**ABSTRACT**

of the dissertation titled:

**"PROCESSING OF HEAP LEACH SOLUTIONS OF COPPER WITH REDUCED CRUD FORMATION DURING SOLVENT EXTRACTION UNDER THE CONDITIONS OF AKTOGAY MINING AND PROCESSING PLANT"**

submitted for the degree of Doctor of Philosophy (PhD)
in the specialty 8D07204 – Metallurgical Engineering
by **YESSIRKEGENOV MEIRBEK IBRAGIMOVICH**

**Objective of the study.**

The aim of the dissertation is to improve the processing technology of copper heap leach solutions with reduced crud formation during solvent extraction under the conditions of the Aktogay Mining and Processing Plant.

**Research Objectives**

– To conduct a technological assessment of the low-grade oxidized copper ore deposits of Almaly and Aktogay;

– To carry out a patent and literature review on potential processes for intensifying the SX-EW copper electroextraction technology;

– To perform a thermodynamic analysis of the processes of leaching, extraction, stripping (re-extraction), and crud formation;

– To determine the conditions for the formation and suppression of crud in the extraction process of copper recovery from heap leach solutions; to construct McCabe–Thiele isotherms for the extraction and stripping processes;

– To conduct laboratory and pilot-scale tests on the processing technology of copper heap leach solutions with reduced crud formation during solvent extraction;

– To apply energy-dispersive X-ray spectroscopy (EDX) to identify the causes and mechanisms of the influence of silica in crud;

– To carry out laboratory tests on the use of surface-active additives (coagulants and flocculants) to reduce crud formation;

– To perform mathematical modeling and an economic evaluation of the application of crud-reduction technology in copper electroextraction;

– To develop a process flowsheet for copper extraction from sulfuric acid solutions, which reduces sulfuric acid consumption, improves copper recovery and cathode copper quality, and minimizes the formation of the third phase (crud), which accumulates as a separate phase in the extract along with the raffinate and negatively affects phase separation, copper extraction, and the removal of non-ferrous metal impurities.

The methodologies and objectives presented in this dissertation are aimed at achieving the overall goal of the study.

**The object of the research**

The object of the research is the productive copper-bearing sulfuric acid leach solutions (PLS) from the Almaly and Aktogay deposits. The Almaly PLS contains copper in the range of 0.2 to 2.5 g/dm³, while the Aktogay PLS has a copper concentration of approximately 1.25 g/dm³.

**Methods of Research**

The study employed digital systems for processing thermodynamic data, including the HSC Outokumpu Ou and NETZSCH software; and modern analytical instruments: inductively coupled plasma atomic emission spectroscopy (Optima 8300DV), flame photometer PFP 7 (Jenway, UK), energy-dispersive X-ray spectroscopy, and infrared absorption spectra recorded using an FTIR spectrometer "Avatar 370" in the range of 400–4000 $cm^{-1}$ using capillary layers in KRS-5 windows. The experiment used the Transmission E.S.P. accessory. Data processing was performed using OMNIC 6 software with electronic libraries: HR Aldrich FT-IR Collection Edition II (18454 spectra), Aldrich Organometallic, Inorganic, Boron, Deuterium Compounds (632 spectra). Nicolet Instrument Corp. 1995. Literature sources were used to retrieve information absent from the electronic libraries. X-ray fluorescence analysis was carried out using the wavelength-dispersive spectrometer Axios PANalytical (Netherlands). X-ray phase analysis was performed on a D8 ADVANCE diffractometer "BRUKER AXS GmbH" (Germany), α-C radiation, tube voltage 40 kV, current 40 mA. Diffraction data processing and interplanar spacing calculations were performed using EVA software. Phase identification was carried out using the SeaCRh/match program with the PDF-2 database of the International Centre for Diffraction Data (ICDD, USA). A bench-scale pilot extraction unit with 2 extraction and 1 stripping stage was used.

**Key Provisions (Proven Scientific Hypotheses and Other New Findings Subject to Defense)**

1. Results of the thermodynamic analysis of copper dissolution processes.
2. Results of copper extraction from pregnant leach solutions (PLS) with crud suppression methodology from the Almaly deposit.
3. Results of copper extraction from pregnant leach solutions with crud suppression methodology from the Aktogay deposit.
4. Results of using surfactants in the copper extraction process.
5. Results of the development of a method and process flow diagram for copper extraction from sulfuric acid solutions.

The study was conducted at the Department of "Metallurgical Processes, Thermal Engineering and Special Materials Technology" of KazNITU named after K.I. Satpayev, Almaty.

**Justification of the Research Necessity**

The persistent decline in copper content in Kazakhstan's oxidized ores—from 0.37% in 2018 to 0.26–0.28% in 2024—demonstrates the urgent need for additional measures and scientific research aimed at improving copper recovery, solving the problem of crud formation, and reducing the cost of extractants.

**Description of Main Research Results**

The first section analyzes Kazakhstan's oxidized copper ores, their mineralogical composition, and their importance for hydrometallurgical processing. The solvent extraction (SX-EW) technology of copper is described, including the use of extractants and extraction equipment. Factors affecting process efficiency are considered, as well as methods for reducing crud formation using the ACORGA CR60 reagent to enhance stability and lower costs.

The second section provides a thermodynamic analysis of leaching and extraction processes using sulfuric acid and various extractants. The systems involving copper, manganese, silicon, and vanadium are examined, along with their effects on SX-EW processes. "Potential–pH" diagrams revealed the stability regions of various phases such as $Cu^{2+}$ ions, copper sulfides, oxides, and hydroxides. Thermodynamically stable compounds like dioptase ($Cu_6Si_6O_{18}\cdot 6H_2O$) and vanadium silicides ($V_5Si_3$, $VSi_2$, $V_3Si$) were identified. Manganese, silicon, and vanadium negatively impact extraction and electrolysis processes by forming hard-to-separate phases and increasing energy consumption. Suggested mitigation methods include the use of modified extractants, precipitation, and pH control.

The third section presents copper extraction studies from PLS of the Almaly and Aktogay deposits using different extractants. The results showed that maintaining pH at 1.7 significantly improves extraction efficiency, minimizes crud formation, and increases extractant selectivity. Experiments with Acorga 5640 and Lix 984N at specific pH levels achieved high copper recovery and minimized iron and silicate transfer into the organic phase.

The fourth section describes the developed technology to reduce crud formation during copper extraction from Aktogay PLS. The use of various extractants and additives such as CR60 stabilized the process and significantly reduced interfacial waste (crud). IR spectroscopy, X-ray phase analysis, and chemical composition helped determine optimal extraction parameters minimizing crud formation. A methodology was developed to enhance SX with crud-suppressing agents.

A mathematical model and Python-based optimization program for copper extraction from Aktogay PLS were developed. The economic benefit is achieved through process parameter optimization: copper concentration (1–1.25 g/dm$^3$), pH, extraction duration, and sulfuric acid concentration. The model increases copper recovery up to 88–90% and enhances process efficiency via optimal conditions. The optimization program ensures maximum copper extraction, improving throughput and reducing operating costs.

The techno-economic indicators of the process for Aktogay PLS are provided. The SX-EW scheme achieves 75% copper extraction at 2.5 g/L PLS concentration. The process consumes 533.33 m³ of PLS per ton of cathode copper, reducing waste mass and increasing output. Crud reduction provides an additional 525.6 tons of copper, equivalent to USD 3.7 million. The payback period is 1.1 years with a profitability of 45%.

**Scientific Novelty and Importance of the Results**

The scientific novelty lies in developing a technology for reducing third-phase (crud) formation by dissolving polymerized silicon bonds in crud using modified aldoxime extractants (ACORGA M5774, M5640), a surface-active complex of sodium alkylsulfonate, CR60 additive, and coagulating agents like POLYPACS-30. This technology includes a counter-current extraction scheme with 2–3 stages.

New scientific findings include:

A novel method for copper extraction from sulfuric acid solutions using 2–3-stage counter-current SX with 10 vol% aldoxime extractant and phase separation via settling. Crud suppression occurs via poly(4-styrenesulfonate sodium) and alkylsulfonate sodium surfactants at O:A = 1:2 and 20±5 °C.

First-time demonstration that adding 1% POLYPACS-30, CR60, and ACORGA 5640 to crud and centrifuging at 5000 rpm for 5–7 min reduces crud formation by 60–70%, improving SX quality and reducing extractant loss.

EDX spectroscopy revealed that high silica content in crud and its influence are due to monomeric $Si(OH)_4$, which at high concentrations forms colloidal gels that hinder flotation.

Polycondensation rate of silica depends strongly on pH: minimum at pH 2–3; accelerated by $H^+$ at lower pH and decelerated by $OH^-$ at higher pH.

High extractant content in crud is due to chelation and hydrogen bonding between oxime molecules and $Si(OH)_4$ or SiOH groups.

**Technological Innovation**

– A two-stage scheme for reducing crud formation has been developed for the first time. The first stage involves the use of an optimal mixture of the extractant ACORGA 5640 and the crud suppressant CR 60, which enables maximum copper extraction and reduces the content of colloidal silica. The second stage consists of the addition of 1 cm³ of a 1% POLYPACS-30 coagulant solution directly into the crud phase, followed by centrifugation at 5000 rpm for 5–7 minutes. This methodology allows for a 60–70% reduction in crud phase formation.

**Significance of the Obtained Results:**

– The developed technology significantly improves the process of copper extraction from sulfuric acid solutions, reduces the amount of crud formation, and enhances the efficiency of flotation and extractant recycling.

**Compliance with Scientific Development Priorities or National Programs**

The topic of this dissertation was carried out within the framework of grant funding for 2022–2024 under the project IRN AP14871587 “Development of an integrated technology for reducing crud formation during copper solvent extraction,” as part of the “Zhas Galym” project for 2023–2025 under IRN AR19175411 “Development of an integrated technology for intensifying the electrolysis process in cathode copper production,” and also within the framework of the PCF task IRN BR21881939 “Development of resource-saving energy-generating technologies for the mining and metallurgical complex and the creation of an innovative engineering center,” implemented in Laboratory No. 6 – “Laboratory of Metallurgical Processes, Heat Engineering and Powder Metallurgy” of the Innovative Engineering Center.

**Author’s Personal Contribution**

The author’s personal contribution lies in conducting the experimental research presented in the dissertation, including the development of experimental methodologies, execution of experiments, analysis, and presentation of the results in the form of publications and scientific reports.

**Thesis Approbation**

Based on the dissertation research, 8 printed works have been published, including 4 articles in international peer-reviewed scientific journals indexed in the Scopus/Web of Science databases:

1. T. Chepushtanova, M. Yessirkegenov, K. Mamyrbayeva, Ata Akcil & T. Gaipov. Extraction of Copper from Pregnant Leach Solution (PLS) and Reduction of Crud Formation. Mineral Processing and Extractive Metallurgy Review: An International Journal. April 14, 2024. https://doi.org/10.1080/08827508.2024.2340545. Q1, Percentile 89. Pages 1–13.
2. T. Chepushtanova, M. Yessirkegenov, Ye. Bochevskaya, A. Sharipova, O. Baigenzhenov, Y. Merkibayev, A. Altmyshbayeva. The Testing Results of ACORGA, LIX Extractants and CR60 Crud Mitigation Reagent Influence during SX-EW Copper Extraction. MDPI Sustainability, Q2, Percentile 88. Published: September 8, 2024. https://doi.org/10.3390/su16177815. Pages 1–17.
3. T.A. Chepushtanova, M.I. Yessirkegenov, A. Nikoloski, Y.S. Merkibayev, A.Zh. Altmyshbayeva. Development of an Enhanced Method for Copper Extraction from Sulfuric Acid Solutions. Kompleksnoe Ispolzovanie Mineralnogo Syra. Vol. 334, No. 3, 2025. Published: June 20, 2024. Q4. Pages 99–109. https://doi.org/10.31643/2025/6445.32.
4. T. A. Chepushtanova, M.I. Yessirkegenov, K.K. Mamyrbayeva, Y.S. Merkibayev. Investigations of the Extraction of Copper and Crud Formation from a Pregnant Leached Solution of the Almaly Deposit. Non-ferrous Metals, 2023 (2), Pages 11–19. DOI: 10.17580/nfm.2023.01.02. https://www.rudmet.ru/journal/2217/article/36739/
5. Chepushtanova, T. A.; Yessirkegenov, M. I.; Mamyrbayeva, K. K.; Merkibayev, Y. S.; Nikoloski, A. Testing of the Optimum Extractant for Solvent-

Extraction of Almaly Deposit Copper. Kompleksnoe Ispolzovanie Mineralnogo Syra. Jan–Mar 2023 (1), Pages 43–49. Q4.

6. T.A. Chepushtanova, M.I. Yessirkegenov, K.K. Mamyrbayeva, A. Nikoloski, A.K. Tulepbergenov. Study of the Extraction Process of Key Components (Copper, Iron, and Silica) from the Almaly Deposit Leach Solution. KarGTU Journal "University Proceedings", No. 1 (90), April 2023, Pages 23–29. DOI: 10.52209/1609-1825_2023_1_23.

7. M.I. Yessirkegenov, A.Ö. Mukangaliyeva, A.Zh. Altmyshbayeva, T.A. Chepushtanova, A. Nikoloski. Impact of Crud Formation on the Solvent Extraction of Copper at Kazakh Enterprises. Proceedings of the International Scientific Conference “Satpaev Readings 2022” – Almaty: KazNITU, 2022. Vol. 3. Pages 147–151.

8. T.A. Chepushtanova, M. Yessirkegenov, K.K. Mamyrbayeva, A. Nikoloski, V.A. Luganov. Interphase Formations in Copper Extraction Systems. Selected papers from the 63rd International Scientific Conference, October 23, 2020, Sofia, Bulgaria. Journal of Mining and Geological Sciences. Volume 63. Pages 31–37.

*Patent application:*

Invention application submitted: “Method of Solvent Extraction of Copper from Sulfuric Acid Solutions” No. 20524/0449.1 dated June 3, 2024. (Chepushtanova T.A., Yessirkegenov M.I., Mamyrbayeva K.K., Merkibayev E.S.)

*Monograph:*

T.A. Chepushtanova, M.I. Yessirkegenov, K.K. Mamyrbayeva, E.S. Merkibayev. Sustainable Development of Copper Hydrometallurgy – Principles and Technologies for Crud Reduction in Solvent Extraction. ISBN 978-601-08-4140-6. 136 pages.