into the sulfide phase even without additional reducer. In sulfidizing VF smelt slag, the copper content in slag decreased to lower than ~0.1%, and to ~0.2% in converter slag. The copper concentrations in slag before and after cleaning being equal, the recovery of copper into slag during sulfidization with elemental sulfur is better than that when using ordinary iron-containing sulfidizing agents such as pyrite, pyrrhotine, concentrate, or ore since the amount of slag decreases during sulfidization because some of the iron goes from slag to matte.

Sulfidizing slag with elemental sulfur decreases the content of magnetite in slag, but its deep reduction does not occur. In the experimental conditions used, the magnetite content of slag decreased to ~5–8%.

It has been shown that during direct sulfidization of slag with elemental sulfur, a major portion of sulfur goes to gas, the melt taking up no more than ~49% of sulfur. This should be taken into account in developing new process solutions.



Karyaev: Experimental data on the reduction-sulfidization of slag at a temperature of 1325 °C [16];

Nagamori 1: Experimental data on the equilibrium in the slag–matte system rich in iron (iron crucible) and silicon dioxide at a temperature of 1200 °C in a nitrogen atmosphere [17];

Nagamori 2: Modeling of the content of dissolved copper in iron-silicate slag rich in γ-Fe at a temperature of 1200 °C [17];

Takeda 1: Experimental data on the equilibrium in the slag–matte system with slag rich in silicon dioxide at 1300 °C in 10% SO_2 atmosphere [18];

Takeda 2: Model of the content of dissolved copper in iron-silicate slag rich in silicon dioxide and magnesium oxide at 1300 °C [18];

Yazawa 1: Experimental results on the equilibrium of the slag–matte system rich in metal at 1300 °C [19];

Yazawa 2: Experimental results on the equilibrium of the slag–matte system rich in metal and 11% CaO at 1300 °C [19].

Fig. 7. Dependence of the content of copper in slag on the copper content in matte compared with data of other authors.

It is of interest to further study the theoretical and applied aspects of the sulfidization of copper-smelting and copper–nickel slags with elemental sulfur, including in reduction conditions (at a lower content of magnetite) in order to optimize the consumption of sulfur and its amount in gas and to better understand the distribution of sulfur and non-ferrous metals in wider range of sulfur–slag reaction conditions.

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