

ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD) in the specialty 8D07202 – “Metallurgy”

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“RESEARCH AND DEVELOPMENT OF A TECHNOLOGY FOR THE RECOVERY OF VALUABLE COMPONENTS FROM METALLURGICAL SLAGS BY ELECTROCHEMICAL HYDROCHLORINATION”

Relevance of the topic. Copper and associated non-ferrous metals remain an important part of the economy of the Republic of Kazakhstan. The quality of primary raw materials is declining: the average copper content of mined ores has fallen from 8–10% in the 19th century to 0.52% in 2022, and the copper deficit may reach 30% by 2035. Therefore, the growing industrial demand for copper increasingly has to be met from technogenic sources. Large-tonnage dumps of copper smelting slags that pollute the environment have accumulated at the sites of operating non-ferrous metallurgy enterprises, while the existing industrial technologies do not provide sufficiently deep recovery of copper from dump slags. Dump slags differ from fresh slags in that, during long-term storage, the surface of copper-bearing sulfides oxidizes and becomes coated with secondary phases, which reduces the efficiency of flotation. Known technological solutions have been developed mainly for fresh slags; therefore, their performance cannot be transferred to dump material without experimental verification. Chloride methods are promising for slag processing but require the transportation and storage of gaseous chlorine. Electrochemical hydrochlorination removes this limitation, since chlorine is generated directly in the solution. No data on the application of this method to copper smelting slags have been found in the available literature; therefore, a technology for processing such raw material requires scientific substantiation. Copper was adopted as the target component, while the behavior of associated components is considered in terms of process selectivity and the environmental safety of the solid residue. The research direction is consistent with the priorities of the state policy of the Republic of Kazakhstan in the field of rational use of natural resources, development of the manufacturing industry and environmental safety of technogenic territories.

Scientific novelty of the obtained results:

– A comprehensive study of the dump slag of the Balkhash Copper Smelting Plant was carried out, which established its current state after long-term storage in the dump: phase and mineralogical composition, forms of copper occurrence and their changes in comparison with fresh slag. It was shown that physical preconcentration methods (magnetic separation, gravity concentration, flotation) do not provide effective separation of copper from the dump slag, which justifies the transition to its direct chemical processing.

– The fundamental possibility of recovering copper from dump copper smelting slags by electrochemical hydrochlorination with generation of active chlorine directly in the pulp from sodium chloride solution was experimentally proven for the first time. Without preliminary concentration and without continuous dosing of hydrochloric acid, copper recovery amounted to 70.0% from the dump

slag of the Balkhash Copper Smelting Plant and 45.0% from the dump slag of the Zhezkazgan Copper Smelting Plant, which was additionally studied to verify the applicability of the method to a different type of slag; the difference in recovery is consistent with the proportion of accessible copper forms in these slags.

– It was established that the selectivity of copper and iron separation during electrochemical hydrochlorination of dump slag is ensured by pH control rather than by acid consumption. Copper phases are decomposed in an acidic chloride medium at pH 1.2–1.5, and the subsequent increase in pH to 3.0–4.0 transfers iron(III) to the solid residue while copper remains in solution in the form of chloro complexes; the upper limit of the process is pH 4.0–4.5. It was shown that the process proceeds in a self-acidifying mode: the acid formed during the oxidation of sulfides compensates for the cathodic formation of hydroxide ions, which makes it possible to eliminate continuous dosing of hydrochloric acid without reducing copper recovery. Under the established conditions, about 1.0% of the initial iron passes into the final pregnant solution.

– Regularities of the influence of current, sodium chloride concentration, process duration and liquid-to-solid (L:S) ratio on copper recovery and co-extraction of iron were revealed. It was shown that the decisive electrical parameter is the specific charge per unit mass of slag, and that exceeding the sufficient electrical load or increasing the NaCl concentration to 300 g/dm³ does not increase copper recovery but intensifies the dissolution of the iron silicate matrix and the redistribution of copper to the cathode.

The purpose of the dissertation work is the scientific substantiation and development of a technology for recovering copper from dump slags of the Balkhash Copper Smelting Plant by electrochemical hydrochlorination that provides higher copper recovery than physical concentration methods and limits the transfer of iron into solution.

Provisions submitted for defense:

1. The current state of the dump slags of the Balkhash and Zhezkazgan copper smelting plants has been determined – material composition, forms of occurrence of copper and associated metals, and structure; the inefficiency of physical preconcentration methods for deep recovery of copper has been proven, which justifies the transition to chemical decomposition.

2. Electrochemical hydrochlorination has been applied to copper smelting slags for the first time, and it has been shown that active chlorine generated at the anode directly in the pulp from sodium chloride decomposes copper sulfide phases without an external chlorine supply; the region in E–pH coordinates in which copper remains in solution while iron(III) hydrolyzes has been established. The behavior of other valuable metals (lead, zinc and silver) during slag treatment has also been studied; no transfer of gold into solution was detected.

3. Selective separation of copper and iron during electrochemical hydrochlorination of slags has been scientifically substantiated and experimentally confirmed for the first time: it is achieved by controlling the natural change of pH in the self-acidifying mode, which was identified in exploratory tests and does not require continuous dosing of acid.

4. Copper recovery and the behavior of iron are determined by the combined effect of current, sodium chloride concentration, duration and L:S ratio: above the optimum, each of these parameters intensifies side processes without a significant increase in copper recovery; therefore, the operating mode is determined by joint optimization of current, NaCl concentration and duration according to a Box–Behnken design at L:S = 6:1. These regularities have been established for copper smelting slags for the first time using an electrolyzer of original design, and the established mode has been verified on the slag of the Zhezkazgan plant and confirmed by material balances.

5. Processing of dump copper smelting slag by electrochemical hydrochlorination is feasible in principle according to a scheme with a closed electrolyte loop without continuous dosing of hydrochloric acid and, according to a preliminary assessment, is economically viable under the conditions of the Balkhash Copper Smelting Plant.

Practical significance of the work – a technology for processing dump copper smelting slags has been developed that provides deeper copper recovery than the existing industrial methods of processing dump slags. The results of the work can be used in the design of industrial slag processing units at operating copper smelters of the Republic of Kazakhstan and the countries of the Commonwealth of Independent States. The data obtained on the physicochemical properties of the slags of the Balkhash Copper Smelting Plant and on the regularities of electrochemical hydrochlorination can serve as a basis for further research and development work in the field of processing technogenic raw materials of non-ferrous metallurgy.

Approbation of the work: a utility model patent of the Republic of Kazakhstan No. 12292 “Method for processing metallurgical slags” (Bulletin No. 21 dated 29.05.2026) has been obtained.

Three papers have been published based on the materials of the dissertation, including:

– an article in a journal indexed in the Scopus (Chemical Engineering (miscellaneous), Q2) and Web of Science databases:

1. Kurmangaliyev D., Abdulina S. Physicochemical characteristics of copper smelting slags from Kazakhstan and their potential for secondary resource recovery // Processes. – 2026. – Vol. 14, No. 1. – Art. 113.

– articles in publications recommended by the Committee for Control in the Sphere of Education and Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan:

1. Kurmangaliyev D.B., Abdulina S.A., Mamyachenkov S.V. Promising methods for hydrometallurgical processing of copper slag // Complex Use of Mineral Resources. – 2022. – No. 4(323). – pp. 46–50.

2. Kurmangaliyev D.B., Abdulina S.A., Krykpaeva A.A., Mamyachenkov S.V. A method for extracting valuable components from copper smelter slag // Bulletin of D. Serikbayev EKTU. – 2023. – No. 3. – pp. 80–87.

Structure and scope of the dissertation.

The dissertation consists of an introduction, four chapters, a conclusion, a list of 101 references and three appendices. The work is presented on 104 pages of typewritten text and contains 32 tables, 22 figures and 18 numbered formulas.