

Article

Thermodynamic and Experimental Study of Combined Sulfation Roasting of Copper Sulfide Concentrates

Kalkaman Zhumashev¹ , Aitbala Narembekova^{2,*} , Natalya Lu¹ , Feruza Berdikulova³ 
and Yelena Zhinova¹ 

¹ Chemical and Metallurgical Institute Named After Zh. Abishev, Karaganda 100009, Kazakhstan; innovaciya_zh@mail.ru (K.Z.)

² The Metallurgy and New Materials Department, Karaganda Technical University Named After A. Saginov, Karaganda 100027, Kazakhstan

³ RSE “National Center for Integrated Processing of Mineral Raw Materials of the Republic of Kazakhstan”, Almaty 050036, Kazakhstan

* Correspondence: ay.narembekova@ktu.edu.kz; Tel.: +7-7212-433161

Abstract

This article is devoted to the development of a combined sulfation method (CSM) for processing low-grade copper-sulfide concentrates with a copper grade of 0.34–3.5%. The relevance of the study is driven by the depletion of Kazakhstan’s high-grade copper deposits and the need to incorporate off-balance sulfide raw materials into processing. CSM is based on the spatial separation of two thermally coupled zones in the filter bed of a shaft furnace: a zone of endothermic sulfation of sulfide minerals with ammonium hydrosulfate at 360–650 °C and a zone of exothermic oxidative roasting of residual sulfur at 640–660 °C. Excess oxidation heat compensates for the thermal losses of sulfation, ensuring an auto-genous process without sintering of the charge. Flotation enrichment of off-balance ore from the Annenskoye deposit yielded a concentrate with a Cu grade of 7.59% and a copper recovery of 89.13–92.13%. Thermodynamic modeling was used to validate the temperature conditions for sulfation of individual minerals, and analytical relationships were developed for calculating reagent consumption and sulfur distribution. Laboratory tests confirmed the adequacy of the calculation model; the discrepancy between calculated and experimental data did not exceed 1.5%. The feasibility of regenerating ammonium hydrosulfate and extracting copper from the processed products was demonstrated. A basic flow chart for waste-free processing of low-grade copper-sulfide raw materials was proposed.

Keywords: copper; sulfur; enrichment; roasting; gas recovery; ore; concentrate



Academic Editors: Chaobo Tang
and Tianxiang Nan

Received: 9 June 2026

Revised: 3 July 2026

Accepted: 7 July 2026

Published: 10 July 2026

Copyright: © 2026 by the authors.
Licensee MDPI, Basel, Switzerland.
This article is an open access article
distributed under the terms and
conditions of the [Creative Commons
Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

The progressive depletion of rich copper deposits is a key challenge facing the modern non-ferrous metals industry. Globally, the mineral resource base is shifting toward the processing of low-grade sulfide ores and concentrates with reduced copper and sulfur content, necessitating the development of new, efficient processing technologies. This issue is particularly pressing for Kazakhstan, which possesses substantial reserves of sub-marginal copper ores; their commercial exploitation is currently limited by the low economic efficiency of existing technologies when copper content falls below 0.34 wt. %. In this regard, the development of energy-efficient and environmentally safe technologies for extracting valuable components from low-grade raw materials is one of the priority tasks of modern metallurgy [1–3].

Traditional copper production technology is based on the sequential processes of roasting, smelting, and converting. Despite being a well-established industrial practice, the efficiency of pyrometallurgical processing drops significantly when low-grade concentrates are used, due to the feedstock's insufficient thermal potential, higher impurity content, and increased specific energy consumption. Furthermore, the generation of large volumes of sulfurous gases necessitates the use of costly gas-cleaning systems, thereby increasing the capital and operating expenses of metallurgical plants [4–6]. In this regard, significant attention has been paid in recent years to combined technologies that integrate selective roasting processes with subsequent hydrometallurgical metal recovery [7–9].

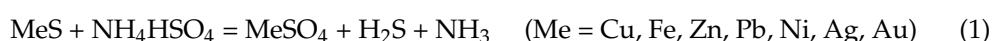
One of the most promising approaches is sulfatizing roasting, which ensures the selective conversion of copper into water-soluble sulfate, while iron predominantly remains in the form of oxides or sparingly soluble compounds. This significantly enhances the selectivity of the subsequent leaching and copper recovery processes. Experimental studies have demonstrated that the optimal selection of roasting conditions enables effective separation of copper and iron through the preferential formation of CuSO_4 [5,6].

Processes employing ammonium sulfate and ammonium hydrogen sulfate as sulfating agents are of particular interest. Their advantages include high reactivity, relatively low roasting temperatures (300–450 °C), reduced energy consumption, and the potential for reagent regeneration. According to a recent systematic review, ammonium sulfate roasting technology is considered one of the most promising methods for processing low-grade mineral and technogenic raw materials, owing to high metal recovery rates, good selectivity, and environmental benefits [10,11]. Similar results were obtained during the processing of copper–nickel concentrates, converter slags, and other sulfide materials, where preliminary sulfation significantly increased the recovery of copper, nickel, and cobalt during subsequent water leaching [12–15].

Despite the extensive research conducted, the majority of published studies focus on the processing of high-grade concentrates, converter slags, or anthropogenic raw materials. Issues regarding the sulfation of low-grade copper-sulfide concentrates with ammonium hydrogen sulfate, the interaction between the endothermic and exothermic stages of the process, and the formation of the phase composition of roasting products remain insufficiently investigated [16–20]. Furthermore, only a few studies combine thermodynamic modeling, thermal analysis, X-ray phase identification of products, and process testing of leaching within a single, comprehensive study.

This paper proposes a combined method for processing low-grade copper-sulfide concentrates using ammonium hydrogen sulfate, based on the sequential occurrence of an endothermic sulfation stage and an exothermic oxidation stage for residual sulfides.

This paper proposes a fundamentally different solution: a combined sulfation method (CSM) based on the energetic coupling of two thermally opposing processes within a single unit. Excess thermal energy released during the exothermic oxidation of sulfide minerals by atmospheric oxygen is utilized to drive the endothermic reaction in which the same minerals are decomposed by ammonium hydrogen sulfate (AHS):



The spatial separation of endothermic and exothermic reaction zones within the filtering bed of the shaft furnace allows for targeted control of the roasting temperature, prevents charge sintering, and ensures the complete breakdown of refractory sulfide minerals across a wide range of sulfur content in the concentrate. Gaseous reaction products (NH_3 and H_2S) are captured by a circulating solution and returned to the production cycle, thereby eliminating atmospheric emissions and enabling reagent regeneration.

The scientific novelty of the proposed approach lies in considering ammonium hydrogen sulfate not only as a sulfating reagent but also as an active regulator of the reaction system's thermal state.

The aim of this work is the theoretical substantiation and experimental verification of a combined sulfation method applied to the processing of low-grade copper sulfide concentrate from the Annenskoye deposit (Kazakhstan).

2. Materials and Methods

2.1. Feedstock Characteristics

Off-balance copper-sulfide ore from the Annenskoye deposit (Zhezkazgan region, Kazakhstan) was used as the feedstock. The chemical composition of the feedstock ore sample is presented in Table 1.

Table 1. Main chemical composition of the feedstock ore sample.

Component	Content, %	Component	Content, %
Copper	0.34	Iron	2.89
Lead	0.079	Silver, g/t	12
Molybdenum, g/t	3.0	Sulfur	0.434
Cadmium	0.002	Aluminum	2.15
Silicon	20.97	Calcium	3.21

The phase composition of copper minerals in the ore (Figure 1) was as follows: secondary sulfides (covellite CuS and chalcocite Cu_2S)—76.5%, chalcopyrite CuFeS_2 —14.7%, oxygen compounds—8.8%.

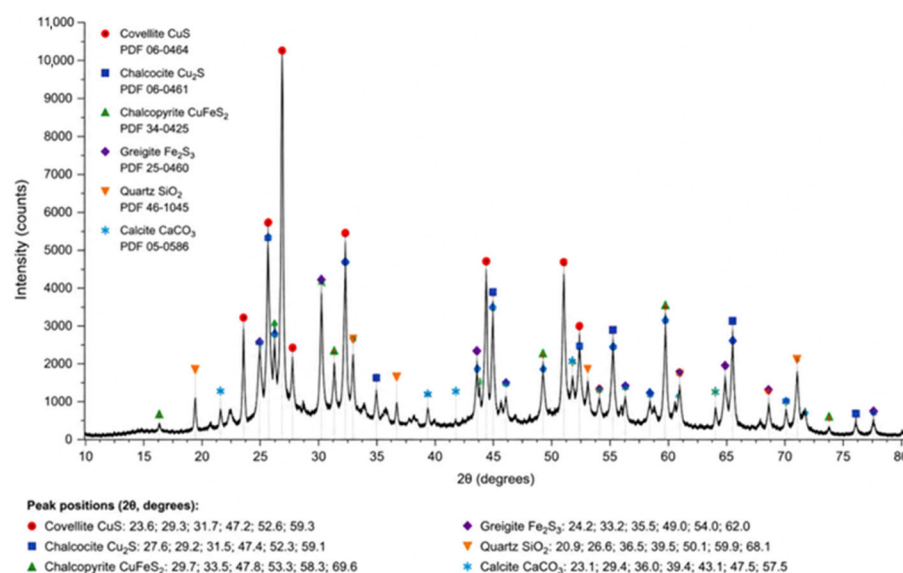


Figure 1. X-ray phase analysis of the raw ore.

The prepared sample, after averaging, crushing, and grinding, contained 86% of the minus 0.071 mm class.

2.2. Flotation Enrichment of the Ore

Concentrates were obtained by flotation enrichment in a laboratory flotation machine of the Mekhanobr type (Mekhanobr, Saint Petersburg, Russia) with a cell volume of 1.0 dm³.

The flotation flowsheet for the experiments is shown in Figure 2.

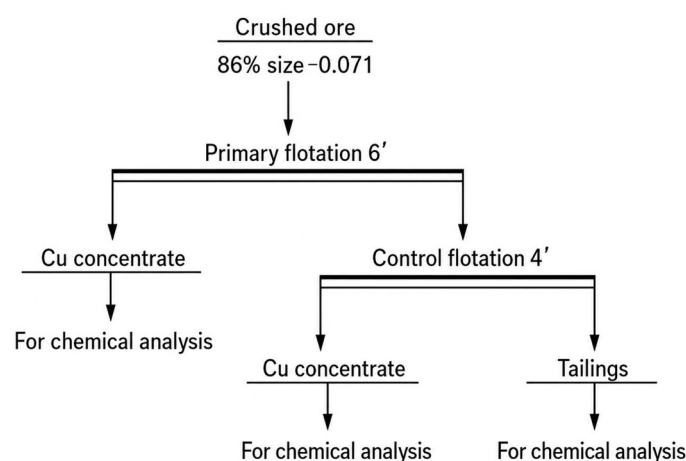


Figure 2. Open flotation flow chart for producing rougher flotation concentrate.

An open flotation flowsheet with primary and secondary stages was used. Flotation conditions: pH = 9.0; xanthate (ks) consumption in primary flotation—80 g/t; methyl isobutyl carbinol (MIBKC)—40 g/t; xanthate consumption in control flotation is 5 g/t.

To obtain a higher-grade concentrate used in roasting experiments, closed-loop flotation experiments were also conducted with two cleaning runs of the rougher concentrate at the same reagent flow rates. The chemical and phase compositions of the rough concentrate (4% yield) are presented in Tables 2 and 3.

Table 2. Chemical composition of rough concentrate, %.

Cu	S	Fe	Ca	SiO ₂	Al ₂ O ₃	Ag, g/t	Ti	Mg	K
7.59	5.81	3.60	2.73	39.13	2.31	98.7	0.3	0.71	1.52

Table 3. Phase analysis of concentrate for copper species content.

Copper Species	Content, abs. %	Share, rel. %	S ^{2−} , abs. %
Sulfates	<0.01	—	—
Carbonates	<0.09	2.3	—
Oxides, silicates	<0.2	—	—
Secondary sulfides (covellite CuS + chalcocite Cu ₂ S)	6.473 (5.547 + 0.925)	85.28 (73.1 + 12.18)	2.093 (1.860 + 0.233)
Chalcopyrite CuFeS ₂	1.116	14.7	1.124
Iron sulfides (Fe ₂ S ₃)	—	—	2.588
Total	7.59	100.0	5.810

2.3. Preparation of the Batch and Granulation

To test the combined sulfation method (CSM), three batch variants with different sulfide sulfur contents were prepared: 2.5%; 5.81%, and 10%. Samples with the specified sulfur content were obtained by mixing the original ore with high-grade concentrate (sulfur content 11.93%). According to the calculated data, ammonium hydrosulfate (AHS, NH₄HSO₄) was added to each batch in an amount determined by the formula:

$$M(\text{AHS}) = 3.45 ([\text{S}^{2-}] - [\text{S}^{2-}]_2),$$

where $[S^{2-}]$ is the total sulfide sulfur content in the concentrate, %; $[S^{2-}]_2$ is the sulfur fraction sent to the oxidative roasting zone, calculated using the equation:

$$[S^{2-}]_2 = 2.5 + 0.1471 ([S^{2-}] - 2.5) \text{ (at a target temperature of } 650^\circ\text{C)}.$$

The batches were pelletized in a laboratory granulator with a bowl diameter of 0.35 m, a side height of 12 cm, and a rotation speed of 25 rpm with water spray. The strength of dry granules measuring 3–5 mm was assessed by dropping them from a height of 1.2 m: the retention rate was 98%, which is sufficient for transportation and loading into the roasting unit.

2.4. Oxidative–Sulfatizing Roasting

The roasting process was studied in a laboratory sintering pan made of quartz glass with a grid bottom and a diameter of 50 mm (Figure 3).

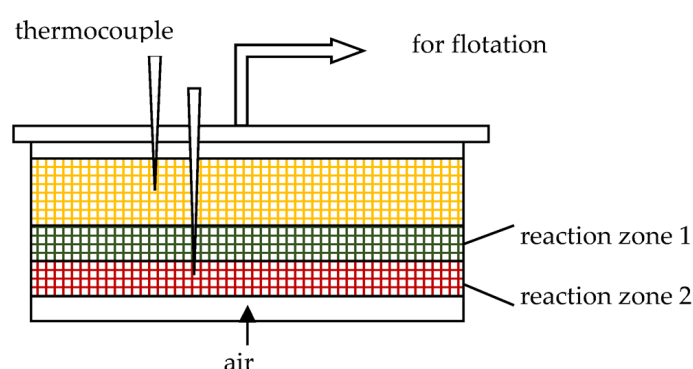


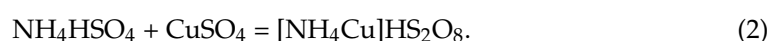
Figure 3. Schematic diagram of a sintering pan with top suction.

The bed height of granules with a diameter of 3–5 mm was approximately 100 mm. The sintering pan was equipped with a tightly sealed lid with thermocouple covers and a draft tube connected to the rotameter of a laboratory flotation cell.

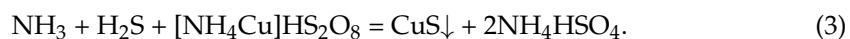
The air intake rate was set at 8 mL/s. Ignition was achieved by blowing hot air (400 °C) from below using a heat gun. Once the lower thermocouple reached 500 °C, the heat gun was removed, and autogenous roasting (autogenous roasting refers to a process in which, following initial ignition, all the necessary thermal energy is generated through the exothermic oxidation of sulfide minerals, without the need for additional external heat input. In contrast, traditional roasting typically requires a continuous external source of thermal energy to maintain the required temperature) continued with the air drawn in until the entire mass was completely roasted. The maximum temperature was recorded by the upper thermocouple as it passed through the roasting zone. A thermodynamic analysis of the reactions of HSA with sulfide minerals and their oxidation by oxygen was conducted using the HCS-5.1 Chemistry (Outokumpu, Pori, Finland) and Astra-4 (STC “Astra”, Moscow, Russia) software packages in the temperature range of 100–700 °C.

2.5. Leaching of Cinder and Collection of Gaseous Products

The calcined material (calcined) was ground and subjected to leaching for 60 min in a 3-L agitator at a temperature of 22–50 °C using a recycled HSA solution (filtrate). During leaching, copper is released into solution as complex ammonium copper hydrosulfate according to the reaction (2):



Gaseous roasting products (NH_3 and H_2S) were captured with an ammonium copper hydrogen sulfate solution. Copper precipitates as CuS sulfide, and the ammonium copper hydrogen sulfate solution is regenerated and returned for leaching (3):



The phase composition of the sulfation product at 360°C was confirmed by X-ray phase analysis on a DRON-3 (Bourevestnik, Saint Petersburg, Russia) automated diffractometer with $\text{CuK}\alpha$ radiation (β filter, conditions: $U = 35\text{ kV}$, $I = 20\text{ mA}$, θ – 2θ acquisition, detector speed 2 deg/min). Phase identification confirmed the formation of copper sulfate (CuSO_4).

2.6. Analytical Methods

The chemical composition of ores and concentrates was determined at the accredited chemical analysis laboratory of the Zh. Abishev Chemical Institute (Karaganda). Phase analysis of copper-bearing minerals was performed using a selective dissolution method. X-ray phase analysis of the roasting products was performed using a DRON-3 diffractometer. Thermodynamic calculations were performed using the HCS-5.1 Chemistry and Astra-4 software packages.

Thermogravimetric and differential scanning calorimetry analyses were conducted to experimentally verify the sequence of thermal transformations predicted by thermodynamic calculations. The TG–DTG curves for the mixture of concentrate and NH_4HSO_4 revealed three characteristic mass-loss stages, corresponding to the decomposition of ammonium bisulfate, the sulfation of copper sulfides, and the oxidation of the remaining sulfide phases (Figure 4). An endothermic peak was observed on the DSC curve in the 320 – 430°C range, associated with sulfation reactions, followed by an intense exothermic peak at 560 – 670°C caused by sulfide oxidation. These results experimentally confirm the existence of the two thermally coupled reaction zones proposed in the present work.

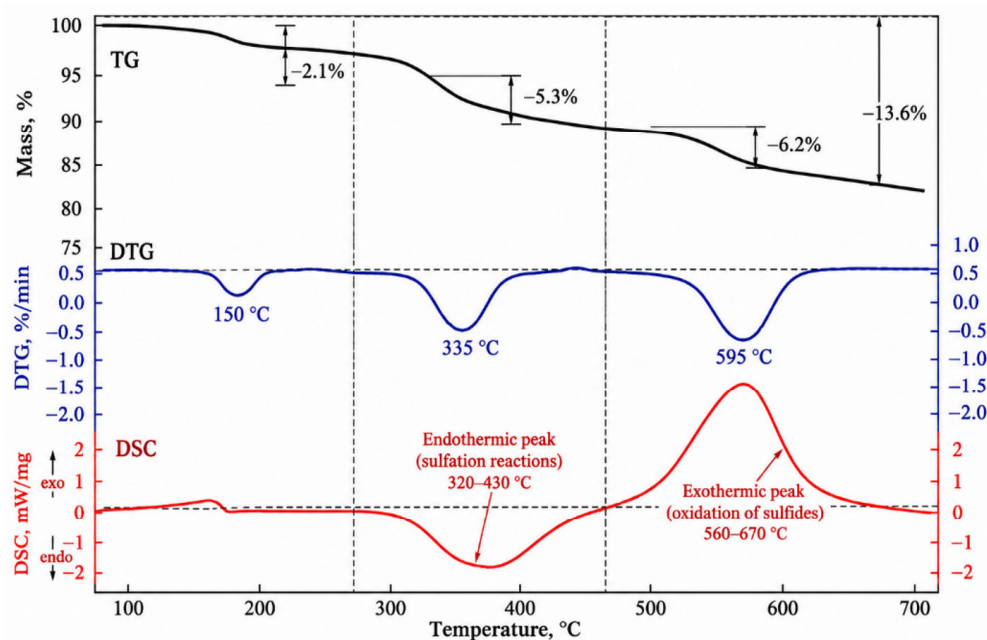


Figure 4. TG-DTG-DSC curves of the mixture of copper concentrate and NH_4HSO_4 with stages of thermal transformations.

3. Results

3.1. Flotation Beneficiation Results

Flotation tests were conducted using an open-loop design to maximize copper recovery in the rough concentrate. In five parallel tests, with a concentrate yield of 8.35–10.36%, a total copper recovery of 89.13–92.13% was achieved at a copper grade of 3.01–3.67% (Table 4). The copper grade in the final tailings was 0.029–0.041%, confirming the high efficiency of flotation.

Table 4. Results of flotation enrichment for the target component (copper).

Experiment No.	Product	Yield, %	Cu Content, %	Cu Recovery, %
1	Total concentrate	8.83	3.52	92.02
1	Dump tailings	91.17	0.029	7.99
2	Total concentrate	8.35	3.67	90.13
2	Dump tailings	91.65	0.037	9.87
3	Total concentrate	9.00	3.36	89.13
3	Dump tailings	91.00	0.041	10.87
4	Total concentrate	9.64	3.21	91.01
4	Dump tailings	90.36	0.034	8.99
5	Total concentrate	10.36	3.01	92.13
5	Waste tailings	89.64	0.030	7.87

Analysis of the dependence of copper content and recovery on concentrate yield (Figure 5) showed that with a yield of 10–12%, a maximum recovery of about 92% is achieved.

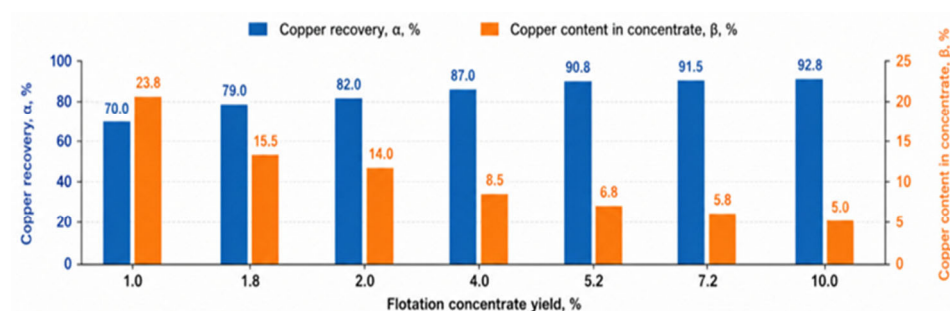


Figure 5. Copper recovery (α) and content (β) in the concentrate.

The closed circuit flotation process produced a high-grade concentrate with a copper grade of 23.8%, a recovery of 70%, and a yield of 0.99%; silver recovery in concentrate was up to 76%.

Sulfur recovery (Figure 6) is slightly lower than that of copper, but its content in the concentrate (2.5–5.81% S^{2-}) ensures autogenous roasting.

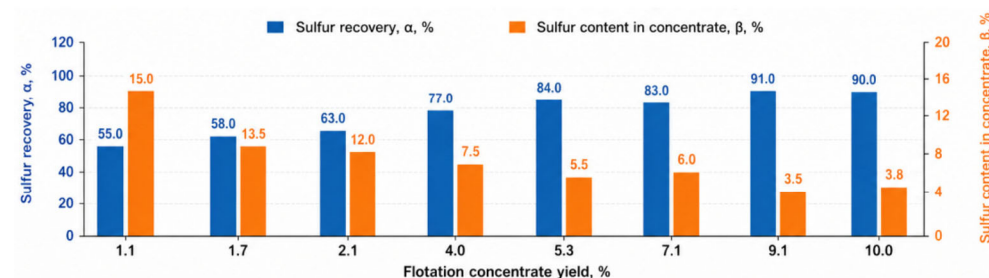


Figure 6. Sulfur recovery (α) and content (β) in the concentrate as a function of concentrate yield at optimal reagent dosages.

Economic efficiency of processing is achieved with copper recovery above 90%, taking into account associated components—silver, rhenium, and iron.

3.2. Thermodynamic Analysis of Sulfation Reactions with Ammonium Hydrosulfate (Zone 1)

Thermodynamic calculations have shown that the interaction of ammonium hydrosulfate (AHS) with sulfide minerals is endothermic and occurs in the temperature range of 300–650 °C. The key reactions and their characteristics at the most significant temperature points are given in Table 5.

Table 5. Thermodynamic characteristics of the reactions of sulfide minerals with GSA (sulfation zone).

Reaction	T, °C	ΔH, kcal	ΔG, kcal	Note
$\text{CuFeS}_2 + 2\text{NH}_4\text{HSO}_4 = \text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{S} + 2\text{NH}_3$	400	+86.96	−24.18	The reaction is thermodynamically probable at $T > 300$ °C
$\text{CuS} + \text{NH}_4\text{HSO}_4 = \text{CuSO}_4 + \text{H}_2\text{S} + \text{NH}_3$	500	+50.62	−8.66	The reaction is probable at $T > 400$ °C
$\text{Cu}_2\text{S} + \text{NH}_4\text{HSO}_4 = \text{Cu} + \text{CuSO}_4 + \text{H}_2\text{S} + \text{NH}_3$	600	+50.46	−3.83	The reaction is probable at $T > 550$ °C
$\text{Fe}_2\text{S}_3 + 3\text{NH}_4\text{HSO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{S} + 3\text{NH}_3$	300	+31.50	−5.23	The reaction is probable at $T > 250$ °C

X-ray phase analysis of the product of aging a mixture of covellite and GSA at 360 °C (DRON-3 diffractometer) confirmed the formation of copper sulfate CuSO_4 with the following unit cell parameters: $a = 8.401$ Å, $b = 6.699$ Å, $c = 4.837$ Å. Thus, already at 360 °C, copper sulfide minerals are transferred to the GSA melt, forming the target sulfate.

The total thermal effect of sulfation of all forms of sulfide sulfur in the concentrate (5.81% S^{2-}) in Zone 1 was +2.864 kcal per 100 g of concentrate at a consumption of 20.044 g of GSA. The specific energy absorption is 0.143 kcal/g of GSA.

3.3. Thermodynamic Analysis of Oxidative Roasting Reactions (Zone 2)

The oxidation reactions of sulfide minerals with atmospheric oxygen are strongly exothermic and thermodynamically highly probable over the entire temperature range studied (Table 6). The total thermal effect of oxidation of the same sulfur sample (5.81 g S^{2-}) was −31.795 kcal at 700 °C.

Table 6. Thermodynamic characteristics of the oxidation reactions of sulfide minerals with oxygen (zone 2).

Reaction	T, °C	ΔH, kcal	ΔG, kcal	Thermal Effect on S^{2-} in Concentrate, kcal
$\text{CuFeS}_2 + 4\text{O}_2 = \text{FeSO}_4 + \text{CuSO}_4$	700	−360.77	−195.03	−6.336
$\text{CuS} + 2\text{O}_2 = \text{CuSO}_4$	700	−168.33	−85.86	−9.784
$4\text{Cu}_2\text{S} + 9\text{O}_2 = 2\text{Cu}_2\text{O} + 4\text{CuSO}_4$	700	−740.54	−336.71	−1.348
$\text{Fe}_2\text{S}_3 + 6\text{O}_2 = \text{Fe}_2(\text{SO}_4)_3$	700	−531.47	−310.71	−14.327
Total	700	—	—	−31.795

Comparing the thermal effects of the two zones allowed us to calculate the Gibbs free energy at 700 °C:

$$\Delta G_{700}^{\circ} \text{C} = \Delta H - T \Delta S = -31.795 - (-14.786 \times 923) = -18,147.5 \text{ kcal}.$$

It follows that upon reaching 700 °C, only a portion of the sulfide sulfur, equivalent to 2.499 g S^{2-} , burns. The specific calorific value of the sulfide sulfur concentrate was 5472.5 cal/g S^{2-} . To compensate for the heat loss in zone 1, zone 2 requires an additional 0.524 g S^{2-} per 100 g of concentrate.

3.4. Calculation of the Heat Balance and Sulfur Distribution by Zone

Based on thermodynamic analysis, analytical relationships were derived to determine the proportion of sulfide sulfur in each zone and the consumption of the gas-acid mixture depending on the sulfur content in the concentrate. At a target firing temperature of 650 °C:

$$[S^{2-}]_2 = 2.5 + 0.1471 ([S^{2-}] - 2.5),$$

$$[S^{2-}]_1 = [S^{2-}] - [S^{2-}]_2,$$

$$M(\text{GSA}) = 3.45 ([S^{2-}] - [S^{2-}]_2).$$

The formulas are applicable for concentrates with an S^{2-} content above 2.5%, since this value corresponds to the lower limit of the autogenous mode without the addition of GSA. The calculated data for five concentrate composition variants and the results of their experimental verification are summarized in Table 7.

Table 7. Calculated sulfur distribution, GSA consumption, and experimental roasting temperatures.

№	$[S^{2-}]$ Total, %	$[S^{2-}]_2$, r (Oxidation Zone)	$[S^{2-}]_1$, r (GSA Zone)	GSA Consumption, g	Roasting Temperature, °C (exp.)
1	5.81	2.987	2.823	9.739	647
2	2.50	2.500	0.000	0.000	652
3	5.00	2.867	2.133	—	—
4	10.0	3.602	6.398	16.762	643
5	11.62	3.841	7.779	—	—

The calculated temperature values are in good agreement with the experimental data: for the three tested batch compositions (5.81%; 2.5%; 10% S^{2-}), the recorded maximum temperatures were 647, 652, and 643 °C, respectively—within the specified range of 640–660 °C. This confirms the adequacy of the developed calculation formulas.

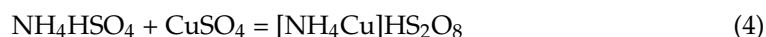
3.5. Results of Oxidative–Sulfatizing Roasting

Three batches of granulated charge were roasted in a laboratory sintering pan at an air intake rate of 8 mL/s. After ignition from an external source (hot air at 400 °C), roasting proceeded in autogenous mode: the combustion zone moved upward through a 100 mm-high granule layer.

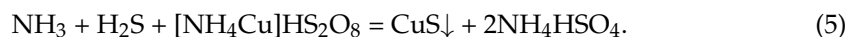
The recorded maximum temperatures for concentrates with sulfur contents of 2.5%, 5.81%, and 10% were 652, 647, and 643 °C, respectively. This temperature range (640–660 °C) ensures complete oxidation of sulfide sulfur and a sufficient degree of sulfation of the target components for their subsequent extraction by aqueous leaching. Visual inspection showed that no granule sintering was observed; the filter layer remained permeable throughout the process.

3.6. Leaching of Cinder and Closed Reagent Cycle

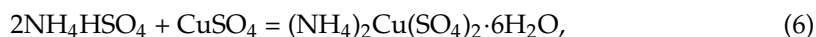
Leaching of crushed cinder with recycled GSA solution allowed copper to be dissolved as the complex compound $[\text{NH}_4\text{Cu}]\text{HS}_2\text{O}_8$:



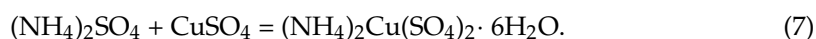
Gaseous roasting products, NH_3 and H_2S , were captured by the same solution, resulting in copper precipitation as CuS sulfide and regeneration of the GSA:



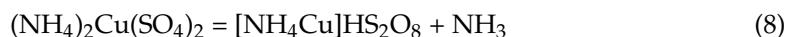
As the solution became saturated, Tutton's salt— $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ —was isolated by crystallization:



formed by the interaction of regenerated GSA with copper sulfate from the cinder. Tutton's salt can be sent to electrolysis to produce cathode copper and ammonium sulfate solution, which is then returned to the leaching cycle:



Thermolysis of Tutton's salt regenerates ammonia and restores the working solution of ammonium sulfate, closing the reagent cycle:



Thus, the proposed scheme enables the creation of a virtually waste-free closed cycle with ammonium hydrosulfate regeneration, toxic gas capture, and sequential copper recovery from both the calcine (leaching) and the gas phase (CuS precipitation).

4. Discussion

4.1. The Place of the Combined Sulfation Method Among Known Approaches

The depletion of high-grade copper deposits is forcing the industry to process off-balance sulfide ores and low-grade concentrates with copper grades of 0.34–3.5% and lower sulfur content. The traditional pyrometallurgical matte smelting process is unprofitable with these raw material parameters, and existing alternative methods have fundamental limitations (Table 8).

Table 8. Comparative characteristics of low-grade copper-sulfide concentrate processing methods.

Processing Method	Advantages	Disadvantages	Applicability to Low-Grade Concentrates
Hydrometallurgy (H_2O_2 , HNO_3)	High sulfide recovery	Expensive reagents, wastewater disposal	Limited
Autoclave leaching (O_2)	Complete chalcopryrite recovery	High pressure, capital costs	Unprofitable
Oxidative-chlorinating roasting	Complete recovery, chloride distillation	Problems with Cl_2 availability and disposal	Complicated
Steam-oxidizing roasting	Moderate temperatures	High steam generation costs (~400 °C)	Limited
Autogenous oxidative roasting	Without external fuel	Sintering at $\text{S}^{2-} > 2.5\%$; No temperature control	Only for $\text{S}^{2-} \leq 2.5\%$
KMS (proposed method)	Heat balance control, closed reagent cycle, gas capture	Requires precise GSA dosing	Effective for $\text{S}^{2-} > 2.5\%$

A common drawback of all the methods considered is the lack of effective heat balance control. During conventional autogenous roasting of concentrates with S^{2-} content above 2.5%, excess heat generation leads to sintering of the batch and disruption of the bed's gas

permeability, making the process uncontrollable. The proposed combined sulfatization method (KMS) eliminates this drawback through a fundamentally different approach—the energetic coupling of two thermally opposed processes in a single unit.

4.2. The Principle of Energetic Coupling and Its Rationale (Figure 2)

The key idea of the KMS is the spatial separation of the zones of endothermic and exothermic reactions in the filter bed of a shaft furnace. In zone 1 (upper, low-temperature), endothermic sulfation of sulfide minerals with ammonium hydrosulfate occurs according to reaction 1.

In zone 2 (lower, high-temperature), exothermic oxidation of the remaining sulfide sulfur by atmospheric oxygen occurs, releasing heat that, according to the second law of thermodynamics, is transferred to zone 1, meeting its energy requirements. This combination allows, on the one hand, to absorb excess oxidation heat, preventing sintering, and on the other, to specifically open up “resistant” sulfide minerals without external heating. Thermodynamic calculations confirmed the fundamental feasibility of this scheme: the total thermal effect of zone 2 (−31.795 kcal per 100 g of concentrate with 5.81% S^{2-}) is more than ten times greater than the thermal consumption of zone 1 (+2.864 kcal), ensuring a large heat balance reserve and stability of the autogenous regime.

4.3. Significance and Practical Applicability of Calculated Dependencies

An important scientific and practical result of the work is the derivation of analytical formulas linking three interdependent process parameters: the sulfide sulfur content in the concentrate $[S^{2-}]$, the sulfur distribution across zones ($[S^{2-}]_1$ and $[S^{2-}]_2$), and the GSA consumption. At a target temperature of 650 °C:

$$[S^{2-}]_2 = 2.5 + 0.1471 ([S^{2-}] - 2.5),$$

$$M(\text{GSA}) = 3.45 ([S^{2-}] - [S^{2-}]_2).$$

It is crucial that the dependence of the sulfur share by zone on the total S^{2-} content is nonlinear: as the sulfur content increases, the share sent to the GSA zone increases disproportionately. This means that for sulfur-rich concentrates (10–12% S^{2-}), GSA consumption increases significantly faster than for moderately rich concentrates (5–6% S^{2-}), which must be taken into account in process design.

The formulas are applicable for concentrates with $S^{2-} > 2.5\%$, since this value is the lower limit of process autogeneity without the addition of GSA. For concentrates with $S^{2-} \leq 2.5\%$, standard oxidative roasting is sufficient. Thus, KMS seamlessly complements existing technology, expanding the range of feedstocks processed.

4.4. Interpretation of Firing Results and the Role of the Filter Layer

Experimentally recorded firing temperatures for three batches of charge (643, 652, and 647 °C) within the specified design range of 640–660 °C demonstrate the high accuracy of the proposed calculation relationships—the error does not exceed 1.5%. This indicates that the process’s thermal balance is determined primarily by chemical reactions rather than by external factors (heat loss, heat capacity of the apparatus), which is a characteristic feature of the filter layer.

The filter layer of a shaft furnace plays a key role in implementing the KMS for several reasons. First, it creates conditions for spatial separation of zones: the combustion front moving from bottom to top forms a clear boundary between the oxidation zone and the sulfation zone. Second, the counter-current airflow preheats the charge in zone 1 with heat from the exhaust gases in zone 2, which, in accordance with the second law

of thermodynamics, increases the overall heat transfer efficiency. Third, the granulated charge maintains gas permeability throughout the process, eliminating sintering—the main problem with sulfur-rich concentrates.

The strength of the granules (98% retention when dropped from 1.2 m) proved sufficient for industrial transportation and loading conditions, confirming the feasibility of the proposed approach to charge preparation.

4.5. Closed Reagent Cycle as a Factor in Economic Efficiency

One of the fundamental advantages of the KMS is the ability to organize a completely closed reagent cycle. Ammonium hydrosulfate consumed in sulfation is regenerated through two processes: gas capture (NH_3 and H_2S) from the roasting zone with precipitation of copper sulfide CuS (reaction 10) and thermolysis of Tutton's salt $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (reaction 13). This fundamentally distinguishes the closed-loop process from chlorination roasting, where the reagent (Cl_2) is irretrievably lost with the gas phase and requires expensive disposal.

The closed-loop process also ensures the environmental safety of the process: toxic NH_3 and H_2S gases are not emitted into the atmosphere, but are completely captured and returned to production. Copper is extracted from two streams: from the calcine leaching solution (in the form of Tutton's salt and subsequently electrolytic copper) and from the CuS precipitate from gas recovery (sent to the converter).

A simplified flow chart for processing off-balance sulfide ores is shown in Figure 7.

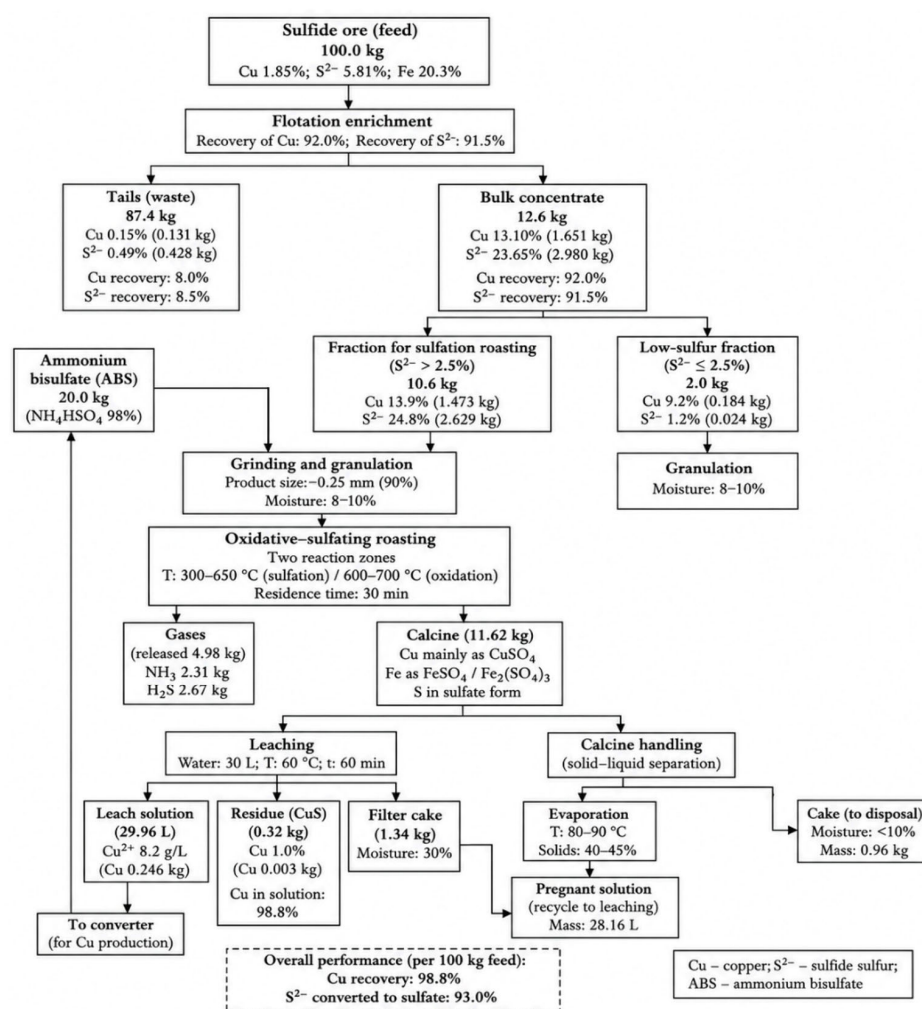


Figure 7. Simplified process flow diagram for the processing of off-balance-sheet sulfide ores.

It should be noted that the leachate is enriched with copper sulfate, which, upon accumulation, forms Tutton’s salt (reaction 6), which crystallizes at room temperature. This allows copper to be extracted by simple crystallization without additional energy input—a significant advantage over the extraction–re-extraction processes of hydrometallurgy.

4.6. Characteristics of the Final Product

Upon completion of the sulfating roasting process, the final product consists of a mixture of water-soluble copper and iron sulfates, oxide phases, and a small amount of residual sulfide minerals. Figure 8 shows the diffraction pattern of the product obtained by holding reaction mixture 2 at 360 °C, while the tabulated interpretation data below demonstrate the formation of copper sulfate (Table 9).

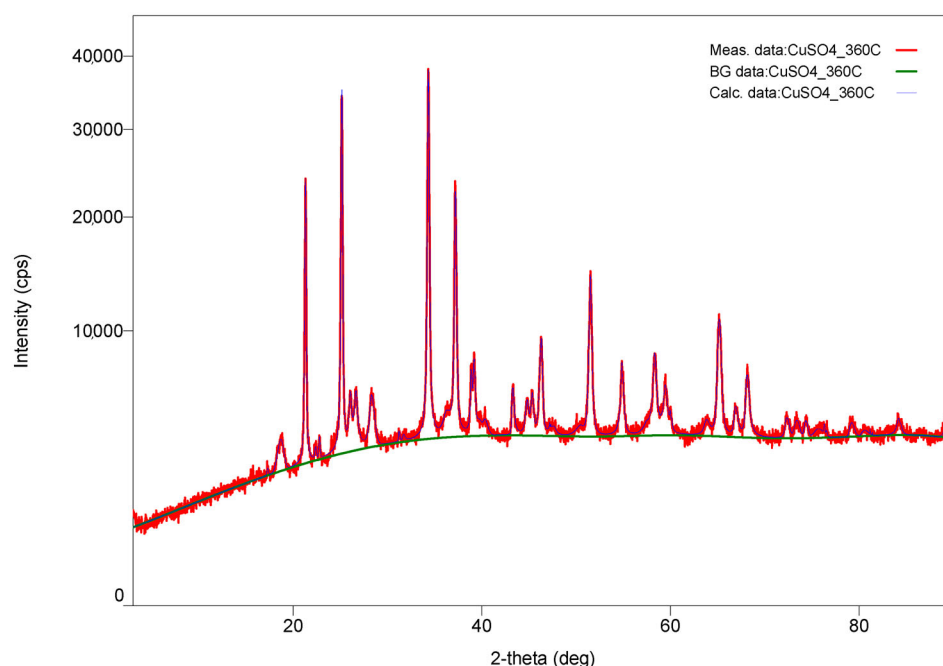


Figure 8. X-ray diffraction pattern of the product obtained by holding the mixture according to reaction 2 (Table 5), recorded on an automated DRON-3 diffractometer using CuK α radiation and a β -filter under the following conditions: U = 35 kV, I = 20 mA, θ –2 θ scan mode, detector speed 2 deg/min.

Table 9. Analysis results

Data set name	a (Å)	b (Å)	c (Å)	alpha (deg)	beta (deg)	gamma (deg)
CuSO ₄ _360C	8.400737	6.699120	4.836656	90.000000	90.000000	90.000000
CuSO ₄ _360C	5.161278	5.029501	7.562220	108.400002	108.599998	90.930000
Phase name	a (Å)	b (Å)	c (Å)	alpha (deg)	beta (deg)	gamma (deg)
Copper Sulfate	8.400737	6.699120	4.836656	90.000000	90.000000	90.000000
Poitevinite, syn	5.161278	5.029501	7.562220	108.400002	108.599998	90.930000

X-ray phase analysis of the calcined product confirmed the formation of crystalline copper sulfate (CuSO₄), the primary target phase of the process. Reflections corresponding to the orthorhombic modification of CuSO₄—with unit cell parameters a = 8.401 Å, b = 6.699 Å, and c = 4.837 Å—were identified in the diffraction pattern, indicating the completion of the sulfation of copper-bearing minerals.

The formation of water-soluble CuSO_4 ensures the effective transfer of copper into solution during subsequent sulfuric acid leaching. Process test results showed a copper recovery rate of up to 92%, confirming the high reactivity of the resulting product and the effectiveness of the selected roasting parameters.

Thus, the final product is characterized by a predominance of water-soluble copper sulfate, a reduced residual sulfide content, and high suitability for subsequent hydrometallurgical copper recovery.

Thermogravimetric and differential scanning calorimetry analyses revealed an absence of significant thermal effects following the roasting process, indicating the completion of major phase transformations and the formation of a thermally stable product.

5. Conclusions

Based on the theoretical and experimental studies conducted, the following conclusions have been formulated.

1. A combined method for the sulfation of low-grade copper sulfide concentrates using ammonium hydrogen sulfate has been developed and experimentally tested; it is based on the energetic coupling of the endothermic sulfation stage and the exothermic oxidation stage of residual sulfides. The proposed approach enables control of the process's thermal regime without the need for additional external heat input.
2. Thermodynamic modeling demonstrated that the reactions between sulfide minerals and ammonium hydrogen sulfate are thermodynamically favorable in the 300–650 °C range, whereas the subsequent oxidation of residual sulfides is accompanied by significant heat release. For a concentrate containing 5.81% S^{2-} , the total thermal effect was +2.864 kcal/100 g for sulfation and −31.795 kcal/100 g for oxidation, confirming the feasibility of offsetting the heat requirements of the endothermic stage using the process's internal heat resources.
3. Based on thermodynamic analysis, analytical relationships were developed to calculate the distribution of sulfide sulfur between the sulfation and oxidation zones, as well as the ammonium hydrogen sulfate consumption. Experimental verification demonstrated good agreement between calculated and actual roasting temperatures: at sulfur contents of 2.5%, 5.81%, and 10%, the maximum process temperatures were 652, 647, and 643 °C, respectively.
4. X-ray phase analysis of the calcination products confirmed the formation of crystalline copper sulfate (CuSO_4)—the primary target phase of the process—at a temperature as low as 360 °C. Thermal analysis (TG–DTG–DSC) revealed an endothermic sulfation effect in the 320–430 °C range and a subsequent exothermic sulfide oxidation effect at 560–670 °C, experimentally confirming the sequential occurrence of two interconnected process stages.
5. Flotation beneficiation of the feed ore yielded a concentrate with a copper recovery of up to 92%, while subsequent combined sulfatizing roasting preserved the product's high reactivity for hydrometallurgical copper recovery. Throughout the process, the filter bed maintained gas permeability, and no granule sintering was observed.
6. The results obtained confirm the potential of the combined sulfation method for processing low-grade copper sulfide concentrates and lay the foundation for developing an energy-efficient technology featuring an autogenous thermal regime, internal regeneration of ammonium hydrogen sulfate, and a closed-loop reagent cycle.

Author Contributions: Conceptualization: A.N., K.Z. and F.B.; methodology: A.N. and K.Z.; Validation: A.N. and K.Z.; formal analysis: Y.Z. and N.L.; visualization: A.N., Y.Z. and N.L.; resources: A.N., K.Z. and F.B.; data curation: A.N., K.Z. and F.B.; writing and preparation of the original text: A.N., K.Z. and F.B.; review and editing of the text: A.N. and Y.Z.; funding acquisition: K.Z.; scientific

supervision: K.Z. and F.B.; project administration: A.N. and K.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the Committee of Industry of the Ministry of Industry and Construction of the Republic of Kazakhstan under program-targeted funding for scientific research for 2024–2026, BR23991563: «Creation of Innovative Resource-Saving Technologies for Mining and Integrated Processing of Mineral and Technogenic Raw Materials».

Data Availability Statement: All data related to the article are available upon request via the authors' email.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Ju, J.; Feng, Y.; Li, H.; Xu, C.; Xue, Z.; Wang, B. Extraction of Valuable Metals from Minerals and Industrial Solid Wastes via the Ammonium Sulfate Roasting Process: A Systematic Review. *Chem. Eng. J.* **2023**, *457*, 141197. [CrossRef]
- Watling, H.R. Review of Biohydrometallurgical Metals Extraction from Polymetallic Mineral Resources. *Hydrometallurgy* **2014**, *140*, 163–180. [CrossRef]
- Ozer, M.; Acma, E.; Atesok, G. Sulfation Roasting Characteristics of Copper-Bearing Materials. *Asia-Pac. J. Chem. Eng.* **2017**, *12*, 365–373. [CrossRef]
- Sokolov, A.; Kasikov, A. Processing of Chalcopyrite Concentrate by Sulfating Roasting. *Tsvetnye Met.* **2024**, *4*, 33–42. [CrossRef]
- Wan, X.; Shi, J.; Taskinen, P.; Jokilaakso, A. Extraction of Copper from Copper-Bearing Materials by Sulfation Roasting with SO₂–O₂ Gas. *JOM* **2020**, *72*, 3436–3446. [CrossRef]
- Davenport, W.G.; King, M.; Schlesinger, M.; Biswas, A.K. *Extractive Metallurgy of Copper*, 6th ed.; Elsevier: Oxford, UK, 2011; 648p.
- Goryachev, A.A.; Mikhailov, V.G.; Fedorov, P.Y.; Medvedev, A.S. Sulfation Roasting of Copper–Nickel Sulfide Materials with Ammonium Sulfate. *Metals* **2021**, *11*, 422. [CrossRef]
- Sukla, L.B.; Panda, S.C.; Jena, P.K. Sulphatizing Roasting of Complex Sulphide Materials. *Hydrometallurgy* **1986**, *16*, 135–146. [CrossRef]
- Kritskii, A.; Fuentes, G.; Deveci, H. A Critical Review of Hydrothermal Treatment of Sulfide Minerals with Cu(II) Solution in H₂SO₄; Media. *Hydrometallurgy* **2025**, *231*, 106413. [CrossRef]
- Castleman, B.A.; van der Merwe, E.M.; Doucet, F.J. Thermochemical Purification of Talc with Ammonium Sulphate as Chemical Additive. *Miner. Eng.* **2021**, *164*, 106815. [CrossRef]
- Chanturiya, V.A.; Bocharov, V.A. Modern state and basic ways of technology development for complex processing of non-ferrous mineral raw materials. *Tsvetnye Met.* **2016**, *11*, 11–18. [CrossRef]
- Sun, J.; Xie, Z.; Jiang, T.; Shen, P.; Liu, D. Experimental and Mechanistic Study on the Recovery of Copper, Iron, Zinc and Cobalt from Copper Slag by Low-Temperature Roasting with Sulfuric Acid–Ammonium Persulfate Combined with Water Leaching. *Chem. Eng. J.* **2025**, *521*, 166710. [CrossRef]
- McNulty, T.; Parameswaran, K. Sulfation Roasting of Copper Sulfide Concentrates: Re-Imagining and Improving an Old Process. In *Proceedings of the 63rd Conference of Metallurgists (COM 2024)*; Springer: Cham, Switzerland, 2025; pp. 925–930. [CrossRef]
- Li, X.; Liu, Y.; Yang, W.; Ma, B.; Chen, Y.; Wang, C. Phase Transformation and Roasting Kinetics of Cobalt-Rich Copper Sulfide Ore in Oxygen Atmosphere Assisted by Sodium Sulfate. *J. Ind. Eng. Chem.* **2023**, *117*, 108–119. [CrossRef]
- Geng, Q.; Han, G.; Wen, S. Flotation of Copper Sulfide Ore Using Ultra-Low Dosage of Combined Collectors. *Minerals* **2024**, *14*, 1026. [CrossRef]
- Xiao, T.; Mu, W.; Shi, S.; Xin, H.; Xu, X.; Cheng, H.; Luo, S.; Zhai, Y. Simultaneous Extraction of Nickel, Copper, and Cobalt from Low-Grade Nickel Matte by Oxidative Sulfation Roasting–Water Leaching Process. *Miner. Eng.* **2021**, *174*, 107254. [CrossRef]
- Sun, Q.; Cheng, H.; Mei, X.; Liu, Y.; Li, G.; Xu, Q.; Lu, X. Efficient Synchronous Extraction of Nickel, Copper, and Cobalt from Low-Nickel Matte by Sulfation Roasting–Water Leaching Process. *Sci. Rep.* **2020**, *10*, 9916. [CrossRef] [PubMed]
- Lv, X.; Cui, F.; Ning, Z.; Free, M.L.; Zhai, Y. Mechanism and Kinetics of Ammonium Sulfate Roasting of Boron-Bearing Iron Tailings for Enhanced Metal Extraction. *Processes* **2019**, *7*, 812. [CrossRef]
- Grudinsky, P.; Pankratov, D.; Kovalev, D.; Grigoreva, D.; Dyubonov, V. Comprehensive Study on the Mechanism of Sulfating Roasting of Zinc Plant Residue with Iron Sulfates. *Materials* **2021**, *14*, 5020. [CrossRef] [PubMed]
- Geidarov, A.A.; Abbasova, N.I.; Guliyeva, A.A.; Jabbarova, Z.A.; Alyshanly, G.I. Selective Extraction of Copper and Aluminum from Oxidized Copper Ores. *Russ. Metall. (Met.)* **2025**, *2*, 88–96. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.