# ANNOTATION

**Dissertation for the degree of Doctor of Philosophy (PhD) in educational program 8D07201 (6D070900) – «Metallurgy»**

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## «RESEARCH AND DEVELOPMENT OF HYDROMETALLURGICAL SCHEME OF JOINT PROCESSING OF TECHNOLOGICAL SOURCES AND «E-WASTE»»

**Relevance of the dissertation topic.** Non-ferrous metals such as copper, gold, silver, platinum and palladium play a key role in modern industry due to their unique properties - high electrical conductivity, resistance to corrosion and ability to participate in catalytic processes. With the development of technology, their use in the electronics industry has increased significantly, especially in the production of microchips, contacts, connectors and other components. However, the decrease in the volume and quality of traditional mineral raw materials leads to the need to search for alternative sources of extraction of valuable metals.

One of the promising solutions to this problem is the recycling of technogenic raw materials and electronic waste (e-waste), which contain a significant amount of non-ferrous metals. The growth of e-waste volumes worldwide, including Kazakhstan, makes the issue of their utilization and recycling particularly urgent. According to the concept of «green economy», by 2050 Kazakhstan plans to increase the level of industrial waste recycling to 60%, which requires the introduction of advanced technologies in this area. In addition, the «Business Roadmap – 2025» defines waste collection and recycling as one of the priority sectors of the country's economy.

Involvement of technogenic and electronic waste in the production cycles of enterprises not only contributes to the rational use of natural resources, but also reduces the ecological load on the environment. Hydrometallurgical technologies for the extraction of non-ferrous metals are a promising direction for the processing of secondary resources, providing a high degree of their recovery with minimal impact on nature. Thus, the study and development of hydrometallurgical scheme of processing of technogenic raw materials and e-waste is an urgent scientific and technical task, which has an important economic and environmental significance for Kazakhstan and the world industry.

**The purpose of the dissertation** work is to study the form of non-ferrous metals in technogenic raw materials and “e-waste” to increase the recovery of copper, gold and silver by intensification of hydrometallurgical processing using modern methods and apparatus - technological design processes

**Research objectives.**

- Determination of composition of slags of Balkhash smelter, tailings of flotation enrichment of Maikain factory №1
- determination of composition of “e - waste” (printed circuit boards of

smartphones);

- determination of possibility of joint processing of slags of Balkhash smelter and tailings of flotation enrichment of Maikain factory №1;

- determination of possibility of hydrometallurgical processing of “e - waste”;

- study of thermodynamic and kinetic parameters of the process of extraction of non-ferrous metals;

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**Objects of research**

1) Tailings of enrichment of Maikain enrichment plant No.1. Location Pavlodar region, RK.

2) The lying waste slags of Balkhash copper smelting plant, Karaganda region, RK.

3) E-waste raw materials. Printed circuit boards of computers and smartphones.

**Scientific novelty.**

Based on the obtained kinetic data for the first time:

- determined the mechanism of the process of sulfuric acid leaching of copper from waste slags of the Balkhash smelter with the influence of ultrahigh-frequency radiation. The influence of super high-frequency radiation on increase of copper extraction rate at temperatures from 25°C to 85°C at the expense of activation energy decrease from 19,108 kJ/mol (without microwave) to 15,517 kJ/mol that testifies to decrease of threshold of diffusion limitation of leaching process rate is substantiated;

- the mechanism of reaction flow of gold leaching with thiourea aqueous solution from tailings of flotation enrichment MZF-1 with pretreatment of raw materials with super high-frequency radiation was established. The increase in gold recovery by increasing the opening of pyrite from 94.7 (without microwave) to 97.35 (microwave) containing gold inclusions by direct heating of metal inclusions with ultra-high frequency radiation, which leads to a decrease in the activation energy of the process by reducing the layer of waste rock and reducing the diffusion limitation, was justified.

- the effect of intensifying ultrasonic radiation on the extraction of gold and silver from e-waste, in aqueous solution of thiourea, at temperatures from 25 ° C to 60 °C, expressed in the reduction of the activation energy of the process of extraction of gold and silver from 31, 087 kJ/mol (without ultrasonic) to 14,941 kJ/mol and from 26,618 kJ/mol (without ultrasonic leaching) to 13,098 kJ/mol, respectively, which indicates a lowering of the threshold of diffusion limitation of the leaching process rate.

- a five-factor mathematical model of the process of gold extraction by leaching in aqueous thiourea solution with intensification of the process by ultrasound from mixed technogenic waste and “e-waste” was obtained.

**Practical significance.**

The technological scheme of joint processing of technogenic raw materials

and «e-waste» by hydrometallurgical method, which passed pilot-laboratory tests, is recommended for implementation by «Incom» LLP and received an expert opinion from JSC «Maikainzoloto».

The developed and patented method allows to carry out joint processing of technogenic raw materials and “e-waste”.

The technology of processing of technogenic and “e-waste” raw materials by hydrometallurgical method was tested by pilot laboratory tests. A patent for useful model “Method of gold extraction from refractory ores, secondary and technogenic raw materials” was obtained. Patent for useful model No. 8276. From 21.07.2023.

The reliability of the research results is confirmed by the use of the following certified equipment of the accredited laboratories of Center of Excellence «Veritas»:

-mass spectrometer with inductively coupled plasma ICP-MS 7500 cx to determine the content of elements by spectral method was used;

-X-ray diffractometer X'Pert PRO company Panalitical for the study of phase composition was used;

-raster electron microscope JSM-6390LV produced by "JEOL Ltd. “(Japan) with energy dispersive microanalysis system INCA EnergyPenta FET X3 by ”OXFORD InstrumentsAnalyticalLimited" (UK) for the study of topography and microstructure of the surface of samples and specimens (including dielectrics - in low vacuum mode), qualitative and quantitative elemental microanalysis in the point area, etc.

- HSC9 software package for thermodynamic modeling of processes;

**Provisions for defense**

1. Influence of microwave (P=1 kW, frequency 2,45 GHz), at joint processing of technogenic raw materials: slags of Balkhash copper smelting plant (BCSP) and tailings of flotation enrichment of JSC “Maikainzoloto” at the stage of oxidative roasting at leaching of copper with aqueous solution of sulfuric acid increases copper recovery from 82% to 89%, and reduces E act from 19,108 kJ/mol (without microwave) to 15,517 kJ/mol

2. Exposure to ultrasonic intensified leaching (P=50 W, frequency 35 kHz) in an aqueous thiourea solution during e-waste recycling by leaching, increases the recovery of gold from 79, 4% to 88.6% and silver from 41% to 56.3%, by reducing the E act from 31.087 kJ/mol (without ultrasonic ) to 14.941 kJ/mol (with ultrasonic ) for gold and from 26.618 kJ/mol (without ultrasonic) to 13.098 kJ/mol (with ultrasonic ) for silver.

3. Mathematical model obtained by probabilistic-deterministic method of experiment planning with the possibility of extrapolating the results with high probability and degree of adequacy for:

- process of gold extraction from mixed technogenic wastes (slag of BCSP and tailings of JSC Maikainzoloto) using an aqueous solution of thiourea (model correlation coefficient R = 0.99; significance of the correlation coefficient $t_R$ = '86.5);

- process of gold extraction from e-waste (model correlation coefficient R = 0.86; significance of correlation coefficient $t_R$ = 11.5 ' 2)

4. Justification of economic efficiency of the proposed technological solutions

**Publications and approbation of the work: the main scientific results of the thesis work are presented: 1. In five publications in journals included in the Scopus database:**

- Shoshay Zh, Sapinov R.V., Sadenova M.A., Varbanov P.S., 2021, Hydrometallurgical Methods for Extracting Non-ferrous Metals from Electronic Gadgets Chemical Engineering Transactions 88, 139-144. DOI: 10.3303/CET2188023 - Scopus (Q3 (3 quartile), percentile 35)

- Shoshay Zh, Sapinov R.V., Sadenova M.A., Varbanov P.S., 2021, Intensification of the Process of Extracting Non-Ferrous Metals from Kazakhstani Technogenic Raw Materials Chemical Engineering Transactions 88, 1069-1074. DOI:10.3303/CET2188178 - Scopus (Q3 (3 quartile), percentile 35)

- Shoshay Z., Sapinov R.V., Sadenova M.A., Beisekenov N.A., Varbanov P.S., Suyundikov M., 2022, Application of Probabilistic-Deterministic Method For Experiment Planning Of Hydrometallurgical Processing Of Various Wastes For Gold Extraction, Chemical Engineering Transactions, 94, 1135-1140 DOI:10.3303/CET2294189. DOI: 10.3303/CET2294189 - Scopus (Q3 (3 quartile), percentile 28)

- Shoshay Zh., Sadenova M.A., Suyundikov M.M., Sapinov R.V., Varbanov P.S., Absolyamova D.R. Investigation of ultrasonic influence on the kinetics of extracting gold from electronic waste. Metalurgia 62 (2023) 2, 207-210. https://hrcak.srce.hr/290058 - Scopus (Q3 (3 quartile), процентиль 35)

- Shoshay Z., Sapinov R.V., Sadenova M.A., Varbanov P.S., Bayeva A.B., 2023, Kinetic Features of Technogenic Raw Material Leaching in Aqueous Sulphuric Acid Solution with Microwave Intensification, Chemical Engineering Transactions, 103, 547-552. DOI: 10.3303/CET23103092 - Scopus (Q3 (3 quartile), percentile 27)

**One publication in a journal from the list of editions recommended by the Committee for Quality Assurance of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan**

1. Шошай Ж., Сапинов Р. В., Саденова М. А., Баева А. Б., Корабаев Б. С. Изучение влияния микроволновой активации на гидрометалургический процесс извлечения золота из техногенных отходов. Научный журнал «Наука и техника Казахстана». – 2023. - № 3. – С. 184–196.

A patent for utility model of the Republic of Kazakhstan “Method of gold extraction from refractory ores, secondary and technogenic raw materials” was obtained.

The main results were reported at 5 international conferences:

1. 24-я конференция по интеграции процессов, моделированию и оптимизации для энергосбережения и сокращения загрязнения – PRES'21, Брно, Чешская Республика Октябрь 2021 г. онлайн

2. 25$^{th}$ Conference on Process Integration, Modelling, and Optimisation for Energy Saving and Pollution Reduction Sustainable Process Integration Laboratory (SPIL), Brno University of Technology, Technická 2896/2, 616 00 Brno, Czech Republic. Сентябрь 2022 г. онлайн

3. Шошай Ж., Сапинов Р.В., Саденова М.А., Варбанов П.С. Техногендік және электронды қалдықтардан алтынды алу мүмкіндіктерімен мәселелері. Международная научно-практическая конференция «Проблемы и перспективы металлургической отрасли: теория и практика». 2023. Стр. 217-220

4. Shoshay Zh., Sadenova M., Varbanov P. Recovery of silver from electronic scrap (methods, features and prospects) //III International Scientific Conference on “Sustainable and Efficient Use of Energy, Water and Natural Resources” (19-24 April 2021 Saint-Petersburg): Saint-Petersburg 2021 pp.273

5. The 24th conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction - PRES'21 has been organised by the Sustainable Process Integration Laboratory - SPIL, NETME Centre, Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czech Republic. The venue took place 31 October – 3 November 2021. c. 139–144. Online

**Structure and scope of the thesis. The dissertation consists of the introduction,** 4 chapters, conclusion and 6 appendices. The work is laid out in 142 pages of typewritten text, contains 49 tables and 68 figures. The list of used sources includes 125 titles.