ABSTRACT

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Borsynbayev Askhat Sakenovich

Study of physical and chemical characteristics of the process of metal extraction from waste of Zhezkazgan and Karagaily concentrators by means of electro-hydropulse discharge

General description of work. The dissertation is devoted to the study of physical and chemical processes of copper and other non-ferrous metals extraction from waste of Zhezkazgan and Karagaily concentrating plants by electro-hydropulse discharge (EHD) and electrochemical methods, as well as the study of new methods using leaching.

The relevance of the work. All over the world, the extraction and processing of metal-containing ores is associated with the formation of a large amount of waste in various physical states. Further accumulation of mining waste leads to a sharp deterioration in the environmental situation on Earth, in particular in Kazakhstan. In addition, the global non-ferrous metallurgy industry is experiencing a shortage of raw materials due to the depletion of the main raw material base. In this regard, it is necessary to create new environmentally friendly, energy-saving technologies for processing both minerals, focused on their maximum use, as well as the involvement of accumulated waste from processing enterprises in the production cycle.

The relevance of the research topic is determined by the need for new sources of raw materials for non-ferrous metals, the involvement of the enrichment stage in the production cycle of metal-containing waste, and the solution of environmental problems in places where mining and metallurgical enterprises are located. Further successful development of the copper industry in Kazakhstan is directly related to the introduction of new innovative and environmentally friendly methods for the complex processing of ores and waste, including unused waste located in dumps. In this work, such a method was the use of an electro-hydropulse discharge, which allows to achieve a quantitatively high yield of metals from the waste of Zhezkazgan concentrating plants (ZCP) № 1,2,3 and Karagaily concentrating plants (KCP) with relatively low energy consumption.

The purpose of the thesis – study of physical and chemical characteristics of the process of metal extraction from waste of Zhezkazgan and Karagaily concentrators by means of electro-hydropulse discharge

Research objectives. The main objectives are:

1. Analysis of literature data on the problem of processing non-ferrous metal ores and their waste and methods of using electro-hydropulse discharge;

2. Conducting granulometric analysis of samples with the possibility of using sieving methods for raw material enrichment;

3. Study of the elemental and mineral composition of waste from KCP, ZCP № 1,2,3;

4. Analysis of the processes of extracting metals from waste from KCP, ZCP № 1,2,3 into the solution after electro-hydropulse impact based on a multifactorial experiment;

5. Comparison of the efficiency of the method of exposure to electro-hydropulse discharge on the process of extracting metals from tailings from KCP, ZCP № 1,2,3 with and without ammonium difluoride

6. X-ray diffraction studies on a powder diffractometer and EDX analysis of samples before and after EHD processing;

7. Infrared (IR) spectroscopy and ion-chromatographic analysis for monitoring of the qualitative changes in the composition of a solution under the influence of EHD;

8. Studying the process of changing the structure of waste using a scanning electron microscope;

9. Obtaining electrolytic copper by processing concentrated working solutions.

Object and subject of research. The objects of study are waste samples obtained from concentrating plants (CP). Sample labels include Current Tailings from the Karagaily concentrating plant (KCP), Aged Tailings from Zhezkazgan concentrating plants (ZCP №1, 2), Current Tailings (ZCP №. 1, 2), and "Aged Tailings" (ZCP № 3). The subject of the research is the application of electro-hydropulse discharge and electrochemical methods to develop an effective method for extracting metals from depleted ores and tailings from the Zhezkazgan and Karagaily concentrating plants.

Research methods. The study employed modern analytical methods, including atomic absorption spectroscopy using a Varian AA-140 spectrometer (USA), atomic emission spectroscopy with microwave plasma (Agilent 4210 MP-AES, Agilent Technologies, Bayan Lepas Free Malaysia), semi-quantitative spectral analysis by laser-induced breakdown spectroscopy (SPEX LAES Matrix Continuum, Russia), X-ray phase analysis using a powder diffractometer (D8 Advance Eco, Bruker, Germany), elemental microscopic analysis with a Micromed POLAR 2 microscope (China), infrared spectroscopy (FSM-1201, LLC "Infraspek", Russia), ion analysis on an ion chromatograph (881 COMPACT IC PRO, Switzerland), and scanning electron microscopy (TESCAN MIRA, Czech Republic).

The scientific novelty. This research is the first to introduce a method to address the utilization of concentrating plant tailings, which contain valuable metals (Cu, Fe, Zn, etc.) and represent a potential raw material for producing concentrates of valuable elements.

1) For the first time, studies on the mineralogical composition, chemical analysis, and semi-quantitative spectral analysis (SQA) of the tailings from the Zhezkazgan and Karagaily concentrating plants were conducted both before and after leaching.

2) The studied objects (tailings) were analyzed using X-ray diffraction, spectral analysis, and scanning electron microscopy (SEM). It was found that copper is present in the tailings in the form of chalcopyrite, chalcocite, and bornite. After leaching with ammonium difluoride and electro-hydropulse discharge, these minerals were decomposed, and copper transitioned into a phosphoric acid-containing solution as a complex.

3) The activation energy of the leaching process for the Zhezkazgan and Karagaily concentrating plants tailings was determined for the first time, measured at 11.52 kJ/mol.

4) Through repeated introduction of tailings in the form of an aqueous layer into the solution, the copper concentration was increased to a level suitable for electrolytic deposition on a stainless steel plate. This was achieved using a novel combined electro-hydropulse method and an environmentally friendly electrolysis technique under alternating and direct currents.

5) A new method was developed for transferring non-ferrous metals from chemical concentrating plant waste into solution, followed by the identification of optimal conditions for recovering these metals as products.

Compliance with the directions of scientific development or state programs. The research was conducted under the agreement between LLP "Kazakhmys Corporation" and Karaganda State University named after E.A. Buketov, Contract №. D1941-190943-126581/371-2 dated May 17, 2019, as part of the project «Development of a technology for extracting metals from depleted ores, tailings, and mining and metallurgical industry waste using electrochemical processes and hydro-pulse discharge (HPD) energy for the extraction of copper (and other non-ferrous metals)». Laboratory analyses were carried out at LLP Tentrgeoanalyt (Karaganda), the Research Center "Applied Chemistry," the Engineering Profile Laboratory "Physicochemical Research Methods," the Institute of Molecular Nanophotonics, and the Scientific Center for Nanotechnology and Functional Nanomaterials at Karaganda University named after E.A. Buketov.

Theoretical and practical significance. The theoretical and practical significance of this thesis lies in the identification of the physicochemical behavior of metals (Cu, Fe, Zn, etc.) during electro-hydropulse treatment of waste (tailings) from the Zhezkazgan and Karagaily concentrating plants. It was determined that the decomposition of refractory minerals containing target metals requires the use of fluoride-containing reagents. The role of fluoride in the mineral decomposition process and the transition of metals into the working solution was elucidated. Multifactor analysis established the optimal ratio of ammonium difluoride to acid, ensuring maximum metal extraction. These findings contribute to the fields of inorganic chemistry, physical chemistry, and metallurgical chemistry.

The practical significance of the work is in the first-time investigation of concentrating plant waste and tailings as potential raw materials for extracting non-ferrous metals. It was demonstrated that electro-hydropulse treatment of aqueous pulp from waste with minimal reagents is an energy-efficient and environmentally friendly method for transferring valuable components into solution. The economic benefits of applying the new technology were calculated. A laboratory setup was

developed for experimental work on the electro-hydropulse treatment of depleted ores and tailings from concentrating plants. Metallic copper was obtained by electrolysis from pre-concentrated working solutions. A new method for extracting non-ferrous metals from concentrating plant waste was developed (Patent No. 6516 for a utility model, Republic of Kazakhstan, October 15, 2021).

The main provisions for defense:

1. In the studied waste, the target metal (Cu) is unevenly distributed depending on the granulometric fraction. Quantitative analysis of the metal in samples, conducted by sieving through various screens ($d > 0.4$; $0.16 < d < 0.4$; $0.08 < d < 0.16$; $d < 0.08$ mm), showed that copper concentrates in the fractions with diameters of $0.16 < d < 0.4$ and $0.08 < d < 0.16$.

2. To transfer metals into solution from the waste of Zhezkazgan and Karagaily concentrating plants, the electro-hydropulse process (EHP) was conducted in a solution containing ammonium difluoride, with the medium acidification using orthophosphoric acid to a pH of 1-2. During the EHP process, the decomposition of refractory silicate minerals occurs, along with the chemical interaction of reagents with target substances, their oxidation, fluorination, and the formation of ammonium-copper complexes in the aqueous phase.

3. Among the studied factors, the greatest efficiency of metal leaching from the waste is achieved (copper extraction rate into solution of 80-85%) under the following parameters: solid-to-liquid ratio (g/g) – 1:1; ratio of Cu to F (g/g) – 1:0.6; sulfuric acid concentration (g/L) – 40; duration of experiment – 30 minutes; discharge voltage – 10 kV.

4. Triple circulation of the working solution in the EHP setup, with the addition of new portions of waste, allows for the raise in the concentration of copper in the solution to 0.25 mol/L. Subsequently, using electrolysis with a ruthenium-titanium anode and a stainless steel cathode, copper with a purity of 99.99% was obtained.

The author's personal contribution to the thesis includes the analysis of literary and patent sources, the conduction of experimental and computational work on the constructed laboratory setup, and the interpretation, generalization, and discussion of the obtained experimental data.

Publications and approbation of the work. The main results of the thesis research have been published in 8 works, including 1 article in peer-reviewed scientific journals indexed in the Web of Science and Scopus databases, 3 articles in publications approved by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, and 4 conference abstracts at international conferences. A patent for a utility model has been obtained in the Republic of Kazakhstan.

The results of the work were discussed at international conferences: "Innovations in Natural Sciences as the Basis for Export-Oriented Industrialization of Kazakhstan: Materials of the International Scientific and Practical Conference" (April 4-5, 2019, Almaty, 2019, pp. 189-192), "Chemistry and Chemical Technology in the 21st Century: Materials of the 20th International Scientific and Practical Conference Named After Professor L.P. Kulev for Students and Young

Scientists" (May 20-23, 2019, Tomsk, 2019, pp. 43-44), "Chemistry, Physics, Biology, Mathematics, Theoretical and Applied Research: Materials of the 38th International Scientific and Practical Conference" (No. 7(27), Moscow, "Internauka" Publishing House, 2020, pp. 54-61), "30th Anniversary of Independence of the Republic of Kazakhstan: Materials of the 12th Traditional International Scientific and Practical Conference for Students" (March 19, 2021, Semey, 2021, pp. 241-244).

The structure and scope of the thesis. The dissertation work is presented in the amount of 103 pages and includes standard sections: normative references, definitions, designations and abbreviations, introduction, literature review, experimental part, experimental results and their discussion, including 57 figures and 29 tables, conclusion, list of 192 used sources and an appendix.