

**INVESTIGATION OF THE SULFATE LEACHING PROCESS OF SULFATED  
RESIDUE OBTAINED FROM COPPER SULFIDE CONCENTRATE**

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It is widely recognized that several methods exist for processing copper concentrates. In most cases, the processing of concentrates begins with oxidative roasting, or as it is often referred to, “dead roasting,” which results in the formation of calcine, whose primary components are metal oxides. Subsequently, the calcine undergoes the conventional “smelting-converting-fire refining-electrolytic refining” sequence to yield pure copper.

However, during concentrate processing, attention is almost exclusively focused on the main components of the concentrates, while little consideration is given to the recovery of other valuable metals such as zinc, lead, iron, and others. Traditional pyrometallurgical processes generally do not address this issue, as these metals either transition into the slag phase or remain in metallic by-products in various compound forms. In the conventional pyrometallurgical processing of concentrates, iron is completely disregarded, as it irreversibly passes into the slag.

For this reason, it is essential to implement technological principles that enable the comprehensive recovery of valuable elements contained in the concentrates at various stages of metallurgical processing.

The process of sulfate leaching of sulfated residue obtained from copper sulfide concentrate is presented. The objective is to transfer the valuable metals contained in the sulfated residue into a solution for their subsequent selective and comprehensive recovery. The sulfate leaching of the residue was conducted in a 9% sulfuric acid solution at a temperature of 80°C under continuous stirring conditions.

It has been shown that copper, zinc, and iron are almost completely extracted during the leaching process: the extraction rate of copper is 99.6%, zinc - 99.5%, and iron - 75.7%. The remaining iron transitions into the solid residue. Lead sulfate remains entirely in the solid residue after acid leaching. Insoluble sulfide silver also passes into the residue because it does not oxidize during the roasting process and, as a result, does not dissolve.

**Keywords:** sulfated residue, sulfuric acid, leaching, solid residue.

**Introduction.** There is growing interest in the processing of sulfide concentrates containing copper and other metals, particularly from the perspective of selective recovery of valuable metals. Typically, during various stages of technological processing, the main focus is on the primary components of the concentrates, neglecting the recovery of metals like zinc, lead, and iron. Traditional pyrometallurgical processes generally overlook these issues, with these metals either transferring into slag phases or remaining in the metallic residues in various compound forms. For instance, during the traditional pyrometallurgical processing

of concentrates, iron is entirely disregarded and irreversibly transitions into slag, primarily in the forms of  $\text{FeSiO}_3$  or  $\text{Fe}_2\text{SiO}_4$ .

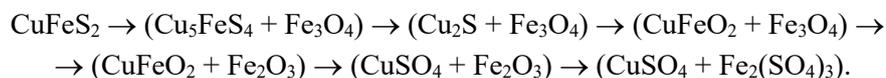
Thus, it is necessary to apply technological principles that allow the comprehensive recovery of valuable elements contained in concentrates during metallurgical processing. These principles must also comply with environmental requirements. At the current stage of technological development, hydrometallurgical processes are rapidly advancing and being applied alongside pyrometallurgical processes. Hydrometallurgical methods nearly eliminate emissions into the environment and enable comprehensive recovery of valuable metals from mineral resources. Moreover, the loss of valuable metals is minimized under this approach. As a rule, hydrometallurgical processes produce minimal waste and are manageable.

This study focuses on investigating the sulfate leaching process of sulfated residue obtained from copper sulfide concentrate, aimed at transferring the valuable metals in the residue into a solution for their subsequent selective and comprehensive recovery.

**Research Methods.** The chemical compositions of the sulfate leaching products of the sulfated residue obtained from copper sulfide concentrate were determined using standard methods.

The sulfate leaching experiments of the sulfated residues were conducted in chemically stable glass containers. After preparing the aqueous solution of sulfuric acid with the required concentration, a pre-weighed portion of the residue was added to it. Following the leaching process, the solid residue remaining at the bottom of the container, along with the precipitate formed during the subsequent purification of the solution, was separated using double-layer filtration and weighed on an electronic scale. The materials used for the purification of the resulting solution were also pre-weighed.

**Discussion of the research results.** It is known that the main component of copper sulfide concentrates is chalcopyrite (recognized as the most refractory sulfide), which undergoes phase transformations during sulfating roasting, as determined by the partial pressure diagrams of the Cu-Fe-S-O system [1]:



In study [2], the critical role of ferric sulfate formed during the low-temperature oxidation of pyrite in roasting mixtures was demonstrated in the sulfation reactions of chalcopyrite, sphalerite, galena, and other associated sulfide minerals. The addition of heated water vapor into the air flow during the roasting of concentrates significantly enhances the sulfation process due to the high equilibrium constant values of the interaction reactions.

For the research, a sulfated residue obtained from the sulfating roasting of a multicomponent copper sulfide concentrate (18.1% Cu, 32.36% S, 22.77% Fe, 8.25% Zn, 9.32% Pb, 4.84% SiO<sub>2</sub>, 2.56% Al<sub>2</sub>O<sub>3</sub>, 1.0% CaO, 0.8% MgO) is selected. The residue consists of phases such as CuSO<sub>4</sub>, ZnSO<sub>4</sub>, PbSO<sub>4</sub>, FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO, SiO<sub>2</sub>, CaO + MgO, and Al<sub>2</sub>O<sub>3</sub>. The average chemical composition of the sulfated residue, calculated by elements, is presented in Table 1, which shows that the main components of the residue are sulfate compounds, most of which dissolve well in water.

*Table 1*

*Chemical Composition of the Sulfated Residue Obtained from Copper Sulfide Concentrate*

Type of Roasted Material	Average chemical composition of the roasted material calculated by elements, %				
	CuSO <sub>4</sub>	ZnSO <sub>4</sub>	PbSO <sub>4</sub>	FeSO <sub>4</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Sulfated roasted material	26.60	12.12	13.70	11.16	22.32
	Fe <sub>2</sub> O <sub>3</sub>	CuO	SiO <sub>2</sub>	CaO + MgO	Al <sub>2</sub> O <sub>3</sub>
	1.54	1.35	5.90	2.19	3.12

The presence of certain amounts of copper and iron oxides-CuO and Fe<sub>2</sub>O<sub>3</sub>-in the roasted material is due to the exothermic reactions occurring during the sulfatization roasting of copper sulfide concentrate. The heat released during these reactions causes an increase in the furnace temperature, especially at temperatures above 650°C, where the primary component of the concentrate, chalcopyrite, begins to partially oxidize, forming copper and iron oxides.

During the sulfatization roasting of copper sulfide concentrate, the gangue minerals present (SiO<sub>2</sub>, CaO, MgO, Al<sub>2</sub>O<sub>3</sub>) are transferred unchanged into the sulfatized roasted product, and they are either very poorly soluble or insoluble in the aqueous sulfuric acid solutions used for leaching [3].

The primary advantage of sulfatized roasted products over oxidized roasted products lies in the fact that most of the compounds in sulfatized roasted products are primarily sulfates (CuSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeSO<sub>4</sub>, ZnSO<sub>4</sub>, PbSO<sub>4</sub>), which, except for PbSO<sub>4</sub>, are well soluble in dilute sulfuric acid solutions. This creates favorable conditions for the extraction of copper and zinc. After the leaching of sulfates, the iron and copper oxide compounds in the sulfatized roasted product are transferred to the leachate.

Based on the above, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was selected as the most effective reagent for the leaching of the sulfatized roasted product, as it is a good solvent for copper and other easily decomposable oxides (according to the general reaction MeO + H<sub>2</sub>SO<sub>4</sub> = MeSO<sub>4</sub> + H<sub>2</sub>O).

The leaching of the sulfatized roasted product was carried out in an 8-10% aqueous solution of sulfuric acid at temperatures of 75–85°C, with a solid-to-liquid ratio of 1:6. During the leaching process, in addition to the presence of expelled air, the trivalent iron sulfate  $\text{Fe}_2(\text{SO}_4)_3$  in the sulfatized roasted product served as a hydro oxidant. The leachate was continuously stirred during the process.

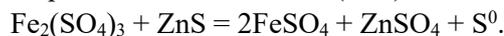
It is crucial to note that the concentrate roasting should be thoroughly completed beforehand, so that unroasted sulfides-especially chalcopyrite-do not remain in the sulfatized roasted product. This is important because the leaching of residual sulfides, particularly chalcopyrite, in aqueous sulfuric acid solutions is challenging.

As seen from the table above, the sulfatized roasted product contains a significant amount of trivalent iron sulfate  $\text{Fe}_2(\text{SO}_4)_3$ . Even in the presence of small amounts of sulfides in the roasted product, the substantial amount of trivalent iron sulfate is sufficient to leach the residual sulfides in the aqueous environment, according to the following general reaction:



where Me = Cu, Fe, Zn, Pb.

In the case of the presence of zinc sulfide (ZnS):



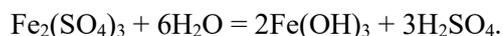
The reaction mentioned proceeds at a high rate, as the change in enthalpy of the reaction at 373 K has a large negative value,  $\Delta H^0 = -249 \text{ kJ/mol}$  [4].

The trivalent iron sulfate consumed in the above reactions is continuously regenerated during the leaching process through the interaction of the formed divalent iron sulfate and sulfuric acid, with the participation of oxygen:

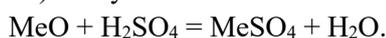


For this reaction, the change in enthalpy at 373 K has a large negative value,  $\Delta H^0 = -207 \text{ kJ/mol}$  [5].

Therefore, the hydrolysis of trivalent iron sulfate will be practically excluded as the leaching environment of the sulfatized roasted product is acidic (pH < 4.5-5.0):



The divalent oxides of metals present in small amounts in the sulfatized roasted product (CuO, FeO) easily dissolve in dilute sulfuric acid solutions:

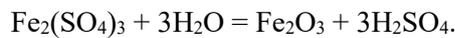


At the beginning of the leaching process, the partial formation of zinc oxide (ZnO) is likely, which may influence the leaching process to some extent. This is associated with the surface nature of zinc oxide, as ZnO, being a partial dissociation product of  $\text{ZnSO}_4$  ( $\text{ZnSO}_4 = \text{ZnO} + \text{SO}_3$ ), forms a thin layer over the  $\text{ZnSO}_4$  particles,

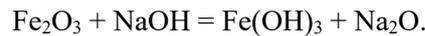
thereby isolating them from direct interaction with the solution. Since the leaching reaction of ZnO ( $\text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O}$ ) occurs much more slowly than the hydrolysis of the sulfate solid phase, the leaching process of the roasted product may proceed in stages.

It is known that when the pH of the leaching solution is  $\text{pH} < 5.5$ ,  $\text{Fe}_2(\text{SO}_4)_3$  dissolves completely. At the same time, the gold and silver, as well as the compounds  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$  that were transferred unchanged from the concentrate to the roasted product, do not dissolve in the sulfuric acid solution and will remain in the residue along with  $\text{PbSO}_4$ .

Trivalent iron sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) can transform into red iron ore ( $\text{Fe}_2\text{O}_3$ ) at a concentration of  $\text{H}_2\text{SO}_4$  of 40–50 g/l:



This would allow the separation of iron (III) oxide from the solution after leaching by precipitation with sodium hydroxide:



During the leaching process, the solution was continuously stirred. After the leaching process, both the remaining residue (chemically analyzed) and the filtered solutions (using atomic absorption spectroscopy, AAS) were analyzed.

The leaching efficiency was evaluated by the percentage of the main metal, copper, that passed into the solution, calculated by the formula:

$$q = (\text{Me}_{\text{leached}} - \text{Me}_{\text{remaining}}) / (\text{Me}_{\text{leached}} \cdot 100\%),$$

where  $\text{Me}_{\text{leached}}$  is the total content of the metal leached from the roasted product, and  $\text{Me}_{\text{remaining}}$  is the content of the metal in the residue.

Table 2 presents the results of the analysis of the sulfuric acid leaching products of the sulfatized roasted product.

Table 2

*Analysis data of the sulfuric acid leaching products of the sulfated roasted material*

Liquid product (solution)	The main ionic concentration 19,2 g/l $\text{Cu}^{2+}$ , 18,1 g/l $\text{Fe}^{3+}$ , 8,5 g/l $\text{Zn}^{2+}$ , 11 g/l $\text{H}_2\text{SO}_4$					
Solid residue	Main mineralogical composition, %					$\text{Al}_2\text{O}_3$ and other insoluble residue, %
	$\text{Fe}_2\text{O}_3$	$\text{PbSO}_4$	$\text{Ag}_2\text{S}_3$	$\text{SiO}_2$	$\text{CaO}+\text{MgO}$	
	18.6	19.2	0.8	28.6	13.2	19.6

Chemical, AAS, and photocolorimetric analyses were conducted in the laboratories of the Institute of Mining Metallurgy CJSC.

A comparison of the experimental results with the calculated data shows that copper, zinc, and iron are almost completely leached during the process. The

leaching degree of copper is 99.6%, zinc - 99.5%, and iron - 75.7%. The remaining iron is transferred to the solid residue.

Lead sulfate ( $\text{PbSO}_4$ ) remains in the undissolved residue in the solid phase, as it does not decompose with  $\text{H}_2\text{SO}_4$  [6]. The sulfide silver also passes into the insoluble residue, as it does not oxidize during the roasting process and, consequently, does not undergo leaching.

The optimal leaching conditions for the sulfatized roasted product are: the leaching temperature is  $80^\circ\text{C}$ , the sulfuric acid concentration is 9%, the constant stirring,  $\text{pH} = 0.8-1.0$ , and the leaching duration is 60-80 minutes.

Copper can be recovered from the leaching solution through cementation with iron, while zinc can be recovered by electrolysis. The lead sulfate in the residue can be dissolved first in a saturated sodium chloride aqueous solution, and then the resulting filtrate can be treated with iron chips for cementation.

**Conclusion.** The leaching degree of copper from the sulfatized roasted product into the sulfuric acid solution is 99.6%, zinc - 99.5%, and iron - 75.7%. The remaining iron passes into the solid residue. Lead sulfate remains entirely in the acidic leaching residue.

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*Received on 04.02.2025.*

*Accepted for publication on 04.06.2025.*

**ՍՈՒԼՖԻԴԱԴՂՆՁԱՅԻՆ ԽՏԱՆՅՈՒԹԻՑ ՍՏԱՑՎԱԾ ՍՈՒԼՖԱՏԱՑՎԱԾ  
ԲՈՎՎԱԾՔԻ ՏԱՐՐԱԼՈՒԾՄԱՆ ԳՈՐԾԸՆԹԱՑԻ ՀԵՏԱԶՈՏՈՒՄԸ**

**Ա.Մ. Հովհաննիսյան, Ն.Ռ. Մանուկյան, Դ.Գ. Վարդանյան**

Պղնձային խտանյութերի վերամշակման համար հայտնի են մի շարք եղանակներ: Առավել հաճախ խտանյութերի վերամշակումը սկսվում է խտանյութի օքսիդարար բովմամբ կամ, ինչպես շատ հաճախ ընդունված է անվանել, «մեռյալ բովմամբ», որի վերջնարդյունքում ստացված բովվածքի հիմնական բաղադրիչները հանդիսանում են մետաղների օքսիդներ: Այնուհետև բովվածքից «հալում-կոնվերտացում-հրային գտում-էլեկտրոլիզային գտում» ավանդական հայտնի սխեմայով ստանում են մաքուր պղինձ:

Սակայն խտանյութերի վերամշակման ժամանակ գրեթե միշտ հիմնական ուշադրությունը սևեռված է խտանյութերի հիմնական բաղադրիչների վրա, ուշադրություն չդարձնելով խտանյութերում առկա այնպիսի մետաղների կորզմանը, ինչպիսիք են ցինկը, կապարը, երկաթը և այլն: Ավանդական պիրոմետալուրգիական գործընթացները սովորաբար այսպիսի հարցերի չեն անդրադառնում. հիմնականում նշված մետաղները կամ տեղափոխվում են խարամային ֆազում, կամ էլ տարբեր միացությունների տեսքով մնում են մետաղական սորախցուկներում: Խտանյութերի ավանդական պիրոմետալուրգիական վերամշակման դեպքում երկաթն ամբողջովին անտեսվում է: Այն անվերադարձ ձևով անցնում է խարամների մեջ:

Այդ պատճառով անհրաժեշտ է կիրառել այնպիսի տեխնոլոգիական սկզբունքներ, որոնք հնարավորություն կտան մետալուրգիական վերամշակման փուլերում համալիր ձևով կորզել խտանյութերում պարունակվող արժեքավոր տարրերը:

Ներկայացված է սուլֆիդապղնձային խտանյութից ստացված սուլֆատացված բովվածքի սուլֆատային տարրալուծման գործընթացը, որի նպատակն է սուլֆատացված բովվածքում առկա արժեքավոր մետաղներն անցկացնել լուծույթ՝ դրանց հետագա ընտրողական սկզբունքով համալիր կորզման համար: Սուլֆատացված բովվածքի տարրալուծումն իրականացվել է 9 %-անոց ծծմբական թթվի լուծույթում 80°C ջերմաստիճանի և անընդհատ խառնման պայմաններում:

Ցույց է տրված, որ պղինձը, ցինկը և երկաթը տարրալուծման ընթացքում գրեթե ամբողջովին կորզվում են. պղնձի կորզման աստիճանը կազմում է 99,6%, ցինկինը՝ 99,5 %, իսկ երկաթինը՝ 75,7%: Երկաթի մնացած մասն անցնում է պինդ սորախցուկի մեջ: Կապարի սուլֆատն ամբողջությամբ մնում է թթվային տարրալուծման սորախցուկում: Անլուծելի նստվածքի մեջ է անցնում նաև սուլֆիդային արծաթը, քանի որ այն բովման գործընթացում չի օքսիդանում և որպես հետևանք չի տարրալուծվում:

**Առանցքային բառեր.** սուլֆատացված բովվածք, ծծմբական թթու, բովվածքի տարրալուծում, սորախցուկ:

## ИССЛЕДОВАНИЕ ПРОЦЕССА ВЫЩЕЛАЧИВАНИЯ СУЛЬФАТИРОВАННОГО ОГАРКА, ПОЛУЧЕННОГО ИЗ СУЛЬФИДНО- МЕДНОГО КОНЦЕНТРАТА

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Как известно, существует ряд методов переработки медных концентратов. Чаще всего переработка концентратов начинается с окислительного обжига, или, как его часто называют, “мертвого обжига”, в результате которого основными компонентами полученного материала становятся оксиды металлов. Далее из обожжённого материала традиционной схемой “плавка – конвертирование – огневое рафинирование – электролитическое рафинирование” получают чистую медь. Однако при переработке концентратов основное внимание практически всегда уделяется извлечению главных целевых компонентов, не принимая во внимание такие металлы, как цинк, свинец, железо и др. Традиционные пирометаллургические процессы, как правило, не затрагивают эти вопросы: указанные металлы либо переходят в шлаковую фазу, либо остаются в виде различных соединений в остатках. В традиционной пирометаллургической переработке железо из концентрата полностью игнорируется и безвозвратно переходит в шлак.

По этой причине необходимо применять такие технологические принципы, которые позволят комплексно извлекать содержащиеся в концентрате ценные элементы на различных стадиях металлургической переработки.

В данной работе представлен процесс выщелачивания сульфатированного огарка, полученного из сульфидно-медного концентрата, с целью перевода содержащихся в нем ценных металлов в раствор для их дальнейшего селективного комплексного извлечения. Выщелачивание сульфатированного огарка проводилось в 9%-ном растворе серной кислоты при температуре 80°C в условиях постоянного перемешивания.

Показано, что медь, цинк и железо практически полностью извлекаются в процессе выщелачивания: степень извлечения меди составляет 99,6%, цинка – 99,5%, железа – 75,7%. Оставшееся количество железа переходит в твердый остаток. Сульфат свинца полностью остается в остатке кислотного выщелачивания. В нерастворимый остаток также переходит сульфидное серебро, так как в процессе обжига оно не окисляется и, следовательно, не растворяется.

**Ключевые слова:** сульфатированный огарок, серная кислота, выщелачивание огарка, кек.