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Metallurgy

Development of an Enhanced Method for Copper Extraction from Sulfuric Acid Solutions

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ABSTRACT

The paper presents a method for the extraction of copper from sulfuric acid solutions, which reduces the consumption of sulfuric acid, increases the extraction of copper and the quality of cathode copper, and reduces the undesirable formation of the third-phase crud. The main results of copper extraction, including 2-3 stepwise extraction of copper, are presented. The extraction is carried out by mixing sulfuric acid solutions with a solution of a chelating, selective extractant of the aldoxime group (10 vol.%) and separating the mixture by settling to obtain a copper-containing extract and extraction raffinate, with the suppression of the third phase-crud due to the dissolution of polymerized silicon bonds in the cruds with a monomeric polymer $(H2C{=}CHC6H4SO3Na)n$ poly(4-sodium styrene sulfonate). This is achieved by adding 5 cm^3 of the polymer, influenced by the surfactant complex of sodium alkyl sulfonate, with an O/A ratio of 1:2 and a temperature of 20±5°C. Subsequent re-extraction of copper from the extract is carried out by mixing the extract with a sulfuric acid solution and separating the mixture by settling to obtain a copper-containing re-extraction and an extractant solution. The re-extract is purified from impurities, and copper is extracted electrically from the purified re-extract to obtain cathode copper and waste electrolyte. A method for calculating the technical and economic choice of an extraction apparatus has also been developed.

Keywords: SX-EW; copper; solvent extraction; crud, intensifying method; sulfuric acid solutions

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Introduction

Today, producing energy from renewable sources requires significantly more copper than producing energy from traditional sources. For example, an offshore wind farm may require five times more copper than a coal-fired power plant. Copper is also used in the manufacture of wind turbine cables to connect elements of complex installations (particularly deep-sea cables) and to transmit power to shore. Increasing demand from renewable energy sources, which require large amounts of copper, is driving the development of new technologies and the intensification of existing copper extraction technologies. KAZ Minerals Group achieved record copper production of 403 kt in 2023, up 6% from 2022, driven by increased production at Aktogay following the launch of its second world-class sulphide concentrator in 2022. Management's constant focus on operational improvement resulted in all ore processing plants exceeding design capacity throughout the year.

Methods that solve the problem of intensifying the extraction process and reducing the consumption of reagents are relevant. There is a method for the extraction of copper from sulfuric acid solutions, which includes extraction by mixing sulfuric acid solutions with a solution of a cation-exchange organic selective extractant and subsequent separation of the mixture by settling to obtain a copper soda hot extract and raffinate extraction [1]. The process is characterized by the formation of three phases: raffinate, extract, and the third phase - crud, which is concentrated in the extract as a separate phase. Re-extraction of copper from the extract is carried out by mixing the extract with a solution of sulfuric acid, followed by separation of the mixture by settling to obtain a copper-containing re-extraction and extractant solution. The re-extract is then purified by flotation with subsequent filtration or coalescence, and copper is electroextracted from the purified re-extract to obtain copper cathode and spent electrolyte. The spent electrolyte is used for copper re-extraction.

The technical result is a reduction in sulfuric acid consumption, increased copper extraction, reduced copper losses with waste solutions, and improved quality of copper cathode. The disadvantage of this method is that it does not provide for the suppression or reduction of the third phase - crud, containing various types of impurities, with silicon as the main component at 17.58% and above. This reduces the extraction of copper and affects the quality of commercial copper during electroextraction due to the use of the extractant LIX 984N, a ketoxime derived from a ketone. In the IR spectrum of this extractant, there are bands of stretching vibrations of C-H aliphatic hydrocarbons at 2957, 2926, 2871, 2856 cm-1, deformation vibrations of aliphatic hydrocarbons δ(CH3), δ(CH2) at 1464, 1378 cm-1, and stretching vibration ν(OH) at 3374 cm-1, aimed specifically at selectivity for copper rather than other metals in the liquid phase.

The interaction in the D2EHPA - $In2(SO_4)_3$ - $Fe_2(SO_4)_3$ - $Ti2(SO_4)_3$ - $ZnSO_4$ - H_2O system was studied, showing that the basis of cruds is the salt InR3, resulting from the secondary interaction of indium ions in solution with compounds formed in the extract [[2], [3]]. The formation of interphase suspensions containing osmium during the extraction of rhenium from acid wash solutions in copper production was examined. Secondary interaction of salts with compounds formed in the extract also occurs when the extractant contains iron and titanium [4], [[5], [6], [7]], [[8], [9], [10], [11], [12]]. This interaction greatly contributes to crud formation in the raffinate when in contact with the original indium-containing solution.

Methods for selecting extractants of the ACORGA class are discussed in works considering the suppression of iron and silicon impurities [[13], [14], [15], [16], [17]]. These works propose mechanisms for silicon polymerization, albeit with different initial solution compositions and preparation histories than those considered in the present study.

Let's consider the factors influencing the efficiency of extractors. The operation of the extraction apparatus depends on many technological parameters, controlled and uncontrolled. To carry out the process under optimal conditions, it is necessary to determine the values of the controlled parameters at which, considering the existing limitations, the most advantageous technological regime would be ensured. The efficiency of the extraction apparatus is influenced not only by the mode of the process carried out in it but also by the correct choice of the structural type of the apparatus itself, which contributes to the achievement of the specified technological parameters [18].

Continuous action devices are subject to various requirements, the main ones being: 1) maximum productivity and work intensity; 2) low energy consumption during operation; 3) high degree of extraction of valuable components; 4) simplicity of the device and low cost of production; 5) ease of control and automatic regulation. Currently, devices of mainly two types are used in practice: periodic and continuous, and the use of continuous devices is more effective due to their greater productivity and the possibility of automated control of their operation. Batch-type devices are usually used in industries with small volumes of reacting phase flows [[19], [20], [21], [22]].

The operation of extraction equipment is characterized by a close relationship between its productivity, quality, and the cost of the products produced since the cost depends on the optimal time for the actual residence of the raw materials in the apparatus. If raw materials are unjustifiably delayed in the devices, the overall productivity of the equipment decreases, the cost of production increases, and in some cases, the quality of the products may decrease. An unjustified reduction in the residence time of raw materials in devices, although it increases the overall productivity of the equipment, reduces the efficiency of using raw materials and the volume of the device, and also leads to a deterioration in product quality [[23], [24]].

Thus, when choosing the type of continuous extractor, it is necessary, first of all, to consider the residence time of the phase flows in the apparatus to achieve the specified economic efficiency of the process being carried out. Having information about the residence time of flow elements in the apparatus, it is possible to assess the operating efficiency of the apparatus itself, i.e., determine the proportion of the apparatus volume occupied by particles kept in the apparatus for a given time interval, the value of which was determined earlier in the process of laboratory or pilot-scale tests in periodic devices.

The purpose of the research was to develop a method for intensifying the extraction of copper from sulfuric acid solutions of the Aktogay deposit and to develop a technique for the technical and economic assessment of the choice of extraction apparatus.

Materials and Methods

The research focused on investigating copper extraction processes using different extractants. The main object of study was a productive copper-containing sulfate solution, commonly referred to as PLS (Pregnant Leach Solution). This solution was obtained through processing ore derived from the Aktogay deposit, with a solution pH of approximately 1.7.

Methods of Analysis: Analytical methods were employed to analyze the samples in this study. The quantitative determination of major elements in brines was conducted using an Optima 8300DV inductively coupled plasma atomic emission spectrometer and a PFP 7 flame photometer (Jenway, England).

Infrared absorption spectra were recorded using an Avatar 370 IR-Fourier spectrometer across the range of 400 - 4000 cm-1 from capillary layers in KRS-5 windows. The experimental setup included the “Transmission E.S.P.” attachment. Data processing was performed using OMNIC 6 software, along with electronic libraries including HR Aldrich FT-IR Collection Edition II (containing 18,454 spectra) and Aldrich Organometallic, Inorganic, Boron, Deuterium Compounds (consisting of 632 spectra) published by Nicolet Instrument Corp. in 1995. In cases where information was not available in the electronic libraries, literary sources were consulted.

X-ray fluorescence analysis was carried out using an Axios PANalytical wavelength dispersive spectrometer (Netherlands). X-ray phase analysis was performed using a D8 ADVANCE diffractometer (BRUKER AXS GmbH, Germany) equipped with Cu Kα radiation, a tube voltage of 40 kV, and a current of 40 mA. Data processing of the obtained diffraction patterns and calculation of interplanar distances were accomplished using EVA software. Sample interpretation and phase identification were achieved using the Search/Match program, utilizing the PDF-2 database from the International Center for Diffraction Data (ICDD, USA).

Extraction Experiment Procedure: Extraction experiments were conducted under controlled room temperature conditions of 20 ± 5°C. Temperature stability was ensured using a LOIP-105A thermostat. The investigation focused on studying the volume ratio of the organic and aqueous phases, ranging from 1:2 to 1:10 with a step size of 2. The contact time between phases was determined based on the time-dependent behaviour of the copper distribution coefficient (DCu), set at 5 minutes. The extraction process was carried out in conventional separatory funnels, followed by phase separation through settling. Aqueous solutions were filtered through a designated paper filter labelled "red ribbon" before sampling for analysis. Mechanical mixing was employed to achieve homogenization of the phases. Depending on the experimental objectives, the resulting solutions were analyzed for their copper content.

Materials. The results of the chemical analysis of a sample of the productive solution are presented in Table 1.

Table 1 – Chemical composition of the initial solution, g/dm^3

Cu	Fe	Mo	Mn	Zn	Al	Ca	Mg
1.25	4.23	-	1.47	0.16	29.10	0.69	12.98
Si	Co	Ni	Cr	Cd	P	Pb	H_2SO_4
0.51	0.033	0.007	0.002	0.0017	0.55	0.02	2.22

As shown in Table 1, the concentration of copper in the solution is 1.25 g/dm³, while sulfuric acid has a concentration of 2.22 g/dm³. The concentrations of aluminum, magnesium, total iron, calcium, and phosphorus are 29.1, 12.98, 4.23, 0.69, and 0.55 g/dm³, respectively. Silicon is also present in the solution with a concentration of 0.51 g/dm³. Other elements in the solution have relatively low levels.

To determine the composition of the solid residue obtained after evaporating the sulfuric acid solution to wet salts, X-ray fluorescence analysis (XRF) was performed. Table 2 presents the results of the XRF analysis of the solid residue.

Table 2 - Content of elements in solid residue

Element	Content, %	Element	Content, %
O	59.394	Ti	0.067
Na	0.346	V	0.008
Mg	3.818	Mn	0.386
Al	4.883	Fe	5.048
Si	0.304	Co	0.014
P	0.296	Ni	0.016
S	14.984	Cu	0.746
Cl	0.263	Zn	0.073
K	0.019	Y	0.004
Ca	0.114	Th	0.013

According to Table 2, the residue contains significant amounts of aluminum (4.9%), magnesium (3.8%), and iron (5.1%). The sulfur content is approximately 15%, which can be attributed to the presence of metal sulfates in the solution. The presence of the $SO4^{2-}$ group is confirmed by infrared (IR) analysis of a sample of the productive solution.

In the spectrum, absorption bands corresponding to water are observed at wave numbers of ν(OH) 3368 cm^{-1} and δ(HOH) 1647 cm^{-1}. The presence of the $SO4^{2-}$ group is evidenced by absorption bands at wave numbers 1108, 979, 671, and 620 cm^{-1}. The band with a peak at a wave number of 698 cm-1 corresponds to the manifestation of deformation vibrations of Me-O-H.

Based on the results obtained from chemical, infrared spectroscopic, and X-ray fluorescence (XRF) analyses, it can be concluded that the productive solution contains silicates of aluminum, magnesium, iron, and calcium, in addition to sulfates. These silicates are the primary components responsible for the formation of impurities. However, the solid residue has a relatively low silicon content of approximately 0.3%. This suggests that insoluble hydroxides, such as $Al(OH)_3$ and $Fe(OH)_3$, which are generated through the hydrolysis of metal salts in the original sulfuric acid solution, may also contribute to the presence of impurities.

To further investigate the process and optimize the extraction of copper, different classes of extractants were tested, including ketoximes (derivatives of ketones) and aldoximes (derivatives of aldehydes). The goal was to identify the most effective extractant for suppressing the formation of copper during the extraction process.

Results

Selecting an Extractant to Reduce Crud Formation During the Extraction of Copper from Sulfuric Acid Solutions.

The copper extraction method is carried out from leaching solutions of oxidized, sulfide, or sulfide-oxidized copper ore or flotation copper concentrate, derived from productive solutions obtained after percolation leaching. At least 5 dm³ of a representative batch of the productive solution is filtered, with a solution pH of approximately 1.7. Purified solutions are collected in a separate container to study their chemical and material composition and conduct further research.

The copper concentration in the solution was 1.25 g/dm³ or less, and sulfuric acid was 2.22 g/dm³. The concentrations of aluminum, magnesium, total iron, calcium, and phosphorus are 29.1, 12.98, 4.23, 0.69, and 0.55 g/dm³, respectively. In addition to these elements, silicon is also present in the solution at a concentration of 0.51 g/dm³. The remaining elements have relatively low content.

The productive solution contained, in addition to sulfates, silicates of aluminum, magnesium, iron, and calcium. Silicates are the main crud-forming components. The silicon content in the solid residue can be approximately 0.3%. Therefore, the crud-forming components can also be insoluble hydroxides $Al(OH)_3$ and $Fe(OH)_3$, which are formed in the original sulfuric acid solution due to the hydrolysis of salts of these metals.

The choice of extractant during the extraction process largely depends on its extraction ability and the initial concentration of the metal in the process solutions. Other important parameters for the effective operation of extraction technology are the low solubility of the extractant in the aqueous phase, its chemical stability under operating conditions, which ensures low losses of the extractant, the possession of acceptable values of the flash point and viscosity of the extract (to ensure effective phase separation), as well as the commercial availability of reagents.

Extraction is carried out at room temperature (20 ± 5°C). Temperature regulation and consistency are ensured by a thermostat (LOIP-105A). The ratio of the volumes of the organic and aqueous phases is controlled in the range of 1:2 to 1:10, with a step of 2; the phase contact time is established based on the time dependence of the copper distribution coefficient (DCu) – 5 minutes. Separatory funnels are used to carry out the extraction process. Phase separation is carried out by settling. Before sampling for analysis, aqueous solutions after extraction are filtered through a paper filter marked "red ribbon." Mixing of the phases is carried out mechanically. Depending on the task, the resulting solutions are analyzed for copper content.

The volume ratio of extractant and diluent is 10-20% to 80-90%. Aliphatic kerosene is used as a diluent. The organic phase is a solution of 10 vol.% of the studied extractants in kerosene, previously purified.

Two classes of extractants are used as reagents for the extraction of copper from acidic leaching solutions: ketoximes and aldoximes. However, it is necessary to take into account the selectivity of elements of these extractants, as well as the formation of the third phase - crud.

The extractant used in this work is ACORGA M5774, which is a modified aldoxime (5-nonyl salicylaldoxime). A distinctive feature of the IR spectrum of the ACORGA M5774 extractant is the presence of a stretching vibration of the carbonyl group ν(C=O) – 1736, 1712 cm-1. In the range of 1400-1000 cm-1, vibrations of the C–O–H group appear. The band at a wave number of 1271 cm-1 also falls into the range of –C–N– vibrations in compounds of the type: ArNHR.

A productive sulfuric acid solution is used, containing 1.25 g/dm^3 Cu and 2.22 g/dm^3 H_2SO_4. Table 1 presents the results of the influence of the extractant ACORGA M5774 and the O/A phase ratio on the formation of cruds and the extraction of copper from the productive solution.

When extracting copper with aldoxime ACORGA M5774 from a productive solution at a phase ratio O/A = 1:2, the degree of copper extraction into the extract is approximately 67%. An increase in the O/A ratio towards the aqueous phase during extraction leads to a significant decrease in the degree of copper extraction; at O/A = 1:4, the extraction into the extract decreases to 17.44%.

Extraction is characterized by the formation of three phases: raffinate, extract, and cruds, which are concentrated in the extract as a separate phase. When using the extractant ACORGA M5774, regardless of the O/A ratio, the phases divide quickly. However, with an increase in O/A, the amount of cruds in the organic matter decreases, so at an O/A of 1:10, only a small amount of sediment is formed.

Table 3 - Effect of the extractant ACORGA M5774 and the O: A phase ratio on the formation of cruds and the extraction of copper from the productive solution

№	O: A*	Content Cu in raffinate, g/dm^3	Extraction, %		Note
			raffinat	extract	
1	3	4	5	6	7
1	1:2	0.412	32.96	67.04	Extraction at O:A 1:2: the raffinate is transparent, brown in color. The organic matter contains a marsh-colored sediment. Phase separation time is 5 minutes.
2	1:4	1.032	82.56	17.44	Extraction at O: A 1:4: after filtration, the colour of the raffinate is dark brown with a greenish tint.
3	1:6	1.250	100.0	-	Extraction at O: A 1:6: after filtration, the colour of the raffinate is dark brown with a greenish tint.
4	1:8	1.250	100.0	-	Extraction at O: A 1:8: phase separation occurs quickly. The raffinate was filtered, its colour is dark green. No precipitate formed in this sample.
5	1:10	1.250	100.0	-	Extraction at O: A 1:10: phases separate well. Raffinate is brownish-greenish in colour. A precipitate is observed in the organic phase.

O: A* - ratio of organic phase to aqueous

At higher pH values, the solution turns yellow due to hydrolysis, and if the pH is above 2-3, further condensation occurs, and the formation of colloidal gels begins, eventually forming a reddish-brown precipitate of hydrated iron(III) oxide.

The content of the main components in the third phase, in percentages, is silicon 17.58%, nickel 3.13%, total iron 2.31%, aluminum 2.14%, and magnesium 2.023%. The remaining elements have relatively low content. Two compounds predominate in the crud sample: alunogen

$[Al(H_2O)_6]2(SO_4)_3$ $(H_2O)_5$ (28.3%) and quartz SiO2 (28.1%). There is a small amount of the compound nuyakasite (7.6%), a complex silicate of iron and aluminum with sodium and silicon oxide of variable composition (3.9%).

Analysis of IR spectroscopic data confirms that during the copper extraction operation, the formation of crud leads to the loss of the extractant. Thus, we can draw the following conclusion that in most cases, the main components of crud are:

Silicic acid is contained in solutions in the form of colloidal particles, which cannot be isolated even by careful filtration, and inorganic sulfates.

Solid compounds present in aqueous solutions: ore material, metal oxides and hydroxides, etc.

The next stage of extraction is to use an alternative method that helps suppress the third phase (crud) formation during the copper extraction process by adding a monomeric polymer, poly(sodium 4-styrene sulfonate), with the chemical formula $(H_2C{=}CHC_6H_4SO_3Na)n$. The sulfonate ion contains the functional group $-S(=O)_2-O^-$. The general formula is RSO2O−, where R is a radical; sodium alkyl sulfonate functionally acts as a surfactant.

When this additive is used in the form of a monomeric polymer, the formation of crud in settling tanks is reduced, thereby increasing the volume available for flows of productive sulfuric acid solutions (PLS) and organics, which directly leads to an increase in plant productivity. The process of liquid extraction in the presence of silicon dioxide in PLS solutions is challenging; however, with the addition of the monomeric polymer poly(sodium 4-styrene sulfonate), stable operation of the process is observed with a pronounced decrease in the formation of the third phase.

Table 4 - Extraction of PLS solution with the addition of $(H_2C{=}CHC_6H_4SO_3Na)_n$

Name extractant	O:W	Volume of raffinate, cm^3	Volume of extract, cm^3	Concentration of Cu in raffinate, g/dm^3	Recovery, into extract, %
ACORGA M 5774	1:2	82	43	0.947	24

Table 4 presents the results of the copper extraction process in the presence of the additive (H2C═CHC6H4SO3Na)n to reduce the formation of crud. Copper extraction is carried out using the extractant ACORGA M5774 – 10 vol.% with the addition of the additive (H2C═CHC6H4SO3Na)n in an amount of 5 cm³.

When extracting with the extractant ACORGA M5774 and the additive $(H_2C{=}CHC_6H_4SO_3Na)n$, the phases separate quickly, but the raffinates remain turbid. The raffinates are left to settle for a day and then filtered through a red ribbon filter. The resulting raffinates are pure transparent solutions, without sediment, and have a light brown colour with a yellowish tint.

The rich organic phase is filtered separately through a blue ribbon filter. Filtration proceeds quickly, and there is no sediment on the filter. The amount of sediment is sharply reduced and becomes ultradispersed.

The use of a reagent to reduce the formation of crud $(H_2C{=}CHC_6H_4SO_3Na)n$ in an amount of 5 cm³ in a productive sulfuric acid solution before it is subjected to the liquid extraction operation leads to a significant reduction in the formation of interfacial crud.

The use of surfactants to reduce the formation of the third phase - crud - allows several problems to be solved: returning the extractant and copper-containing solution to circulation and reducing the number of cruds sent for disposal.

Thus, the optimal technological parameters of extraction with the process of reducing the formation of the third phase - crud - are as follows: ACORGA M5774 extractant is used at a concentration of 10 vol.%. Kerosene is used as a diluent. The O/A ratio is 1:2, temperature 20-25°C, process duration 5 minutes, and phase settling time 1 day. The volume of the additive $(H_2C{=}CHC_6H_4SO_3Na)n$ is 5 cm³. The pH value of the initial solution should be between 1.5 and 3.0, which helps prevent the decomposition of the organic phase and avoids the formation of various types of precipitation that can contaminate the organic phase and prevent phase separation, reducing the technical characteristics of the process. To increase the degree of extraction, extraction and re-extraction are carried out in several stages (2-3), determined by the concentration of copper in the raffinate and extractant after extraction.

Development of a technique for technical and economic assessment of the choice of extraction apparatus.

The economic efficiency of using an extraction apparatus is determined, on the one hand, by the achieved degree of extraction of the substance, and on the other hand, by the costs of conducting the process. To assess the economic efficiency of using this type of extraction apparatus, an optimality criterion is used, which depends on the cost per unit volume of interacting phases at the entrance to and exit from the apparatus, the compositions and volumetric flow rates, operating costs (energy costs for ensuring the movement of flows and heat exchange, costs for depreciation of equipment, labour costs, etc.). Conditional cost savings (Sc) and present income (Ip) can be used as optimality criteria. Conditional cost savings are determined using one of the following equations:

$$S_c = (C_p - C)\,Q \qquad S_c = C_pQ - (C_f + C_v)$$

$$S_c = R_{ex}\,C_{ex} - R_{en}\,C_{en} - C_t \quad (1)$$

Where,
C_{p} - planned cost
C - actual cost
S_c - conditional cost savings
I_p - present income
Q- quantity of product produced
C_f - fixed costs
C_v - variable costs
R_{en} - volumetric flow rates at the entrance
R_{ex} - volumetric flow rates at the exit
C_{en} - cost per unit volume of interacting phases at the entrance
C_{ex} - cost per unit volume of interacting phases at the exit
C_t - total costs associated with equipment operation

Where C_p, C planned and actual compared cost of products; Q - quantity of product produced; C_f - fixed production costs that do not depend on productivity and quality of management; C_v - variable costs determined by the productivity and quality of the technological process; R_{en}, R_{ex} - volumetric flow rates at the entrance to and exit from the apparatus; C_{en}, C_{ex} - cost per unit volume of interacting phases at the entrance to the apparatus and exit from it; C_t - total costs associated with equipment operation.

Another quantitative measure of the technical and economic effect of using an extractor is the present income, equal to the difference between the income from the sale of commercial products and the total present costs and determined per unit of output

$$I'_p = (\textstyle\sum_{i=1}^{N} P_i - C_v)\mathrm{O} - \mathrm{E}C_i = (\sum_{i=1}^{N} P_i - C_v)\mathrm{O} - (\,C_i/P_p) \quad (2)$$

or the total present income from the release of all products

$$I'_p = \textstyle\sum_{i=1}^{N} P_i O_i - C_v - \mathrm{E}C_i \quad (3)$$

Here P_i - price of 1 product: O - annual output of product i; E - standard investment efficiency ratio; C_i - capital investment; P_p - standard payback period; O - annual output of all products. The value of the reduced income is one of the most universal criteria for optimality since it indicates both the volume of production and the quality of products, as well as operating and capital costs. The maximum amount of present income is achieved at a minimum cost or present costs, or a maximum profit.

$I`_p$ - present income, equal to the difference between income from the sale of commercial products and total present costs and determined per unit of output
P_i - price of 1 product
O - annual output of product i
E - standard investment efficiency ratio
C_i - capital investment
P_p - standard payback period

Dependency (VIII.35) can be rewritten in a video

$$I'_p = (\sum_{i=1}^{N} \bar{E}_i\,(\tau) O_i \mathrm{H}_i - C_{0\Sigma})\mathrm{B_o} - (C_i/P_p) \quad (4)$$

Where $\bar{E}_i\,(\tau)$- extraction; O_i. — conditional production of commercial products per unit of raw materials (with complete extraction); $C_{0\Sigma}$ costs of processing a unit of raw materials; P_{o} raw material productivity.

If the volume of output is strictly determined, then to carry out technical and economic calculations, you can use the average value of the reduced costs per unit of output:

$$I_p = C_v + (\frac{C_i}{\mathrm{O}P_p}) \quad (5)$$

Optimizing the process when using dependencies (VIII.33)-(VIII.37) comes down to finding the maximum of the optimality criterion I_p

when using dependency (VIII.36) and its minimum when using dependency (VIII.37).

In the case of a sufficiently low price of the obtained by-products, the reduced income can be determined by the formula:

$$I_p = P_t O - \left[\frac{P_r O}{E(\mathrm{i})} + C_{var} O + C_{fix}\right] \qquad (6)$$

where, P_r, P_t - total price per unit of raw materials and target product; C_{var} - variable costs per unit of product produced; C_{fix} - fixed costs per unit of time.

An increase in the value of Ppr can be achieved by regulating the following factors:

1) Improving the conditions of the process (with unchanged installation productivity;

2) Making additional capital investments when an increase in output leads to an increase inI_p i.e., when $d\,C_{fix}/dE(i) < P_rO/E^2(i)$, or in the case of an increase in productivity and volume of marketable products;

3) Increasing the productivity of the installation.

4) Increasing product yield and reducing variable costs (especially the cost of raw materials, heat, and energy costs).

If variable and fixed costs are much higher than the cost of raw materials (i.e. $C_{var}O+C_{fix} >> P_rO/E(\tau)$), then they should be reduced to a minimum, and the extractor productivity should be increased to a maximum value, provided that the depreciation of the apparatus significantly affects total fixed costs.

In the case where the cost of raw materials significantly exceeds other costs (i.e. $P_rO/E(\tau) >> C_{var}O+C_{fix}$) the output value at the installation should be maximized by improving the process conditions.

In general, when searching for an optimality criterion in practice, it is necessary to vary various independent variables, the limit values of which are determined by technological conditions. Optimization of continuous devices is achieved in two ways: static (in which they strive to carry out the process with maximum efficiency according to the optimized criterion at each moment in time) and dynamic (in which the process is subject to frequent disturbances and practically proceeds in a dynamic mode).

Since solving the problem of achieving the maximum value of the optimality criterion in a general form is impossible, in practice the optimum is found according to one or, in rare cases, two or three indicators, which may include productivity, degree of extraction, cost, product yield, etc. Other main variables that can be changed to optimize an industrial extractor are the process temperature, the type of extractor, the reaction time and the residence time of the material in the apparatus, the concentration of reagents, the number of apparatuses in the cascade, etc. For multi-stage devices, the selected indicator is optimized for each link, moving from the next stage to the previous one.

Conclusion

A method has been developed for the extraction of copper from sulfuric acid solutions, which reduces sulfuric acid consumption, increases copper extraction and the quality of cathode copper, and reduces the formation of the third phase (crud). Crud, which is concentrated as a separate phase in the extract along with the raffinate, negatively affects phase separation, copper extraction, and the removal of non-ferrous metal impurities. The introduction of the monomeric polymer poly(4-sodium styrene sulfonate) ($(H_2C{=}CHC_6H_4SO_3Na)_n$) into the process dissolves and destroys polymerized silicon bonds in crystals, enhancing the process by more than 25%.

After completing calculations to optimize all compared options for using the extraction apparatus, preference is given to the option that corresponds to the maximum value of Ppr, found for the optimal values of the studied independent technological parameters. If the values of Ppr for the compared options differ slightly from each other, preference is given to the option characterized by better working conditions, a shorter payback period, and improved flow organization of the reacting phases.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Күкірт қышқылы ерітінділерінен мысты алудың жетілдірілген әдісін жасау

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ТҮЙІНДЕМЕ

Мақалада күкірт қышқылының ерітінділерінен мысты алу әдісі ұсынылған, ол күкірт қышқылының шығынын азайтады, мыстың алынуын және катодты мыстың сапасын арттырады, сонымен қатар үшінші фаза-крадтың қажетсіз түзілуін азайтады. Мыс алудың негізгі нәтижелері, соның ішінде 2-3 сатылы мыс алу келтірілген. Күкірт қышқылды ерітінділерді хелаттаушы, селективті экстрагент альдоксимдер тобынан (10 көлем. %) ерітіндімен араластыру және қоспаны тұндыру арқылы мыс құрамды экстракт және экстракциялық раффинат алу арқылы экстракция жүргізіледі. Крадтағы полимерленген кремний байланыстарын мономерлі полимер $(H_2C{=}CHC_6H_4SO_3Na)_n$ поли (4-натрий стиролсульфонаты) пайдаланып еріту арқылы үшінші фаза-крадтың пайда болуын азайтады. Бұл натрий алкилсульфонатының ПАВ кешенінің әсерінен, О/А қатынасы 1:2 және температура 20±5°C болғанда 5 $см^3$ полимер қосу арқылы жүзеге асырылады. Құрамында мыс бар реэкстракт және экстрагент ерітіндісін алу үшін экстрактты күкірт қышқылының ерітіндісімен араластырып, одан кейін қоспаны тұндырып бөлу арқылы жүзеге асырылады. Реэкстракт қоспалардан тазартылады және катодты мыс пен пайдаланылған электролитті алу үшін тазарған реэкстракттан мыс электролиттік жолмен алынады. Сондай-ақ, экстракциялық аппаратты техникалық және экономикалық таңдау әдісі әзірленді.

Түйін сөздер: SX-EW; мыс; экстракциялау; крад; интенсификация әдісі; күкірт қышқылды ерітінділер.

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Разработка усовершенствованного метода извлечения меди из сернокислых растворов

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АННОТАЦИЯ

В статье представлен метод извлечения меди из сернокислых растворов, который снижает потребление серной кислоты, увеличивает извлечение меди и качество катодной меди, а также уменьшает нежелательное образование третьей фазы (крада). Основные результаты извлечения меди, включая 2-3 этапное извлечение меди, представлены. Извлечение осуществляется путем смешивания сернокислых растворов с раствором хелатирующего, селективного экстрагента группы альдоксимов (10 об.%) и разделения смеси путем отстаивания для получения медьсодержащего экстракта и экстракционного раффината, с подавлением третьей фазы (крада) за счет растворения полимеризованных кремниевых связей в крудах с использованием мономерного полимера $(H_2C{=}CHC_6H_4SO_3Na)_n$ поли(4-натрий стиролсульфоната). Это достигается добавлением 5 см^3 полимера, под влиянием комплекса ПАВ из алкилсульфоната натрия, с соотношением О/В = 1:2 и температурой 20±5°С. Последующая реэкстракция меди из экстракта проводится путем смешивания экстракта с раствором серной кислоты и разделения смеси путем отстаивания для получения медьсодержащего реэкстракта и раствора экстрагента. Реэкстракт очищается от примесей, и медь извлекается электролитически из очищенного реэкстракта для получения катодной меди и отработанного электролита. Также разработан метод расчета технического и экономического выбора экстракционного аппарата.

Ключевые слова: SX-EW; медь; жидкостная экстракция; крад; метод интенсификации; сернокислые растворы.

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References

[1] Pat. 2339713 RU. МПК C22B 15/00, C22B 3/30. Opubl. 27.11.2008, bull. 33.

[2] Pat. 2178342 RU. МПК B03B 7/00, C22B 3/04, C22B 3/26. Opubl. 20.01.2002, bull. 2.

[3] Zagorodnyaya A N, Abisheva Z S, Sadykanova S E, Bobrova V V, & Sharipova A S. The characterisation and origins of interphase substances (cruds) in the rhenium solvent extraction circuit of a copper smelter. Hydrometallurgy. 2010; 104(2):308-312. https://doi.org/10.1016/j.hydromet.2010.05.013

[4] Panda S, Parhi P K, Pradhan N, Mohapatra U B, Sukla L B, & Park K H. Extraction of copper from bacterial leach liquor of a low grade chalcopyrite test heap using LIX 984N-C. Hydrometallurgy. 2012; 121-124:116-119. https://doi.org/10.1016/j.hydromet.2012.03.008

[5] Nobahar A, Melka A B, Pusta A, et al. A New Application of Solvent Extraction to Separate Copper from Extreme Acid Mine Drainage Producing Solutions for Electrochemical and Biological Recovery Processes. Mine Water Environ. 2022; 41:387-401. https://doi.org/10.1007/s10230-022-00858-7

[6] Shakibania S A, Mahmoudi A, Mokmel M, & Rashchi F. The effect of chloride ions on copper solvent extraction from sulfate-chloride medium using LIX 984N. Minerals Engineering. 2020; 156:106498. https://doi.org/10.1016/j.mineng.2020.106498

[7] Chepushtanova TA, Merkibayev YS, Mamyrbayeva K K, Sarsenbekov T, & Mishra B. Mechanism and technological results of sulfidation roasting of oxidized lead compounds. Kompleksnoe Ispolzovanie Mineralnogo Syra=Complex use of mineral resources. 2025; 332(1):119-132. https://doi.org/10.31643/2025/6445.11

[8] Cole P. Understanding aqueous-in-organic entrainment in copper solvent extraction. J. S. African Institute of Mining and Metallurgy. 2016; 116(6):525-531. http://dx.doi.org/10.17159/2411-9717/2016/v116n6a6

[9] Kenzhaliev BK, Kvyatkovsky SA, Kozhakhmetov S M, Sokolovskaya L V, Semenova A S. Depletion of waste slag of balkhash copper smelter. Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources; 2018; 306(3):45-53. (in Russ.). https://doi.org/10.31643/2018/6445.16

[10] Bochevskaıa E G, Abısheva Z S, Sharıpova A S, & Sargelova E A. Obrazovanıe osmıısoderjaıh mejfaznyhvzveseı prı ekstraktsıı renııa ız promyvnoı kısloty mednogoproızvodstva. Izvestııa Natsıonalnoı Akademıı Naýk[Formation of organic compounds containing

meiotic fluids by extracting the extracted product from the industrial acidity of honey production. Report by the National Academy of Sciences.]. Shemistry and technology. 2022; 3(452):42-56. (in Russ.).

[11] Solvent Extraction Principles and Practice, Revised and Expanded, by Jan Rydberg, Michael Cox, Charles Musikas, and Gregory R. Choppin was published on March 3, 2004.

[12] Agarwal S, Ferreira A E, Santos S M C, Reis M T A, Ismael M R C, & Correia M J N. Separation and recovery of copper from zinc leach liquor by solvent extraction using ACCORGA M5640. International Journal of Mineral Processing. 2010; 97(1-4):85-91. https://doi.org/10.1016/j.minpro.2010.08.009

[13] Alguacil F J, Cobo A, & Alonso M. Copper separation from nitrate/nitric acid media using ACCORGA M5640 extractant: Part I: solvent extraction study. Chemical Engineering Journal. 2002; 85(2-3):259-263. https://doi.org/10.1016/S1385-8947(01)00166-8

[14] Chepushtanova T, Yessirkegenov M, Mamyrbayeva K, Akcil A, & Gaipov T. Extraction of Copper from Pregnant Leach Solution (PLS) and Reduction of Crud Formation. Mineral Processing and Extractive Metallurgy Review. 2024, 1-13. https://doi.org/10.1080/08827508.2024.2340545

[15] Chepushtanova TA, Yessirkegenov MI, Mamyrbayeva KK, Merkibayev YS. Investigations of extraction of copper and crud formation components of productive solution of Almaly deposit. Non-ferrous Metals. 2023; 54(1):11-19 https://doi.org/10.17580/nfm.2023.01.02

[16] Li X H, Zhou G Y, Huang S T, & Wen J K. Effect of Bioleaching Microorganisms and Solid Ore Particles on Formation of Interfacial Crud in Solvent Extraction Plants. Advanced Materials Research. 2013; 825:335-339. https://doi.org/10.4028/www.scientific.net/AMR.825.335

[17] Autef A, Joussein E, Gasgnier G, & Rossignol S. Role of the silica source on the geopolymerization rate. Journal of Non-Crystalline Solids. 2012; 358:2886-2893. https://doi.org/10.1016/j.jnoncrysol.2012.07.015

[18] Watling H R. Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate–chloride and sulfate–nitrate process options. Hydrometallurgy. 2013; 140:163-180. https://doi.org/10.1016/j.hydromet.2013.09.013

[19] Ferreira A E, Agarwal S, Machado R M, Gameiro M L F, Santos S M C, Reis M T A, Carvalho J M R. Extraction of copper from acidic leach solution with ACCORGA M5640 using a pulsed sieve plate column. Hydrometallurgy. 2010; 104(1):66-75. https://doi.org/10.1016/j.hydromet.2010.04.013

[20] Petersen J. Heap leaching as a key technology for recovery of values from low-grade ores – A brief overview. Hydrometallurgy. 2016; 165(1):206-212. https://doi.org/10.1016/j.hydromet.2015.09.001

[21] Pat. (11) 2 339 713(13) C1 RU. Sposob ekstraktsıımedı ız sernokıslyh rastvorov [Method of extracting medicine from sulfite seeds]. Bulletin, Opubl. 27.11.2008, bull.33.

[22] Jumadilov T, Abilov Z, Grazulevicius J, Zhunusbekova N, ...Agibayeva L, Akimov A. Mutual activation and sorption ability of rare cross-linked networks in intergel system based on polymethacrylic acid and poly-4-vinylpyridine hydrogels in relation to Lanthanum ions. Chemistry and Chemical Technology. 2017; 11(2):188-194.

[23] Yelubay M, Yerzhanova D, Bakibaev A, ...Amitova A, Aitkaliyeva G. Selection of an Effective Activating Agent for Coke Production Waste. Polish Journal of Environmental Studies. 2024; 33(1):467-476. https://doi.org/10.15244/pjoes/171656

[24] Sperline RP, Song YE, Freiser Ma H. Organic constituents of cruds in Cu solvent extraction circuits: I. Separation and identification of diluent-soluble compounds. Hydrometallurgy. 1998; 50(1):1-21. https://doi.org/10.15244/pjoes/171656