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Study of the basic laws of dissolution of gold and copper in solutions with an ultra-low concentration of sodium cyanide

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Abstract. The work sets out to study the basic physicochemical dissolution patterns of gold, copper, and natural copper-containing minerals (chalcopyrite, bornite and azurite) in solutions with an ultra-low concentration of sodium cyanide (from $0.102 \cdot 10^{-3}$ to $4.08 \cdot 10^{-3}$ mol/L). The influence of various factors on the rate of dissolution of Au and Cu in solutions with ultra-low NaCN concentrations was studied by the rotating disk method; for natural copper minerals, the powder diffraction method was used. The concentration of gold and copper in solutions was determined by atomic absorption analysis. The chemical composition of the studied copper minerals was determined using the X-ray phase method, while the specific surface of the minerals was detected using a laser granulometer. The process of gold dissolution is shown to proceed in both diffusion and kinetic regions. In the diffusion region, the rate constant was $0.334 \cdot 10^{-6}$ $L \cdot cm^{-2} \cdot s^{-1/2} \cdot rad^{-1/2}$; in the kinetic region – $0.919 \cdot 10^{-6}$ $L \cdot cm^{-2} \cdot s^{-1/2}$. The calculated value of the apparent activation energy for the diffusion region was 22.5 kJ/mol; for the kinetic region – 40.1 kJ/mol. The addition of glycine to a solution with an ultra-low concentration of sodium cyanide is shown to increase the specific dissolution rate of gold by 1.2 times: from $0.692 \cdot 10^{-9}$ to $0.82 \cdot 10^{-9}$ $mol/cm^2 \cdot s$. The process of copper dissolution is shown to take place in the diffusion region. The rate constant was $0.496 \cdot 10^{-6}$ $L \cdot cm^{-2} \cdot s^{-1/2} \cdot rad^{-1/2}$ at an activation energy of 17.0 kJ/mol. With a fractional supply of sodium cyanide, the dissolution rate of copper minerals is reduced by 10–30% compared to a single load. The calculated apparent activation energy values for chalcopyrite, bornite, and azurite were 22.03, 24.2, and 24.1 kJ/mol, respectively. Thus, the use of ultra-low concentrations of NaCN in the process of cyanidation of gold and copper has a positive effect, which can be used in the processing of gold-copper raw materials to significantly reduce the consumption of sodium cyanide.

Keywords: gold, copper, sodium cyanide, dissolution kinetics, rate constant, activation energy

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МЕТАЛЛУРГИЯ

Научная статья
УДК 532.7:66.06

Изучение основных закономерностей растворения золота и меди в растворах с ультранизкой концентрацией цианида натрия

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Резюме. Цель – изучение основных физико-химических закономерностей растворения золота, меди и природных медьсодержащих минералов (халькопирит, борнит и азурит) в растворах с ультранизкой концентрацией цианида натрия (от $0,102 \cdot 10^{-3}$ до $4,08 \cdot 10^{-3}$ моль/л). Влияние различных факторов на скорость растворения Au и Cu в растворах с ультранизкой концентрацией NaCN изучали методом вращающегося диска, природных медных минералов – методом порошков. Концентрацию золота и меди в растворах определяли атомно-абсорбционным методом анализа. Химический состав исследуемых медных минералов – рентгенофазовым методом, удельную поверхность минералов выявляли с помощью лазерного гранулометра. Установлено, что процесс растворения

золота протекает в двух областях – в диффузионной и кинетической. Константа скорости в диффузионной области составила 0,334·10^{-6} л·см$^{-2}$·с$^{-1/2}$·рад$^{-1/2}$, в кинетической – 0,919·10^{-6} л·см$^{-2}$·с$^{-1/2}$. Рассчитанное значение кажущейся энергии активации для диффузионной области составило 22,5 кДж/моль, кинетической – 40,1 кДж/моль. Показано, что добавление глицина в раствор с ультранизкой концентрацией цианида натрия способствует повышению удельной скорости растворения золота в 1,2 раза: с 0,692·10^{-9} до 0,82·10^{-9} моль/см^{2}·с. Установлено, что процесс растворения меди протекает в диффузионной области. Константа скорости составила 0,496·10^{-6} л·см$^{-2}$·с$^{-1/2}$·рад$^{-1/2}$, энергия активации – 17,0 кДж/моль. Показано, что при дробной подаче цианида натрия скорость растворения медных минералов снижается на 10–30% в сравнении с разовой загрузкой. Рассчитанные значения кажущейся энергии активации составили для халькопирита, борнита и азурита, соответственно, кДж/моль: 22,03, 24,2 и 24,1. Таким образом, применение ультранизких концентраций NaCN в процессе цианирования золота и меди дает положительный эффект, что может быть использовано при переработке золотомедного сырья, и, как следствие, позволит существенно снизить расход цианистого натрия.

Ключевые слова: золото, медь, цианид натрия, кинетика растворения, константа скорости, энергия активации

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INTRODUCTION

Currently, the search for rational ways to extract valuable components from man-made raw materials, which include such items as roasted pyrite and enrichment tailings obtained during the processing of [1] polymetallic ores, has become rather urgent.

Among the various methods for extracting valuable components from man-made raw materials, cyanidation represents one of the most effective approaches. However, the formation of copper cyanide complexes as a result of leaching during gold extraction results in a high consumption of sodium cyanide and correspondingly increased operating costs [1–9].

The works of Australian researchers [10–12] describe a method for extracting precious metals from gold-copper ores using a mixture of sodium cyanide and glycine as leaching agents, which offers a number of advantages compared with other amino acids due to its stability and biodegradability, resulting in increased environmental friendliness [2]. The addition of glycine (2–10 g/dm^{3}) to cyanide (0.8–1.2 g/dm^{3}) during leaching is shown to increase the extraction of precious metals by 1.5–1.8 times.

Test experiments carried out to investigate the leaching of noble metals from man-made raw materials using solutions having an ultra-low concentration of sodium cyanide with the aim of reducing the consumption of sodium cyanide in the cyanidation process (< 1.02·10^{-3} mol/dm^{3}) have demonstrated satisfactory results [13]. However, there is no information in the literature about the basic dissolution behaviours of gold and copper in solutions with low concentrations of sodium cyanide (less than 4.08·10^{-3} mol/dm^{3}).

In this regard, it seems appropriate to study the basic patterns of dissolution of gold and copper in solutions having an ultra-low concentration of sodium cyanide (0.102·10^{-3} – 4.08·10^{-3} mol/dm^{3}) using the rotating disk method, which was successfully applied by Professor I.A. Kakovsky to study the dissolution kinetics of precious metals using various reagents. This method, which provides good reproducibility of experimental results, can be used to identify factors that determine the reaction rate, on the basis of which certain practical conclusions can be drawn[4] [14, 15].

EXPERIMENTAL PROCEDURE

For the experiments, gold and copper disks with a fineness of 999.9 were used. Prior to the start of each experiment, each disk was carefully sanded, polished, washed with water and wiped with ethyl alcohol. These operations were carried out in order to prevent the disk surface from changing during the experiment, which could affect the reproducibility of the results.

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[4] Kholmanskikh Yu.V. *Dissolution kinetics of noble metals and their alloys in cyanide solutions: PhD thesis in Engineering Sciences.* Sverdlovsk; 1961. / Холманских Ю.В. Кинетика растворения благородных металлов и их сплавов в цианистых растворах: дис. … канд. техн. наук: Свердловск, 1961.

At the beginning and end of each experiment, the pH and concentration of dissolved oxygen in the solution were measured according to the potentiometric method. The oxidiser of gold was atmospheric oxygen, whose concentration in the solution was in the range of 8.3–7.9 mg/dm^3 and practically did not change throughout all the experiments.

The amount of dissolved metal, determined by sampling and analysing solution samples, was calculated by the formula [14]:

$$Q = \frac{C_{Me} \cdot V}{A_{Me} \cdot 1000 \cdot S}, \tag{1}$$

where C_{Me} – concentration of the metal in solution (mol/L); V – volume of the solution (L); A_{Me} – atomic mass of metal; S – disk surface area (cm^2); Q – amount of dissolved metal (mol/cm^2).

The amount of metal in the samples selected for analysis and the change in the total volume of the solution were taken into account. The concentration of metal in solutions was determined by atomic absorption analysis.

The dissolution rate was calculated according to the formula [14]:

$$v = \frac{Q}{\tau}, \tag{2}$$

where v – rate of metal dissolution (mol/cm$^2 \cdot$ s); S – disk surface area (cm^2); τ – duration of dissolution (s).

To eliminate errors, the experimental data were processed using the least squares method, allowing the average value of the rate to be obtained from several data points. The error in determining the gold dissolution rate was 4% with a probability of 96%.

STUDY OF THE GOLD DISSOLUTION RATE IN SOLUTIONS WITH AN ULTRA-LOW CONCENTRATION OF SODIUM CYANIDE

Dependence of the gold dissolution rate on the disk rotation frequency. To determine the nature of the gold dissolution process at ultra-low concentrations of sodium cyanide, the dependence of the gold dissolution rate on the disk rotation frequency (n) in the range from 4.19 to 41.87 rad/s was studied. The selection of the specified range of mixing speeds was carried out taking into account that the value of the Reynolds number (Re) should be within $10^1 \div 10^4$ (when Re < 10^1 – edge effects; when Re > 10^4 – turbulent mode) [15–20]. The Reynolds number was calculated using the formula:

$$Re = \frac{\omega \cdot R^2}{\upsilon}, \tag{3}$$

where ω is the angular velocity of rotation of the disk (rad/s); υ – kinematic viscosity of the liquid (cm^2/s); R is the radius of the disk (cm).

For a disk having a radius of 1.5 cm in the selected rotation frequency interval, the value of the Reynolds number was in the range from 942.75 to 9420.75. Within this range, conditions of the laminar flow regime of the disk surface area are observed.

The experiments were carried out under the following constant conditions: temperature – 25°C; pH – 11.0; NaCN concentration – $0.612 \cdot 10^{-3}$ mol/dm^3. The resulting graph of the dependence of the rate of dissolution of gold on the number of revolutions of the disk is shown in Fig. 1.

Graphical data show that, with an increase in the speed of rotation of the disk, the rate of dissolution of gold increases only up to a certain limit – 15.7 rad/s (150 rpm). At the same time, the dissolution rate increases from $3.22 \cdot 10^{-10}$ to $5.43 \cdot 10^{-10}$ mol/cm^{2}s and further does not depend on the mixing intensity, since the dissolution process passes from the diffusion region to the kinetic [15]. That is, when the disk rotation speed is up to 15.7 rad/s, the limiting stage of this process is the supply of reagents to the disk surface or the removal of the resulting reaction products. Further, the rate of dissolution of gold no longer depends on the intensity of mixing, but is determined by the rate of the chemical reaction.

Thus, when studying the influence of various factors on the rate of dissolution of gold, it is necessary to pay special attention to the intensity of mixing of the solution (the number of revolutions of the disk). Therefore, the influence of various factors on the rate of gold dissolution was studied in two areas: in diffusion – at 4.19 rad/s; and kinetic – at 31.4 rad/s.

Dependence of the gold dissolution rate on the concentration of sodium cyanide. Further studies into the effect of sodium cyanide concentration on the rate of gold dissolution in the diffusion and kinetic regions were undertaken.

The experiments were carried out at a concentration of NaCN from $0.102 \cdot 10^{-3}$ to $4.08 \cdot 10^{-3}$ mol/ dm^3 (from 5 to 200 mg/dm^3); pH – 11.0; number of disk revolutions – 4.19 rad/s for diffusion mode and 31.4 rad/s for kinetic; temperature – 25°C. The results of the experiments are shown in Fig. 2.

Fig. 2 shows that the rate of gold dissolution in the diffusion region increases from $0.66 \cdot 10^{-10}$ to $8.85 \cdot 10^{-10}$ mol/$cm^2 \cdot s$ with an increase in the concentration of sodium cyanide from $0.102 \cdot 10^{-3}$ to $4.08 \cdot 10^{-3}$ mol/dm^3. However, after $0.41 \cdot 10^{-3}$ mol/dm^3, the rate growth slows down; this may be due to the formation of a film on the disk surface, whose thickness depends on the cyanide concentration, mixing intensity, temperature and duration of dissolution [15–17].

In the kinetic region, in the range of sodium cyanide concentrations from $0.10 \cdot 10^{-3}$ to $2.04 \cdot 10^{-3}$ mol/dm^3, a linear relationship is observed between the gold dissolution rate and the concentration of the complexing agent. The dissolution rate of the noble metal increases from $0.94 \cdot 10^{-10}$ to $16.5 \cdot 10^{-10}$ mol/$cm^2 \cdot s$.

The process of gold dissolution takes place in the pre-limit region, in which the dissolution rate is proportional to the sodium cyanide concentration.

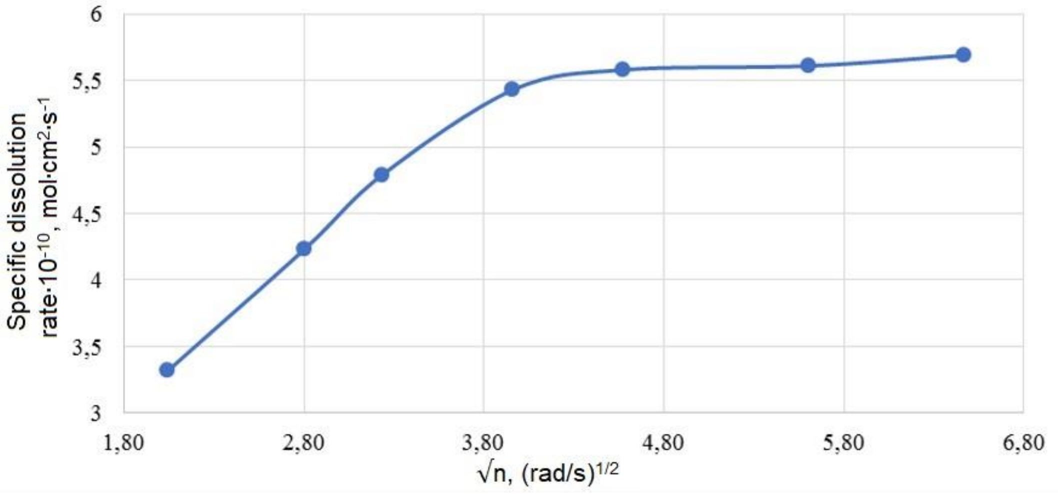

Fig. 1. Gold dissolution rate vs disc angular rotation rate
Рис. 1. Зависимость скорости растворения золота от угловой скорости вращения диска

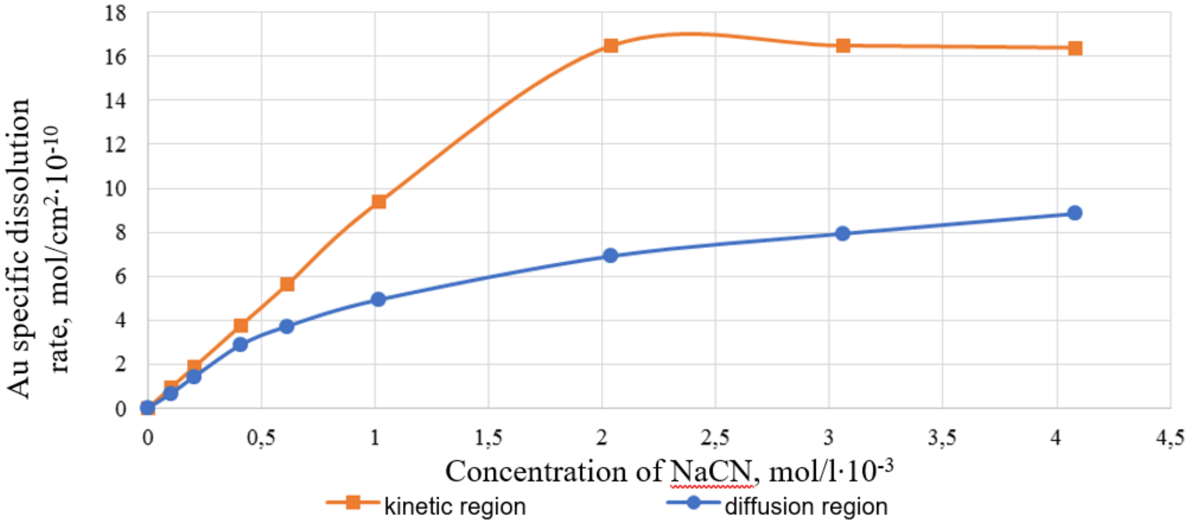

Fig. 2. Gold dissolution rate vs sodium cyanide concentration
Рис. 2. Зависимость скорости растворения золота от концентрации цианида натрия

The dissolution rate constant of gold in the diffusion region is calculated by the formula:

$$К = \frac{v}{C\cdot\sqrt{n}}, \qquad (4)$$

where K – reaction rate constant (L·cm^{-2}· s$^{-1/2}$· rad$^{-1/2}$); v – dissolution rate of gold (mole·cm^{-2}·s^{-1}); C – concentration of sodium cyanide (mol/L); n – number of revolutions of the disk (rad/s), comprising 0.334·10^{-6} dm^{3}· cm^{-2}· s$^{-1/2}$· rad$^{-1/2}$.

The dissolution rate constant of gold in the kinetic region is calculated by the formula:

$$K = \frac{v}{C}, \qquad (5)$$

where K – reaction rate constant (L·cm^{-2}·s-$^{1/2}$); υ – dissolution rate of gold (mole·cm^{-2}·s^{-1}); C – concentration of sodium cyanide (mol/L); comprising 0.919 ·10^{-6} dm^{3}·cm^{-2}·s$^{-1/2}$.

The theoretical velocity constant was calculated from the flow equation:

$$j = \frac{10^{-3}\cdot Д^{2/3}\cdot S\cdot C\cdot \omega^{1/2}\cdot t}{0.89\sqrt[3]{6}\cdot v^{1/6}}, \qquad (6)$$

where D – diffusion coefficient of sodium cyanide (cm^{2}/s); ω – angular velocity (rad/s); v – viscosity of the solution (cm^{2}/s); S – disk surface area (cm^{2}); C – concentration of the solvent (mol/L).

The theoretical velocity constant value was 0.428·10^{-6} dm^{3}· cm^{-2}· s$^{-1/2}$· rad$^{-1/2,}$ which is 78% of the calculated experimental value (0.334·10^{-6} dm^{3}· cm^{-2}· s$^{-1/2}$· rad$^{-1/2}$). According to the literature data, this is explained by the formation of a film on the surface of the dissolving metal, most likely gold hydroxide, which should be considered as an additional intradiffusion resistance [16, 18].

Dependence of the gold dissolution rate on temperature. The effect of temperature on the rate of dissolution of gold in cyanide solution was studied in the range of 288–308 K. Two series of experiments were conducted. One was carried out in diffusion mode with a disk speed of 4.19 rad/s, while the other was carried out at a speed of 31.4 rad/s. NaCN concentration – 0.612·10^{-3} mol/dm, pH – 11.0.

Based on the obtained experimental data, a graph was plotted in LgK-1/T coordinates in the diffusion (Fig. 3) and kinetic regions (Fig. 4).
The activation energy of the process [16] is determined from the tangent of the slope angle of the curve in accordance with the Arrhenius equation:

$$E_a = 2.303R|tg\alpha|, \qquad (7)$$

where R – gas constant (R = 8.314 J/(mol·K)).

The activation energy in the diffusion mode was 22.5 kJ/mol; in kinetic mode – 40.1 kJ/mol. The increased value of the activation energy in diffusion mode confirms the fact of the formation of a film on the surface of the disk.

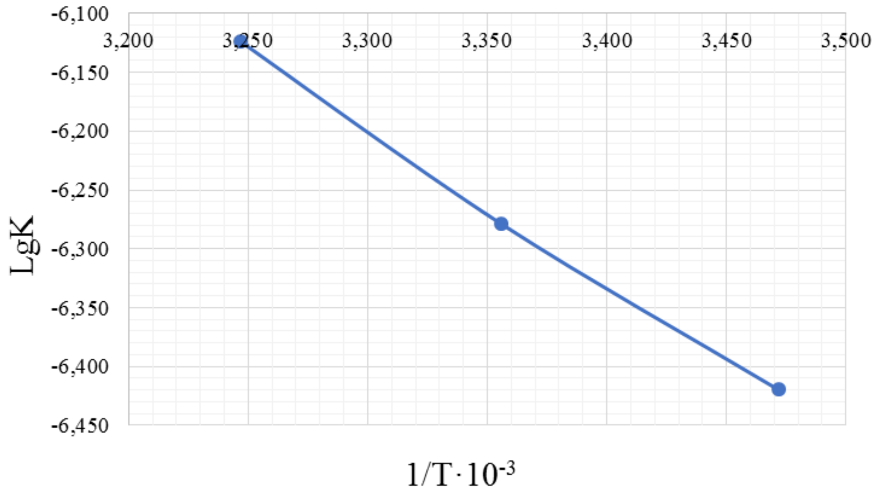

Fig. 3. Gold dissolution rate vs temperature in the diffusion mode
Рис. 3. Зависимость скорости растворения золота от температуры в диффузионном режиме

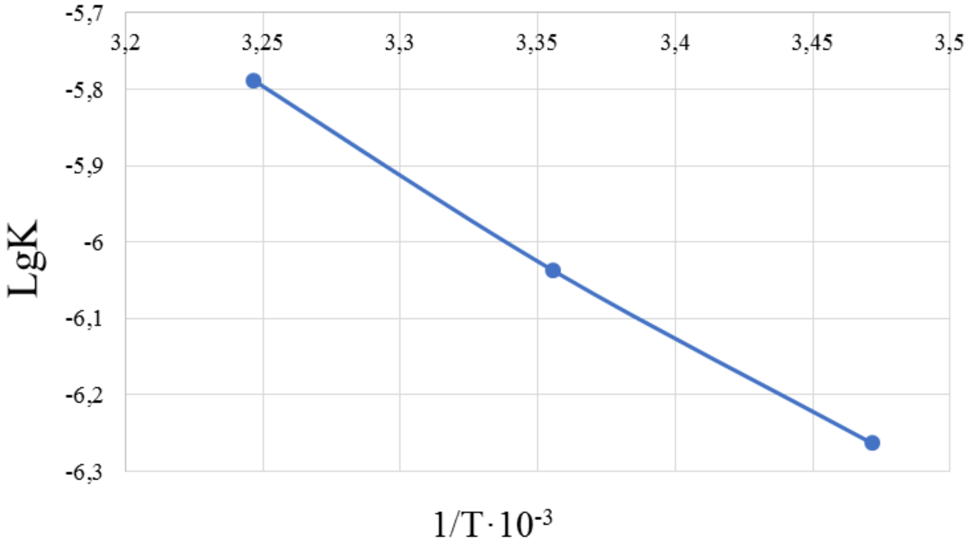

Fig. 4. Gold dissolution rate vs temperature in the kinetic mode
Рис. 4. Зависимость скорости растворения золота от температуры в кинетическом режиме

The obtained results indicate that the process of gold dissolution in a cyanide solution at an ultra-low NaCN concentration proceeds in the diffusion and kinetic regions; this is confirmed by the results of experiments on the dependence of the gold dissolution rate on the intensity of mixing.

Effect of glycine addition on the rate of gold dissolution. To determine the effect of the addition of glycine to a solution with an ultra-low concentration of sodium cyanide on the rate of dissolution of gold, an experiment was conducted under the following conditions: pH = 11.0; angular velocity of rotation of the disk – 4.19 rad/s; t = 25°C; concentration of sodium cyanide – $2.04 \cdot 10^{-3}$ mol/dm^3; glycine concentration – $0.27 \cdot 10^{-3}$ mol/dm^3. The results are shown in Fig. 5.

As follows from the data presented in Fig. 5, the addition of glycine to sodium cyanide increases the specific dissolution rate of gold from $0.692 \cdot 10^{-9}$ to $0.82 \cdot 10^{-9}$ mol /cm^{2}s (i.e., by 1.2 times).

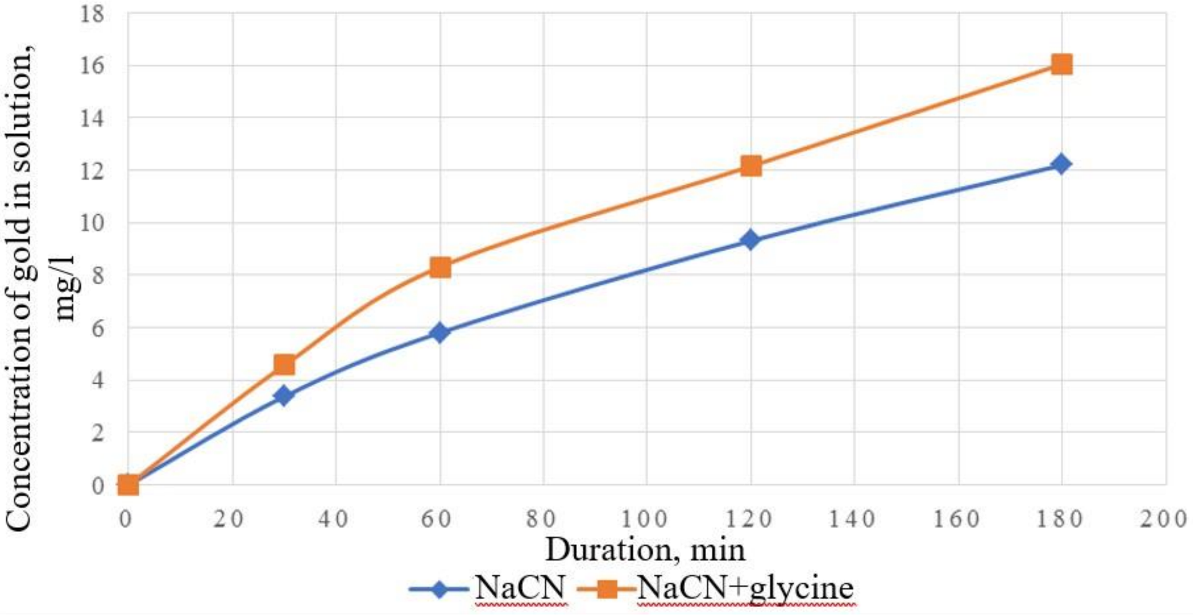

Fig. 5. Kinetics of gold dissolution by ultra-low NaCN concentration solutions in glycine presence
Рис. 5. Кинетика растворения золота растворами с ультранизкой концентрацией NaCN в присутствии глицина

STUDY OF THE COPPER DISSOLUTION RATE IN SOLUTIONS WITH AN ULTRA-LOW CONCENTRATION OF SODIUM CYANIDE

The high consumption of sodium cyanide during gold leaching is explained by the additional presence of non-ferrous metals in technogenic raw materials, primarily copper. Therefore, to evaluate the behaviour of copper [21] at ultra-low concentrations of sodium cyanide, experiments were conducted to study the rate of its dissolution using the rotating disk method.

Dependence of the rate of dissolution of copper on the speed of rotation of the disk. The dependence of the copper dissolution rate on the disk rotation frequency was initially studied in the range from 4.19 to 52.33 rad/s. With a disk radius of 0.62 cm, the selected rotation frequency interval corresponds to a Reynolds number value varying from 163.4 to 5632.6 [16].

The experiments were carried out under the following constant conditions: temperature – 25°C; pH – 11.0; NaCN concentration – $0.612 \cdot 10^{-3}$ mol/dm. The resulting graph of the dependence of the rate of dissolution of copper on the number of revolutions of the disk is shown in Fig. 6.

From the presented data, it can be seen that the rate of dissolution of copper increases in proportion to the square root of the number of revolutions from $6.2 \cdot 10^{-10}$ to $38.0 \cdot 10^{-10}$ $mol \cdot cm^{-2} s^{-1}$ in the range of disk rotation speeds from 4.19 to 146.53 rad/s (from 40 to 1400 rpm). Thus, in the studied interval of the disk rotation frequency, the process of copper dissolution proceeds in the diffusion region.

Dependence of the copper dissolution rate on the concentration of sodium cyanide. Experiments to determine the dependence of the dissolution rate of copper on the concentration of sodium cyanide (Fig. 7) were carried out using the following parameters: angular velocity – 4.19 rad/s; pH – 11.0; t – 25°C; sodium cyanide concentration – from $0.612 \cdot 10^{-3}$ to $3.061 \cdot 10^{-3}$ mol/dm^3 (from 30 to 150 mg/dm^3).

From the presented graph, the dissolution rate of copper can be seen to increase to $22.7 \cdot 10^{-10}$ $mol/cm^{2} \cdot s$; moreover, this dependence is linear to the concentration of NaCN – $2.04 \cdot 10^{-3}$ mol/dm^3 (up to 100 mg/dm) – that is, the reaction has a cyanide first order. Further, the dissolution process has slowed down due to the formation of a film on the surface of the copper disk, consisting of copper cyanide (CuCN) [18].

The calculated value of the copper dissolution rate constant was $0.496 \cdot 10^{-6}$ $dm^3 \cdot cm^{-2} \cdot s^{-1/2} \cdot rad^{-1/2}$.

An assumption about the density of the product shell can be made according to the value of the Pilling–Bedworth criterion – the ratio of the molar volumes of the reaction product and the starting substance:

$$K_{П-Б} = \nu \frac{\frac{M_{prod}}{d_{prod}}}{\frac{M_{start}}{d_{start}}}, \qquad (8)$$

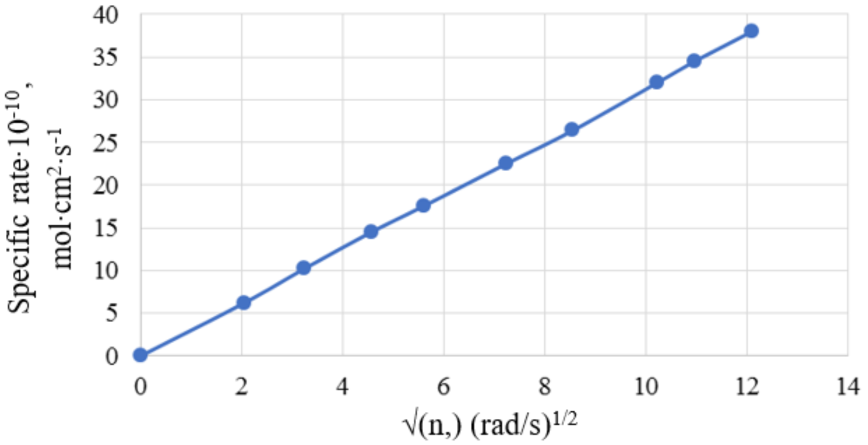

Fig. 6. Copper dissolution rate vs disc angular rotation rate
Рис. 6. Зависимость скорости растворения меди от угловой скорости вращения диска

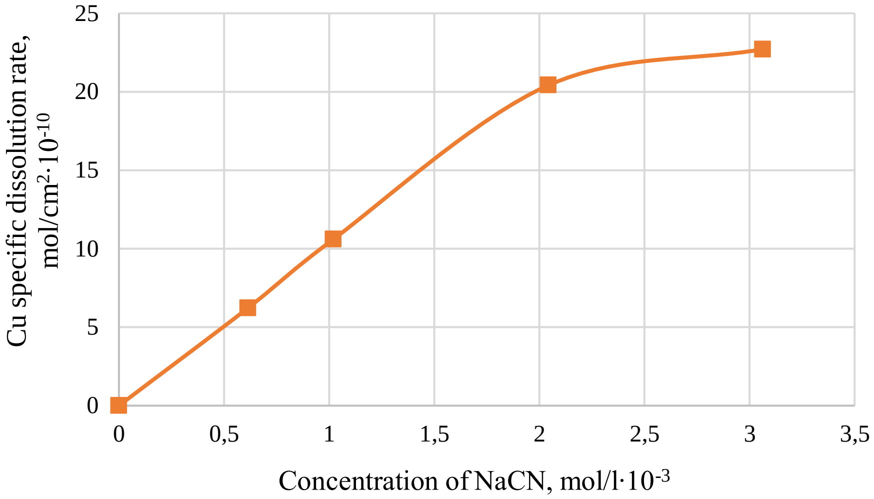

Fig. 7. Copper dissolution rate vs NaCN concentration
Рис. 7. Зависимость скорости растворения меди от концентрации NaCN

where ν – number of moles of solid product formed from 1 mole of the initial substance; M_{prod} and M_{start} – molecular weights of the product and the initial substance, respectively; d_{prod} and d_{start} are the densities of the product and the initial substance.

The ratio of molar volumes of copper and copper cyanide was 4.3, indicating the formation of a dense film[5].

Dependence of copper dissolution rate on temperature. The effect of temperature on the copper dissolution rate was studied in a temperature range from 288 to 308 K, a disk rotation speed of 4.19 rad/s, and a sodium cyanide concentration of $0.612 \cdot 10^{-3}$ mol/dm³. Based on the obtained experimental data, a graph was plotted in the LgK-1/T coordinates (Fig. 8).

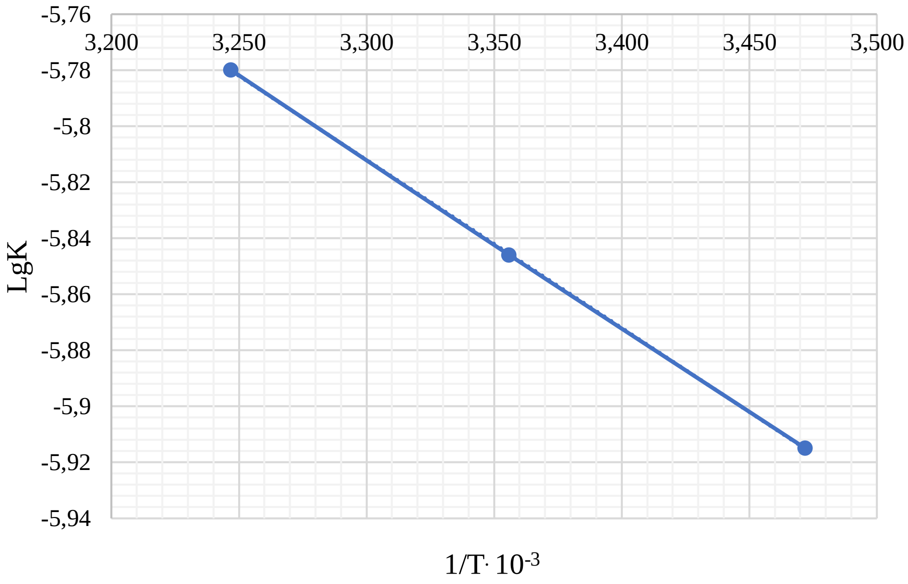

Fig. 8. Copper dissolution rate vs temperature
Рис. 8. Зависимость скорости растворения меди от температуры

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[5] Zelikman A.N., Vol'dman G.M., Belyavskaya L.V. *Theory of hydrometallurgical processes*. Moscow: Metallurgiya; 1975, 504 p. / Зеликман А.Н., Вольдман Г.М., Белявская Л.В. Теория гидрометаллургических процессов. М.: Металлургия, 1975. 504 с.

The activation energy of the process was 17.0 kJ/mol, which confirms the process occurring in the diffusion region.

Table 1 presents the main kinetic characteristics of the dissolution of gold and copper obtained as a result of experiments in comparison with the data obtained by I.A. Kakovsky and Yu.B. Kholmanskikh, who studied the process of dissolution of these metals in cyanide solutions with a sodium cyanide concentration of 200 mg/dm^3 (4.08·10^{-3} mol/dm^3) [9].

Based on the comparison of the obtained characteristics of the process of dissolution of gold and copper, it can be concluded that the process of cyanidation of gold and copper is effective at ultra-low solvent concentrations. The faster rate of the process taking place in the kinetic region at ultra-low concentrations of sodium cyanide is possibly due to the absence of diffusion complications (films).

RESULTS OF EXPERIMENTS ON THE DISSOLUTION OF COPPER MINERALS IN SOLUTIONS WITH A LOW CONCENTRATION OF SODIUM CYANIDE

Due to the fact that the presence of copper in man-made raw materials takes the form of natural minerals [22], experiments were conducted to assess the dissolution rate of such natural minerals as bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$) and azurite ($2CuCO_3{\cdot}Cu(OH)_2$) in solutions with a low concentration of sodium cyanide. The results of X-ray phase analysis of minerals are presented in Table 2.

According to Table 2, the copper content in chalcopyrite is 31.1%; in bornite – 35.5%; in azurite – 21.6%. The content of iron and sulfur in chalcopyrite is 13.3% and 10.88%, respectively; in bornite – 28.6% and 30.6%; in azurite – 6.25% and 0.088%.

The experiments were carried out on test sample powders having a particle size of minus 0.1 plus 0.074 mm with mechanical stirring under the following conditions: weighed weight – 250 mg; solution volume – 200 cm^3; temperature – 25°C; duration – 1 h; NaOH concentration – 0.002 mol/dm^3 (pH 11.0); NaCN concentration 0.41·10^{-3} – 2.04·10^{-3} mol/dm^3.

Following the end of each test, the concentration of copper in the solution was determined by atomic absorption analysis; the specific surface area of the mineral was determined using a Malvern Mastersizer 3000 laser granulometer.

Fig. 9 shows the dependence of the specific dissolution rate of natural copper minerals on the concentration of sodium cyanide.

From the data presented, it can be seen that the specific dissolution rate of copper sulfide minerals, such as chalcopyrite and bornite, increases to a certain limit (for chalcopyrite 8.84·10^{-8} mol/cm^2·s; for bornite – 10.48·10^{-8} mol/cm^2·s); the fact that no further increase in the concentration of sodium cyanide (>1.02·10^{-3} mol/dm^3) leads to a significant increase in the dissolution rate is explained by the formation of a film of simple copper cyanide on the surface of minerals.

Table 1. Main kinetic characteristics of metal dissolution in cyanide solutions
Таблица 1. Основные кинетические характеристики растворения металлов в цианистых растворах

Source of information	**Diffusion regime**				**Kinetic regime**	
	Gold		Copper		Gold	
	Rate constant dm^3·cm^{-2}·s$^{-1/2}$·rad$^{-1/2}$	Activation energy, kJ/mol	Rate constant dm^3·cm^{-2}·s$^{-1/2}$·rad$^{-1/2}$	Activation energy, kJ/mol	Rate constant dm^3·cm^{-2}·s$^{-1/2}$·rad$^{-1/2}$	Activation energy, kJ/mol
This paper	0.334·10^{-6}	22.5	0.496·10^{-6}	17.0	0.919·10^{-6}	40.1
[14]	0.332·10^{-6}	14.56	0.414·10^{-6}	13.4	0.51·10^{-6}	59.1
[15]	0.332·10^{-6}	14.6	0.410·10^{-6}	13.2	0.55·10^{-6}	59.0

Table 2. Chemical composition of natural copper minerals
Таблица 2. Химический состав природных минералов меди

Mineral	**Element content, %**							
	Cu	Fe	S	Al	SiO_2	$C_{общ}$	Ca	Na
Chalcopyrite	31.1	13.3	10.85	n/d*	n/d*	n/d*	n/d*	n/d*
Bornite	35.5	28.6	30.6	n/d*	n/d*	n/d*	n/d*	n/d*
Azurite	21.6	6.25	0.088	4.19	32.6	0.88	0.414	0.40

*n/d – not determined.

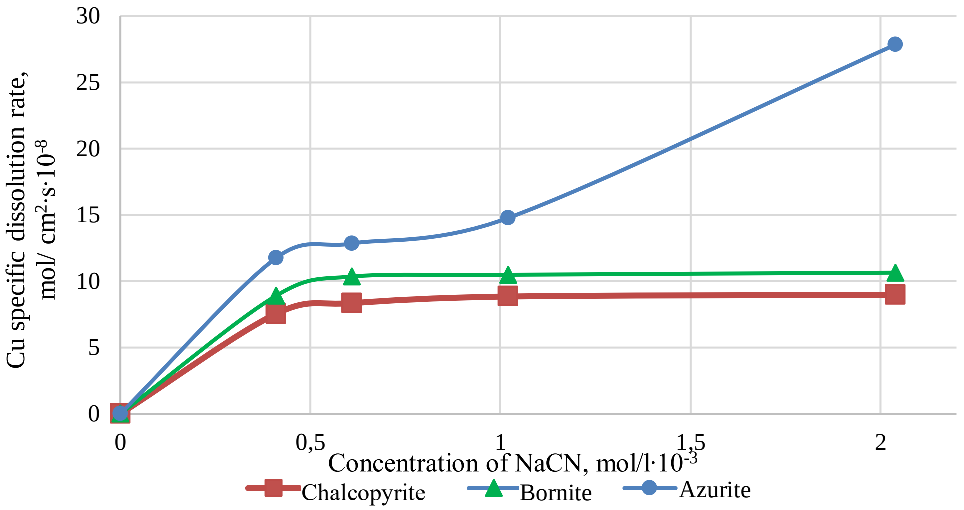

Fig. 9. Copper natural mineral dissolution rate vs sodium cyanide concentration
Рис. 9. Зависимость степени растворения природных минералов меди от концентрации цианида натрия

The specific dissolution rate of the oxidised copper mineral (azurite) increases to $27.84 \cdot 10^{-8}$ mol/cm^2·s with an increase in the concentration of sodium cyanide to $2.04 \cdot 10^{-3}$ mol/dm^3; however, in the range of concentrations from $0.41 \cdot 10^{-3}$ mol/dm^3 to $1.02 \cdot 10^{-3}$ mol/dm^3, this increase is less pronounced.

A patent describing a method of extracting gold from a copper-containing mineral raw material by cyanidation under stirring is based on the fractional supply of a diluted solution of sodium cyanide in the process [20]. The authors note that the positive effect in this case is achieved due to a slowdown in chemical reactions of non-targeted consumption of sodium cyanide.

For this reason, it seemed appropriate to study the effect of the method of feeding sodium cyanide into the cyanidation process on the dissolution rate of copper.

Test conditions were as follows: weighed amount – 250 mg; solution volume – 200 cm^3; temperature – 25°C; duration – 1 h; NaOH concentration – 0.002 mol/dm^3 (pH 11.0); NaCN concentration $0.41 \cdot 10^{-3}$ – $0.61 \cdot 10^{-3}$ mol/dm^3 (20–30 mg/dm^3).

In the first case, NaCN was loaded at 100% of the target concentration at the beginning of the experiment (single load); in the second case, 50% (at a concentration of 20 mg/dm^3) and 33.3% at a concentration (30 mg/dm^3) every 20 minutes from the beginning of the experiment. The results of the experiments are presented in Figs. 10–12.

The obtained data confirm that the method of feeding sodium cyanide into the cyanidation process influences the specific dissolution rate of copper. With a fractional supply of NaCN, the dissolution rate of copper minerals is reduced by 10–30% as compared to a single load.

The calculated activation energy values were 22.03 kJ/mol, 24.2 kJ/mol, and 24.1 kJ/mol for chalcopyrite, bornite and azurite, respectively, which corresponds to the conditions of the process in the intra-diffusion region. The high activation energy values confirm the formation of a film of copper cyanide on the surface of minerals.

CONCLUSION

The basic patterns of dissolution of gold and copper in solutions with an ultra-low concentration of sodium cyanide were studied using the rotating disk method. The obtained results demonstrated the effectiveness of ultra-low concentrations of sodium cyanide: the dissolution rate constant of gold in the diffusion region was $0.334 \cdot 10^{-6}$ dm^3· cm^{-2}· c$^{-1/2}$· rad$^{-1/2}$; in the kinetic region – $0.919 \cdot 10^{-6}$ dm^3· cm^{-2}· c$^{-1/2}$. The copper dissolution rate constant in the diffusion region was $0.414 \cdot 10^{-6}$ dm^3· cm^{-2}· c$^{-1/2}$· rad$^{-1/2}$. The presence of glycine in a solution with an ultra-low concentration of sodium cyanide allowed the specific dissolution rate of gold to be increased from $0.692 \cdot 10^{-9}$ to $0.82 \cdot 10^{-9}$ mol/cm^{2}s (i.e., by 1.2 times).

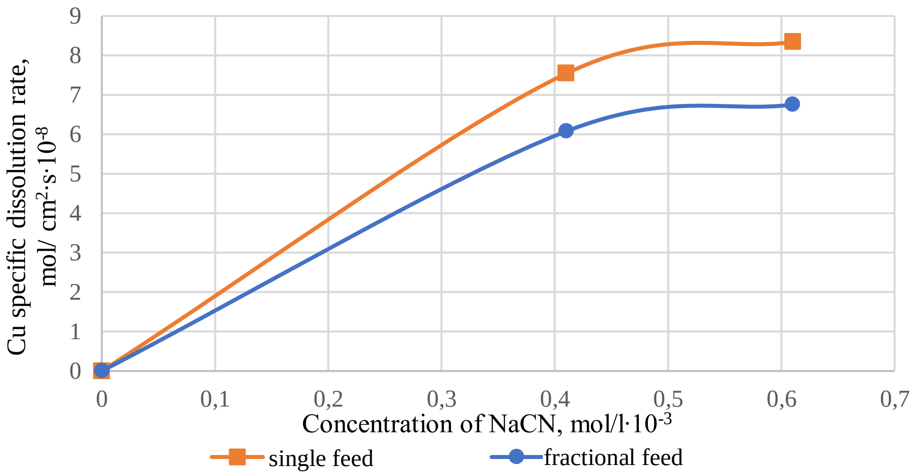

Fig. 10. Chalcopyrite specific dissolution rate vs NaCN addition method
Рис. 10. Зависимость удельной скорости растворения халькопирита от способа подачи NaCN

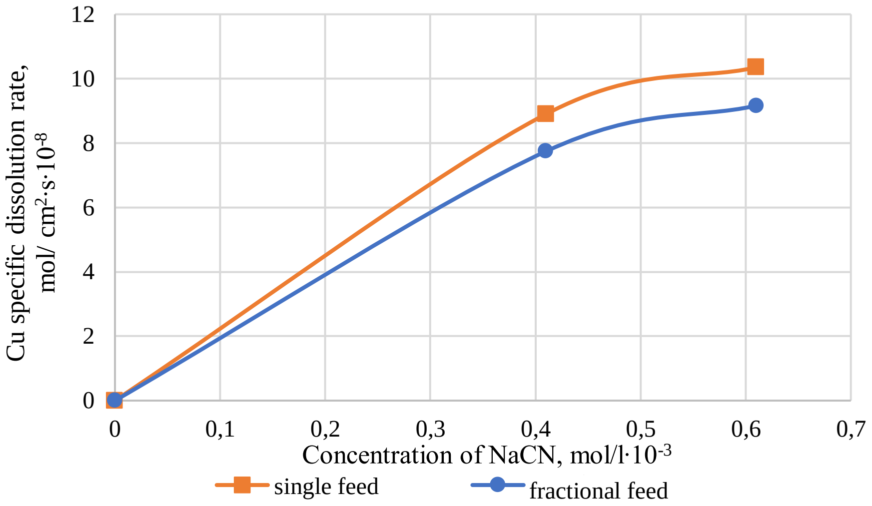

Fig. 11. Bornite specific dissolution rate vs NaCN addition method
Рис. 11. Зависимость удельной скорости растворения борнита от способа подачи NaCN

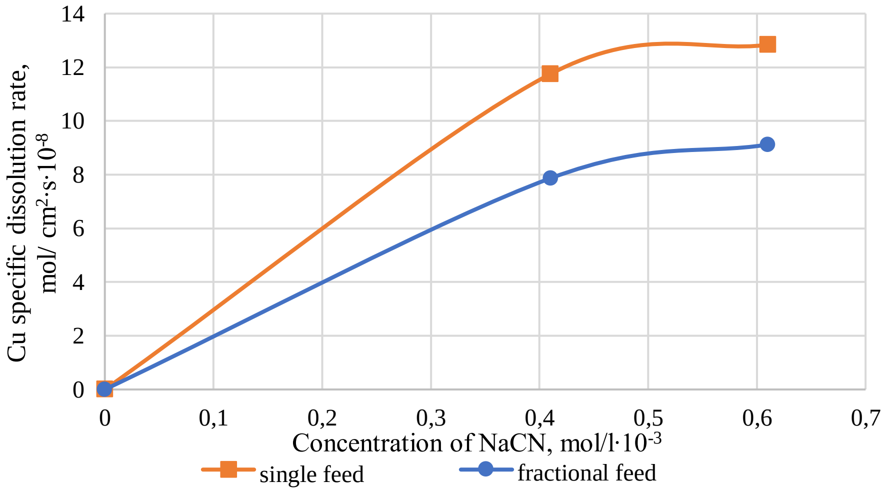

Fig. 12. Azurite specific dissolution rate vs NaCN addition method
Рис. 12. Зависимость удельной скорости растворения азурита от способа подачи NaCN

The influence of various factors on the dissolution rate of natural copper minerals in solutions with an ultra-low concentration of sodium cyanide using the powder method was also studied. It is noted that a fractional supply of sodium cyanide in the cyanidation process reduces the dissolution rate of copper by 10–30% as compared to a single loading, which is a positive effect when cyanidating gold-copper raw materials.

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Conflict of interests

The authors declare no conflicts of interests.

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