

THERMODYNAMIC ANALYSIS SULFATIZING ROASTING OF STALE NICKEL-COBALT-CONTAINING WASTES FROM OPERATING PLANTS

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ABSTRACT

Metallurgy is one of the leaders in terms of the amount of accumulated waste worldwide. Every year the amount of waste placed in dumps, sludge ponds, tailings ponds only grows. However, at present, tailings, slag, dust, etc. of metallurgical enterprises are considered the most promising for secondary use and the extraction of valuable metals from tailings is an important problem in the world.

In Kazakhstan, the technology of processing nickel-cobalt-containing tailings is practically undeveloped. Sokolov-Sarybai Mining Production Association Joint-Stock Company (SSGPO JSC) in Kazakhstan, loses more than 7 thousand tons of nickel and 14 thousand tons of cobalt per year. For processing this type of raw material, a combined technology that includes preliminary roasting and leaching processes is acceptable.

The aim of the work is a thermodynamic analysis of the roasting process of wet magnetic separation (wms) tailings of the SSGPO JSC, containing such main components as nickel, cobalt and iron sulfides.

Thermodynamic analysis of the roasting of wms tailings in the temperature range from 500 to 750°C showed that in the presence of a limited amount of oxygen, the formation of iron sulfides of the following compositions is possible: $\text{Fe}_{0.877}\text{S}$, FeS , Fe_2S_3 , Fe_7S_8 . Nickel and cobalt sulfides are converted into Ni_3S_2 , Ni_3S_4 and $\text{CoS}_{0.89}$, CoS , respectively. In this temperature range, within the homogeneity region, the transformation of cobalt and nickel sulfides also occurs. The calculated values of the Gibbs free energy confirm the possibility of reactions of formation of low-sulfide compounds and the optimal condition for firing is the temperature range of 600-700°C. Depending on the firing conditions, interconversion of iron, nickel and cobalt sulfides occurs.

The results of thermodynamic analysis confirm the possibility of extracting iron, nickel and cobalt from wms tailings in the form of soluble low-sulfide compounds with subsequent extraction from the tailings in the form of individual metal powders. Combined technology for processing this type of raw material will be a good example of the use of circular economy principles.

Keywords: thermodynamic analysis, roasting, nickel sulfide, cobalt sulfide, wastes.

INTRODUCTION

Smartphones, electric vehicles, renewable solar panels, wind turbines, and new clean energy technologies are highly dependent on metals, including lithium, nickel, copper, cobalt, chromium, and manganese [1]. Consequently, a reliable supply of these minerals is crucial to ensuring the transition to sustainable energy, driving up demand.

The gradual depletion of mineral reserves [2-3] is leading to a mismatch between current production rates and projected demand for these metals.

The Republic of Kazakhstan has substantial reserves of nickel and cobalt, primarily found in low-grade oxidized ores like those at Kempirsai, Gornostayev, and Bozshakol, as well as iron-bearing ores and concentrates from Sokolovsky and Sarbaisky. The complex mineralogy, including intergrowths of cobalt and iron minerals and isomorphic substitution of cobalt in pyrite, combined with the low nickel and cobalt content, renders standard metallurgical processes ineffective. As a result, there is currently no nickel or cobalt production in Kazakhstan [4].

It is essential to consider alternative raw materials, including water resources, low-grade ores, tailings, slags, and electronic waste. The growing demand for nickel has stimulated research into recovering nickel from secondary sources like wet magnetic separation tailings [5]. Two primary approaches for nickel extraction from these waste materials are: hydrometallurgical processing, involving leaching of the waste and subsequent nickel recovery; and pyrometallurgical processing, which involves thermal treatment of the waste [6].

Significant quantities of nickel and cobalt are lost in tailings and metallurgical process residues. For instance, the SSGPO JSC annually loses over 7,000 tons of nickel and 14,000 tons of cobalt. The non-standard composition of pyrite-cobalt concentrates produced at this plant necessitates the development of new technologies for their efficient processing and recovery of valuable components.

In this context, the research, development, and implementation of optimal technologies for the production of nickel and cobalt from low-grade nickel and cobalt-bearing raw materials, concentrates, and technogenic waste is a pressing issue.

Pre-roasting, followed by leaching and selective extraction with subsequent metal or compound refining, is an effective combined technology for increasing the metal concentration in feed materials, including tailings [7, 8].

Nevertheless, simple roasting of ores does not always provide the expected results. Research has demonstrated that high-temperature sulfatization of oxidized ores, employing a sulfuric acid dosage of 0.7 g per gram of ore at 420 °C, significantly enhanced nickel extraction, reaching 80-82%.

As demonstrated in studies [9, 10], the most promising technologies for processing pyrite-containing materials involve smelting or activating dissociative roasting of the feedstock followed by hydrometallurgical or pyrometallurgical processing of the calcine. When smelting low-grade nickel-bearing ores using pyrite concentrates as a sulfidizing agent, nickel and cobalt concentrate in the matte. For more complete nickel and cobalt recovery, the matte should be low-grade. Dissociative roasting of pyrite-containing materials can be carried out under various conditions: in vacuum, in an inert gas atmosphere, in combustion products, sulfur dioxide, air, etc., at different

temperatures, with or without melting of the processed products, and in various roasting units [1]. Hydrometallurgical methods, which provide high-complexity processing of various types of feedstock, are considered the most promising for further processing of calcines or low-grade mattes.

To provide a thermodynamic basis for the pre-roasting process, we have performed a thermodynamic analysis of systems containing nickel, cobalt, iron, sulfur, and oxygen under thermal processing conditions.

MATERIALS AND METHODS

The initial materials and reagents

In this study were used tailings from the wet magnetic separation process at the SSGPO JSC, obtained during the processing of iron ores, were used as the feedstock. Physicochemical analysis was conducted using X-ray diffraction, atomic emission spectroscopy, and chemical analysis.

A thermodynamic analysis of sulfide behavior under activating roasting conditions was conducted using HSC Chemistry 5.11 software from Outokumpu Technology. The analysis was based on the equilibrium conditions of heterogeneous chemical reactions involving gaseous substances. Thermodynamic characteristics of the main reactions were calculated, and isothermal sections of phase equilibrium diagrams were constructed for the Fe-O-S (Fig. 1 a), Ni-O-S (Fig. 1 b), and Co-O-S (Fig. 2) systems at temperatures ranging from 600 to 800°C.

RESULTS AND DISCUSSION

Physicochemical analysis of SSGPO JSC wms tailings samples revealed the presence of iron, nickel, and cobalt sulfides, as well as other impurities (hereinafter referred to as pyrite concentrate). The chemical composition of the wms tailings is presented in Table 1.

Table 1: Chemical composition of the wms tailings.

Chemical composition, %												
Fe ₀₆ III	Cu	Co	Ni	S _{06III}	Pb	Zn	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	As
12,62	0,05	0,013	0,0081	3,46	0,019	0,069	37,23	12,97	12,59	4,72	0,59	0,006

The main minerals in the tailings are pyrite, diopside, clinocllore, albite, and others. Nickel and cobalt content is low, with millerite and heazlewoodite being the primary minerals.

As the SO₂ concentration decreases, iron disulfide undergoes a series of transformations, forming lower iron sulfides: $\text{FeS}_2 \rightarrow \text{Fe}_2\text{S}_3 \rightarrow \text{Fe}_7\text{S}_4 \rightarrow \text{Fe}_{0,877}\text{S} \rightarrow \text{FeS}$. When pyrite is thermally treated in the presence of roasting gases, the aforementioned lower iron sulfides, as well as Fe₃O₄ and possibly FeSO₄, are formed.

To predict the behavior of sulfides under activating roasting conditions, the following partial pressure diagrams were selected and studied: Fe-S-O, Ni-S-O, and Co-S-O.

It is well known that the composition of the gas phase during thermal treatment plays a decisive role and determines the composition of the cinder. The thermodynamics of transformations in the Fe-O-S, Co-O-S, and Ni-O-S systems have been analyzed in detail in works [11].

Analysis of the $\log p_{\text{SO}_2} - f(\log p_{\text{O}_2})$ partial pressure diagram for the Fe-S-O system revealed that at 900 K and a partial pressure of sulfur dioxide close to atmospheric $\lg p_{\text{SO}_2} = 0$, pyrite undergoes the following transformations: $\text{FeS}_2 \rightarrow \text{Fe}_2\text{S}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3$ (Fig. 1a).

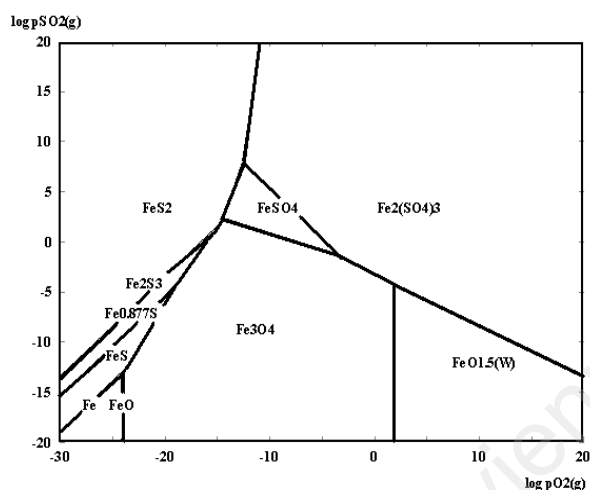


Figure 1 a – Isothermal section of the phase equilibrium diagram for the Fe-O-S system at 900 K

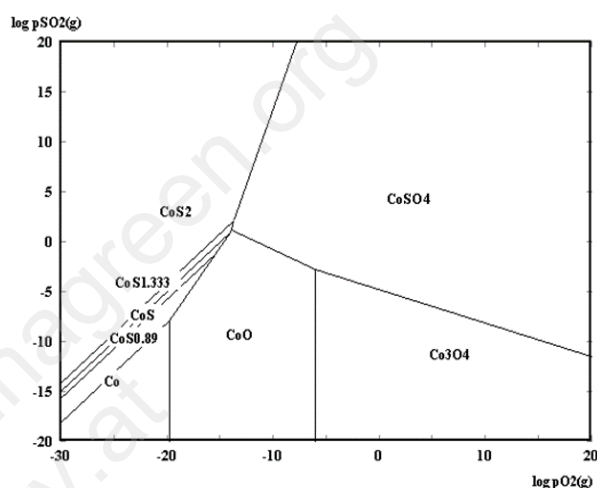


Figure 1b – Isothermal section of the phase equilibrium diagram for the Co-O-S system at 900 K

Analysis of the phase equilibrium diagrams in the Co-O-S system reveals that the oxidation of cobalt sulfide at 900 K and a partial pressure of sulfur dioxide of $\lg p_{\text{SO}_2} = 0$ proceeds sequentially through the phases $\text{CoS}_2 \rightarrow \text{CoS}_{1.333} \rightarrow \text{CoS} \rightarrow \text{CoO} \rightarrow \text{CoSO}_4$ (Fig. 1b). When the SO_2 concentration in the gas phase decreases, thermal dissociation of cobalt disulfide occurs with the sequential formation of lower cobalt sulfides: $\text{CoS}_2 \rightarrow \text{CoS}_{1.333} \rightarrow \text{CoS} \rightarrow \text{CoS}_{0.89}$. Under thermal treatment conditions with a deficiency of oxygen and in the presence of roasting gases, the formation of the aforementioned lower cobalt sulfides, as well as CoO , CoSO_4 , and a small amount of Co_3O_4 , is possible.

The oxidation of nickel sulfide at 900 K under a near-atmospheric sulfur dioxide partial pressure proceeds sequentially through the phases $\text{NiS}_2 \rightarrow \text{Ni}_3\text{S}_4 \rightarrow \text{NiS} \rightarrow \text{NiO} \rightarrow \text{NiSO}_4$, as shown in figure 2.

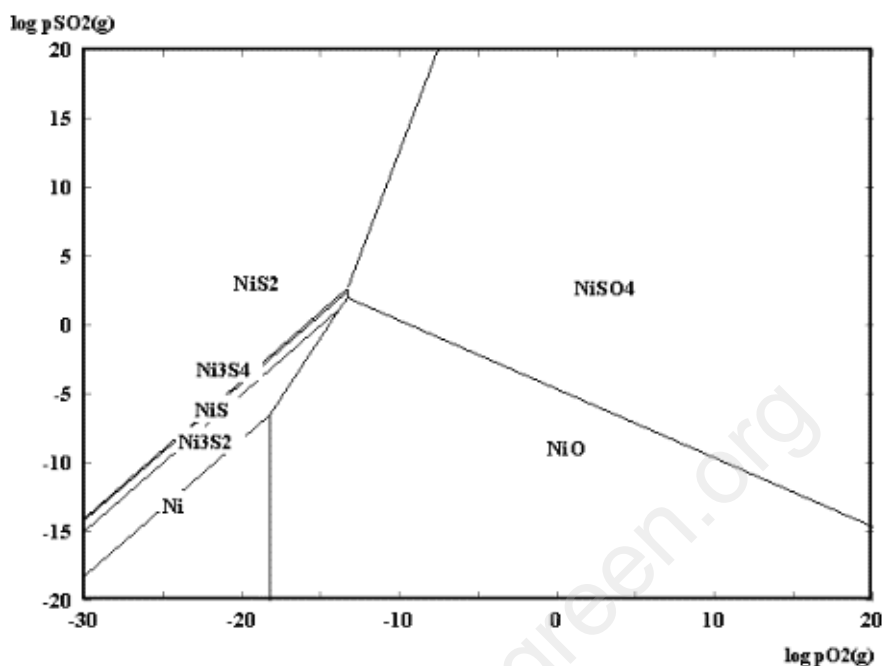


Figure 2: Isothermal section of the phase equilibrium diagram for the Ni-O-S system at 900 K

An analysis of the isothermal sections of partial pressure diagrams (Figures 1-2) indicates that during the roasting of nickel-cobalt-containing materials in a wide range of gas phase compositions ($O_2 + SO_2$), the following compounds are the most stable: FeS, $Fe_{0.877}S$, Fe_2S_3 , FeS_2 , Fe_3O_4 , $FeSO_4$, $Fe_2(SO_4)_3$, CoS_2 , $CoS_{1.333}$, CoS , $CoS_{0.89}$, CoO , $CoSO_4$, Co_3O_4 , NiS_2 , Ni_3S_4 , Ni_3S_2 , NiS , NiO , $NiSO_4$.

In the event of oxygen deficiency, sulfur-containing compounds such as FeS, $Fe_{0.877}S$, Fe_2S_3 , FeS_2 , CoS_2 , $CoS_{1.333}$, CoS , $CoS_{0.89}$, NiS_2 , Ni_3S_4 , Ni_3S_2 , NiS are the most stable. As the oxygen potential in the system increases, the thermodynamic probability of forming metal oxides and sulfates increases. Moreover, sulfate formation primarily occurs from oxidized compounds.

A thermodynamic analysis of the roasting process for iron, nickel, and cobalt sulfides was conducted.

Gibbs free energy calculations were performed for the likely primary reactions during the thermal treatment of nickel-cobalt-containing sulfide ores (Table 2).

Table 2 – Thermodynamic analysis of potential reactions during the dissociative roasting of materials.

Chemical reaction		ΔG° , kJ/mol	
		273 K	900 K
1.	$\text{FeS}_2 + 1/2\text{O}_2 = 1/2\text{Fe}_2\text{S}_3 + 1/2\text{SO}_2$	-130,30	-143,19
2.	$\text{FeS}_2 + 0,86\text{O}_2 = 1,14 \text{Fe}_{0,877}\text{S} + 0,86 \text{SO}_2$	-208,20	-245,42
3.	$\text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2$	-241,97	-280,78
4.	$\text{FeS}_2 + 6/7\text{O}_2 = 1/7\text{Fe}_7\text{S}_8 + 6/7\text{SO}_2$	-203,90	-237,17
5.	$\text{Fe}_2\text{S}_3 + 5/7\text{O}_2 = 2/7\text{Fe}_7\text{S}_8 + 5/7\text{SO}_2$	-147,20	-187,95
6.	$\text{Fe}_2\text{S}_3 + 0,719\text{O}_2 = 2,281\text{Fe}_{0,877}\text{S} + 0,719 \text{SO}_2$	-155,60	-204,28
7.	$\text{Fe}_2\text{S}_3 + \text{O}_2 = 2\text{FeS} + \text{SO}_2$	-223,34	-275,17
8.	$\text{Fe}_7\text{S}_8 + \text{O}_2 = 7\text{FeS} + \text{SO}_2$	-266,49	-305,26
9.	$\text{Fe}_{0,877}\text{S} + 0,123\text{O}_2 = 0,877\text{FeS} + 0,123\text{SO}_2$	-29,66	-31,05
10.	$\text{CoS}_2 + \text{O}_2 = \text{CoS} + \text{SO}_2$	-250,42	-268,37
11.	$\text{CoS}_2 + 1,11\text{O}_2 = \text{CoS}_{0,89} + 1,11\text{SO}_2$	-279,36	-295,41
12.	$\text{CoS}_{1,333} + 0,333\text{O}_2 = \text{CoS} + 0,333\text{SO}_2$	-80,14	-86,00
13.	$\text{CoS}_{1,333} + 0,443\text{O}_2 = \text{CoS}_{0,89} + 0,443\text{SO}_2$	-109,07	-113,03
14.	$\text{CoS} + 0,11\text{O}_2 = \text{CoS}_{0,89} + 0,11\text{SO}_2$	-28,94	-27,04
15.	$\text{NiS}_2 + 2/3\text{O}_2 = 1/3\text{Ni}_3\text{S}_4 + 2/3\text{SO}_2$	-172,08	-183,36
16.	$\text{NiS}_2 + 4/3\text{O}_2 = 1/3\text{Ni}_3\text{S}_2 + 4/3\text{SO}_2$	-344,68	-360,84
17.	$\text{Ni}_3\text{S}_4 + \text{O}_2 = 3\text{NiS} + \text{SO}_2$	-263,38	-272,94
18.	$\text{Ni}_3\text{S}_4 + 2\text{O}_2 = \text{Ni}_3\text{S}_2 + 2\text{SO}_2$	-517,79	-532,46
19.	$\text{NiS} + 1/3\text{O}_2 = 1/3\text{SO}_2 + 1/3\text{Ni}_3\text{S}_2$	-84,81	-86,50

During the roasting of FeS_2 in the presence of limited oxygen, iron sulfides with various compositions can be obtained via reactions (1-4): $\text{Fe}_{0,877}\text{S}$, FeS , Fe_2S_3 , Fe_7S_8 within the homogeneity range. Additionally, depending on the roasting conditions, these iron sulfides can undergo mutual transformations according to reactions (4-9).

Nickel and cobalt sulfides exhibit similar behavior. According to reactions 10 and 11, cobalt disulfide can transform into $\text{CoS}_{0,89}$ and CoS , while reactions 15 and 16 describe the conversion of nickel disulfide to Ni_3S_2 and Ni_3S_4 . Reactions 12-14 and 17-19 represent transformations of cobalt and nickel sulfides within their homogeneity ranges. In the presence of excess oxygen, oxygen-containing compounds of iron, nickel, and cobalt, such as metal oxides and sulfates, are formed.

Based on the phase diagrams of the $\text{Fe}(\text{Ni}, \text{Co})\text{-S}$ systems, it can be concluded that the presence of wide homogeneity ranges allows for the formation of low-sulfur iron compounds with a broad range of compositions, as well as variable composition cobalt and nickel sulfides under thermal treatment conditions (700-1100 K).

CONCLUSION

For the efficient processing of pyrite concentrates obtained from the tailings of wet magnetic separation at SSGPO JSC, a combined method involving preliminary roasting and subsequent leaching of valuable components is optimal. Thermodynamic analysis conducted under thermal treatment conditions at temperatures of 650-700 °C confirmed the possibility of forming low-sulfur iron compounds with various compositions, as well as cobalt and nickel sulfides with variable compositions.

The thermodynamic properties of these natural sulfide compounds (Fe_7S_8 , $\text{Fe}_{0.877}\text{S}$, Fe_2S_3 , FeS , $\text{CoS}_{1.333}$, CoS , $\text{CoS}_{0.89}$, Ni_3S_4 , Ni_3S_2 , NiS), as determined experimentally within their respective homogeneity ranges, can serve as foundational data for thermodynamic modeling and analysis of processes involving these sulfides.

These results indicate that the roasting process not only enhances the recovery of valuable components but also allows for the modification of the composition of the final goods, thus opening up new opportunities for optimizing the processing of pyrite concentrates. The combined approach based on thermal treatment can significantly improve the efficiency of leaching processes and, consequently, enhance the economic performance of the overall process.

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