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Effectiveness of secondary copper electrolytic refining slime decopperization

S.O. Vydysh, E.V. Bogatyreva

National University of Science and Technology "MISIS"
4 Bld. 1 Leninsky Prosp., Moscow 119049, Russia

✉ Elena V. Bogatyreva (Helen_Bogatureva@mail.ru)

Abstract: The relevance of replacing the slime–H_2SO_4–H_2O system used for processing slimes from secondary copper electrolytic refining (SCER) with a slime–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O system has been substantiated. Comprehensive studies of the characteristics of SCER slime samples were conducted. It was found that about 90 % of the copper is distributed between the Cu_2O phase and other phases, with a total copper content of 55.12 %. A new phase, $Cu_4(OH)_6SO_4$, corresponding to the mineral brochantite, was discovered, with a content in the slime of 6.40 %. Silver, with a concentration of 2.43 % in the slime, is present in metallic form at 69.1 %, with the remainder in the form of AgCl. The contents of associated components $PbSO_4$, $BaSO_4$, and SnO_2 are 13.52 %, 9.33 %, and 4.73 %, respectively. To substantiate the feasibility of low-temperature hydrometallurgical opening of the slime components and the conditions necessary for its implementation, determined by the specific qualitative and quantitative compositions of the slime, a thermodynamic analysis of the slime–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O system was performed. This analysis allowed for the discovery and mathematical description of the dependencies of copper leaching indicators on the composition of the ammonia-ammonium mixture (ammonia buffer). A nomogram for the theoretical calculation of the minimum excess $NH_3 \cdot H_2O/NH_4^+$ over the stoichiometrically necessary amount required for the complete formation of the copper ammine complex was constructed according to the equilibrium ammonia-ammonium solution's pH and copper concentration. Thermodynamic calculations determined the optimal composition and consumption of ammonia-ammonium solutions, as well as the characteristics of the leach pulp, such as the concentration of $[Cu(NH_3)_4]^{2+}$ and the redox potential. Technological studies demonstrated the possibility of effective and selective extraction of copper from SCER slimes at a rate of no less than 99 % in the slime–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O system, which was confirmed experimentally. Studies of the kinetics of copper leaching from slime in the slime–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O system were conducted. The activation energy of the ammonia-ammonium copper leaching process from SCER slime ($E_a = 5 \pm 0.25$ kJ/mol) was determined within the temperature range from 15 to 45 °C at a total buffer system concentration $[NH_3 \cdot H_2O] + [NH_4^+]$ of 1 and 2 mol/L, as well as the order of reaction at a temperature of 24±1 °C, which is 0.24±0.02 and 0.91±0.05 for $[NH_3 \cdot H_2O] + [NH_4^+]$ concentrations above 1.5 mol/L and below 1.5 mol/L, respectively. A change in the kinetic mode of leaching with the limitation of the reaction rate by adsorption of reagents on the surface of solid particles to diffusion was detected when the total buffer system concentration $[NH_3 \cdot H_2O] + [NH_4^+]$ was reduced below 1.5 mol/L. The equation for the formal kinetics of the investigated process in the slime–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O system was determined.

Keywords: copper, silver, secondary copper, slime, phase composition, thermodynamic analysis, leaching, kinetics, kinetic models, leaching rate, buffer systems, resource conservation.

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Эффективность обезмеживания шламов электролитического рафинирования вторичной меди

С.О. Выдыш, Е.В. Богатырева

Национальный исследовательский технологический университет «МИСИС»
Россия, 119049, г. Москва, Ленинский пр-т, 4, стр. 1

✉ Елена Владимировна Богатырева (Helen_Bogatureva@mail.ru)

Аннотация: Обоснована актуальность замены системы шлам–H_2SO_4–H_2O для переработки шламов электролитического рафинирования вторичной меди (ЭРВМ) системой шлам–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O. Выполнены комплексные исследования характеристик образца шлама ЭРВМ. Установлено, что около 90 % меди распределено между фазами Cu_2O и прочими при общем содержании Cu 55,12 %. Обнаружена новая фаза $Cu_4(OH)_6SO_4$, соответствующая минералу брошантит, содержание которой в шламе составляет 6,40 %. Серебро при его концентрации в шламе 2,43 % на 69,1 % присутствует в металлическом состоянии, остальное в соединении AgCl. Содержание попутных компонентов $PbSO_4$, $BaSO_4$ и SnO_2 составляет 13,52, 9,33 и 4,73 % соответственно. Для обоснования возможности низкотемпературного гидрометаллургического вскрытия компонентов шлама и необходимых для его реализации режимов, обусловленных особенностями качественного и количественного составов шлама, выполнен термодинамический анализ системы шлам–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O, позволивший обнаружить и математически описать зависимости показателей процесса выщелачивания меди от состава аммиачно-аммонийной смеси (аммиачного буфера). Построена номограмма теоретического расчета минимального избытка $NH_3 \cdot H_2O/NH_4^+$ от стехиометрически необходимого количества, требуемого для полного протекания реакции комплексообразования аммиаката меди в соответствии с величинами pH равновесного аммиачно-аммонийного раствора и концентрации в нем меди. Термодинамическими расчетами определены оптимальный состав аммиачно-аммонийных растворов и их расход, а также характеристики пульпы выщелачивания: концентрация $[Cu(NH_3)_4]^{2+}$ и окислительно-восстановительный потенциал. Технологические расчеты показали возможность эффективного и селективного извлечения меди из шламов ЭРВМ не менее чем 99 % в системе шлам–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O, что подтверждено экспериментально. Проведены исследования кинетики выщелачивания меди из шлама в системе шлам–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O. Определена энергия активации процесса аммиачно-аммонийного выщелачивания меди из шлама ЭРВМ (E_a = 5±0,25 кДж/моль) в интервале температур от 15 до 45 °C при суммарной концентрации буферной системы $[NH_3 \cdot H_2O] + [NH_4^+]$ 1 и 2 моль/л, а также порядок по реагенту при температуре 24±1 °C, равный 0,24±0,02 и 0,91±0,05 для $[NH_3 \cdot H_2O] + [NH_4^+]$ более 1,5 моль/л и менее 1,5 моль/л соответственно. Обнаружена смена кинетического режима выщелачивания с лимитированием скорости процесса адсорбцией реагентов на поверхности твердых частиц на диффузионный при снижении суммарной концентрации буферной системы $[NH_3 \cdot H_2O] + [NH_4^+]$ ниже 1,5 моль/л. Определено уравнение формальной кинетики исследованного процесса в системе шлам–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O.

Ключевые слова: медь, серебро, вторичная медь, шлам, фазовый состав, термодинамический анализ, выщелачивание, кинетика, кинетические модели, скорость выщелачивания, буферные системы, ресурсосбережение.

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Introduction

The global economic recovery in the post-COVID period led to a sharp increase in demand for refined copper in 2023, amounting to 4.6 % compared to 2022, while the growth in primary copper production was only 0.5 % [1]. The deficit in refined copper was compensated by the inclusion of secondary copper resources in processing, which, for the first time, increased the share of secondary copper above 20% in the production of refined copper [2; 3]. The depletion of global copper ore reserves at the current level of production is estimated to occur within the next 50—100 years, but a deficit in refined copper production may already reach more than 8 million tons in the next decade [4; 5]. According to forecasts, by 2030, the production of refined copper is expected to decrease by 10 % compared to 2025, while consumption is projected to increase by 22 % [5].

By 2030, the development of new copper deposits is planned, which could increase global copper production by 1.7 to 3.3 million tons per year [5]. The increased processing of secondary copper resources could contribute not only to offsetting the global deficit of refined copper but also to stabilizing copper prices on the stock market.

The copper refining technology, both for primary and secondary raw materials, according to GOST 859-2014, consists of two stages—fire refining and electrolytic refining [6]. During the process of electrolytic copper refining, anode slimes are formed, which act as concentrators for rare and precious metals. The composition of these slimes is determined by the electrolysis parameters and the composition of the anode copper, and it varies widely [7; 8], with mass percentages as follows:

Cu	1.00—53.40	Te	0.01—9.00
Ag	0.10—24.00	Pb	0.60—51.40
Au	0.02—5.40	Sn	0.10—12.10
Se	0.10—21.00	Ni	0.01—10.90

A distinctive feature of secondary copper electrolytic refining slimes (SCER) is the increased content of tin and nickel and the decreased content of selenium and tellurium. The processing of SCER and primary copper electrolysis slimes is similar, but lead and tin remain unextracted and end up in the production waste—slag from the Dore alloy smelting [7—13]. In addition to the low utilization of raw materials, Dore alloy smelting has the following disadvantages [7; 14; 15]:

— high capital costs for pyrometallurgical processing;

— high energy consumption;

— elevated concentrations of lead in the workplace air, ranging from 0.5 to 3.0 mg/m^3, which is 50 to 300 times higher than the maximum allowable concentrations (MAC) in the workplace air;

— significant generation of solid waste (slag output ranges from 0.9 to 1.2 tons per ton of slime).

In accordance with modern requirements for diversified raw material utilization and the potential increase in SCER slime volumes, the development of technology for deeper processing of these slimes with the simultaneous extraction of lead and tin is a timely and relevant task. Hydrometallurgical methods appear to be the most promising solution for this challenge.

Hydrometallurgical technologies for processing anode slimes have not yet found widespread application due to the following drawbacks [7; 9; 11; 13; 14]:

— multi-stage processes;

— production of solutions with low precious metals concentration and contaminated with impurities of base metals;

— generation of significant volumes of waste solutions that require disposal.

However, improvements in hydrometallurgical slime processing, aimed at reducing or eliminating these drawbacks, will simplify the management and control of technological processes, which is particularly relevant in the context of implementing the “Industry 4.0” program. This program focuses on the digitalization of technological processes to improve production efficiency [16; 17].

Most technological schemes of modern enterprises for processing copper-electrolyte slimes begin with decopperization—copper removal, which is carried out under autoclave conditions in a sulfuric acid solution with a concentration of 100 to 250 g/L at temperatures ranging from 80 to 140 °C, pressure up to 0.7 MPa, a liquid-to-solid ratio (L/S) of (5÷10) : 1, and the supply of oxygen as an oxidant for 8—16 hours [7—9; 11—15]. The use of sulfuric acid is justified by the feasibility of returning Cu-containing solutions to the main copper production process. During autoclave oxidative leaching of copper-electrolyte slime, the destruction of copper selenides and tellurides occurs effectively, contributing to the increased extraction of copper into the leach solution, reaching 99 %, as well as the dissolution of nickel oxide, compared to atmospheric decopperization of anode slime through aeration in a sulfuric acid solution. However, given the low content of selenium and tellurium in SCER slime, the use of capital-intensive autoclave leaching is irrational, while atmospheric decopperization of anode slime through aeration in a sulfuric acid solution has low specific productivity in terms of decopperized slime (up to 67.5 kg/m^3 per operation) [7].

Intensification of the sulfuric acid leaching process of copper from slime can be facilitated by using hydrogen peroxide as an oxidizer instead of oxygen [18]. The rate of copper dissolution during atmospheric leaching in a solution of 200 g/L H_2SO_4 and 12.5 g/L H_2O_2 is $7{,}4\cdot10^{-8}$ g-ion/(cm$^2\cdot$s), which is 76.6 % lower than during autoclave treatment — $2{,}8\cdot10^{-7}$ g-ion/(cm$^2\cdot$s). However, the use of hydrogen peroxide as an oxidizer may lead to silver losses in the leach solution due to its oxidation. Additionally, sulfuric acid methods for SCER slime decopperization have the following drawbacks:

— the necessity of using corrosion-resistant equipment;

— difficulty in filtering sulfuric acid pulps containing tin and barium, due to the possible formation of metastannic acid H_2SnO_3 or recrystallization of $BaSO_4$.

These drawbacks can be mitigated by transitioning from the slime—H_2SO_4—H_2O_2—H_2O system to the less aggressive and neutral to tin dioxide system of slime—$NH_3\cdot H_2O$—$(NH_4)_2SO_4$—H_2O—O_2, where oxygen from the air can be used as the oxidizer [19]. The application of ammonia-ammonium (AA) leaching for copper-bearing mono- and polymetallic raw materials has been studied in works [19—29]. It is known that the oxidative dissolution of copper proceeds stepwise through the following reactions [28; 30]

$$\mathrm{Cu} + 2\mathrm{NH_3} + 0.25\mathrm{O_2} + 0.5\mathrm{H_2O} = \\ = [\mathrm{Cu(NH_3)_2}]^+ + \mathrm{OH}^-, \quad (1)$$

$$[\mathrm{Cu(NH_3)_2}]^+ + 2\mathrm{NH_3} + 0.25\mathrm{O_2} + 0.5\mathrm{H_2O} = \\ = [\mathrm{Cu(NH_3)_4}]^{2+} + \mathrm{OH}^-, \quad (2)$$

$$[\mathrm{Cu(NH_3)_4}]^{2+} + \mathrm{Cu} = 2[\mathrm{Cu(NH_3)_2}]^+. \quad (3)$$

In the initial stage, the process follows the electrochemical mechanism according to reactions (1) and (2), but as the concentration of $[Cu(NH_3)_4]^{2+}$ ions increases, an autocatalytic mechanism of copper dissolution according to reaction (3) is initiated, which enhances the dissolution rate [20—25; 30]. In raw materials with high contents of oxidized Cu-bearing components, copper leaching may initially proceed via the autocatalytic mechanism. In the absence of copper sulfides and chalcogenides, the use of autoclave leaching with oxygen supply is irrational, as it may lead to silver losses with the ammonia-ammonium solution [27]. Nickel also tends to form ammoniacal complex compounds, allowing its co-extraction with copper into the solution [29; 31]. However, depending on the concentration ratios of ammonia and copper, the forms of the resulting complexes and their proportion in the solution may vary (Fig. 1) [30], which can influence the AA-leaching process of copper from SCER slime.

The evaluation of the thermodynamic and kinetic characteristics of metallurgical and chemical-metallurgical processes not only supports the justification of their operating modes but also provides the opportunity for mathematical modeling to develop an automatic control scheme [30]. The study of leaching kinetics is necessary to determine the mechanism of the process, the rate-limiting stage, to justify the technological modes of the process, to identify directions for its intensification, and for management and automation [32].

The aim of this work is to improve the efficiency, resource, and energy conservation of SCER slime decopperization in the process of low-temperature ammonia-ammonium leaching.

Objectives of the work:

— To determine the characteristics of the research object—SCER slime;

— To conduct a thermodynamic analysis of the SCER slime decopperization process in the slime—$NH_3 \cdot H_2O$—$(NH_4)_2SO_4$—H_2O—O_2 system to assess the composition and consumption of the AA-leach solution, ensuring copper extraction into the solution of no less than 99 %;

— To test the developed decopperization modes on the research object;

— To determine the activation energy and order of reaction for the ammonia buffer $[NH_3 \cdot H_2O] + [NH_4^+]$ in the AA-leaching process of SCER slime, leading to the derivation of the formal kinetics equation.

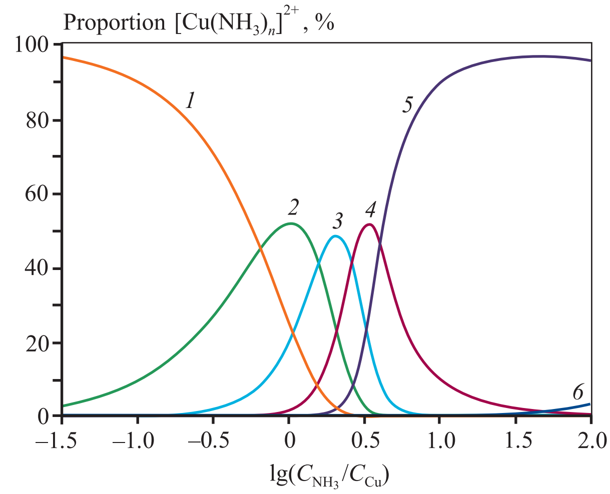

Fig. 1. Dependence of the proportion of various copper cations in an ammonia-ammonium solution on the molar ratio of ammonia to copper in the solution at $C_{Cu} = 0.01$ mol/L [30]
1 – Cu^{2+}; *2* – $[Cu(NH_3)]^{2+}$; *3* – $[Cu(NH_3)_2]^{2+}$; *4* – $[Cu(NH_3)_3]^{2+}$; *5* – $[Cu(NH_3)_4]^{2+}$; *6* – $[Cu(NH_3)_5]^{2+}$

Рис. 1. Зависимость доли различных катионов меди в аммиачно-аммонийном растворе от мольного соотношения аммиака и меди в растворе при $C_{Cu} = 0{,}01$ моль/л [30]
1 – Cu^{2+}; *2* – $[Cu(NH_3)]^{2+}$; *3* – $[Cu(NH_3)_2]^{2+}$; *4* – $[Cu(NH_3)_3]^{2+}$; *5* – $[Cu(NH_3)_4]^{2+}$; *6* – $[Cu(NH_3)_5]^{2+}$

1. Characteristics and methods of research on slime from secondary copper electrolytic refining

Analyses of the composition of SCER slime and the processing products were conducted using modern research methods and equipment, such as:

transmission electron microscopy using the S-3400N scanning electron microscope (SEM) by Hitachi High-Technologies Corporation (Japan), equipped with a NORAN *X*-ray energy-dispersive spectrometer;

— *X*-ray fluorescence analysis on the ARL9900 WorkStation (“Thermo Fisher Scientific”, Switzerland);

— granulometric analysis on the MicroSizer-201 laser particle size analyzer;

— density assessment of the research object using the AccuPyc 1340 helium pycnometer (Micromeritics, USA);

— determination of copper content in the leach solution and residue by iodometric titration with sodium thiosulfate;

— determination of silver content by gravimetric analysis (precipitation of silver iodide from solution) [33; 34].

The results of the chemical and phase analyses of the secondary copper electrolytic refining slime are presented below, wt.%:

Cu	55.12
Ag	2.43
Pb	9.24
Sn	3.72
Ba	5.45
SiO_2	1.21
Others	22.83

Cu_2O	26.3
$PbSO_4$	13.5
$BaSO_4$	9.3
$Cu_4(OH)_6SO_4$*	6.4
SnO_2	4.8
Cu	2.0
Total crystalline phases	62.3

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* Corresponding to brochantite.

It is evident that the "others" category in the research object amounts to 22.83 %, of which more than 72 % consists of oxygen and sulfur. The total amount of crystalline phases in the slime corresponds to 62.3 %, with the remaining 37.7 % represented by *X*-ray amorphous phases. This underscores the importance of calculating the rational composition of the slime (Table 1).

Information about the presence of the $Cu_4(OH)_6SO_4$ phase, corresponding to the mineral brochantite, in copper-electrolyte slimes is absent in the available literature [7—15]. Copper, which constitutes 55.12 % of the slime, is distributed among the Cu_2O, $Cu_4(OH)_6SO_4$, metallic copper, and other phases at 42.4 %, 6.5 %, 3.6 %, and 47.5 %, respectively. The high copper content in the "others" category is associated with unidentified reflections in the *X*-ray phase analysis. Silver is concentrated in two phases: metallic silver, which contains 69.1 % of the total silver content, and silver chloride.

It can be seen from Table 2 that SCER slime is a fine-grained material, with over 80 % of the particles being smaller than 48.2 μm. The specific surface area of the particles in the research object was 115.14 dm^2/g, and the density of the slime was 5260 kg/m^3.

Fig. 2 presents a micrograph of SCER slime obtained by SEM and analyzed at points using energy-dispersive *X*-ray spectroscopy. Copper (I) oxide is represented by spheroidal particles, lead sulfate by dendritic particles, and tin oxide by acicular particles.

The following reagents were used in the study: aqueous ammonia, ammonium sulfate, ammonium bicarbonate, sodium thiosulfate pentahydrate, and potassium iodide (all of analytical grade).

Leaching of the slime (**Method I**) was carried out at a molar ratio of $\Theta = [NH_3 \cdot H_2O] : [(NH_4)_2SO_4] = 4$ mol/mol and with a minimal excess of $NH_3 \cdot H_2O/NH_4^+$ over the stoichiometrically necessary quantity (SNQ) for reaction (31) (see below) of $\chi = 20$ %, which, based on the results of thermodynamic analysis, in the AA-solution in the slime—$NH_3 \cdot H_2O$—$(NH_4)_2SO_4$—H_2O—O_2 system, are preferable for achieving the goal of resource and energy conservation. Air was used as the oxidizer, with a flow rate of 190 ± 2 L/h. The solution, at a liquid-to-solid ratio (L/S) of 12 : 1, without heating ($t = 24$°C), was mixed with a sample of the research material with a total mass of 80 g. The process continued until the redox potential (ORP) of the pulp reached +260 ± 10 mV relative to the standard hydrogen electrode (52 ± 10 mV relative

Table 1. **Rational composition of secondary copper electrolytic refining slime**

Таблица 1. Рациональный состав шлама электролитического рафинирования вторичной меди

Phase	Content, wt.%									Total
	Cu	Pb	Ba	Sn	Ag	SiO_2	S	O	Others	
Cu_2O	23.36	–	–	–	–	–	–	2.94	–	26.30
$PbSO_4$	–	9.24	–	–	–	–	1.43	2.85	–	13.52
$BaSO_4$	–	–	5.45	–	–	–	1.27	2.54	–	9.26
$Cu_4(OH)_6SO_4$	3.60	–	–	–	–	–	0.45	2.35	–	6.40
SnO_2	–	–	–	3.72	–	–	–	1.01	–	4.73
Cu	2.00	–	–	–	–	–	–	–	–	2.00
Ag	–	–	–	–	1.68	–	–	–	–	1.68
SiO_2	–	–	–	–	–	1.21	–	–	–	1.21
AgCl	–	–	–	–	0.75	–	–	–	0.25	1.00
Others	26.16	–	–	–	–	–	1.66	–	6.08	33.90
Total	55.12	9.24	5.45	3.72	2.43	1.21	4.81	11.69	6.33	100.00

Table 2. **Integral granulometric composition of secondary copper electrolytic refining slime**

Таблица 2. Интегральный гранулометрический состав шлама электролитического рафинирования вторичной меди

Maximum particle diameter of the fraction, μm	1.88	4.09	9.49	16.7	22.8	29.3	37.0	48.2	69.7	600
Percentage of particles with diameter from 0 to maximum within the fraction, %	10	20	30	40	50	60	70	80	90	100

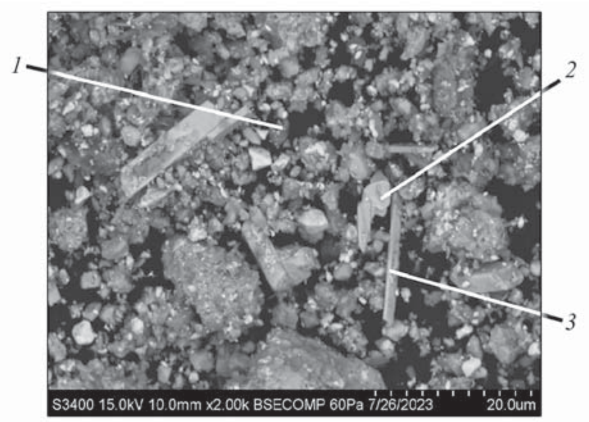

Fig. 2. Micrograph of the research object – SCER slime
1 – Cu_2O, ***2*** – $PbSO_4$, ***3*** – SnO_2

Рис. 2. Микрофотография объекта исследования – шлама ЭРВМ
1 – Cu_2O, ***2*** – $PbSO_4$, ***3*** – SnO_2

to the silver chloride electrode). The resulting pulp was filtered using a Buchner funnel through a “blue ribbon” filter; the residue on the filter was washed with ammoniacal water with a concentration of 0.1 mol/L (L/S ~ 1 : 1) and then with distilled water (L/S ~ 1 : 5). The leach solution and the wash water were combined and analyzed for copper content (iodometric titration with sodium thiosulfate) and silver content (gravimetrically—by precipitating silver iodide, drying, and weighing it on XS 204 analytical scales (Mettler-Toledo, Switzerland)). The leaching residue was dried in a 2B 151 laboratory oven (SNOL, Russia) and weighed on SPS 202 laboratory technical scales (OHAUS, USA) to determine its yield.

Kinetic studies of AA-leaching of slime (**Method II**) were conducted at a molar ratio of $[NH_3\cdot H_2O]$: : $[(NH_4)_2SO_4]$ = 4 mol/mol and a concentration of $C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]} = 0.5\div3.5$ mol/L. Oxygen from the air was used as the oxidizer, with a flow rate ranging from 18 ± 1 to 155 ± 2 L/h. A sample of the research material weighing 5 g was added to the solution at a liquid-to-solid ratio (L/S) of 100 : 1 and a temperature of 15—45 °C. The total duration of the process ranged from 5 to 30 minutes. During the experiment, samples of the leach solution were taken and analyzed for copper content using iodometric titration with sodium thiosulfate. The total volume of the samples taken did not exceed 5 % of the solution volume. Based on the results obtained, the dependencies of the degree of leaching on the duration of the process were plotted for $t = 15\div45$ °C and buffer mixture concentrations $C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]} = 1$ and 2 mol/L to determine the activation energy, as well as for $C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]} = 0.5\div3.5$ mol/L and $t = 25$ °C to evaluate the reaction order. The dependencies of $\ln(d\alpha/d\tau)$ — $1/T$ and $\ln(d\alpha/d\tau)$ — $\ln C$ (where $d\alpha/d\tau$ are the slope coefficients of the tangents at the values of the leaching degree $\alpha = 0$) were plotted, and from the tangents of their slopes, the activation energy and reaction orders were determined, respectively.

2. Results and discussion

2.1. Thermodynamic analysis

The thermodynamic analysis of the slime—$NH_3\cdot H_2O$—$(NH_4)_2SO_4$—H_2O—O_2 system was carried out due to the need to justify effective conditions for the extraction of SCER slime components. This is related to selecting the composition of the leaching solution that ensures high copper recovery in the AA-leaching process.

Thermodynamic calculations of the probable reactions in the studied slime— $NH_3\cdot H_2O$—$(NH_4)_2SO_4$—H_2O—O_2 system were performed using reference data on the thermodynamic parameters of the slime components and the potential products of their interaction with the leaching system [31; 35; 36].

In work [29], it was recommended that copper dissolution in ammonia solutions $[NH_3\cdot H_2O]$ and $[NH_4^+]$ be conducted in the pH range of 9—11, which ensures the maximum activity of $[Cu(NH_3)_4]^{2+}$ ions participating in the autocatalytic oxidation reaction of copper. To oxidize $[Cu(NH_3)_2]$ + ions to $[Cu(NH_3)_4]^{2+}$, according to the mechanism described by reactions (1)—(3), oxygen from the air is supplied to the system. The oxidation potential of oxygen depends on the pH and, under normal conditions, can be calculated using the equation [37]:

$$E^0 = 1.228 - 0.059\text{pH}, \qquad (4)$$

where pH is the hydrogen ion concentration.

According to equation (4), for pH values of 9, 10, and 11, the oxidation potential of the oxygen half-reaction:

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad (5)$$

is E^0 = +0.697, +0.638 and +0.579 V, respectively.

The results of the Gibbs energy calculation, equilibrium constants, and redox potentials of probable reactions in the slime—$NH_3\cdot H_2O$—$(NH_4)_2SO_4$—H_2O—O_2 system for the phases Cu, Ag, and Pb are presented in Table 3. The analysis of these data showed that most chemical reactions (6)—(8), (10), (12), (14), (16), (18)—(20), (22)—(28) are thermodynamically probable. However, for processes (11)—(16), (21), and (22), which are not redox reactions, the dissolution reactions of metal compounds and the formation of their ammine complexes

Table 3. **Results of Gibbs energy (ΔG^0_{298}), equilibrium constants, and redox potential calculations of probable reactions in the slime–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O–O_2 system**

Таблица 3. Результаты расчета энергии Гиббса (ΔG^0_{298}), констант равновесий и окислительно-восстановительного потенциала вероятных реакций в системе шлам–$NH_3 \cdot H_2O$–$(NH_4)_2SO_4$–H_2O–O_2

№	Reaction	E^0, V	ΔG^0_{298}, kJ/mol Me	$\lg K_a$
(6)	$Cu + 2NH_3 \cdot H_2O + 0.25O_2 = [Cu(NH_3)_2]^+ + OH^- + 1.5H_2O$	+0.817 (pH = 9)	−78.8	+13.8
		+0.758 (pH = 10)	−73.1	+12.8
		+0.699 (pH = 11)	−67.5	+11.8
(7)	$[Cu(NH_3)_2]^+ + 2NH_3 \cdot H_2O + 0.25O_2 = [Cu(NH_3)_4]^{2+} + OH^- + 1.5H_2O$	+0.707 (pH = 9)	−68.2	+12.0
		+0.648 (pH = 10)	−62.5	+11.0
		+0.589 (pH = 11)	−56.8	+10.0
(8)	$0.5[Cu(NH_3)_4]^{2+} + 0.5Cu = [Cu(NH_3)_2]^+$	+0.110	−5.3	+0.9
(9)	$Cu + 2NH_4^+ + 0.25O_2 + OH^- = [Cu(NH_3)_2]^+ + 1.5H_2O$	–	−106.0	+18.6
(10)	$[Cu(NH_3)_2]^+ + 2NH_4^+ + 0.25O_2 + OH^- = [Cu(NH_3)_4]^{2+} + 1.5H_2O$	–	−87.2	+15.3
(11)	$0.5Cu_2O + 2NH_3 \cdot H_2O = [Cu(NH_3)_2]^{2+} + OH^- + 1.5H_2O$	–	+21.2	−3.7
(12)	$0.5Cu_2O + 2NH_4^+ + OH^- = [Cu(NH_3)_2]^{2+} + 1.5H_2O$	–	−31.9	+5.6
(13)	$CuO + 4NH_3 \cdot H_2O = [Cu(NH_3)_4]^{2+} + 2OH^- + 3H_2O$	–	+41.5	−7.3
(14)	$CuO + 4NH_4^+ + 2OH^- = [Cu(NH_3)_4]^{2+} + 3H_2O$	–	−64.8	+11.4
(15)	$Cu(OH)_2 + 4NH_3 \cdot H_2O = [Cu(NH_3)_4]^{2+} + 2OH^- + 4H_2O$	–	+34.8	−6.1
(16)	$Cu(OH)_2 + 4NH_4^+ + 2OH^- = [Cu(NH_3)_4]^{2+} + 4H_2O$	–	−71.4	+12.5
(17)	$0.25Cu_4(OH)_6SO_4 + 4NH_3 \cdot H_2O = [Cu(NH_3)_4]^{2+} + 0.25SO_4^{2-} + 1.5OH^- + 4H_2O$	–	+24.7	−4.3
(18)	$0.25Cu_4(OH)_6SO_4 + 4NH_4^+ + 2.5OH^- = [Cu(NH_3)_4]^{2+} + 0.25SO_4^{2-} + 4H_2O$	–	−81.5	+14.3
(19)	$Ag + 2NH_3 \cdot H_2O + 0.25O_2 = [Ag(NH_3)_2]^+ + OH^- + 1.5H_2O$	+0.330 (pH = 9)	−31.9	+5.6
		+0.271 (pH = 10)	−26.2	+4.6
		+0.212 (pH = 11)	−20.5	+3.6
(20)	$Ag + 2NH_4^+ + 0.25O_2 + OH^- = [Ag(NH_3)_2]^+ + 1.5H_2O$	–	−57.6	+10.1
(21)	$AgCl + 2NH_3 \cdot H_2O = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$	–	+12.6	−2.2
(22)	$AgCl + 2NH_4^+ + 2OH^- = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$	–	−40.5	+7.1
(23)	$AgCl + 2NH_3 \cdot H_2O + Cu = [Cu(NH_3)_2]^+ + Ag + Cl^- + 2H_2O$	+0.342	−33.0	+5.8
(24)	$AgCl + 2NH_4^+ + Cu + 2OH^- = [Cu(NH_3)_2]^+ + Ag + Cl^- + 2H_2O$	–	−88.9	+15.6
(25)	$AgCl + [Cu(NH_3)_2]^+ + 2NH_3 \cdot H_2O = [Cu(NH_3)_4]^{2+} + Ag + Cl^- + 2H_2O$	+0.232	−22.4	+3.9
(26)	$AgCl + [Cu(NH_3)_2]^+ + 2NH_4^+ + 2OH^- = [Cu(NH_3)_4]^{2+} + Ag + Cl^- + 2H_2O$	–	−70.1	+12.3
(27)	$[Ag(NH_3)_2]^+ + Cu = [Cu(NH_3)_2]^+ + Ag$	+0.487	−47.0	+8.2
(28)	$[Ag(NH_3)_2]^+ + [Cu(NH_3)_2]^+ = [Cu(NH_3)_4]^{2+} + Ag$	+0.377	−36.4	+6.4

with the ammonium ion are thermodynamically more probable than with the ammonia hydrate. Therefore, it is necessary to establish the dependence of the equilibrium concentration of copper and silver ammines on the concentration of free ammonia hydrate ($[NH_3 \cdot H_2O]$) and ammonium ion ($[NH_4^+]$), as well as on the pH value, which depends on the molar ratio of ammonia hydrate and ammonium ion in the solution, i.e., on Θ [38]. The $[NH_3 \cdot H_2O]$ + $[NH_4^+]$ mixture, in the form of an ammonium salt of a strong acid, creates a buffer system [39]:

$$NH_3 \cdot H_2O \rightleftarrows NH_4^+ + OH, \qquad (29)$$

and therefore, it is assumed that the equilibrium pH of the system equals the initial value.

To determine the effect of the equilibrium pH and the total concentration of free $NH_3 \cdot H_2O$ and NH_4^+ ions (i.e., not bound in complexes $[NH_3 \cdot H_2O + NH_4^+]_{free}$), considering the buffer system equilibrium from reaction (29), on the concentrations of copper and silver ammines, the reactions (11) and (12), (13) and (14), (15) and (16), (21) and (22) from Table 3 were combined, yielding the following equations:

$$\begin{gathered} 0.5Cu_2O + 2x[NH_3 \cdot H_2O] + \\ + 2(1-x)NH_4^+ + 2(1-x)OH^- = \\ = [Cu(NH_3)_2]^+ + OH^- + 1.5H_2O, \end{gathered} \tag{30}$$

$$\begin{gathered} CuO + 4x[NH_3 \cdot H_2O] + \\ + 4(1-x)NH_4^+ + 4(1-x)OH^- = \\ = [Cu(NH_3)_4]^{2+} + 2OH^- + 3H_2O, \end{gathered} \tag{31}$$

$$\begin{gathered} Cu(OH)_2 + 4x[NH_3 \cdot H_2O] + \\ + 4(1-x)NH_4^+ + 4(1-x)OH^- = \\ = [Cu(NH_3)_4]^{2+} + 2OH^- + 4H_2O, \end{gathered} \tag{32}$$

$$\begin{gathered} AgCl + 2x[NH_3 \cdot H_2O] + \\ + 2(1-x)NH_4^+ + 2(1-x)OH^- = \\ = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O, \end{gathered} \tag{33}$$

where x and $(1-x)$ are the molar fractions of $NH_3 \cdot H_2O$ and NH_4^+ in the ammonia-ammonium solution, respectively.

It is known that the solubility of $[Cu(NH_3)_4]SO_4$ in water is 16.9 g/100 g H_2O, corresponding to a concentration of $[Cu(NH_3)_4]^{2+}$ 0.74 mol/L [31]. The solubility of copper ammines is primarily influenced by the concentration of free ammonia, and at $C_{NH_3 \cdot H_2O} =$ = 7.2 mol/L and $C_{(NH_4)_2SO_4} = 2.3$ mol/L a concentration of $[Cu(NH_3)_4]^{2+}$ 1.7 mol/L was achieved [40]. However, in the study [41], it was found that increasing the concentrations of ammonia and ammonium chloride to 10.84 and 5.44 mol/L, respectively, promoted the solubility of copper tetraammine to 2.8 mol/L. It is probable that the ratio of ammonia molecules to ammonium ions in the solution, as well as the type of ammonium salt, affects the solubility of copper ammines. Therefore, in this study, it is assumed that the maximum concentration of $[Cu(NH_3)_4]^{2+}$ is 2.8 mol/L, by analogy with $NH_3 \cdot H_2O$—NH_4Cl—H_2O solutions.

The dependencies of the equilibrium concentrations of $[Cu(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$, and $[Ag(NH_3)_2]^+$ ions on the solution pH and $[NH_3 \cdot H_2O + NH_4^+]_{free}$ for reactions (30)—(33), without considering the influence of additional factors on the system, are shown in Fig. 3.

From Fig. 3, it can be seen that the maximum solubility of $[Cu(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$ in AA-solutions is achieved at pH = 9.37, which corresponds to a molar fraction of $NH_3 \cdot H_2O$ in the solution of 0.57 (see Fig. 4). As this increases, the pH of the AA-solution and the solubility of AgCl rise, which may lead to undesirable silver losses in the leach solution and reduce the selectivity of decopperization.

However, in the study [41], it was found that increasing the molar fraction of ammonia hydrate in the AA-solution positively affects the transition of oxidized copper into the leach solution. The solubility of oxygen in the solution, which is influenced by the salt content, significantly affects the course of oxidative leaching. The increase in $NH_3 \cdot H_2O$ concentration in the solution has little effect on this parameter, but at a concentration of 1 mol/L $(NH_4)_2SO_4$, the solubility of oxygen in the solution decreases by 35 % compared to its solubility in water [42—44].

Given the above, for effective copper extraction with AA-solutions, a pH range of 9.25—10.00 is recommended, corresponding to a molar fraction of ammonia hydrate $[NH_3 \cdot H_2O] = 50 \div 85$ % (see. Fig. 4) [38].

From Fig. 3, it can be seen that the lowest equilibrium concentration of $[Cu(NH_3)_4]^{2+}$ in the ammonia-ammonium system, under otherwise equal conditions, is observed for reaction (31). The Gibbs free energy values of reactions (13) and (14), which make up the overall reaction (31), are more positive than those for (15) and (16), which make up reaction (32). This indicates that the thermodynamics of $[Cu(NH_3)_4]^{2+}$ complex formation will be least favorable when the AA-solution interacts with copper oxide (CuO). Therefore, the thermodynamically necessary quantity (TNQ) of $NH_3 \cdot H_2O$ and NH_4^+, as well as the minimum excess of $NH_3 \cdot H_2O$ and NH_4^+ over the stoichiometrically necessary quantity (SNQ) for the AA system, must be established for reaction (31). The equilibrium constant, TNQ of $NH_3 \cdot H_2O$ and NH_4^+, and the minimum excess of $NH_3 \cdot H_2O$ and NH_4^+ over SNQ for reaction (31), ensuring 100 % dissolution of Cu, are determined by the following equations [32]:

$$K_a = \frac{\left[[Cu(NH_3)_4]^{2+}\right] \cdot \left[OH^-\right]^2}{[NH_3 \cdot H_2O]^{4x} \cdot [NH_4^+]^{4 \cdot (1-x)} \cdot [OH^-]^{4 \cdot (1-x)}}, \tag{34}$$

$$\begin{gathered} TNQ_{NH_3 \cdot H_2O} = SNQ_{NH_3 \cdot H_2O} + \\ + \sqrt[4]{\frac{\left[[Cu(NH_3)_4]^{2+}\right]}{K_a K_d^{4 \cdot (1-x)} \cdot 10^{2 \cdot (14-pH)}}} \cdot \frac{1}{\left[[Cu(NH_3)_4]^{2+}\right]}, \end{gathered} \tag{35}$$

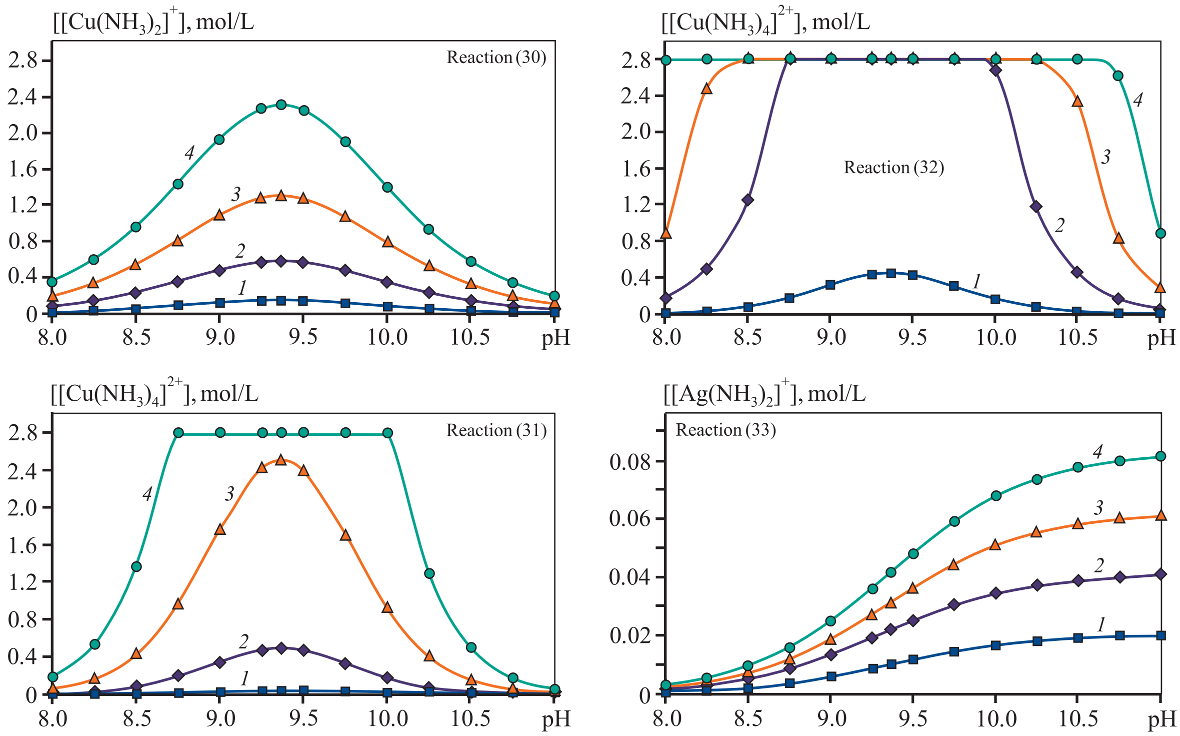

Fig. 3. Dependences of changes in the equilibrium concentrations of $[Cu(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$and $[Ag(NH_3)_2]^+$ ions on the pH of the solution and $[NH_3{\cdot}H_2O + NH_4^+]_{free}$ for reactions (30)–(33)

$[NH_3{\cdot}H_2O + NH_4^+]_{free}$, mol/L: 0.25 (*1*), 0.50 (*2*), 0.75 (*3*) and 1.0 (*4*)

Рис. 3. Зависимости равновесных концентраций ионов $[Cu(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$ и $[Ag(NH_3)_2]^+$ от pH раствора и $[NH_3{\cdot}H_2O + NH_4^+]_{своб}$ для реакций (30)–(33)

$[NH_3{\cdot}H_2O + NH_4^+]_{своб}$, моль/л: 0,25 (*1*), 0,50 (*2*), 0,75 (*3*) и 1,0 (*4*)

$$\mathrm{TNQ}_{NH_4^+} = \mathrm{SNQ}_{NH_4^+} + \sqrt[4]{\frac{[[Cu(NH_3)_4]^{2+}]K_d^{4x}\cdot 10^{2\cdot(14-\mathrm{pH})}}{K_a}}\cdot\frac{1}{[[Cu(NH_3)_4]^{2+}]}, \quad (36)$$

$$\chi_{NH_3\cdot H_2O} = \chi_{NH_4^+} = \left(\frac{\mathrm{TNQ}}{\mathrm{SNQ}} - 1\right)\cdot 100\ \%, \quad (37)$$

where K_a is the equilibrium constant of reaction (31); $K_d = [NH_4^+][OH^-]/[NH_3{\cdot}H_2O] = 10^{-4.75}$ is the dissociation constant of $NH_3{\cdot}H_2O$ in water [31]); $\mathrm{TNQ}_{NH_3\cdot H_2O}$, $\mathrm{TNQ}_{NH_4^+}$ are the thermodynamically necessary quantities of $NH_3{\cdot}H_2O$ and NH_4^+, mol/mol CuO; $\mathrm{SNQ}_{NH_3\cdot H_2O}$, $\mathrm{SNQ}_{NH_4^+}$ are the stoichiometrically necessary quantities of $NH_3{\cdot}H_2O$ and NH_4^+, mol/mol CuO; χ is the minimum excess of $NH_3{\cdot}H_2O/NH_4^+$ over SNQ for reaction (31).

According to equations (35) and (36), the TNQ of $NH_3{\cdot}H_2O$ and NH_4^+ for reaction (31) depends on the molar concentration of the complex ion $[Cu(NH_3)_4]^{2+}$ in the AA-solution and the equilibrium pH, which, like the equilibrium constant K_a, depends on the molar fraction of $[NH_3{\cdot}H_2O]$ in the solution.

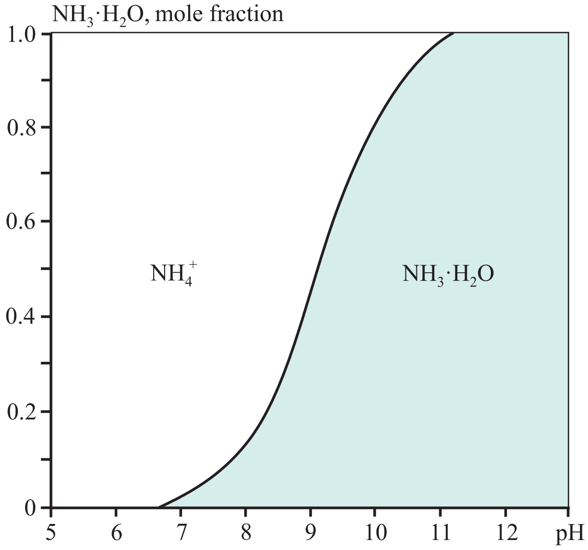

Fig. 4. Dependence of the mole fraction of $NH_3{\cdot}H_2O$ in an ammonia-ammonium solution on pH at an activity coefficient $\gamma_{NH_4^+} = 1$, $t = 25$ °C and $P = 1$ atm [38]

Рис. 4. Зависимость мольной доли $NH_3{\cdot}H_2O$ в аммиачно-аммонийном растворе от pH при коэффициенте активности $\gamma_{NH_4^+} = 1$, $t = 25$ °C и $P = 1$ атм [38]

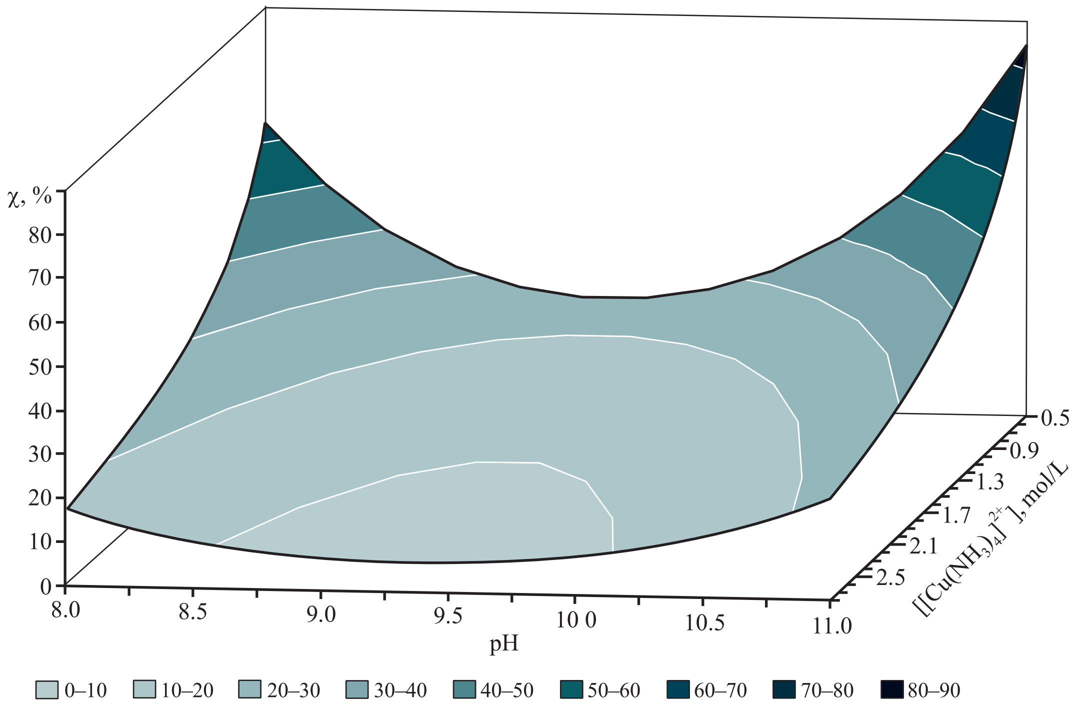

Fig. 5. Surface plot of the dependence of the minimum excess of $NH_3{\cdot}H_2O/NH_4^+$ over SNQ, necessary for the complete progress of reaction (31), on the equilibrium pH of the ammonia-ammonium solution and the concentration of $[Cu(NH_3)_4]^{2+}$

Рис. 5. Поверхность зависимости величины минимального избытка $NH_3{\cdot}H_2O/NH_4^+$ от СНК, необходимого для полного протекания реакции (31), от равновесного pH аммиачно-аммонийного раствора и концентрации в нем $[Cu(NH_3)_4]^{2+}$

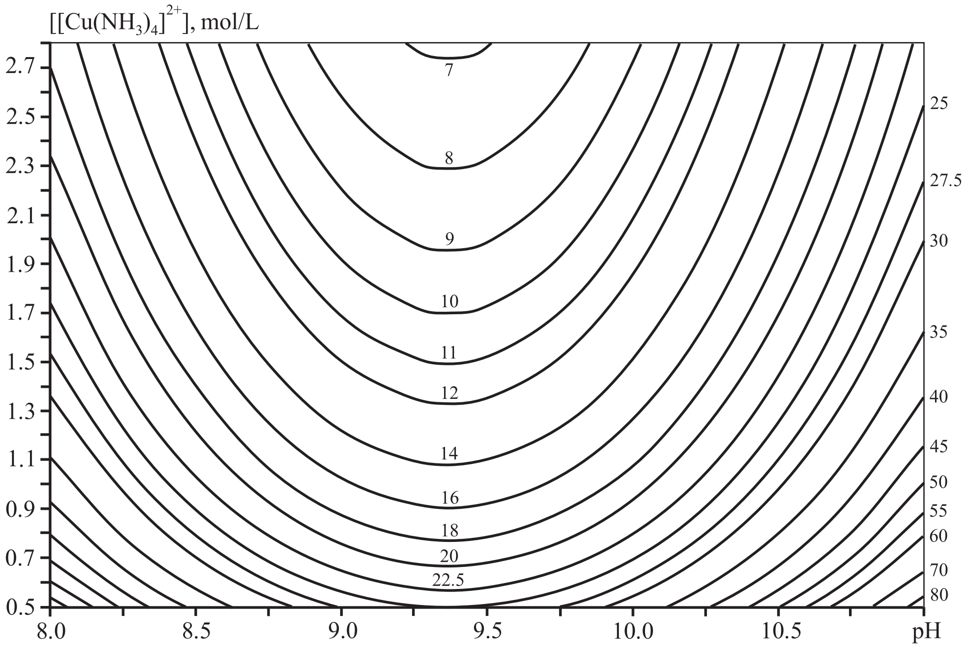

Fig. 6. Nomogram for the theoretical calculation of the minimum excess of $NH_3{\cdot}H_2O/NH_4^+$ over SNQ, necessary for the complete progress of reaction (31), in accordance with the equilibrium pH values of the ammonia-ammonium solution and the concentration of $[Cu(NH_3)_4]^{2+}$

Рис. 6. Номограмма теоретического расчета минимального избытка $NH_3{\cdot}H_2O/NH_4^+$ от СНК, необходимого для полного протекания реакции (31), в соответствии с величинами pH равновесного аммиачно-аммонийного раствора и концентрации в нем $[Cu(NH_3)_4]^{2+}$

Fig. 5 and 6 present, respectively, the surface plot and the nomogram for the theoretical calculation of the minimum excess of $NH_3 \cdot H_2O/NH_4^+$ over SNQ, necessary for the complete progress of reaction (31), depending on the equilibrium pH of the AA-solution and the concentration of $[Cu(NH_3)_4]^{2+}$ in it. It is evident that an increase in the concentration of $[Cu(NH_3)_4]^{2+}$ reduces the required excess of $NH_3 \cdot H_2O$ over SNQ needed for the complete progress of reaction (31). However, the authors of [45] found that as the copper concentration in the ammonia etching solution increases from 0.6 to 1.0 mol/L, the dissolution rate decreases by almost half due to the probable saturation of the diffusion layer with the products of reaction (3) [46]. Therefore, it is advisable to limit the maximum allowable copper concentration in the AA-leaching solution of secondary copper electrorefining slime to no more than 0.8 mol/L for more intensive process progress.

The onset of silver transition during ammonia-ammonium leaching of copper can be monitored by the redox potential (ORP) of the pulp. The standard ORP value for the oxidation of silver in ammonia $[NH_3 \cdot H_2O]$ is +0.367 V, which is significantly higher than that of copper (I) and (II): $E_{[Cu(NH_3)_2]^+/Cu}$ = = −0.120 V, $E_{[Cu(NH_2)_4]^{2+}/Cu}$ = −0.065 V [31]. However, considering the mechanism of copper oxidation in ammonia solutions (reactions (1)—(3)), the ORP of the system may be determined by the half-reaction of oxidation $[Cu(NH_3)_2]^+$ to $[Cu(NH_3)_4]^{2+}$, with a standard value of −0.01 V [35]. According to the Pourbaix diagram for the Cu—NH_3—H_2O system (Fig. 7), the potential of the half-reaction for the oxidation $[Cu(NH_3)_2]^+$ to $[Cu(NH_3)_4]^{2+}$ remains constant at pH > 9.25, when the molar fraction of $[NH_3 \cdot H_2O]$ in the AA-solution is more than 50 %. Figure 8 presents the calculated dependence of the Cu(II) fraction and the concentration of silver in the AA leaching solution for copper on the ORP of the pulp at equilibrium concentrations of $[NH_3 \cdot H_2O + NH_4^+]_{free}$ ranging from 0.5 to 1.0 mol/L and a molar fraction of $[NH_3 \cdot H_2O]$ in the AA-solution greater than 50 %, without considering the influence of additional factors on the system [30; 31; 35].

According to the data in Fig. 8, the concentration of silver ammine in the solution begins to increase when the ORP of the AA-leaching pulp for copper exceeds 130, 145, and 165 mV for equilibrium concentrations of $[NH_3 \cdot H_2O]$ = 1.00, 0.75 and 0.50 mol/L, respectively. However, based on reactions (27) and (28) (Table 3), there is a high thermodynamic probability of $[Ag(NH_3)_2]^+$ reduction by copper and the complex ion $[Cu(NH_3)_2]^+$. Therefore, to avoid incomplete copper transition from SCER slime into the AA-leach-

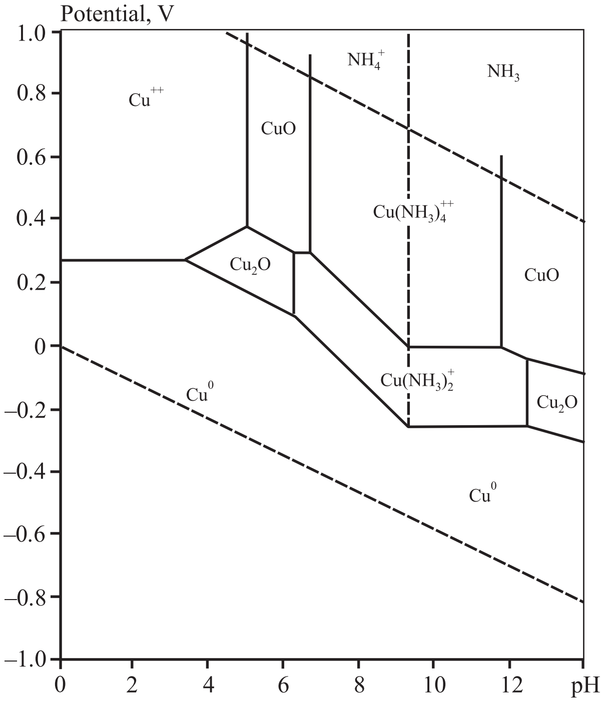

Fig. 7. Pourbaix diagram for the Cu–NH_3–H_2O system [29]
t = 25 °C, P = 1 atm, activity: $a_{Cu^{2+}}$ = 1, a_{NH_3} = 1

Рис. 7. Диаграмма Пурбе Cu–NH_3–H_2O [29]
t = 25 °C, P = 1 атм, активность: $a_{Cu^{2+}}$ = 1, a_{NH_3} = 1

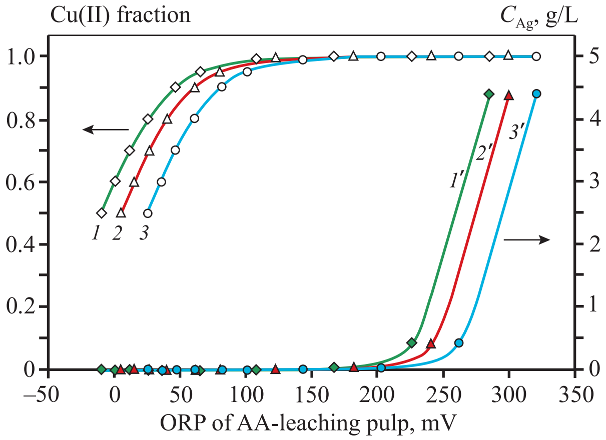

Fig. 8. Calculated dependence of the Cu(II) fraction and silver concentration in the ammonia-ammonium leaching solution for copper on the ORP of the pulp, at equilibrium concentrations of $[NH_3 \cdot H_2O + NH_4^+]_{free}$ = 1.0 mol/L (***1***, ***1′***), 0.75 mol/L (***2***, ***2′***), and 0.5 mol/L (***3***, ***3′***), with a molar fraction of $[NH_3 \cdot H_2O]$ greater than 50 % in the AA solution

Рис. 8. Расчетная зависимость доли Cu(II) и концентрации серебра в растворе аммиачно-аммонийного выщелачивания меди от показателя ОВП пульпы при равновесных концентрациях $[NH_3 \cdot H_2O + NH_4^+]_{своб}$ = 1,0 моль/л (***1***, ***1′***), 0,75 моль/л (***2***, ***2′***) и 0,5 моль/л (***3***, ***3′***) и мольной доли в АА-растворе $[NH_3 \cdot H_2O]$ более 50 %

ing solution, it is advisable to monitor the ORP, which should be maintained at +225 ± 10, +240 ± 10, and +260 ± 10 mV relative to the standard hydrogen electrode (SHE) at $[NH_3{\cdot}H_2O+NH_4^+]_{free}$ = 1.00, 0.75, and 0.50 mol/L, respectively.

To assess the objectivity of the conclusions and recommendations made above based on the thermodynamic analysis, technological studies of the AA-leaching process for copper from SCER slime were conducted.

2.2. Technological studies on ammonia-ammonium leaching of copper from secondary copper electrorefining slime in the $-NH_3{\cdot}H_2O-(NH_4)_2SO_4-H_2O-O_2$ system

According to the results of the thermodynamic analysis, the following regime is recommended for leaching copper from SCER slime (**Method I**): $\Theta = 4$ mol/mol (corresponding to an initial pH = 9.55); L/S = 12 : 1 (to obtain a leach solution with a copper concentration of 0.72 ± 0.01 mol/L); $\chi = 20$ % of the stoichiometrically necessary quantity (SNQ) for reaction (31), and an air flow rate of 190 ± 2 L/h until the ORP reaches +260 ± 10 mV relative to the SHE (52 ± 10 mV relative to the silver chloride electrode (SCE)) at an equilibrium concentration of $[NH_3{\cdot}H_2O+NH_4^+]_{free}$ = = 0.58 mol/L.

Experimental results show that the recommended conditions for the decopperization of SCER slime using an ammonia-ammonium solution ensure the absence of silver in the leach solution at a pulp ORP of +269 mV relative to the SHE and +61 mV relative to the SCE, with a copper recovery rate of 99.4 %.

To manage the decopperization process of SCER slime in the slime—$NH_3{\cdot}H_2O$—$(NH_4)_2SO_4$—H_2O—O_2 system, it is necessary to clarify the mechanism and kinetic patterns of the process.

2.3. Comprehensive studies of the kinetics of the ammonia-ammonium leaching process for secondary copper electrorefining slime in the slime$-NH_3{\cdot}H_2O-(NH_4)_2SO_4-H_2O-O_2$ system

To study the kinetics of leaching, model equations are applied that describe processes occurring in both diffusion and kinetic domains [47—53], using equations such as the "shrinking sphere" model, Ginstling—Brounshtein, Erofeev—Kolmogorov, and others. However, the first two are only suitable for describing the leaching rate of monodisperse material with particles of the same shape [30], and the Erofeev—Kolmogorov equation is not applicable for determining the process regime [54]. Therefore, the identification of the leaching regime was based on the values of activation energy and reaction order, determined using Method II, presented above in Section 1.

The complexation reaction of copper ammine (31) is reversible, but its equilibrium constant at pH = 9.55 in the system and $\Theta = 4$ mol/mol is $K_a = 92.44$ (see Table 4), allowing the copper leaching process from SCER slime to be considered practically irreversible. Then the formal kinetics equation for the investigated copper leaching process from slime into the solution is:

$$\frac{d\alpha}{d\tau} = ke^{-E_a/(RT)} C^{n_1}_{\sum[NH_3\cdot H_2O]+[NH_4^+]} P^{n_2}_{O_2} S, \qquad (38)$$

where k is a constant factor; E_a is the apparent activation energy of the chemical process, J/mol; R = = 8.31 J/(mol·K) is the universal gas constant; T is the process temperature, K; $C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]}$ is the total concentration of $[NH_3{\cdot}H_2O] + [NH_4^+]$ in the solution; P_{O_2} is the oxygen pressure; n_1 is the reaction order for the $NH_3{\cdot}H_2O$—$(NH_4)_2SO_4$; n_2 is the reaction order for oxygen from the air; S is the surface area of the slime particles, dm^2/g.

The apparent activation energy and reaction orders are parameters dependent on the nature of the interaction between components in the system. Investigating the influence of temperature and concentrations on the leaching rate while stabilizing other characteristics will allow their values to be determined and conclusions drawn about the regime of the process.

Fig. 9 shows the dependence of $\ln(d\alpha/d\tau)$ on $\ln C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]}$ for the AA-leaching of copper from SCER slime at a total concentration of $[NH_3{\cdot}H_2O] + [NH_4^+]$ ranging from 0.5 to 3.5 mol/L, with an L/S ratio of 100 : 1, temperature of 24 °C, $[NH_3{\cdot}H_2O] : [(NH_4)_2SO_4]$ = 4 mol/mol (corresponding to pH = 9.55), and an air flow rate of v_{air} = 95±2 L/h. The nature of this dependence indicates a change in the leaching regime around $C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]}$ = 1.5 mol/L. It is suggested that below this concentration, the leaching process occurs in the external diffusion region with a reaction order $n_1 \approx 0.91 \approx 1$, while at $C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]}$ 1.5 mol/L, the process shifts to a kinetic regime, where the rate is limited by the adsorption of reagents on the surface of solid particles, with an apparent reaction order $n_1 = 0.24$.

Accordingly, the determination of the activation energy was carried out on both sides of the transition region: at a total concentration $C_{\Sigma[NH_3\cdot H_2O]+[NH_4^+]}$ = 1 and 2 mol/L. The study results are presented in Fig. 10 as the dependence of $\ln(d\alpha/d\tau)$ on $1/T$, with temperature

Table 4. **Equilibrium constants values for reaction (31) at different pH levels**

Таблица 4. Значения констант равновесия реакции (31) с учетом pH

pH	8.75	9.00	9.25	9.50	9.55	9.75	10.00	10.25
K_a	27.82	75.91	122.08	103.00	92.44	48.98	16.02	4.4

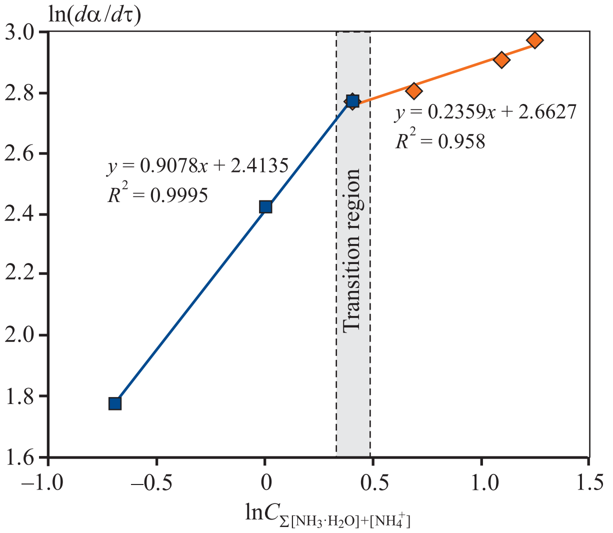

Fig. 9. Dependence of $\ln(d\alpha/d\tau)$ on $\ln C_{\Sigma[NH_3 \cdot H_3O]\,+\,[NH_4^+]}$ for ammonia-ammonium leaching of copper from secondary copper electrolytic refining slime

L : S = 100 : 1; t = 24 °C; $[NH_3 \cdot H_2O] : [(NH_4)_2SO_4] = 4$ mol/mol (corresponds to pH = 9.55); $v_{air} = 95 \pm 2$ L/h)

Рис. 9. Зависимость $\ln(d\alpha/d\tau)$ от $\ln C_{\Sigma[NH_3 \cdot H_3O]\,+\,[NH_4^+]}$ для аммиачно-аммонийного выщелачивания меди из шлама ЭРВМ

Ж : Т = 100 : 1; t = 24 °C; $[NH_3 \cdot H_2O] : [(NH_4)_2SO_4] = 4$ моль/моль (pH = 9,55); $v_в = 95 \pm 2$ л/ч

ranging from 15 to 45 °C, where the upper limit is justified by increased ammonia losses with further temperature increase [24]. It can be seen that in both cases, the apparent activation energy of the process was 5 ± ± 0.25 kJ/mol, which is consistent with the assumptions about the AA-leaching process of copper proceeding in the external diffusion regime at $C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} =$ = 1 mol/L and in the kinetic regime with the rate limited by reagent adsorption on the surface of solid particles at $C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} = 2$ mol/L.

In addition to the ammonia and ammonium salts involved in forming complexes, oxygen from the air is used as a reagent in the slime—$NH_3 \cdot H_2O$—$(NH_4)_2SO_4$—H_2O—O_2 system. However, due to the difficulty of maintaining a certain concentration of oxygen in the solution, this influence was assessed by increasing the air flow rate in the leaching system from 18 to 156 L/h. It was found that changing the air flow rate in the studied range hardly affects the process rate. It is evident that across the entire range, the rate of oxygen supply to the leaching system was significantly higher than its consumption rate, resulting in a constant dissolved oxygen concentration.

For a more unambiguous interpretation of the kinetic study results, a literature review was conducted. It was found in [55] that the diffusion coefficient of copper ammine in solution decreases from $6 \cdot 10^{-6}$ to $2.5 \cdot 10^{-6}$ cm^2/s as the copper concentration in the AA-solution increases from 0.5 to 10 g/L, and further increases in copper concentration to 80 g/L reduce it to $1{,}67 \cdot 10^{-6}$ cm^2/s. These factors, along with the decrease in oxygen solubility in solutions as their salt content increases, can significantly reduce the overall copper transition rate into the ammonia-ammonium solution, as indicated by the results in [45]. Only the application of autoclave ammonia leaching of copper at an oxygen pressure of 7.8 atm promotes the transition from the diffusion regime to the kinetic regime, where the rate-limiting step becomes the formation and dissolution of copper ammines [20; 23]. This confirms the advisability of limiting the final copper concentration to 0.8 mol/L, as recommended based on the thermodynamic analysis.

In [56], it was established that reaction (1) proceeds in the external diffusion region of reaction if the concentration of dissolved oxygen is more than 280 times lower than that of ammonia; otherwise, the rate-limiting step becomes the chemical interaction between the Cu^+ ion and ammonia. Reaction (1) can only determine the overall process rate at a low concentration of Cu(II) in the solution, but as it increases, the oxidation of metallic copper also begins to proceed through reaction (3), where the main electron carriers in the system become $[Cu(NH_3)_4]^{2+}$ ions [21; 24; 57].

In [58], it was found that the autocatalytic dissolution of copper by reaction (3) limits its dissolution in ammonia, while reaction (2) proceeds fairly quickly. This may be due to the use of ammonia solution in the absence of ammonium salts, which promotes the formation of copper hydroxocomplexes and hydroxides on the particle surfaces, complicating the mechanism of oxidative dissolution of copper in ammonia [59]. A similar conclusion is presented by the authors of [22], who consider the rate-limiting step to be the removal of reaction (2) products due to the formation of copper hydroxide on

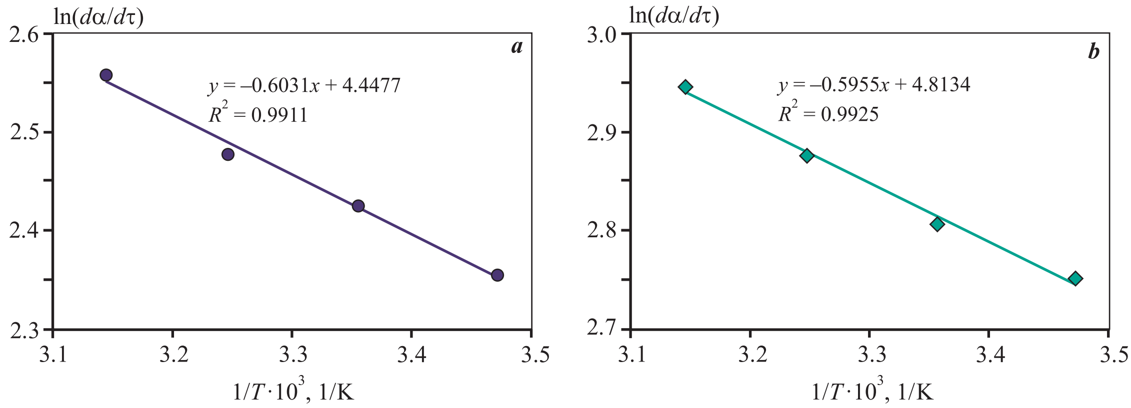

Fig. 10. Dependence of $\ln(d\alpha/d\tau)$ on $1/T$ for ammonia-ammonium leaching of copper from secondary copper electrolytic refining slime

L : S = 100 : 1; $[NH_3{\cdot}H_2O] : [(NH_4)_2SO_4] = 4$ mol/mol; $v_{air} = 95\pm2$ L/h) and total concentration $C_{\Sigma[NH_3\cdot H_2O] + [NH_4^+]} = 1$ mol/L (***a***) and 2 (***b***)

Рис. 10. Зависимость $\ln(d\alpha/d\tau)$ от $1/T$ процесса аммиачно-аммонийного выщелачивания меди из шлама ЭРВМ

Ж : Т = 100 : 1; $[NH_3{\cdot}H_2O] : [(NH_4)_2SO_4] = 4$ моль/моль; $v_в = 95\pm2$ л/ч) и $C_{\Sigma[NH_3\cdot H_2O] + [NH_4^+]} = 1$ моль/л (***a***) и 2 моль/л (***b***)

the Cu particle surfaces because of ammonia deficiency in the reaction zone. The formation of $Cu(OH)_2$ also occurs when oxidized copper dissolves in ammonium salts without the addition of ammonia [60]. In [60], it was established that the activation energy for the dissolution of oxidized copper ore in an NH_4Cl solution is 71 kJ/mol.

The use of ammonia-ammonium solutions significantly reduces the activation energy of the copper dissolution process. For example, in [24], during copper leaching with a solution containing copper, free ammonia, and ammonium sulfate in amounts of 0.2, 2.4, and 0.5 mol/L, respectively, the E_a was 22.8 kJ/mol, and increasing the Cu^{2+} content in the solution increased the copper dissolution rate. The authors consider the rate-limiting step to be the removal of reaction (2) products. In [46; 61], E_a values of 23.3 and 22.5 kJ/mol were obtained for the leaching of copper from oxidized ore with a solution containing 0.5 mol/L $NH_3{\cdot}H_2O$ and 2 mol/L NH_4Cl, and the dissolution of copper from printed circuit boards in a solution composed of $4NH_3{\cdot}H_2O + 1(NH_4)_2SO_4 + 0.63Cu(II)$, finding that the processes are limited by the internal diffusion of the reagent through a layer of non-reactive impurities. The reduction in activation energy when using the ammonia-ammonium leaching system is confirmed in [62], where, during the dissolution of malachite ore in an AA-solution (0.74 mol/L $NH_3{\cdot}H_2O$), CO_3^{2-} ions are released into it, forming $(NH_4)_2CO_3$. In this case, the activation energy is 22.3 kJ/mol, and the reaction order for ammonia is 1, indicating that the process occurs in the diffusion domain. The activation energy for the dissolution of malachite ore in an AA-solution (5 mol/L $NH_3{\cdot}H_2O$ and 0.3 mol/L $(NH_4)_2CO_3$) decreases to 15 kJ/mol [63]. The minimum value of $E_a = 3.8$ kJ/mol was obtained during the leaching of CuO from pyrite cinder with a solution composed of: $7.2NH_3{\cdot}H_2O + 3.8NH_4Cl$ mol/L [64].

From the above, it follows that the activation energy of the copper leaching process decreases as the proportion of oxidized copper in the initial raw material increases, as confirmed by the results of the kinetic studies conducted on copper leaching from SCER slimes. The dissolution of copper in the presence of oxidized forms Cu^+ and Cu^{2+} through reactions (2) and (3) may likely be complicated by the presence of various forms of copper ammine complexes and other compounds.

Based on the above, it can be assumed that AA-leaching of copper from SCER slime at a concentration of the ammonia-ammonium buffer system less than 1.5 mol/L proceeds via reactions

$$0.5Cu_2O_{(s)} + 2NH_3{\cdot}H_2O_{(aq)} = [Cu(NH_3)_2]^+_{(aq)} + OH^-_{(aq)} + 1.5H_2O, \tag{39}$$

$$[Cu(NH_3)_2]^+_{(aq)} + 0.25O_2 + OH^-_{(aq)} + 2.5H_2O = Cu(OH)_{2(s)} + 2NH_3{\cdot}H_2O_{(aq)}, \tag{40}$$

$$Cu(OH)_{2(s)} + 4NH_3{\cdot}H_2O_{(aq)} = [Cu(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)} + 4H_2O, \tag{41}$$

$$[Cu(NH_3)_4]^{2+}_{(aq)} + Cu_{(s)} = 2[Cu(NH_3)_2]^+_{(aq)}, \tag{42}$$

and is accompanied by the formation of an intermediate phase—copper hydroxide, which forms an intradiffusion

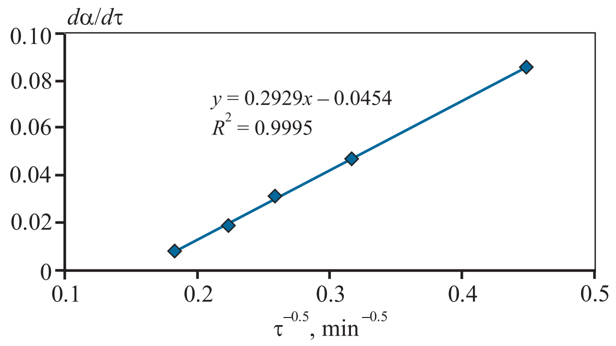

Fig. 11. Dependence of $d\alpha/d\tau$ on $\tau^{-0,5}$
$C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} = 1$ mol/L and $t = 25$ °C

Рис. 11. Зависимость $d\alpha/d\tau$ от $\tau^{-0,5}$
$C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} = 1$ моль/л, $t = 25$ °C

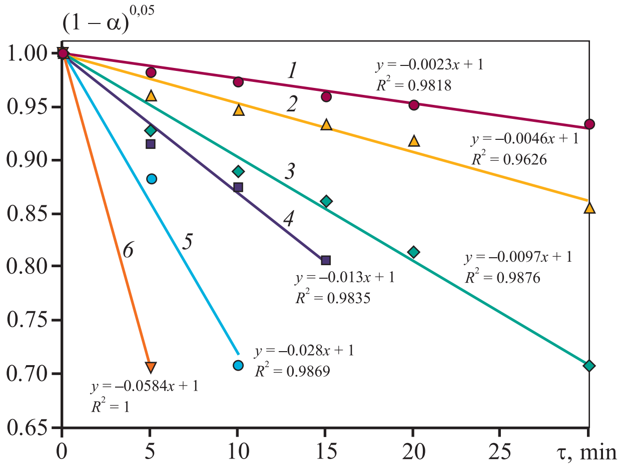

Fig. 12. Dependence of $(1-\alpha)^{(1-\beta)}$ on the duration copper leaching at $\beta = 0.95$ and $C_{\Sigma[NH_3 \cdot H_3O]+[NH_4^+]}$, mol/L: 0.5 (*1*), 1.0 (*2*), 1.5 (*3*), 2.0 (*4*), 3.0 (*5*) and 3.5 (*6*)
L : S = 100 : 1; $t = 24$ °C; $[NH_3 \cdot H_2O] : [(NH_4)_2SO_4] = 4$ mol/mol; $v_{air} = 95 \pm 2$ L/h

Рис. 12. Зависимость $(1-\alpha)^{(1-\beta)}$ от продолжительности выщелачивания меди при $\beta = 0,95$ и $C_{\Sigma[NH_3 \cdot H_3O]+[NH_4^+]}$, моль/л: 0,5 (*1*), 1,0 (*2*), 1,5 (*3*), 2,0 (*4*), 3,0 (*5*) и 3,5 (*6*)
Ж : Т = 100 : 1; $t = 24$ °C; $[NH_3 \cdot H_2O] : [(NH_4)_2SO_4] = 4$ моль/моль; $v_в = 95 \pm 2$ л/ч

layer according to reaction (40) and simultaneously disappears according to reaction (41), as evidenced by the linear nature of the dependence of $d\alpha/d\tau$ on $\tau^{-0.5}$ at a buffer solution concentration of 1 mol/L and a leaching process temperature of 25 °C (Fig. 11).

The leaching rate of copper from SCER slime is directly proportional to the surface area of the particles, which changes during the process. The dependence of the surface area on the degree of leaching can be described by a power function $S = S_0(1-\alpha)^{\beta}$. By integrating equation (38) considering the consumption of the ammonia-ammonium buffer system for the formation of $[Cu(NH_3)_4]^{2+}$, the dependence of the degree of copper extraction from slime on the leaching duration was obtained (43):

$$(1-\alpha)^{1-\beta} = 1-(1-\beta)ke^{-E_a/(RT)} \times$$
$$\times S_0\left(C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} - \nu G_0\alpha\right)^{n_1}\tau, \qquad (43)$$

where S_0 is the initial specific surface area of the particles, dm²/g; β is the reaction order with respect to the solid; n_1 is the reaction order for the $NH_3 \cdot H_2O$—$(NH_4)_2SO_4$, buffer system, equal to 0.24 and 0.91 for $C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} > 1.5$ mol/L and $C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} < 1.5$ mol/L, respectively; G_0 is the mass of copper in the slime, g; $\nu = 0.63$ mol/(L·g) is the change in reagent concentration corresponding to the transition of a unit mass of leached copper from the slime into solution.

The value of the parameter β depends on the nature of the leached material: for monodisperse material with particles of the same shape, they are equal to 2/3, 1/2, and 0 for isometric, columnar, and flat particles, respectively, while in the most common case of leaching polydisperse material with particles of different shapes, β approaches 1 [30]. Fig. 12 shows the results of the mathematical processing of the data from the study of the kinetics of copper leaching from SCER slime using equation (43) with a β value of 0.95, which ensures linear dependencies. It can be seen that the high level of linear approximation (>0.95) for the linear dependencies of $(1-\alpha)^{(1-\beta)}$ on the process duration, achieved at $\beta = 0.95$, corresponds to a constant factor of 0.0096 ± ± 0.0002. Thus, the kinetics of copper leaching from SCER slime, depending on the process duration, with a ratio of $[NH_3 \cdot H_2O] : [(NH_4)_2SO_4] = 4$ mol/mol (pH = = 9.55) and an ammonia-ammonium buffer system concentration greater than 1.5 and less than 1.5 mol/L, can be described by the equations:

$$\frac{d\alpha}{d\tau} = 0.0096e^{-5000/(RT)} \times$$
$$\times\left(C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} - 0.63G_0\alpha\right)^{0.24} S_0(1-\alpha)^{0.95}, \qquad (44)$$

$$\frac{d\alpha}{d\tau} = 0.0096e^{-5000/(RT)} \times$$
$$\times\left(C_{\Sigma[NH_3 \cdot H_2O]+[NH_4^+]} - 0.63G_0\alpha\right)^{0.91} S_0(1-\alpha)^{0.95}, \qquad (45)$$

Conclusions

1. Comprehensive studies of secondary copper electrolytic refining slime revealed an elevated copper content of 55.12 %, underscoring the importance of finding an effective method for extracting copper from this slime. The presence of the $Cu_4(OH)_6SO_4$ phase, corresponding to brochantite, was detected, for which there is no existing data regarding its occurrence in slimes. The total silver content in SCER slime is 2.43 %, with 69.1 % of the silver in metallic form, and the remainder as chloride. The contents of associated components $PbSO_4$, $BaSO_4$, and SnO_2 are 13.52 %, 9.33 %, and 4.73 %, respectively.

2. Based on thermodynamic analysis, the potential for effective and selective copper extraction from SCER slime by a hydrometallurgical method in an ammoniaammonium system without heating was established. The composition of the initial reagent solutions, including ammonia hydrate $NH_3 \cdot H_2O$ and ammonium sulfate $(NH_4)_2SO_4$, their consumption, as well as the characteristics of the leach pulp, were determined.

3. Technological studies confirmed the effectiveness of the recommended conditions for low-temperature ammonia-ammonium leaching ($\Theta = 4$ mol/mol, $\chi =$ $= 20$ % of the SNQ for reaction (31)) and the process control criteria ($[[Cu(NH_3)_4]^{2+}] = 0{,}72 \pm 0{,}01$ mol/L and pulp ORP +260 ± 10 mV relative to SHE (52 ± 10 mV relative to SCE), which ensure 99.4 % copper extraction and prevent silver from dissolving into the leach solution.

4. Kinetic studies of the copper leaching process from SCER slime determined the apparent activation energy to be 5 ± 0.25 kJ/mol within the temperature range of 15 to 45 °C, at total buffer system concentrations of $[NH_3 \cdot H_2O] + [NH_4^+]$ of 1 and 2 mol/L. The reaction order at a temperature of 24 ± 1 °C was found to be 0.24 ± 0.02 and 0.91 ± 0.05 for $[NH_3 \cdot H_2O] + [NH_4^+]$ greater than 1.5 mol/L and less than 1.5 mol/L, respectively. A transition in the leaching regime from external diffusion-controlled to kinetic-controlled, with the rate limited by reagent adsorption on the surface of solid particles, was observed as $[NH_3 \cdot H_2O] + [NH_4^+]$ increased from 0.5—1.5 to 1.5—3.5 mol/L at a temperature of 24 ± 1 °C. The formal kinetics equation for the studied process was determined.

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Information about the authors

Stepan O. Vydysh – Postgraduate Student of the Department of Non-Ferrous Metals and Gold, National University of Science and Technology «MISIS» (NUST MISIS).
https://orcid.org/0009-0007-4742-3966
E-mail: vydyshso@yandex.ru

Elena V. Bogatyreva – Dr. Sci. (Eng.), Professor of the Department of Non-Ferrous Metals and Gold, NUST MISIS.
https://orcid.org/0000-0003-2753-3424
E-mail: Helen_Bogatureva@mail.ru

Информация об авторах

Степан Олегович Выдыш – аспирант кафедры цветных металлов и золота, Национальный исследовательский технологический университет «МИСИС» (НИТУ МИСИС).
https://orcid.org/0009-0007-4742-3966
E-mail: vydyshso@yandex.ru

Елена Владимировна Богатырева – д.т.н., проф., доцент кафедры цветных металлов и золота, НИТУ «МИСИС».
https://orcid.org/0000-0003-2753-3424
E-mail: Helen_Bogatureva@mail.ru

Contribution of the authors

S.O. Vydysh – defined the purpose of the work, conducted experiments, wrote the article.

E.V. Bogatyreva – defined the purpose of the work, conducted experiments, wrote the article.

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