***How to Cite:*** Shlyapov, R.M., Amerkhanova, Sh.K., Uali, A.S., Omarbekov, T.B., & Belgibayeva, D.S. (2022). Thermodynamics of chalcocite dissolving in solutions of flotation reagents. *Bulletin of the University of Karaganda – Chemistry, 105(1), 122-132.* https://doi.org/10.31489/2022Ch1/122-132

---

*Article*

UDC 543.42+519.242.7:351.823 https://doi.org/10.31489/2022Ch1/122-132

R.M. Shlyapov[1], Sh.K. Amerkhanova[1], A.S. Uali[1], T.B. Omarbekov[2], D.S. Belgibayeva[1]

[1]*L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan;*
[2]*Autonomous Cluster Fund "Park of Innovative Technologies", Almaty, Kazakhstan*
*(*Corresponding author's e-mail: rustamshlyapow@gmail.com)*

# Thermodynamics of chalcocite dissolving in solutions of flotation reagents

This work describes the formation of the ionic composition of the sorption layer during the concentration of copper-lead and pyrite-copper-zinc ore. The thermodynamics of the sorption layer of a sulfhydryl collector (sodium diisobutyl thiophosphate and potassium butyl xanthate) on the surface of chalcocite under various conditions of its oxidation has been studied using pH- and redoxometry. The nature of the change in the chalcocite electrode potential depending on the type of modifier and storage device, as well as on pH, has been experimentally clarified. The differences in the collective action of a one-component accumulator and a mixture of flotation reagents were revealed based on the thermodynamics analysis of the flotation process reactions. In addition, the optimal conditions for the flotation were determined. It was found that the quality of the concentrate is mainly influenced by two factors, such as the pulp redox potential and the pH of the medium. Mathematical equations of the optimal reagent and hydrodynamic enrichment regimes with the maximum dissolution of ore minerals in solutions of flotation reagents were modeled.

*Keywords*: flotation, hydrophobicity, sorption layer of collector, the ionic composition of the pulp in a liquid phase, flotation reagents, sulfide minerals.

## *Introduction*

Modernized technologies of the enrichment of ores from new deposits should ensure the production of high-quality products from raw materials of medium and low quality [1–3]. However, most of the resources of ore raw materials in the Republic of Kazakhstan (pyrite-copper-zinc, copper, copper-lead, iron-manganese) are at a great depth and scattered over a large area. In this regard, the intensification of enrichment processes based on an integrated approach, which uses various enrichment methods in one technological scheme and reagent compositions selective for a specific mineral, takes on high relevance [4–6].

Improving polymetallic ores in production is predicated on examining economically profitable and environmentally friendly flotation reagents from a scientific research perspective, providing the necessary enrichment indicators [7–10].

The selection of flotation reagents for ore beneficiation is acquired from the ability of adsorption complexes on the surfaces of minerals. The sorption capacity is determined by the strength of the complex, poorly soluble compounds of metal ions that make up the crystal lattices. In this regard, the literature analysis of sorption processes on the surface of ore minerals is currently considered relevant and forward-looking to select cost-effective storage devices [11–16].

Along with the above, general criteria of selection of collector compositions capable of directional action on the surface of ore material are the quantitative indices of absolute stiffness and electronegativity, according to the theory of HSAB and Pearson principle, the affinity of individual collectors or their mixtures for cations of heavy metals in solution, based on the recovery of valuable components in concentrate [17].

The evaluation sources of physicochemical characteristics of dissolution of sulfide ores and minerals included in their composition have also been analyzed. It was shown that the processes of dissolution of sulfide minerals ($CuFeS_2$) are significantly intensified in the presence of catalysts (Ag). The dissolution mechanism is entirely determined by the semiconductor properties of chalcopyrite, namely, the electronic conductivity [18]. The solubility of minerals increases in the presence of potent oxidizing agents in an acidic medium. In particular, the dissolving ability of an electrolyte containing $H_2SO_4$ and $Fe^{3+}$ has been studied. Moreover, the presence of $Fe^{3+}$ ions plays a key role.

On the other hand, the possibility of dissolution of copper sulfides in solutions of complexing agents is traced [19]. At the same time, the results of elemental and phase analyses of leaching products were used to establish the dissolution mechanism. The complete theoretical description of the mineral dissolution process is given in [20]. In the example of a waste rock mineral (serpentine), using the DLFO theory, a relationship was established between the intensive dissolution of serpentine and a decrease in brucite extraction. However, more attention is paid to the practical side of the issue. The relationship of the physicochemical characteristics of minerals in the dissolution process with the extraction efficiency of valuable components is poorly expressed.

## *Experimental*

Flotation experiments were carried out on an FML-1 laboratory flotation machine with a chamber volume of 0.5 l according to the following procedure: a sample of ore (size 0.074 mm, weight 10 g) is loaded into the flotation cell and mixed with water.

Potentiometric measurements were performed using an ion-selective chalcogenide ($Cu_2S$) electrode based on the pH meter-ionomer (I-500). A chlorinated ESL-1M electrode was used as an electrode for comparison. The solutions were stirred using a magnetic stirrer.

During the experiment, tannin solutions with a concentration of $10^{-4}$ mol/l, potassium bichromate ($K_2Cr_2O_7$) $10^{-2}$ mol/l, hydrogen peroxide ($H_2O_2$) $10^{-2}$ mol/l were used. To maintain the required pH level, solutions of sodium hydroxide (NaOH) and sulfuric acid ($H_2SO_4$) were used in the concentration range from $10^{-2}$–$10^{-6}$ mol/l. A mixture of $(C_4H_9O)_2PSSNa$ (main substance is sodium diisobutyl dithiophosphate (w((i-$C_4H_9O)_2PS_2Na$)= 65 %)) with butyl, potassium xanthogenate was used as a floater agent. All measurements were made in the temperature range 298–318 K. The electrode stationary potential was fixed within 30 minutes.

The values of activation energy, activation enthalpy, and activation entropy of chalcocite dissolution were calculated using the Arrhenius equation and the transition state equation [21]:

$$\lg W = \lg A - \frac{E_a}{2.303RT} \tag{1}$$

$$\Delta S^{\#} = R \ln A - \ln \frac{k}{Th} - 1 \tag{2}$$

$$\Delta H^{\#} = E_a - 2RT \tag{3}$$

The method of the full factorial experiment was chosen for optimal control. This method involves the use of 4 factors 3 level matrices and allows obtaining generalized regression equations that consider the influence of all factors [22]. The calculation and evaluation of the results of flotation studies were carried out by the statistical options of the Excel application.

X-ray phase analysis of ore samples was carried out on an X-ray diffractometer (XRD-7000 Shimadzu, Shimadzu, Japan). The valuable part of copper-lead ore is represented mainly by chalcocite, pyrite, galena, and cuprite. Gangue is silica, aluminosilicates, calcium carbonates. Elemental analysis of the initial ores was carried out on the ore grade instrument (Spektrolab, SPECTRO Analytical Instruments GmbH, Germany). The study of the results showed that sulfide ore>copper-zinc ore>oxide ore>tailings (primary enrichment) are the richest in the content of Cu, Pb, Zn industrial elements.

## *Results and Discussion*

In this work, the process of collective absorption of minerals on the surface of a chalcocite electrode was studied using a mixture of potassium butyl xanthogenate and sodium diisobutyl dithiophosphate as flotation reagents, as well as potassium dichromate as an activator and sodium hydroxide as a depressor.

Considering the experimental data on the potential of a multi-component system, the values of the activation energy, entropy and enthalpy of the process were calculated using the Excel application (Table 1).

Under the data of [15], interpreting the achieved values of the activation energy specified in Table 1 indicates that the electrode potential (E{mV}) in the diffusion mode occurs on the surface of the mineral. Activation energy is diffused during the limitation period.

The negative value of the enthalpy of activation in a weakly alkaline medium has a combined structure, which leads to a decrease in the number of “active” particles. On the contrary, a change to positive values of the enthalpy of activation indicates an increase in the number of “active” particles. By the obtained values of the activation entropy, it can be assumed that compounds of variable composition in the anionic form are formed on the surface of the mineral.

Table 1

**Thermodynamic parameters of the theory of absolute speeds in the system NaOH – $K_2Cr_2O_7$ – $(i\text{-}C_4H_9O)_2PS_2Na$**

| T {K} | 298 | 303 | 308 | 313 | 318 |
|---|---|---|---|---|---|
| pH=8 | | | | | |
| $E_a$ {kJ/mol} | 43.93±0.01 | | | | |
| ΔS#{J/mol K} | -41.59±0.01 | -41.61±0.01 | -41.627±0.01 | -41.643±0.01 | -41.659±0.01 |
| ΔH# {kJ/mol} | -4.95±0.01 | -5.038±0,01 | -5.121±.0.01 | -5.205±0.01 | -5.288±0.01 |
| pH=10 | | | | | |
| $E_a$ {kJ/mol} | 45.81±0.02 | | | | |
| ΔS# {J/mol K} | 102.9±0.01 | 102.89±0.01 | 102.87±0.01 | 102.86±0.01 | 102.84±0.01 |
| ΔH#{kJ/mol} | 40.85±0.01 | 40.77±0.01 | 40.68±0.03 | 40.60±0.01 | 40.52±0.01 |
| pH=12 | | | | | |
| $E_a$ {kJ/mol} | 49.00±0.01 | | | | |
| ΔS# {J/mol K} | 122.80±0.01 | 122.78±0.01 | 122.76±0.01 | 122.75±0.01 | 122.73±0.01 |
| ΔH#{kJ/mol} | 44.05±0.01 | 43.96±0.01 | 43.88±0.01 | 43.80±0.01 | 43.71±0.01 |

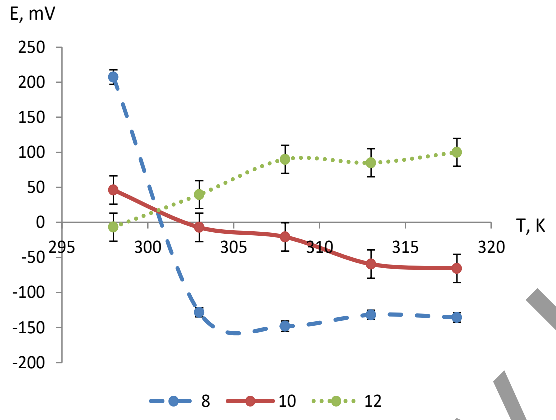

Figure 1. The investigation of the behaviour of the surface potential of the working electrode in solutions ($K_2Cr_2O_7$ – NaOH) with increasing temperature and pH

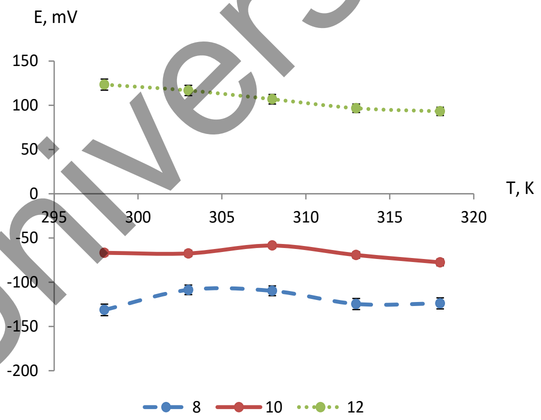

Figure 2. The behaviour of the electrode potential in the $K_2Cr_2O_7$ – NaOH – $(i\text{-}C_4H_9O)_2PS_2Na$ system in the range of temperature 298–318 K and pH 8–12

Figure 1 demonstrates that the working area of the stationary potential of the chalcosine electrode in potassium dichromate solutions (pH =8±0.3) is abruptly shifted to the electronegative region with increasing temperature. Cuprite ($Cu_2O$) formation occurs on the $Cu_2S$ surface in these solutions. The following fact is confirmed by the results of the phase diagram in [23], where the analysis of $CuFeS_2$ oxidation is described in three stages:

$$2CuFeS_2 + 15H_2O = Cu_2S + 2Fe(OH)_3 + 3SO_3^{2-} + 24H^+ + 18e^- \quad (E = -260\{mV\}) \quad (4)$$

$$Cu_2S + 4H_2O = Cu_2O + SO_3^{2-} + 8H^+ + 6e^- \quad (E = -130\{mV\}) \quad (5)$$

$$Cu_2O + 3H_2O = 2Cu(OH)_2 + 2H^+ + 2e^- \quad (E = +157\{mV\}) \quad (6)$$

The E{mV} curve in the $K_2Cr_2O_7$ – NaOH subsystem at pH = (10±0.3) is expressed by the ambiguous destabilization of the electrode potential of the chalcocite dissolution process in potassium dichromate solutions. With a stepwise increase in hydrogen concentration (pH = 12±0.3), the dependence of the electrode potential is formed on an electropositive scale. This indicates the formation of copper chromate, according to reaction (7):

$$Cu_2S + 2CrO_4^{2-} + 3H_2O = 2CuCrO_4 + SO_3^{2-} + 6H^+ + 8e^- \quad (E = +109 \div +20\{mV\}) \quad (7)$$

Analyzing the obtained low values of the electrochemical potential in the system $K_2Cr_2O_7$ – NaOH – $(i\text{-}C_4H_9O)_2PS_2Na$ (Figure 2), we suggest that copper and butyl xanthate interact at (pH = 8) with the formation of $CuC_4H_9OPSS$. In this experiment, the oxidation of chalcocite sulfide sulfur proceeds intensively due to the influence of $Cr_2O_7^{2-}$ ions. The chalcocite electrode potential dependence in an alkaline solution of potassium dichromate in the presence of a mixture of a sulfhydryl collector at pH = 12 confirms the passage of ionic flotation due to the oxidation of sulfide sulfur and dissolution of copper ions. The thermodynamic characteristics, in particular, the activation energy and enthalpy values (Table 1), agree with the above reactions.

Despite specific achievements in expanding the list of effective reagents-fillers for flotation, the domestic industry is experiencing a shortage of its products. Based on the foregoing, in this work, a set of experimental studies has been carried out to develop the subsystems using tannin ($C_{76}H_{52}O_{46}$) as a complexing reagent-collector for refractory ores flotation concentration. The experimental results of the dependence of the $Cu_2S$ potential in the $H_2O_2$-tannin-$H_2SO_4$ system are shown in Figures 3-4.

A stable complex of tannin with copper ions is formed on the surface of the mineral at pH = 4. It was found that the oxidation of sulfide sulfur of chalcocite by dichromate ions promotes the binding of copper ions with tannin (Figure 4). An increase in the pH of solutions leads to a shift in the equilibrium of the reaction. It may be due to the hydrophilization of the chalcocite surface. The calculated values of the reaction thermodynamics in $K_2Cr_2O_7$-Tannin-$H_2SO_4$ confirm the exothermicity of the process of $Cu^{2+}$ binding with tannin at pH = 4 and 318{K} (Table 2).

Table 2

**Thermodynamic factors of the system $K_2Cr_2O_7$-Tannin-$H_2SO_4$**

| T {K} | 298 | 303 | 308 | 313 | 318 |
|---|---|---|---|---|---|
| | pH=4 | | | | |
| $E_a$ {kJ/mol} | 25.3±0.01 | | | | |
| ΔS# {J/mol K} | –391.82±0.01 | –391.94±0.01 | –391.98±0.01 | –391.97±0.01 | –391.99±0.01 |
| ΔH# {kJ/mol} | –49.55±0.01 | –50.38±0.01 | –51.21±0.01 | –52.04±0.01 | –52.87±0.01 |
| | pH=5 | | | | |
| $E_a$ {kJ/mol} | 48.53±0.01 | | | | |
| ΔS# {J/mol K} | 109.05±0.01 | 109.03±0.01 | 109.01±0.01 | 109.01±0.01 | 108.95±0.01 |
| ΔH# {kJ/mol} | 43.63±0.01 | 43.55±0.01 | 43.46±0.01 | 43.38±0.01 | 43.36±0.01 |
| | pH=6 | | | | |
| $E_a$ {kJ/mol} | 32.39±0.01 | | | | |
| ΔS# {J/mol K} | 58.47±0.01 | 58.46±0.01 | 58.44±0.01 | 58.43±0.01 | 58.41±0.01 |
| ΔH# {kJ/mol} | 27.45±0.01 | 27.35±0.01 | 27.27±0.01 | 27.18±0.01 | 27.14±0.01 |

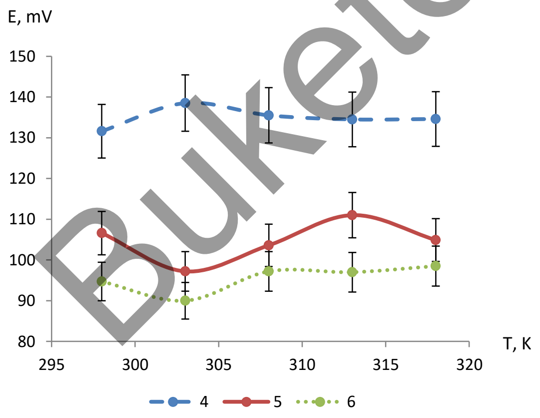

Figure 3. Characteristics of the electrode potential in the solutions ($H_2O_2$ – tannin – $H_2SO_4$) with increasing temperature and pH

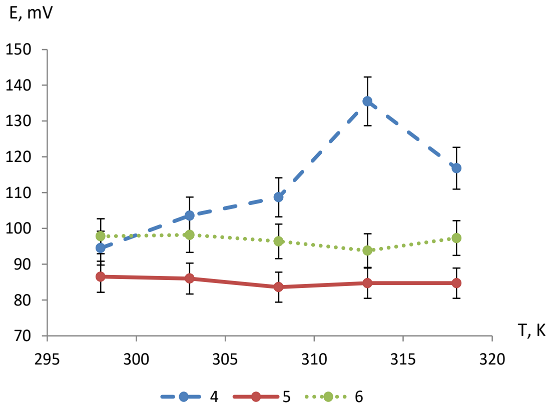

Figure 4. The behaviour of the electrode potential in the $K_2Cr_2O_7$ – tannin – $H_2SO_4$ system with a change in the pH range from 4 to 6

The thermodynamic characteristics of the copper-zinc ore beneficiation process were determined to test the optimal reagent modes of the modified polyfunctional collector (based on a mixture of potassium butyl xanthogenate-sodium diisobutyl dithiophosphate (w((i-$C_4H_9O)_2PS_2Na$)) flotation reagents. The results are presented in Table 3.

Table 3

**Thermodynamic values of the formation of a flotation complex of potassium butylxanthogenate – sodium diisobutyldithiophosphate on the surface of copper-lead ore**

| T{K} | 298 | 303 | 308 | 313 | 318 |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| pH=8 | | | | | |
| $E_a$ {kJ/mol} | 68.89±0.01 | | | | |
| lgA | 11.44 | | | | |
| ΔS# {J/mol K} | 187.93±0.01 | 187.92±0.01 | 187.94±0.01 | 187.87±0.01 | 187.87±0.01 |
| ΔH#{kJ/mol} | 63.94±0.01 | 63.86±0.01 | 63.77±0.01 | 63.69±0.01 | 63.61±0.01 |
| pH=10 | | | | | |
| ΔS# {J/mol K} | -31.28±0.01 | -31.31±0.01 | -31.37±0.01 | -31.33±0.01 | -31.34±0.01 |
| ΔH#{kJ/mol} | 156.02±0.01 | 155.94±0.01 | 155.85±0.01 | 155.77±0.01 | 155.69±0.01 |
| pH=12 | | | | | |
| $E_a$ {kJ/mol} | 173.65±0.01 | | | | |
| lgA | -30.41 | | | | |
| ΔS# {J/mol K} | -613.7±0.01 | -613.72±0.01 | -613.73±0.01 | -613.75±0.01 | -613.77±0.01 |
| ΔH#{kJ/mol} | -178.68±0.01 | -178.62±0.01 | -178.75±0.01 | -178.85±0.01 | -178.94±0.01 |

The indicated activation entropy data suggest that the flotation reagent has an active effect on the interaction of copper with butyl xanthogenate with the formation of $CuC_4H_9OCSS$. Furthermore, the exothermicity of the process is confirmed by the maximum value of work and entropy, which indicates the direction. The potentiometric method results for determining the dependence of the electrode potential in an alkaline medium in the presence of a mixture of flotation reagents are shown in Figures 5-6.

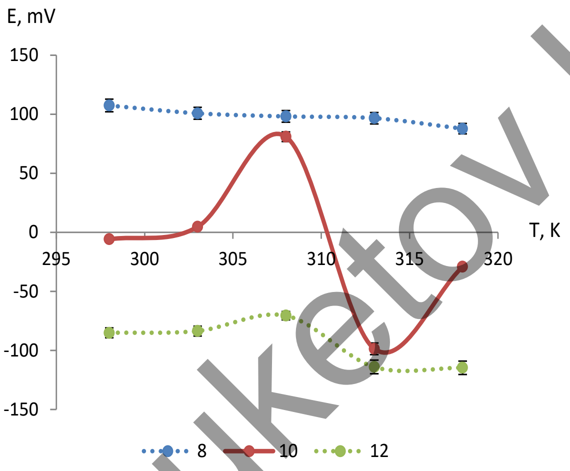

Figure 5. Dependence of the change in the potential of the working electrode in an alkaline medium with increasing temperature

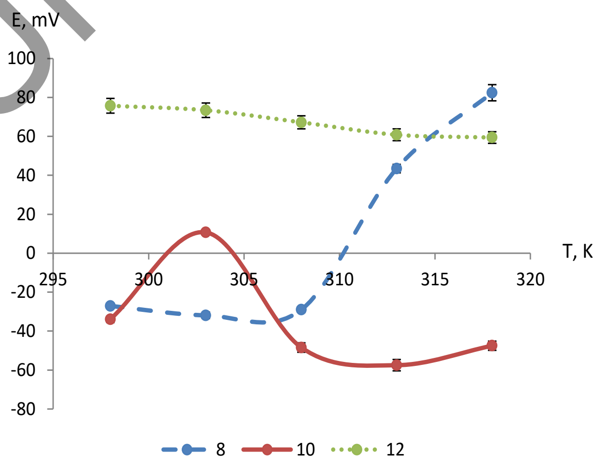

Figure 6. Changes in electrode potential in the system (NaOH – $H_2O_2$ – $(i\text{-}C_4H_9O)_2PS_2Na$) from temperature and pH

The potential shift to the electronegative region at pH = 10 is caused by the formation of poorly soluble copper hydroxides on the surface of the mineral. Sulfide sulfur oxidation to $SO_3^{2-}$ and $SO_4^{2-}$ is due to the adsorption of OH-radicals and atomic oxygen on the $Cu_2S$ surface.

Taking into account all the revealed trends in the various-component systems of the model ore beneficiation process, the activation process of the "intermediate" copper complex occurs. In this study, using the Gauss method in the calculations, the equations of the electrode function are derived with temperature and pH change. The temperature dependence of the $Cu_2S$ potential with a variable value of pH solutions is presented in Figure 7.

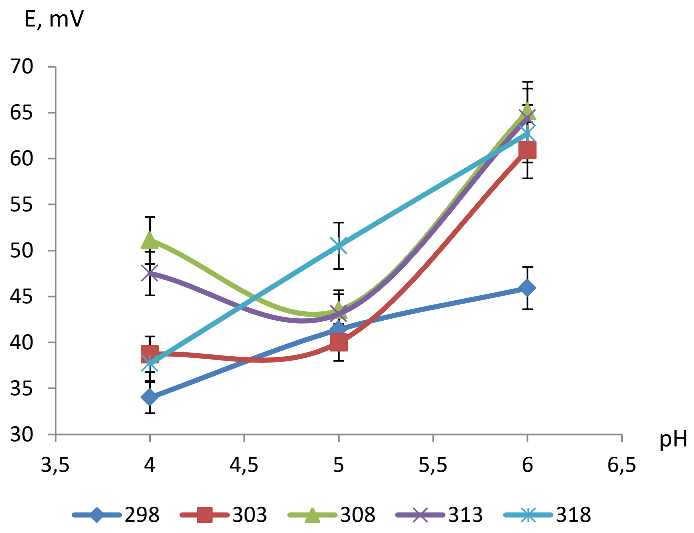

Figure 7. Effect of temperature and pH on the potential of the chalcocine electrode

The optimal mode for the maximum enrichment process of copper-lead and pyrite-copper-zinc ores was found using a mixture of flotation reagents according to the obtained obtained linear equations (8–10):

$$E = 1.9997t^2 - 153.77t + 2764.8 \ (pH=8) \quad (8)$$

$$E = 471.34t^2 - 10562t + 87407 \ (pH=10) \quad (9)$$

$$E = -0.8491t^2 + 61.04t - 1010.1 \ (pH=12) \quad (10)$$

The method of mathematical planning was applied to establish the optimal reagent and hydrodynamic enrichment modes.

Table 4 represents the generalized equation of surface modelling changes in the dissolving mineral raw materials process based on the changed electrode potential in multicomponent flotation process systems.

Table 4

**The generalized equation of surface modelling changes in the process of dissolving mineral raw materials**

| Systems | Mathematical model | R |
|---|---|---|
| $K_2Cr_2O_7$ – NaOH | $y = (20.475 + (-3.061)\cdot(pH) + 0.106\cdot(pH)^2) + ((-1.08) + 0.157\cdot pH + (-0.005)\cdot(pH)^2\cdot t°C) + (0.0124 + (-0.002)\cdot pH + 0.0001\cdot(pH)^2\cdot(t°C)^2)$ | 0.99 |
| $K_2Cr_2O_7$ – $H_2SO_4$ – tannin | $y = ((-107.79 + 73.019\cdot pH + (-5.396)\cdot(pH)2) + ((419.280 + 88.824\cdot pH + (-3.979)\cdot(pH)2\cdot t°C) + (16.48 + (-3.294)\cdot pH + 0.1597\cdot(pH)^2\cdot(t°C)^2)$ | 0.98 |
| $H_2O_2$ – NaOH | $y=((-50.813) + 1.349\cdot pH + (-8.7358)\cdot(pH)^2) + (2.725 + 2.552\cdot pH + (-7.563)\cdot(pH)^2\cdot t°C) + (1.7329 + (-1.756)\cdot pH + (0.0283\cdot(pH)^2\cdot(t°C)^2)$ | 0.99 |
| NaOH – $H_2O_2$ –$(C_4H_9O)_2PS_2Na$ | $y = ((-388.08 + 94.877\cdot pH + (-5.1541)\cdot(pH)^2) + (341.397 + (-82.957)\cdot pH + 0.453\cdot(pH)^2)\cdot t°C) + ((-1.355) + 0.286\cdot pH + (-0.0137)\cdot(pH)^2)\cdot(t°C)^2)$ | 0.99 |

It can be seen that the potential of the halcosin is shifted to the negative area with an increased temperature in a weakly alkaline medium (pH = 8) and to the positive zone in a more alkaline medium, which indicates an intensive occurrence of oxidative processes due to hydroxide and bichromate ions. This model is characterized by the interaction of the mineral in an alkaline oxidant solution; therefore, it may be tested to calculate the values of stationary potentials of copper sulfide (I) in the temperature range and the acidity of the medium.

It should be noted that the steady-state potential data (Figures 1–7) indicate that the sulfur oxidation reactions of copper and lead minerals to thiosulfate ions occur most fully in alkaline media. These ions are replaced by xanthogenate and dibutyldithiophosphate to form complex compounds. Moreover, sulfur oxidation products are thiosulfate and sulfate ions in the medium with high redox potential. These ions, which have a higher ability to hydrate, contribute to the formation of poorly soluble copper xanthates and copper diisobutyldithiophosphates in the volume of the solution, reducing the hydrophobicity of the surface, and consequently the quality of the concentrate [24].

In pursuance of the probabilistic-deterministic approach, the optimization of copper-lead ore concentration was carried out. Likewise, the partial dependences of chemical and technological parameters on variable factors of air supply rate, impeller speed, consumption of the $(C_4H_9O)_2PSSNa$ collector mixture and potassium butyl xanthogenate were obtained (Table 5).

Table 5

**Dependence of the degree of copper extraction and the degree of ore reduction for the process of concentration of copper ore using a mixture of potassium butyl xanthogenate – sodium diisobutyl dithiophosphate**

| Factors ($x$) | $\varepsilon_{Me}$, % ($y$) | R | K ($y$) | R |
|---|---|---|---|---|
| $\upsilon_{air.}$ {l/h} | $y = -0.05x^2 + 4.4819x - 5.6996$ | 0.99 | $y = -0.0063x^2 + 0.3594x + 12.035$ | 0.99 |
| $\nu_{rot.}$ {Hz} | $y = -0.0039x^2 + 0.2767x + 95.093$ | 0.99 | $y = -0.0146x^2 + 0.956x - 10.853$ | 0.99 |
| $C_{flotation}$ {g/t} | $y = -0.0246x^2 + 4.484x - 109.17$ | 0.99 | $y = 0.0042x + 4.1161$ | 0.99 |

For lead minerals, the high redox potential of the pulp initiates the reaction of the formation of poorly soluble lead sulfate at low pH and high pH of lead hydroxocarbonate. Therefore, hydrophobization in the presence of oxidized lead sulfide is difficult, which reduces the amount of metal extracted into the concentrate [25].

The large-scale laboratory studies have been carried out to recommend the use of a mixture of a flotation reagent (potassium butyl xanthogenate and sodium diisobutyl dithiophosphate (w(($i$-$C_4H_9O)_2PS_2Na$) for flotation of copper ore from the Nurkazgan deposit.

## *Conclusions*

The thermodynamic parameters characterizing the chalcocite dissolution process in copper minerals flotation solutions have been determined. The progress of the enrichment process is mainly determined not only by the change in the pulp potential's redox action, but also by the electrode potential of dissolution of chalcogenide minerals.

Due to this fact, it is possible to eliminate the formation of hydroxide compounds at the stage of selective flotation of copper concentrates in alkaline media due to the equalization of the chromate- and xanthogenate ions concentration in the liquid phase.

A qualitatively new approach to the prediction of the behavior of sulfide minerals is proposed. It consists in considering the relationship between the redox ability of minerals and the flotation characteristics of polymetallic ores and the hydrodynamic enrichment regime. It was shown that copper recovery degree into concentrate is closely related to air consumption and dispersion degree of bubbles for copper- lead ore samples. These factors directly affect the oxidation-reduction balance in the pulp. Namely, they increase the probability of the formation reactions of hydroxo complexes, thiosulfates, copper, lead sulfates on the surface of sulfide minerals.

A statistical model was proposed to calculate the value of the relative fractions of the surface sorption layer of the pulp during the flotation of copper ore from the "Nurkazgan" deposit.

This model takes into account the oxidation processes occurring in parallel on the surface of the mixed sorption layer of the collector of potassium butyl xanthogenate and sodium dissobutyl dithiophosphate (w(($i$-$C_4H_9O)_2PS_2Na$).

## References

1 Стрельцова А.А. Флотационные извлечения поверхностно-активных веществ различной природы из смешанных растворов, содержащих высокомолекулярный реагент / А.А. Стрельцова, А.А. Мазурик Е.А. Хромышева // Химическая безопасность. — 2018. — Т. 2, № 1. — С. 116–126. http://chemsafety.ru/index.php/chemsafety/article/view/44

2 Германов А.А. Новые технические средства автоматического контроля технологических параметров в обогатительном производстве / А.А. Германов, А.А. Трушин, Н.О. Тихонов, А.А. Трегубов // Горн. инф.-аналит. бюлл. (Науч.-тех. журн.). — 2019. — № 2. — С. 114–122. https://giab-online.ru/catalog/12694

3 Tinashe O. Ndoro. A Review of the Flotation of Copper Minerals / Tinashe O. Ndoro, Lordwell K. Witika // International Journal of Sciences: Basic and Applied Research (IJSBAR), 2017. — Vol. 34(2). — P. 145–165. https://www.researchgate.net/publication/318284476

4 Авагян А.В. Термодинамическое обоснование процесса сульфидирования окисленных медных минералов серой / А.В. Авагян // Вестн. Нац. политех. ун-та Армении. Металлургия, материаловедение, недропользование. — 2018. — № 2. — С. 34–44. http://test.journals.sci.am/index.php/polytech_banber-metalurgia/issue/view/228

5 Горячев Б.Е. Термодинамика формирования сорбционного слоя тиольных собирателей на поверхности сфалерита при условии окисления сульфидной серы минерала до элементной [Электронный ресурс] / Б.Е. Горячев, А.А. Николаев, Зай Яа Чжо, А.А. Моргун // Цветные металлы. — 2018. — № 4. — С. 2–10. http://www.rudmet.ru/journal/1715/article/29442/

6 Александрова Т.Н. Метод типизации медно-цинковых руд сложного состава с применением нейросетевых моделей / Т.Н. Александрова, Е.К. Ушаков, А.В. Орлова // Горн. инф.-аналит. бюлл. (Науч.-тех. журн.). — 2020. — № 5. — С. 140–147. https://cyberleninka.ru/article/n/metod-tipizatsii-medno-tsinkovyh-rud-slozhnogo-sostava-s-primeneniem-neyrosetevyh-modeley

7 Заварухина Е.А. Влияние дополнительного собирателя на селективность флотационного разделения сульфидов меди и цинка / Е.А. Заварухина, Н.Н. Орехова // Гор. инф.-аналит. бюлл. (Науч.-тех. журн.). — 2017. — № 3. — С. 305–311. https://cyberleninka.ru/article/n/vliyanie-dopolnitelnogo-sobiratelya-na-selektivnost-flotatsionnogo-razdeleniya-sulfidov-medi-i-tsinka

8 Омарова Н.К. Флотация сульфидом медной руды с флотореагентом «PS» / Н.К. Омарова, Р.Т. Шерембаева // Обогащение руд. — 2015. — Т. 356, № 2. — С. 15–17. http://dx.doi.org/10.17580/or.2015.02.03

9 Кондратьев С.А. Оценка собирательной силы флотационного реагента / С.А. Кондратьев, В.И. Рябой // Физико-технические проблемы разработки полезных ископаемых. — 2015. — № 1. — С. 137–144. http://www.rudmet.ru/journal/1428/article/24521/

10 Рябой В.И. Собиратель для медно-мышьяковистых руд / В.И. Рябой, Е.Д. Шепета // Горные науки и технологии. — 2020. — Т. 5, № 4. — С. 297–306. https://doi.org/10.17073/2500-0632-2020-4-297-306

11 Игнаткина В.А. Экспериментальные исследования изменений контрастности флотационных свойств кальциевых минералов / В.А. Игнаткина // Физико-технические проблемы разработки полезных ископаемых. — 2017. — № 5. — С. 113–122. https://elibrary.ru/item.asp? id=30488395

12 Рамазанова В.Р. Перспективы использования нового реагента для флотации окисленых медных руд / В.Р. Рамазанова, А.С. Жилин / Актуальные проблемы развития технических наук: сб. ст. участн. XX Обл. конкурса науч.-исслед. работ «Научный олимп» по направлению «Технические науки». — М.: Эдитус, 2018. — С. 89–91. https://elibrary.ru/item.asp? id=35049070

13 Баласанян С.Ш. Компьютерная модель для стохастического управления технологическим процессом флотации руды с учетом надежности измельчительного оборудования / С.Ш. Баласанян, С.О. Симонян, Э.М. Геворгян // Изв. Том. политех. ун-та. — 2013. — Т. 323, № 5. — С. 50–57. http://earchive.tpu.ru/handle/ 11683/5058

14 Moses Nduna. A model for the zeta potential of copper sulphide/ Moses Nduna, Alison Emslie Lewis, Patrice Nortier // Colloids and Surfaces A: Physicochemical and Engineering Aspects, Elsevier, 2014. — Vol. 441. — P. 643–652. https://www.sciencedirect.com/science/article/abs/pii/S0927775713007784

15 Амерханова Ш.К. Кинетические особенности процесса сорбции серосодержащих собирателей на поверхности медной руды / Ш.К. Амерханова, Р.М. Шляпов, А.С. Уали // Вестн. Воронеж. гос. ун-та. Сер. Химия. Биология. Фармация. — 2017. — № 1. — С. 7–10. https://elibrary.ru/item.asp? id=29025082

16 Матвеева Т.Н. Новые флотационные реагенты для извлечения микро- и наночастиц благородных металлов из упорных руд / Т.Н. Матвеева, Т.А. Иванова, В.В. Гетман, Н.К. Громова // Горн. журн. — 2017. — № 11. — С. 89–93. — http://rudmet.net/media/articles/Article_MJ_11_17_pp.89-93_2.pdf

17 Kondratev, S.A., Bochkarev, I.G. Physically absorbable reagents-collectors in elementary flotation // J. Min. Sci, Elsevier, 2007. — Vol. 43. — P. 530–538. https://doi.org/10.1007/s10913-007-0056-9

18 Zand, L., Vakylabad, A.B. & Masoumi, M.E. Homogeneous Catalytic Dissolution of Recalcitrant Chalcopyrite ($CuFeS_2$)// Top Catal, Elsevier, 2022. https://doi.org/10.1007/s11244-022-01565-x

19 Baba A.A., Balogun A.F., Olaoluwa D.T. Leaching kinetics of a Nigerian complex covellite ore by the ammonia-ammonium sulfate solution // Korean J. Chem. Eng., Elsevier, 2017. — Vol. 34. — P. 1133–1140. https://doi.org/10.1007/s11814-017-0005-5

20 Fu Yf., Yin Wz., Dong Xs. New insights into the flotation responses of brucite and serpentine for different conditioning times: Surface dissolution behavior // Int J Miner Metall Mater., Elsevier, 2021. — Vol. 28. — P. 1898–1907. https://doi.org/10.1007/s12613-020-2158-1

21 Al-Juaid S.S. Inhibition of carbon steel corrosion in hydrochloric acid solutions using polyoxyethylene sorbitan fatty acid esters (tween compounds). Chemistry and Technology of Fuels and Oils, Scopus, 2012. — Vol. 48. — P. 313–320. https://doi.org/10.1007/s10553-012-0374-8

22 Khovanskyi S., Pavlenko I., Pitel J., Mizakova J., Ochowiak M., Grechka I. Solving the coupled aerodynamic and thermal problem for modeling the air distribution devices with perforated plates // Energies, Elsevier, 2019. — Vol. 12. — P. 3488. https://doi.org/10.3390/en12183488

23 Николаев А.А. Термодинамика взаимодействия хромат-ионов с минеральным комплексом полиметаллических руд халькопирит / А.А. Николаев, Б.Е. Горячев // Изв. вузов. Цветная металлургия. — 2013. — № 5. — С. 3–9. https://doi.org/10.17073/0021-3438-2013-5-3-9

24 Vigdergauz V.E., Makarov D.V., Zorenko I.V. Effect exerted by structural features of copper-zinc ores on their oxidation and technological properties// J Min Sci., Elsevier, 2008. — Vol. 44. — P. 413–420. https://doi.org/10.1007/s10913-008-0046-6

25 Chander S. Oxidation/Reduction Effects in Depression of Sulfide Minerals — A Review // Mining, Metallurgy & Exploration, Scopus, 1985. — Vol. 2. — P. 26–35. https://doi.org/10.1007/bf03402591

Р.М. Шляпов, Ш.К. Амерханова, А.С. Уали, Т.Б. Омарбеков, Д.С. Бельгибаева

# Флотациялық реагенттер қоспаларының ерітінділерінде халькозиннің еруінің термодинамикасы

Мыс-қорғасын және колчедан-мыс-мырыш кендерін байыту кезінде сорбциялық қабаттың иондық құрамын қалыптастыру процесі қарастырылды. pH метрия мен редоксометрияны қолдана отырып, халькозин бетінің әр түрлі тотығу жағдайларында сульфогидрил жинағышының сорбциялық қабатының (натрий диизобутилтиофосфаты және калий бутил ксантогенаты) термодинамикасы зерттелді. Халькозин электродының электрод потенциалының pH-ға байланысты модификатор мен жинақтау түріне өзгеру сипаты эксперименталды түрде түсіндірілді. Флотация процесінің реакцияларының термодинамикасын талдау негізінде бір компонентті жинақтау пен флотореагенттер қоспасының ұжымдық әсерінің айырмашылықтары анықталды. Флотация жүргізудің оңтайлы шарттары анықталды, қойыртпақ пен pH ортаның тотығу-тотықсыздану әлеуетінің екі факторының концентрат сапасына басым әсері дәлелденді. Флотациялық реагенттер ерітінділерінде кен минералдарын барынша ерітумен байытудың оңтайлы реагенттік және гидродинамикалық режимдерінің математикалық теңдеулері модельденді.

*Кілт сөздер:* флотация, гидрофобтылық, жинағыштың сорбциялық қабаты, қойыртпақтың сұйық фазасының иондық құрамы, флотациялық реагенттер, сульфидті минералдар.

Р.М. Шляпов, Ш.К. Амерханова, А.С. Уали, Т.Б. Омарбеков, Д.С. Бельгибаева

# Термодинамика растворения халькозина в растворах флотационных реагентов

Рассмотрен процесс формирования ионного состава сорбционного слоя при обогащении медно-свинцовой и колчеданно-медно-цинковой руды. С применением pH и редоксометрии изучена термодинамика сорбционного слоя сульфогидрильного собирателя (диизобутилтиофосфата натрия и бутилового ксантогената калия) на поверхности халькозина в различных условиях его окисления. Экспериментально выяснен характер изменения электродного потенциала халькозинового электрода от типа модификатора и накопителя в зависимости от pH. На основании анализа термодинамики реакций процесса флотации выявлены различия собирательного действия однокомпонентного накопителя и смеси флотореагентов. Определены оптимальные условия проведения флотации, установлено преобладающее влияние двух факторов окислительно-восстановительного потенциала пульпы и pH среды на качество концентрата. Смоделированы математические уравнения оптимальных реагентных и гидродинамических режимов обогащения с максимальным растворением рудных минералов в растворах флотационных реагентов.

*Ключевые слова:* флотация, гидрофобность, сорбционный слой собирателя, ионный состав жидкой фазы пульпы, флотационные реагенты, сульфидные минералы.

## References

1 Strelzova, A.A., Mazuric, A.A., & Hromysheva, E.A. (2018). Flotazionnye izvlecheniia poverkhnostno-aktivnykh veshchestv razlichnoi prirody iz smeshannykh rastvorov, soderzhashchikh vysokomolekuliarnyi reagent [Flotation extraction of surfactants of various nature from mixed solutions containing high-molecular reagents]. *Khimicheskaia bezopasnost — Russian Journal of Chemical safety, 2, 1,* 116–126. http://chemsafety.ru/index.php/chemsafety/article/view/44 [in Russian].

2 Germanov, A.A., Trushin, A.A., Tikhonov, N.O., & Tregubov, A.A. (2019). Novye tekhnicheskie sredstva avtomaticheskogo kontrolia tekhnologicheckikh parametrov [New technical means of automatic control of technological parameters in concentration production]. *Gornyi informatsionno-analiticheskii bulleten (Nauchno-tekhnicheskii zhurnal) — Mining informational and analytical bulletin (scientific and technical journal), 2,* 114–122. https://giab-online.ru/catalog/12694 [in Russian].

3 Tinashe, O. Ndoro, & Lordwell, K. Witika**.** (2017). A Review of the Flotation of Copper Minerals. *International Journal of Sciences: Basic and Applied Research (IJSBAR), 34(2),* 145–165. https://www.researchgate.net/publication/318284476

4 Avagyan, A.V. (2018). Termodinamicheskoe obosnovanie protsessa sulfidirovaniia okislennykh mednykh mineralov seroi [Thermodynamic justification for the sulphide process of oxidized copper minerals with sulfur], *Vestnik Natsionalnogo politekhnicheskogo universiteta Armenii. Metallurgiia, materialovedenie, nedropolzovanie. Herald of the National Polytechnic University of Armenia. Metallurgy, materials science, Subsoil use, 2,* 34–44. http://test.journals.sci.am/index.php/polytech_banber-metalurgia/issue/view/228 [in Russian].

5 Goriachev, B.E., Nikolaev, A.A., Zai Ya, Chzho, & Morgun, A.A. (2018). Termodinamika formirovaniia sorbtsionnogo sloia tiolnykh sobiratelei na poverkhnosti sfalerita pri uslovii okisleniia sulfidnoi sery minerala do elementnoi [Thermodynamics of the

formation of a sorption layer of thiol collectors on the surface of sphalerite under the condition of oxidation of sulfide sulfur of the mineral to elemental] *Tsvetnye metally — Non-ferrous metals, 4,* 2–10. http://www.rudmet.ru/journal/1715/article/29442/ [in Russian].

6 Alexandrova, T.N., Ushakov, E.K., & Orlova, A.V. (2020). Metod tipizatsii medno-tsinkovykh rud slozhnogo sostava s primineniem neirosetevykh modelei [Method of complex copper–zinc ore typification using neural network models]. *Gornyi informatsionno-analiticheskii bulleten (Nauchno-tekhnicheskii zhurnal) — Mining informational and analytical bulletin (scientific and technical journal), 5,* 140–147. https://cyberleninka.ru/article/n/metod-tipizatsii-medno-tsinkovyh-rud-slozhnogo-sostava-s-primeneniem-neyrosetevyh-modeley [in Russian].

7 Zavarukhina, E.A., & Orekhova, N.N. (2017). Vliianie dopolnitelnogo sobiratelia na selektivnost flotatsionnogo razdeleniia sulfidov medi i tsinka [Effect of additional collector on the selectivity of the flotation separation of copper and zinc sulphides]. *Gornyi informatsionno-analiticheskii bulleten (nauchno-tekhnicheskii zhurnal) — Mining informational and analytical bulletin (scientific and technical journal), 3,* 305–311. https://cyberleninka.ru/article/n/vliyanie-dopolnitelnogo-sobiratelya-na-selektivnost-flotatsionnogo-razdeleniya-sulfidov-medi-i-tsinka [in Russian].

8 Omarova, N.K. & Sherembayeva, R.T. (2015). Flotatsiia sulfidom mednoi rudy s flotoreagentom «PS» [Sulfide copper ore flotation with “PS” reagent], *Zhurnal «Obogashchenie rud» — Journal of Russia “Obogashchenie Rud”, 356, 2,* 15–17. http://dx.doi.org/10.17580/or.2015.02.03 [in Russian].

9 Kondratiev, S.A., & Ryaboi, V.I. (2015). Otsenka sobiratelnoi sily ditiofosfatov i ee sviaz s selektivnostiu izvlecheniia poleznogo komponenta [Dithiophosphates collecting ability estimation and its relationship to selectivity of valuable component recovery] *Zhurnal «Obogashchenie rud» — Journal of Russia Obogashchenie Rud, 1,* 137–144. http://www.rudmet.ru/journal/1428/article/24521/ [in Russian].

10 Ryaboy, V.I., & Shepeta, E.D. (2020). Sobiratel dlia medno-myshiakovykh rud [Collector for copper-arsenic ore flotation]. *Gornyi informatsionno-analiticheskii bulleten (Nauchno-tekhnicheskii zhurnal) — Mining informational and analytical bulletin (scientific and technical journal),* 5(4), 297–306. https://doi.org/10.17073/2500-0632-2020-4-297-306 [in Russian].

11 Ignatkina, V.A. (2017). Eksperimentalnye issledovaniia izmeneniia kontrasnosti flotatsionykh svoistv kaltsevykh mineralov [Experimental investigation of change in the contrast between flotation properties of calcic minerals]. *Fiziko-tekhnicheskie problemy razrabotki poleznykh iskopaemykh, 5,* 113–122. https://elibrary.ru/item.asp? id=30488395 [in Russian].

12 Ramazanova, V.R., & Zhilin, A.S. (2018). Perspektivy ispolzovaniia novogo reagenta dlia flotatsii okislennykh mednykh rud [Prospects for using a new reagent for the flotation of oxidized copper ores]. *Zhurnal «Aktualnye problemy razvitiia tehnicheskikh nauk» — Journal of Russia “Aktualnye problemy razvitiia tehknicheskikh nauk”, 2,* 89–95. https://elibrary.ru/item.asp? id=35049070 [in Russian].

13 Balasanyan, S.S., Simonyan, S.O., & Gevorgyan, E.M. (2013). Kompiuternaia model dlia stokhasticheskogo upravleniia tekhnologicheskim protsessom flotatsii rudy s uchetom nadezhnosti izmelchitelnogo oborudovaniia [Computer model for stochastic control of the ore flotation process considering grinding equipment reliability]. *Izvestiia Tomskogo politekhnicheskogo universiteta — Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering, 323(5*), 50–57. http://earchive.tpu.ru/handle/11683/5058 [in Russian].

14 Moses, N., Alison Emslie Lewis, & Patrice Nortier (2014). A model for the zeta potential of copper sulphide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, Elsevier, 441,* 643–652. https://www.sciencedirect.com/science/article/abs/pii/S0927775713007784

15 Amerkhanova, Sh.K., Shliapov, R.M. & Uali, A.S. (2017). Kiniticheskie osobennosti protsesa sorbtsii serosoderzhashchikh sobiratelei na poverkhnosti mednoi rudy [Kinetic features of sorption process of sulfur collectors on the surface of copper ore] *Vestnik Voronezhskogo gosudarstvenogo universiteta. Seriia Khimiia. Biologiia. Farmatsiia — Proceedings of Voronezh State University. Series Chemistry. Biology. Pharmacy, 1,* 7–10. https://elibrary.ru/item.asp? id=29025082 [in Russian].

16 Matveeva, T.N., Ivanova, T.A., Getman, V.V. & Gromova, N.K. (2017). Novye flotatsionnye reagenty dlia izvlecheniia mikro- i nanochastits blagorodnykh metallov iz upornykh rud [New flotation agents for recovery of micro- and nanoparticles of precious metals from rebellious ore]. *Gornyi zhurnal — Journal of Russia “Gornyi Zhurnal”, 1,* 89–93. http://rudmet.net/media/articles/Article_MJ_11_17_pp.89-93_2.pdf [in Russian].

17 Kondratev, S.A., & Bochkarev, I.G. (2007). Physically absorbable reagents-collectors in elementary flotation. *J. Min. Sci, Elsevier, 43, 530–538.* https://doi.org/10.1007/s10913-007-0056-9

18 Zand, L., Vakylabad, A.B., & Masoumi, M.E. (2022). Homogeneous Catalytic Dissolution of Recalcitrant Chalcopyrite ($CuFeS_2$). *Top Catal, Elsevier*. https://doi.org/10.1007/s11244-022-01565-x

19 Baba, A.A., Balogun, A.F., & Olaoluwa, D.T. (2017). Leaching kinetics of a Nigerian complex covellite ore by the ammonia-ammonium sulfate solution. *Korean J. Chem. Eng., Elsevier, 34,* 1133–1140. https://doi.org/10.1007/s11814-017-0005-5

20 Fu, Yf., Yin, Wz., & Dong, Xs. (2021). New insights into the flotation responses of brucite and serpentine for different conditioning times: Surface dissolution behavior. *Int J Miner Metall Mater., 28, 1898–1907.* https://doi.org/10.1007/s12613-020-2158-1

21 Al-Juaid, S.S. (2012). Inhibition of carbon steel corrosion in hydrochloric acid solutions using polyoxyethylene sorbitan fatty acid esters (tween compounds). *Chemistry and Technology of Fuels and Oils, Scopus., 48,* 313–320. https://doi.org/10.1007/s10553-012-0374-8

22 Khovanskyi, S., Pavlenko, I., Pitel, J., Mizakova, J., Ochowiak, M., & Grechka, I. (2019). Solving the coupled aerodynamic and thermal problem for modeling the air distribution devices with perforated plates. *Energies, 12,* 3488. https://doi.org/10.3390/en12183488

23 Nikolaev, A.A. & Goryachev, B.E. (2013). Termodinamika vzaimodeistviia khromat-ionov s mineralnym kompleksom polimetallicheskikh rud khalkopirit [Thermodynamics of interchange of chromate ions with mineral complex of polymetal ores. Chal-

copyrite]. *Izvestiia vuzov. Tsvetnaia metallurgiia — Izvestiya. Non-Ferrous Metallurgy, 5,* 3–9. https://doi.org/10.17073/0021-3438-2013-5-3-9 [in Russian].

24 Vigdergauz, V.E., Makarov, D.V., & Zorenko, I.V. (2008). Effect exerted by structural features of copper-zinc ores on their oxidation and technological properties. *J. Min. Sci., 44,* 413–420. https://doi.org/10.1007/s10913-008-0046-6

25 Chander, S. (1985). Oxidation/Reduction Effects in Depression of Sulfide Minerals — A Review. *Mining, Metallurgy & Exploration, 2,* 26–35. https://doi.org/10.1007/bf03402591

## Information about authors

**Shlyapov, Rustam Maratovich** (corresponding author) — Candidate of Chemical Sciences, Associate Professor, L.N. Gumilyov Eurasian National University, Kazhymukan street, 13, 010000, Nur-Sultan, Kazakhstan, e-mail: rustamshlyapow@gmail.com; https://orcid.org/0000-0003-0696-214X;

**Amerkhanova, Shamshiya Kenzhegazinovna** — Doctor of Chemical Sciences, Full Professor, L.N. Gumilyov Eurasian National University, Kazhymukan street, 13, 010000, Nur-Sultan, Kazakhstan, e-mail: amerkhanovashk@gmail.com; https://orcid.org/0000-0002-2492-4203;

**Uali, Aitolkyn Sailaubekkyzy** — Candidate of Chemical Sciences, Associate Professor, L.N. Gumilyov Eurasian National University, Kazhymukan street, 13, 010000, Nur-Sultan, Kazakhstan, e-mail: ualiaitolkyn@gmail.com; https://orcid.org/0000-0002-5851-6566;

**Omarbekov, Tolegen Bazarovich** — Candidate of Chemical Sciences, Autonomous Cluster Fund "Park of Innovative Technologies", Zhibek-Zholy Ave, 135, 050000, Almaty, Kazakhstan, e-mail: omar_toke@mail.ru;

**Belgibayeva, Dana Sapargalievna** — Candidate of Chemical Sciences, L.N. Gumilyov Eurasian National University, Kazhymukan street, 13, 010000, Nur-Sultan, Kazakhstan, e-mail: dana0577.77@gmail.com; https://orcid.org/0000-0002-4225-600X