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COPPER RECOVERY FROM SULFURIC ACID LEACH SOLUTIONS

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Abstract

Solvent extraction is an effective method for separating and recovering metal ions from aqueous solutions based on their distribution between two immiscible phases. In this process, metal compounds react with organic extractants dissolved in hydrocarbon solvents, such as kerosene, forming hydrocarbon-soluble metal complexes. The extraction and subsequent re-extraction (stripping) of metals can be controlled by adjusting process parameters, particularly the pH of the aqueous phase. The present study focuses on oxidized copper ores located in the dumps of the Kalmakyr deposit. To develop an optimal process for the recovery of valuable metals from productive leach solutions, the initial stage involves evaluating whether the obtained solution can be considered standard and predicting its behavior under conventional extraction conditions. The chemical composition of the solution was analyzed, including the type and concentration of dissolved metals, pH value, presence and concentration of ammonia, chlorides, nitrates, and other relevant components. Based on the established solution characteristics, the feasibility of selectively recovering metals using solvent extraction technology was assessed, providing a foundation for the development of an efficient metal recovery process.

Keywords

oxidized copper, extraction, electro winning, leaching

Introduction. Solvent extraction is one of the most widely used methods for the separation and recovery of components from aqueous solutions and is based on the different distribution of substances between two immiscible phases, typically an aqueous and an organic phase [1]. In hydrometallurgical practice, liquid–liquid extraction is extensively applied for the selective recovery and concentration of metal ions from process solutions obtained during the leaching of ores and technogenic raw materials.

The liquid extraction process involves a chemical interaction between metal ions present in the aqueous phase and an organic extractant dissolved in an organic solvent, such as petroleum distillation products, including kerosene [2]. As a result of this interaction, a hydrocarbon-soluble metal–extractant complex is formed, which is transferred from the aqueous phase into the organic phase. The efficiency and selectivity of this process depend on the chemical nature of the extractant, the composition of the aqueous solution, and the operating conditions.

Chemical transformations occurring during extraction provide the possibility to control the transfer of metal compounds into the organic phase and their subsequent re-extraction (stripping) back into the aqueous phase. This control is achieved by changing process parameters such as pH, redox potential, extractant concentration, and phase ratio [1,3]. Among these factors, the pH of the aqueous medium plays a key role, as it directly affects the speciation of metal ions and the stability of the formed complexes.

The object of the present study is oxidized copper ores located in the dump deposits of the Kalmakyr deposit. These technogenic formations represent a significant source of valuable metals and require the development of efficient processing technologies. To develop an optimal process for the recovery of valuable metals from productive metal-containing solutions with specific physicochemical properties, it is necessary at the initial stage to determine whether the obtained solution can be classified as a standard solution and to predict its behavior under standard solvent extraction conditions [2].

For this purpose, a comprehensive characterization of the initial solution is required. This includes the identification of metals present, determination of their concentrations, measurement of the pH of the medium, and evaluation of the presence and concentrations of ammonia, chlorides, nitrates, and other accompanying components. The chemical composition of the solution significantly influences the extraction behavior of metals, as competing ions and complex-forming agents can affect both extraction efficiency and selectivity.

Knowledge of the specific composition of the productive solution makes it possible to assess which metals can be selectively recovered using solvent extraction technology and to determine the most suitable extraction and stripping conditions. This approach provides a scientific basis for designing an efficient and economically viable process for the recovery of copper and associated valuable metals from oxidized copper ores and technogenic raw materials [3].

In our case, after vat leaching, the solution has the following indicators table

Table 1

Content of individual metals in solution after vat leaching (mg / l) according to ICP-MS data

Elements	Solution	Elements	Solution
Ag	0,051	Nd	0,763
Al	341,2	Ni	0,465
As	0,35	P	131,2
Au	0,014	Pb	0,784
Ba	0,0001	Pr	0,188
Be	0,023	Rb	1,249
Bi	0,06	S	14910
Ca	441	Sb	0,017
Cd	0,006	Sc	0,193
Ce	1,361	Se	0,144
Co	0,574	Sm	0,239
Cr	0,444	Sn	0,045
Cs	0,0001	Sr	2,303
Cu	1606,5	Ta	0,028
Dy	0,2152	Tb	0,004
Er	0,037		

Among the various extractants currently considered for the treatment of the studied copper-containing solution, the most suitable and widely applied in the hydrometallurgical industry is an unmodified mixture of aldoxime and ketoxime. This class of extractants is known for its high selectivity toward copper ions, good chemical stability, and compatibility with hydrocarbon solvents commonly used in industrial operations. The choice of an appropriate extractant is a critical step in developing an efficient and economically viable solvent extraction process [4].

To determine the optimal concentration of the extractant in the organic phase, a series of organic solutions were prepared with varying extractant contents of 10%, 20%, 30%, 40%, and 50% by volume in the corresponding hydrocarbon solvent. These solutions were subsequently employed in a systematic experimental program designed to evaluate their extraction performance.

In each experiment, the prepared organic solution was contacted with a productive aqueous solution containing dissolved copper under controlled conditions. The mixing was carried out at an organic-to-aqueous (O/A) phase ratio of 1:1 using a mechanical stirrer for approximately 3 minutes to ensure thorough contact between the two phases. After the mixing period, the phases were allowed to separate in a standard separatory funnel until clear phase boundaries were observed.

Following phase separation, the residual copper concentration in the aqueous phase was measured using appropriate analytical techniques. This step allowed the determination of the copper extraction efficiency for each extractant concentration. The results obtained from these measurements, summarized in Table 2, provide valuable insights into the relationship between extractant concentration and copper recovery.

The experimental design and results provide a foundation for selecting the most effective extractant concentration, which balances copper recovery, reagent consumption, and process efficiency. Moreover, these findings contribute to the understanding of the underlying chemical interactions between copper ions and the aldoxime–ketoxime mixture, as well as the optimal operating conditions for industrial-scale applications. The methodology described here also establishes a framework for subsequent studies on stripping, phase regeneration, and recycling of the organic extractant, which are essential for the sustainability and cost-effectiveness of the solvent extraction process.

Table 2

Copper content in the aqueous phase after extraction at different contents of the extractant according to the data of chemical analysis

Experiment	Ratio of extractant with solvent	Content of Cu in the aqueous phase, g/l	Extraction of Cu in the organic phase,%
1	LIX984-N – 10% Solvent – 90%	0,45	73,1
2	LIX984-N – 20% Solvent – 80%	0,35	79,0
3	LIX984-N – 30% Solvent – 70%	0,16	90,4
4	LIX984-N – 40% Solvent – 60%	0,14	91,6
5	LIX984-N – 50% Solvent – 50%	0,09	94,6
	Ref. Solution	1,67	

As can be observed from Table 2, increasing the proportion of the extractant LIX984-N in the organic phase leads to a corresponding increase in the extraction of copper into the organic phase. This trend indicates that higher concentrations of the extractant enhance the formation of copper–extractant complexes, thereby improving the overall efficiency of the extraction process. Understanding this relationship is critical for optimizing reagent usage while maximizing copper recovery.

Following this initial study, further experiments were conducted to investigate the influence of agitation time and temperature on the efficiency of copper extraction. For these experiments, the organic phase was prepared with a composition of 50% LIX984-N and 50% solvent, and the organic-to-aqueous (O/A) phase ratio was maintained at 1:1. Controlled agitation was performed to ensure uniform contact between the two phases, and the separation of the organic and aqueous phases was achieved using a standard separatory funnel.

The copper concentrations in the aqueous and organic phases were subsequently analyzed, and the results of these experiments are presented in Tables 3 and 4. The data provide insights into the optimal operational parameters, including the minimum agitation time required to achieve maximum copper transfer and the effect of temperature on the kinetics and equilibrium of the extraction process.

These findings are essential for designing an efficient industrial extraction process, as they allow for the determination of conditions that maximize copper recovery while minimizing energy consumption and reagent usage. In addition, the results form the basis for further studies on stripping, phase regeneration, and process scaling, contributing to the development of a cost-effective and sustainable copper recovery methodology.

Table 3

Copper content in the aqueous phase after extraction at different agitation times according to the data of chemical analysis

Experiment	Agitation time, min	Content of Cu in the aqueous phase, g/l	Extraction of Cu in the organic phase,%
1	1	0,21	87,4
2	3	0,15	91,0
3	5	0,20	88,0
4	10	0,13	92,2
5	15	0,16	90,4
	Ref. Solution	1,67	

Table 4

Copper content in the aqueous phase after extraction at different temperature conditions according to the data of chemical analysis

Experiment	Extraction temperature, t°	Content of Cu in the aqueous phase, g/l	Extraction of Cu in the organic phase,%
1	20	0,076	95,4
2	30	0,079	95,3
3	40	0,065	96,1
4	50	0,069	95,9
5	60	0,067	96,0
	Ref. Solution	1,67	

As can be seen from Tables 3 and 4, variations in agitation time and temperature had minimal effect on the extraction of copper into the organic phase under the tested conditions. This indicates that the formation of copper–extractant complexes with LIX984-N is a rapid process that reaches near-equilibrium even at short contact times and ambient temperatures. Such behavior simplifies the design of the extraction process, as precise control of temperature and prolonged agitation are not critical for achieving high copper recovery.

To further optimize the extraction process, additional experiments were conducted to determine the optimal ratio of the organic and aqueous phases during both extraction and stripping operations. The extraction experiments were performed using an organic phase composed of 50% LIX984-N and 50% solvent, with an agitation time of 3 minutes at room temperature. The organic and aqueous phases were separated using a standard separatory funnel, ensuring clear phase boundaries and complete phase separation.

The results of these experiments, summarized in Table 5, provide important insights into the influence of the phase ratio on the efficiency of copper transfer from the aqueous to the organic phase and back during stripping. These findings are crucial for designing an industrially viable solvent extraction process, as they allow for the selection of an organic-to-aqueous phase ratio that maximizes copper recovery while minimizing reagent consumption and organic solvent use. The data also form a basis for scaling up the process, ensuring consistent performance under practical operating conditions.

Table 5

Extraction results at different ratios of organic and aqueous phases

Experiment	The ratio of organic and aqueous phases	Content of Cu in the aqueous	Extraction of Cu in the organic

		phase, g/l	phase,%
1	5/1	0,11	93,4
2	2/1	0,20	88,0
3	1/1	0,37	77,8
4	1/2	1,24	25,7
5	1/5	1,60	4,2
	Ref. Solution	1,67	

Subsequently, the re-extraction (stripping) of copper from the metal-loaded organic phase was carried out. In this part of the study, the copper-containing organic solution obtained from the extraction experiments was contacted with 15% sulfuric acid as the stripping agent. The experiments were conducted at various organic-to-aqueous (O/A) phase ratios to evaluate the effect of phase proportions on the efficiency of copper transfer from the organic phase back into the aqueous phase.

During each experiment, the organic and aqueous phases were mixed using a mechanical stirrer for approximately 3 minutes to ensure complete interaction between the copper–extractant complexes and the stripping solution. Following agitation, the phases were allowed to separate in a standard separatory funnel until a clear interface was observed.

The concentrations of copper in the aqueous phase after re-extraction were measured, and the results are summarized in Table 6. These data provide essential information regarding the efficiency of the re-extraction process under different phase ratios and confirm the ability to recover copper from the loaded organic phase effectively. The findings serve as a basis for optimizing the stripping stage, ensuring maximum recovery of copper while minimizing the consumption of sulfuric acid and enabling the recycling of the organic extractant for subsequent extraction cycles.

Table 6

Stripping results at different ratios of organic and aqueous phases

Experiment	The ratio of organic and aqueous phases	Cu content in the aqueous phase, g/l
1	5/1	43,3
2	2/1	37,2
3	1/1	32,6
4	1/2	30,8
5	1/5	29,4

As can be observed from Tables 5 and 6, an organic-to-aqueous phase ratio ranging from 2:1 to 1:1 provides the most favorable conditions for both extraction and stripping operations. This range ensures efficient transfer of copper into the organic phase during extraction, as well as effective recovery of copper back into the aqueous phase during re-extraction, while minimizing reagent and solvent consumption.

Following the optimization of phase ratios, further experiments were conducted to evaluate the performance of different extractants under controlled conditions. In these experiments, the organic phase was prepared with 50% of the respective extractant and 50% solvent, while maintaining an organic-to-aqueous phase ratio of 1:1. Agitation was carried out for 3 minutes at room temperature to ensure uniform contact between the phases. Phase separation was then achieved using a standard separatory funnel, and the aqueous and organic phases were analyzed for copper content.

The results of these comparative extraction tests, summarized in Table 7, provide valuable insights into the relative efficiency and selectivity of each extractant. These findings are critical for selecting the most effective reagent for copper recovery, as they allow for the identification of an extractant that maximizes copper transfer into the organic phase while maintaining favorable operational conditions. The data also support further optimization of industrial solvent extraction processes, including considerations for reagent consumption, phase ratios, and potential recycling of the organic phase.

Table 7

Extraction results with different extractants

Experiment	Extractant name	Content of Cu in the aqueous phase, g/l	Extraction of Cu in the organic phase,%
1	LIX984-N	0,11	93,4
2	Mextral 5774	0,12	92,8
3	Mextral 5640H	0,10	94,0
4	Mextral 984H	0,11	93,4
5	Mextral 973H	0,09	94,6

As can be seen from Table 7, the use of different extractants resulted in copper extraction efficiencies ranging from 92% to 94% into the organic phase. This indicates that all tested extractants are highly effective for copper recovery under the selected experimental conditions. The relatively small variation in extraction efficiency demonstrates that the choice of extractant, while important, may be complemented by other operational parameters such as phase ratio, contact time, and concentration to optimize overall process performance.

These results confirm the suitability of the tested extractants for industrial application, as they consistently achieve high copper recovery while maintaining operational simplicity. Furthermore, the data provide a foundation for selecting the most appropriate extractant based on additional criteria, such as reagent cost, chemical stability, selectivity toward copper over other metals, and ease of regeneration during repeated extraction–stripping cycles. This information is essential for designing an efficient, cost-effective, and sustainable solvent extraction process for recovering copper from oxidized ore leach solutions.

Main conclusion. Based on the results of the laboratory studies, the optimal conditions for the extraction and re-extraction of copper from oxidized ores of the Kalmakyr deposit were established. The most effective parameters were found to be an organic phase composed of 50% LIX984-N extractant and 50% solvent, an agitation time of 3 minutes at room temperature (25–30°C), and an organic-to-aqueous phase ratio of 1:1. Under these conditions, copper extraction into the organic phase reached high efficiency, ranging from 92% to 94%, and the subsequent re-extraction into the aqueous phase was similarly effective.

The studies also demonstrated that variations in agitation time and temperature within the tested ranges had minimal impact on copper recovery, indicating that the process is robust and can be conducted under ambient conditions without significant loss of efficiency. Additionally, the ratio of the organic and aqueous phases was identified as a critical factor for maximizing both extraction and stripping performance.

These findings provide a reliable basis for the design of an efficient, cost-effective, and sustainable solvent extraction process for copper recovery from oxidized ore leach solutions. The selected conditions ensure high metal recovery, minimized reagent consumption, and potential for organic phase recycling, making the process suitable for industrial application.

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