Improving cobalt extraction through oxidative blowing of copper-nickel matte

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ABSTRACT

The article presents results of thermodynamic calculations and laboratory studies, focusing on the cobalt behavior during oxidative smelting of copper-nickel mattes. The compositions of the studied solutions are related to the products formed during the second stage of the converting process of copper-nickel matte at the Nadezhdinsky Metallurgical Plant (NMP) of MMC Norilsk Nickel company. These sulfide products typically contain from 1.5 to 12 wt.% of iron. The obtained experimental results and thermodynamic calculations indicate that adjusting the /CaO ratio to increase the proportion of CaO or complete replacement of SiO_2 with fluxes containing CaO leads to a significant increase in cobalt recovery rates in the matte phase (with an iron concentration of 2.5 wt.%) raising them from 30% to 45%. Meanwhile, the recovery rates of copper and nickel remain constant.

INTRODUCTION

Metallic cobalt ranks among the three most treated and valuable non-ferrous metals (Cu, Ni and Co), that are processed at the metallurgical plants of MMC Norilsk Nickel company. These metals are present in sulfide copper-nickel ores, with pentlandite or pyrite serving as the primary minerals containing cobalt. Cobalt concentration in certain particles can reach up to 2.5 wt.%, averaging between 0.2 and 1.2 wt. % [Genkin A.D.,1981; Tsemekhman L. Sh., 2010]. Sulfide minerals extracted from the mineral deposits are subjected to flotational separation to produce Cu and Cu-Ni concentrates. During this stage approximately 14% of all extracted cobalt is lost with tailings, attributed to technological losses.

The application of flotation separation methods results in the distribution of cobalt among various products: around 9% of Co is transferred into the copper concentrate, while 77% Co goes into copper-nickel concentrate, with the remaining 14% ending up with tailings. Subsequent pyrometallurgical treatment of the copper-nickel concentrate yields a commercially valuable product known as the copper-nickel matte, characterized by a high copper concentration. The recovery rates for Cu and Ni in the final product exceed 95%, whereas cobalt recovery is less than 55%. The low Co recovery rates are primarily attributed to its low concentrations in the feed materials, and losses with slags. Figure 1 shows the schematic flowsheet of the pyrometallurgical treatment of sulfide materials.

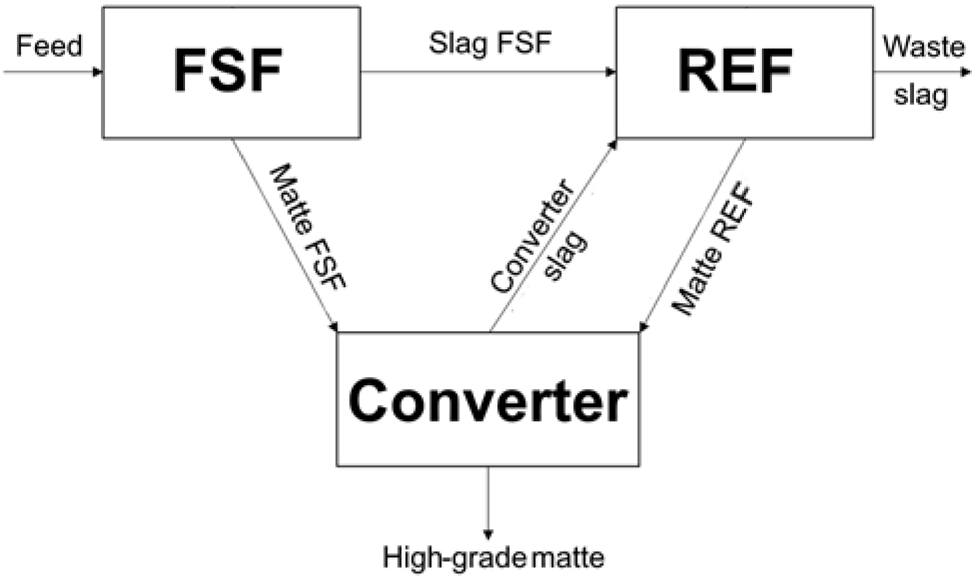

FIG 1 – Scheme of processing nickel-coper sulphide ore at Nadezhdinsky Metallurgical Plant (FSF-flash smelting furnace and REF- slag cleaning furnace)

Sulfide materials are oxidized in a converter to produce high-grade matte. Then the converter slag is conveyed to the slag cleaning furnace, while the matte is returning from the slag cleaning furnace back to converter, leading to circulation of cobalt between the furnaces. Figure 2 illustrates the distribution of cobalt between the materials supplied for converting stage and the products of the slag cleaning furnace. This figure is based on industrial data obtained from a Nadezhdinsky metallurgical plant. The concentration of cobalt in the products is determined by using analytical chemistry methods.

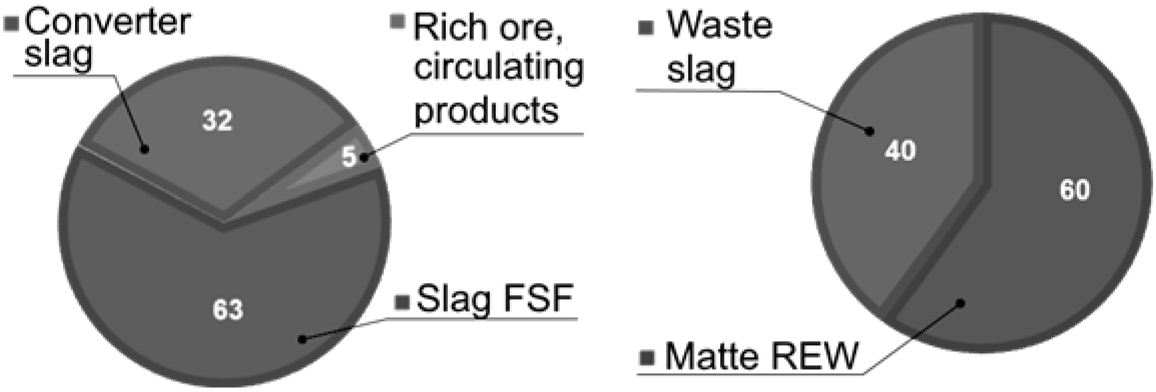

FIG 2 - Distribution of cobalt between processed and obtained products of converter (left image) or slag cleaning furnace (right image) of Nadezhdinsky Metallurgical Plant

Increasing cobalt recovery at the converter process will reduce the amount of circulated cobalt and enhance overall recovery rates. During converting copper-nickel matte, SiO_2-based fluxes are used as additives to significantly lower the melting point of the formed slag, and to facilitate the bonding of resulting FeO and Fe_3O_4 during matte oxidation. However, the converting of matte into high-grade “white matte” is accompanied by significant losses of non-ferrous metals into slag, particularly cobalt. Literature and metallurgical practice indicate that dissolved cobalt contributes significantly to total cobalt losses in slags [Krupnov L. V., 2023, Tsemekhman L. Sh., 2010]. While iron and cobalt exhibit similar behavior in these processes, they differ markedly from nickel and copper, where mechanical losses, such as entrained particles of sulfides or metals in slag greatly affect recovery rates. In ferrous metallurgy, fluorite (CaF_2), limestone or lime are the primary fluxing agents used in the processing of iron feed materials. Given the analogous behavior of cobalt and iron in both non-ferrous and ferrous metallurgy, it is hypothesized that replacing SiO_2 flux with CaO-containing fluxing agents could alter the distribution of cobalt between slag and matte. This hypothesis requires verification through thermodynamic and experimental means.

At the initial stage, thermodynamic calculations were conducted to assess the oxidation of a cobalt-rich sulfide sample using SiO_2 and CaO-based additives in various ratios. Thermodynamic modeling was employed to provide an initial estimation of the distribution of non-ferrous metals. The calculation was focused on determining the required amount of flux and oxygen blow to achieve a matte with the desired composition.

THERMODYNAMIC CALCULATIONS

The calculation of the converting process was performed using the FactSage software version 6.4, utilizing the thermodynamic databases FTmisc and FToxid [Bale C. W., Vol. 54, 2016; Bale C. W., Vol. 54, 2016]. Throughout the matte oxidation calculation, the SiO_2/CaO ratio was varied within the range of 1 to 0.2 and only SiO_2. Operating conditions included a temperature of 1350°C, pressure at 1 atm, and pure oxygen as the oxidizing agent. Table 1 outlines the composition of the matte employed for the calculations. Based on the computational outcomes, a series of graphs depicting the behavior of non-ferrous metals in both matte and slag were generated and are presented in Figures 3 and 4.

TABLE 1 – The concentrations of the main components in the matte used in the calculations

The mass fraction of the component, wt. %				
Cu	Ni	Co	Fe	S
17.19	43.78	2.68	12.68	23.67

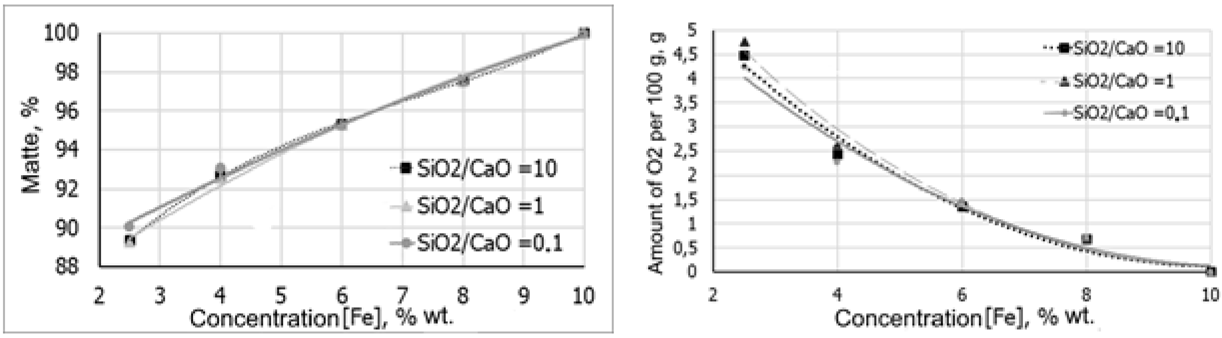

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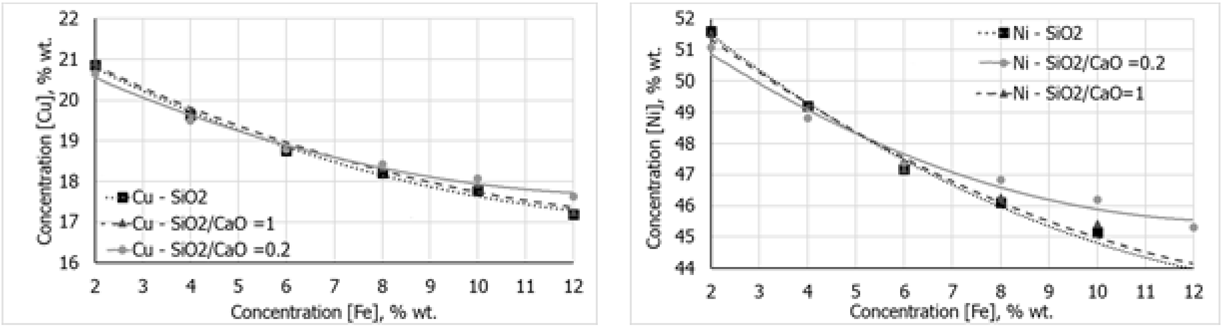
FIG 3 – Output of the matte (a) and oxygen consumption (b) as functions of iron concentration in the matte



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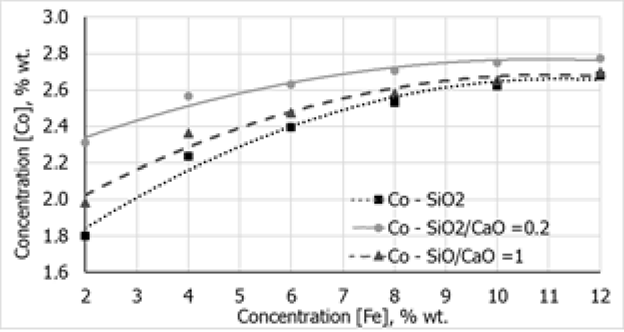

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FIG 4 – The concentrations (wt.%) of Cu (a), Ni (b) and Co (c) in the matte as functions of iron concentration

Figure 3 shows the amount of matte produced and oxygen consumption relative to the iron concentration in the matte phase. According to thermodynamic estimation, varying ratio of fluxing agents does not significantly impact matte output and oxygen consumption.

Figure 4 demonstrates that replacement SiO_2 with CaO has negligible effect on the Cu and Ni concentrations in the matte phase. However, there is a notable change in cobalt proportion with the substitution of SiO_2 by CaO. For instance, when obtaining copper-nickel matte with 2.5 wt.% of Fe, the cobalt concentration increases by 0.5 wt.% when using CaO. Based on the presented data, the evaluation of cobalt recovery into the matte phase suggests potential savings of cobalt up to 4.5% compared to silicate slags.

Following the assessment of theoretical parameters for cobalt recovery, product compositions, and oxidation process conditions, a series of laboratory experiments were conducted.

RESULTS AND DISCUSSION

In total eleven experiments were performed, including 6 experiments with SiO_2-based slag (without Ca addition), and 5 experiments with CaO-based slag with a SiO_2/CaO ratio of 0.2. To estimate the distribution of non-ferrous metals between slag and matte, a synthetic flux composed of FeO, SiO_2 and CaO was used to simulate pyrometallurgical converting slag while maintaining a consistent SiO_2/CaO ratio. The experiments were conducted in an induction furnace at temperatures ranging from 1300 to 1350 °C, under an overall pressure of is 1 atm, using pure oxygen as the oxidizing agent and employing Al_2O_3 crucible. The compositions of the obtained samples were examined using methods of analytical chemistry and EDX-SEM. Experimental conditions are detailed in Table 2, the results of the chemical analysis are presented in Table 3.

TABLE 2 – Experimental conditions

№	Feed composition, g				O_2:		Mass of products, g		SiO_2/CaO
	Matte	SiO_2	CaO	FeO	Vol, l	Gas flow, l/min	matte	slag	
1	61.6	12	-	28	2.57	0.7	54.3	46.1	SiO_2
2	61.6	12	-	28	1.23	0.7	60.0	41.1	SiO_2
3	61.6	12	-	28	2.68	0.7	52.5	48.8	SiO_2
4	61.6	12	-	28	4.78	0.7	47.4	51.2	SiO_2
5	61.6	12	-	28	7.23	0.7	47.0	50.0	SiO_2
6	61.6	12	-	28	8.47	0.7	33.1	55.9	SiO_2
7	61.6	2	10.6	28	2.68	0.7	54.7	45.7	~0.2
8	61.6	2	10.6	28	1.46	0.7	57.4	44.6	~0.2
9	61.6	2	10.6	28	4.96	0.7	47.3	53.2	~0.2
10	61.6	2	10.6	28	6.35	0.7	43.8	40.7	~0.2
11	61.6	2	10.6	28	6.40	0.4	45.7	52.8	~0.2

TABLE 3 – The concentrations of the main components in the matte and slag phases (wt.%)

№	Composition of matte phase, wt.%					Composition of slag phase, wt.%					
	Cu	Ni	Co	S	Fe	Cu	Ni	Co	Fe	SiO_2	CaO
0	***16.9***	***42.9***	***2.95***	***23.0***	***12.45***						
1	17.4	46.6	2.06	24.0	7.18	0.59	1.47	1.38	47.2	25.2	-
2	16.6	43.9	2.16	24.5	8.97	0.56	1.24	1.18	48.0	25.8	-
3	18.0	47.9	1.97	23.7	6.69	0.88	2.33	1.43	47.5	24.2	-
4	19.0	48.7	2.01	23.0	6.81	1.23	3.25	1.72	44.6	19.8	-
5	20.1	52.4	1.50	22.4	3.25	0.95	3.45	2.03	47.9	20.6	-
6	22.9	55.4	0.81	19.3	1.47	1.62	8.19	2.40	41.9	16.7	-
7	17.8	47.2	2.31	23.6	6.6	0.69	2.02	1.09	46.6	3.8	16.8
8	17.1	45.6	2.46	24.3	8.33	0.67	1.41	0.88	46.3	3.4	18.2
9	20.1	52.0	1.60	24.1	2.2	0.64	2.34	1.12	38.2	2.4	15.6
10	20.8	52.7	1.76	22.0	2.18	3.98	1.05	1.73	42.6	3.6	17.7
11	21.3	53.5	1.57	21.7	1.9	0.83	3.61	1.94	49.3	1.8	16.7

Consider the behavior of non-ferrous metals in the matte during oxidation and the use of additives based on SiO_2 and CaO, the results are shown in Figure 5.

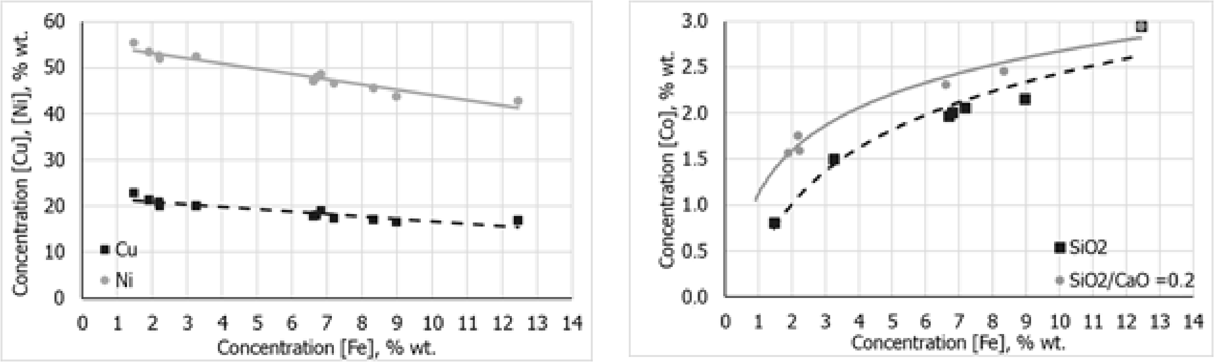

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FIG 5 - The concentrations of non-ferrous metals in the matte phase as functions of iron concentration (wt.%): a- Cu, Ni; b – Co

Analysis of the graphs in Figure 5 indicates that the choice of flux does not influence the t of copper and nickel concentration in matte, confirming the calculation results. However, the cobalt concentration varies significantly depending on the selected flux. For instance, in the copper-nickel matte (with 2.5 wt.% Fe) the cobalt concentration increases from 1.24 wt.% to 1.75 wt. %. (at 40.5 rel.%) with the addition of CaO-based slag. Evaluation of cobalt recovery rates using different types of slags is presented in Figure 6.

The recovery of cobalt in matte or the losses of cobalt with slag were calculated as the ratio of the amount of metal in high-grade matte or slag to the amount of metal in the initial sample, formulas 1 and 2.

$$[Co]_{rec} = \frac{[Co]_{hgm}}{Co_{matte}} \cdot 100\% \qquad (1)$$

$$(Co)_{los} = \frac{(Co)_{slage}}{Co_{matte}} \cdot 100\% \qquad (2)$$

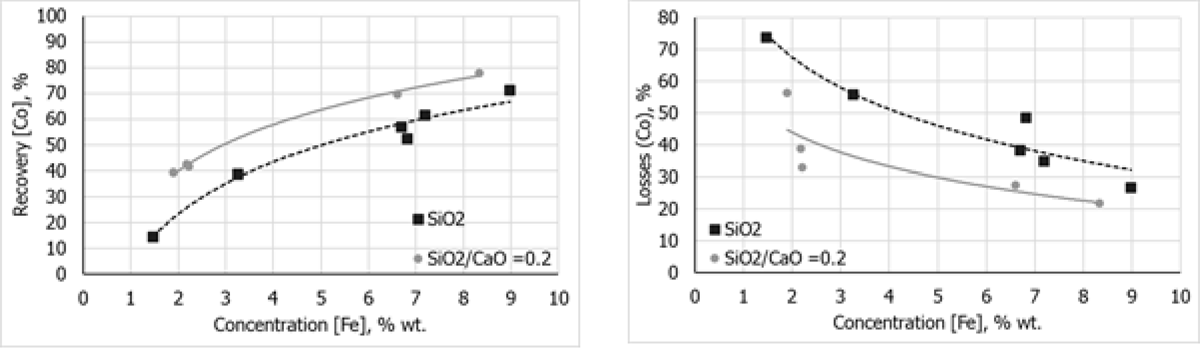

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FIG 6 - Recovery of cobalt into the bottom phase (a) and losses with slag (b) from the iron content in the sulfide mass

Analysis of cobalt recovery and losses with slags during the second stage of converting reveals the effectiveness of incorporating CaO as fluxing additive. The recovery of Co within the examined range of matte compositions (with 2 to 10 wt.% Fe) increases from 11 to 20% with the utilizing of calcium-ferrite slags. It's worth noting that the concentration of cobalt in the slag is assessed without considering mechanically entrained particles, utilizing SEM-EDX methods for analysis. Detailed description of sample preparation methods for SEM-EDX are provided in previous works [Gouldstein J., 1984, 5 Krishtal M. M., 2009]. Figure 7 illustrates the cobalt concentration in slag as function of the iron concentration in the matte phase.

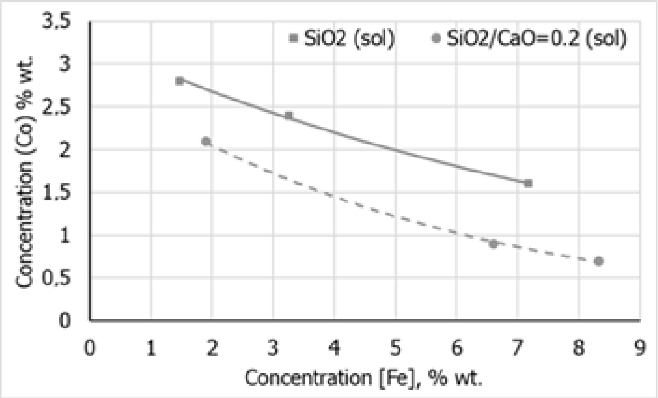

FIG 7 – Cobalt concentration in the matte phase according to SEM- EDX data

The analysis of the microstructures of the samples reveals that in the first scenario, the matrix base comprises an iron-silicate solution with dispersed sulfide-metal particles of varying composition and structure. In the second scenario, the slag matrix consists primarily of the Fe-Ca-O system with a minor presence of residual silicate forming the slag base. Further analysis of the slags using EDX-SEM methods corroborates the potential benefits of employing CaO-based slags over SiO_2-based ones.

A comparison of the practical and calculated results of the behavior of cobalt in slag and high-grade matte, the results are presented in Figure 8.

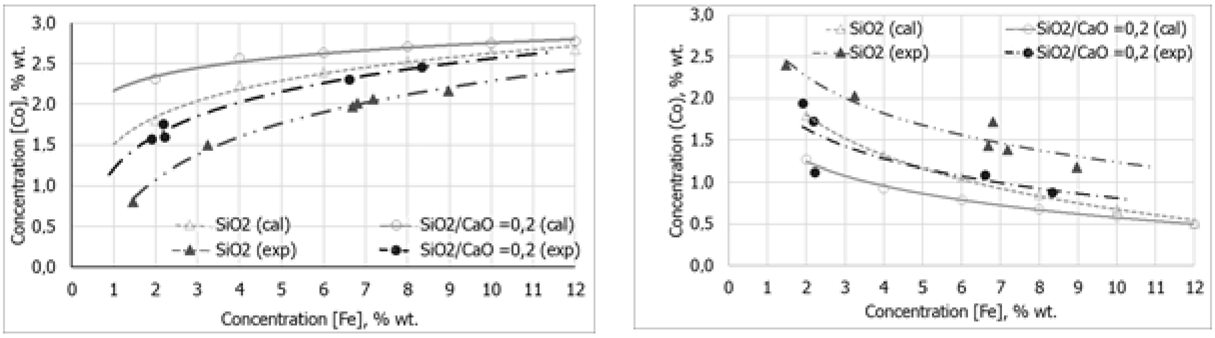

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FIG 8 – Cobalt concentration in matte (a) and slag (b) according to calculation and experimental data

The results of theoretical calculations of cobalt distribution presented in Figure 8 differ significantly from the practical data for two types of slags based on SiO_2 and CaO. The difference in results may be due to incomplete databases that lack data on the distribution of cobalt in sulfide solutions.

CONCLUSIONS

The assessment of cobalt distribution among the products of copper-nickel production of MMS Norilsk Nickel was carried out. The assessment involved thermodynamic calculations and laboratory studies on the converting process of copper-nickel matte to “white” matte using additives based on SiO_2 and CaO. The utilization of CaO-based slags resulted in an increase in cobalt concentration in the matte phase, while the concentrations of Cu and Ni remained unchanged. For instance, in high-grade matte with a 2.5 wt.% Fe concentration, the cobalt concentration increased from 1.24 wt.% to 1.75 wt.%, that makes a 40.5% rise, upon transition to calcium-ferrite slag. Furthermore, the recovery of Co within the considered range of Fe compositions from 10 to 2% increases by 11-20% upon switching to calcium-ferrite slag. Thus, the use of calcium oxide as the primary component of fluxing agents at the converting process of copper-nickel matte will have a positive impact on cobalt recovery rates.

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