ABSTRACT
of the thesis submitted for the degree of Doctor of Philosophy (PhD)
in the educational program "8D05301–Chemistry"
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"Investigation of Amino Acid Leaching Processes
of Copper Sulfide Minerals"

General Characteristics of the Work. The thesis is devoted to the investigation of amino acid leaching processes of copper sulfide minerals – chalcocite (Cu_2S), bornite (Cu_5FeS_4), and chalcopyrite ($CuFeS_2$) – from the Dzhezkazgan deposit using glycine and other amino acids (lysine, betaine, cysteine, methionine) in an alkaline medium in the presence of atmospheric oxygen or hydrogen peroxide under various experimental conditions. The study includes the determination of the kinetic parameters of the leaching process, as well as the examination of the composition, present phases, and surface condition of the minerals before and after leaching using various physicochemical analytical methods.

Relevance of the Research Topic. At present, the depletion of high-grade copper ores necessitates the mining and processing of low-grade raw materials. Under these conditions, traditional pyrometallurgy becomes less efficient due to increased energy consumption, higher operating costs, and environmental pollution caused by toxic emissions (such as furans, sulfur gases, CO_2, and acidic effluents). This situation highlights the need for the development of energy-efficient and environmentally safe methods for processing copper-bearing materials.

A promising alternative is hydrometallurgy based on leaching. The hydrometallurgical approach is characterized by lower costs, comprehensive raw material processing, high selectivity, lower operating temperatures, safer working conditions, and reduced environmental impact. However, conventional inorganic reagents used in leaching are often toxic, non-selective, corrosive, and difficult to recover or reuse, leading to their high consumption during the leaching process.

This study explores the use of glycine as a leaching agent for copper sulfide minerals—chalcocite, bornite, and chalcopyrite. The glycine-based system (aqueous glycine solution, pH modifier, and oxidant) offers effective and selective copper extraction while minimizing environmental and operational risks. Thus, glycine leaching represents a promising alternative to traditional technologies in copper hydrometallurgy and aligns with the strategy of environmentally sustainable resource processing.

The Aim of the Research: To identify the patterns of amino acid leaching processes of copper sulfide minerals – chalcocite (Cu_2S), bornite (Cu_5FeS_4), and chalcopyrite ($CuFeS_2$) – from the Dzhezkazgan deposit in an alkaline medium in the presence of hydrogen peroxide under mild conditions.

The Tasks of the Research:

1. To determine the optimal process parameters (concentrations of glycine, sodium hydroxide, and hydrogen peroxide; reagent ratios; pH; and temperature) affecting the efficiency of glycine leaching of chalcocite, bornite, and chalcopyrite.

2. To compare the leaching ability of amino acids – glycine, lysine, cysteine, methionine, and betaine – under identical conditions and to elucidate the mechanisms of their interaction with chalcocite, bornite, and chalcopyrite in an alkaline medium.

3. To identify the rate-limiting steps in the glycine leaching of chalcocite, bornite, and chalcopyrite using the shrinking core model.

4. To determine the specific leaching rates of chalcocite, bornite, and chalcopyrite based on the Dolivo-Dobrovolsky equation; to establish the reaction order with respect to glycine, sodium hydroxide, and hydrogen peroxide; and to identify optimal conditions for efficient leaching.

5. To apply X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), infrared (IR), Raman, and Mössbauer spectroscopy to study changes in the crystal structure and chemical composition of the minerals before and after glycine leaching.

6. To propose leaching reaction schemes for chalcocite, bornite, and chalcopyrite in an alkaline medium in the presence of hydrogen peroxide based on copper extraction data and physicochemical analysis results.

Research Objects: Chalcocite, bornite, and chalcopyrite from the Dzhezkazgan deposit (Kazakhstan); glycine, lysine, cysteine, and methionine produced by Titan Biotech (India); betaine from Zhejiang Medicines & Health Products (China); sodium hydroxide from OJSC "Reaktiv" (Russia); hydrogen peroxide from LLP "Firma Skat" (Kazakhstan).

Research Subject: Copper leaching from the solid phase of chalcocite, bornite, and chalcopyrite into the solution through the formation of copper (II) glycinate complexes.

Research Methods: Energy-dispersive spectroscopy, scanning electron microscopy, X-ray diffraction, low-temperature nitrogen adsorption-desorption method, Fourier-transform infrared spectroscopy, Raman spectroscopy, Mössbauer spectroscopy, atomic absorption spectroscopy.

The Main Provisions for the Defense:

1. The highest copper extraction degree from chalcocite (22.37 %), bornite (7.99 %), and chalcopyrite (3.80 %) during amino acid leaching in an alkaline medium (0.1 M NaOH) in the presence of hydrogen peroxide (0.1 M) are achieved using glycine, which significantly exceeds the leaching efficiency when using other amino acids (lysine, betaine, cysteine, methionine), where the copper extraction degree ranges from 2.43-7.78 % for chalcocite, 0.76-2.33 % for bornite, and 1.62-2.30 % for chalcopyrite.

2. Among the three main stages considered in the shrinking core model, the rate-limiting step of the glycine leaching process of chalcocite, bornite, and chalcopyrite under varying process parameters (glycine, NaOH, H_2O_2 concentrations, and temperature) is diffusion through the reaction product layer. This is confirmed by the highest correlation coefficient (R^2=0.983-1.000) compared to diffusion through the liquid film (R^2=0.976-0.998) and chemical reaction on the solid surface (R^2=0.976-0.999).

3. According to the reaction order values (α) calculated using the Dolivo-Dobrovolsky equation, the rate of glycine leaching of chalcocite, bornite, and

chalcopyrite in an alkaline medium (0.1 M NaOH) increases with the glycine concentration from 0.1 M to 1 M (α=0.15 for chalcocite; α=0.26 for bornite) and hydrogen peroxide concentration (from 0.05 M to 0.25 M for chalcocite – α=0.33; from 0.05 M to 0.5 M for bornite – α=0.25), while for chalcopyrite, only the increase in hydrogen peroxide concentration from 0.05 M to 0.25 M is significant (α=0.16).

Scientific Novelty of the Research Results:

1. The kinetic regularities of leaching secondary (chalcocite, bornite) and primary (chalcopyrite) copper sulfide minerals in alkaline glycine solutions with hydrogen peroxide as an oxidant under mild conditions have been determined for the first time. Key factors influencing these processes have also been identified.

2. The features of leaching chalcocite, bornite, and chalcopyrite in solutions of various amino acids (glycine, lysine, methionine, cysteine, betaine) in alkaline medium in the presence of hydrogen peroxide have been identified for the first time. It has been established that glycine, compared to other amino acids, is a more effective leaching reagent.

3. The regularities of the influence of the acid-base equilibrium of amino acid solutions on the formation and stability of copper-amino acid complexes, as well as on the kinetics of copper sulfide mineral leaching, have been established for the first time.

4. For the first time, the rate-limiting stages, reaction orders, and specific leaching rates of copper sulfide minerals by glycine in alkaline medium in the presence of hydrogen peroxide have been determined using the shrinking core model and the Dolivo-Dobrovolsky equation.

The Main Results of the Research:

1. Glycine leaching of chalcocite, bornite, and chalcopyrite is a selective process that ensures the preferential extraction of copper with minimal iron leaching (no more than 0.08 %). The optimal process parameters have been determined: a system of 0.1M Gly-0.1M NaOH-0.1M H_2O_2, alkaline medium (pH>9.60), and a temperature of 25 °C. Under these conditions, the copper extraction degrees from chalcocite, bornite, and chalcopyrite were 22.37 %, 7.99 %, and 3.80 %, respectively.

2. Glycine is more effective than lysine, betaine, cysteine, and methionine as a leaching reagent for copper sulfide minerals in alkaline medium in the presence of hydrogen peroxide, due to its ability to form more stable copper complexes ($\log\beta_2$=15.15). In systems with other amino acids, the copper extraction degrees from chalcocite, bornite, and chalcopyrite were lower by 14.59-19.94 %, 5.66-7.23 %, and 1.50-2.18 %, respectively, compared to the glycine systems.

3. Kinetic analysis of glycine leaching of chalcocite, bornite, and chalcopyrite based on the shrinking core model showed that the rate-limiting step of the processes is the diffusion of reagents and products through the reaction product layer.

4. The specific leaching rate (W) and reaction order (α) were calculated using the Dolivo-Dobrovolsky equation. The specific leaching rates of chalcocite, bornite, and chalcopyrite decrease with the increase in process time due to the reduction in the mineral's reactive surface area. The leaching rate of chalcocite and bornite is significantly influenced by changes in glycine concentration (α=0.15-0.26) and hydrogen peroxide concentration (α=0.25-0.33), while for chalcopyrite, only the change in hydrogen peroxide concentration is significant (α=0.16).

5. The results of X-ray diffraction analysis, scanning electron microscopy, infrared, Raman, and Mössbauer spectroscopy confirmed changes in the structure and composition of the minerals after glycine leaching. SEM revealed the dissolution of defective areas and fine fractions. XRD and Raman spectroscopy confirmed the preservation of main phases with a reduction in peak intensity, as well as the disappearance of certain peaks, indicating the formation of new phases. IR spectroscopy detected characteristic vibrations, indicating the interaction of glycine with copper minerals. Mössbauer spectroscopy showed a change in the local environment of iron in bornite and chalcopyrite, confirming structural and morphological modifications.

6. Reaction schemes for glycine leaching of copper sulfide minerals have been proposed. Chalcocite leaches in two stages: rapid conversion of chalcocite to copper ions and covellite, followed by further transformation of covellite at a rate 10 times slower than in the first stage. It was shown that the leaching of bornite and chalcopyrite occurs with the formation of solid solutions $Cu_{5(1-X)}FeS_4$ and $Cu_{1-X}FeS_2$, respectively.

Theoretical Significance of the Work: This work contributes to the theoretical understanding of amino acid leaching of copper sulfide minerals in an alkaline medium with the participation of hydrogen peroxide, by revealing the kinetic patterns and stages of the processes. The principles of copper (II) complexation with amino acids and their influence on leaching efficiency have been identified. The results of the dissertation research have expanded the knowledge in the field of hydrometallurgical processes and established a fundamental basis for improving environmentally friendly technologies for processing copper-bearing raw materials.

Practical Significance of the Work: Glycine is an accessible, inexpensive, environmentally friendly, non-volatile, and easily producible organic reagent. It is almost completely regenerated and reused, reducing operational costs. The powdered form of glycine minimizes transportation expenses and associated risks, while the low corrosive activity of alkaline glycine solutions lowers the requirements for equipment materials, reducing capital expenditures. The glycine-based system can replace conventional acid leaching without significant changes to the technological process. Moreover, glycine leaching reduces the dissolution of undesirable elements (Fe, Cr, Mn, Al, Ca, Mg, Si), thereby improving the purity of the solution for the subsequent extraction stage.

Compliance with scientific development directions or government programs. Physico-chemical studies of copper sulfide mineral samples (chalcocite, bornite, chalcopyrite) using X-ray phase analysis, low-temperature nitrogen adsorption-desorption (Brunauer-Emmett-Teller method), and Mössbauer spectroscopy were carried out at the Institute of Solid State Chemistry and Mechanochemistry (Novosibirsk, Russia) within the framework of the state assignment of the ISSCM SB RAS No. 121032500065-5 “Composite nanomaterials for solid-state electrochemical devices” (2021–2024 yy.).

Approval and Presentation of the Research Results: The results of the dissertation research were presented and discussed at the 9th Interuniversity Conference-Competition (with international participation) of Student Scientific Works named after Corresponding Member of the USSR Academy of Sciences Alexander

Alexandrovich Yakovkin (St. Petersburg, 2020); at the 8th International Russian-Kazakh Scientific and Practical Conference “Chemical Technologies of Functional Materials” (Almaty, 2022); and at the 9th International Russian-Kazakh Scientific and Practical Conference “Chemical Technologies of Functional Materials” (Novosibirsk, 2023).

Publications. The results of the research conducted within the framework of this dissertation were published in co-authorship in 7 scientific works, including: 1 article in the international peer-reviewed journal Physicochemical Problems of Mineral Processing, indexed in the Web of Science database (SCIE, IF = 1.4, Q3); 3 articles in peer-reviewed journals included in the list of journals recommended by the Committee for Quality Assurance in the Sphere of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan; 3 conference abstracts in the proceedings of international scientific conferences.

Personal contribution of the PhD candidate to each publication:

1. Chalcopyrite leaching by amino acid solutions in the presence of hydrogen peroxide // Physicochemical Problems of Mineral Processing (research design, data collection, validation, methodology development, visualization, original draft writing, editing).

2. Kinetics of bornite leaching in the presence of glycine (In Russian) // VESTNIK KazNRTU (planning and conducting experiments, empirical data collection, validation, methodology, visualization, original draft preparation, editing).

3. Glycine leaching kinetics of chalcocite in alkaline medium in the presence of hydrogen peroxide (In Russian) // Chemical Journal of Kazakhstan (development of methodology, processing and interpretation of results, visualization, main text writing, contribution to editing).

4. Interaction of Chalcopyrite with Glycine and Lysine in Alkaline Medium (In Russian) // University Proceedings (acquisition and discussion of experimental data, methodology, visualization, original text preparation, editing).

5. Conference abstracts in international scientific conferences (research, data collection and analysis, methodology, visualization, original text writing).