ABSTRACT

of the dissertation on the topic:

"COMPREHENSIVE PROCESSING OF THE SHALKIYA DEPOSIT OXIDE NATURAL AND SULFIDE TECHNOGENIC ZINC-CONTAINING RAW MATERIALS",

 submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D7220 – "Metallurgy"
MAKHANBETOVA BAKTYGUL ALIMSHANOVNA submitted for the degree of Doctor of Philosophy (PhD)

The purpose of the work.

The purpose of the dissertation is the theoretical and experimental substantiation of developing a technology for the comprehensive processing of the Shalkiya deposit oxidized zinc-containing ores and sulfide ore's concentration tailings with the simultaneous production of silicon ferroalloys and zinc sublimates.

The objectives of the study are:

- to perform thermodynamic modeling of the interaction of zinc, lead, iron sulfides with carbon and magnetite and determine patterns of producing ferroalloys and Zn-Pb sublimates;

- To establish, using thermodynamic modeling coupled with the second-order rotatable designs, the optimal process parameters for the equilibrium extraction degree of silicon into alloy, zinc and lead into sublimates, the concentration of elements in the products during the interaction of Shalkiya oxidized ore, its concentration tailings in a mixture with sulfide ore in the presence of carbon, iron, magnetite;

- To develop mathematical models based on which to determine the optimal process parameters (consumption of coke, steel shavings, magnetite concentrate) for producing high-quality ferrosilicon by electric smelting from Shalkiya deposit oxidized ore, its concentration tailings and their mixtures and extracting zinc and lead into sublimates;

- To study the kinetics of silicon extraction into ferroalloy during electric smelting of Shalkiya oxidized ore and its concentration tailings;

- Conduct large-scale laboratory tests of electric smelting of the Shalkiya deposit ore's concentration tailings mixed with coke, steel shavings, magnetite concentrate and sulfide ore to produce ferrosilicon and catch sublimates containing zinc and lead;

- To calculate economic indicators of the created technology for comprehensive processing of the Shalkiya deposit zinc-containing oxidized ore and its concentration tailings to produce commercial ferrosilicon and Zn-Pb sublimates.

The object of the research is:

The object of the research is oxide natural and sulfide man-made zinccontaining ore of the Shalkiya deposit.

Methods for studying objects

To accomplish the research objectives, the following methods were used in the work: computer thermodynamic modeling using the HSC-6.0 software package (Outokumpu, Finland), based on the principle of minimizing the Gibbs energy; electric smelting in arc laboratory and large-scale laboratory electric furnaces; planning an experiment using the second-order rotatable designs (Box-Hunter plan); creating mathematical models of formation of target products; constructing 3D and planar images with optimization on their basis of conditions for producing commercial ferrosilicon and extracting non-ferrous metals. To analyze raw materials and products, the following instrumental and chemical methods were used: scanning electron microscopy using a scanning electron microscope JSM-6490LV (Japan) with INCA energy-dispersive microanalysis systems; X-ray diffractometry on an automated diffractometer DRON-3 with SiKa radiation, β filter; X-ray spectral microanalysis on a Superprobe 733 electron probe microanalyzer, JEOL (Japan); differential thermal analysis using a derivatograph Q-1000D MOM (Paulik-Erdey, Hungary); pycnometric method; gravimetric method for determination of silicon; complexometric method for determination of zinc.

Main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for the dissertation defense

1. Results of studies of thermodynamic modeling of the interaction of zinc, lead, iron sulfides (and their mixtures), as well as the Shalkiya deposit oxidized and sulfide ores and its concentration tailings with carbon in the presence of iron and magnetite.

2. Results of the kinetics of silicon extraction into ferroalloy from the Shalkiya zinc-containing ore and its oncentration tailings.

3. Optimum conditions ensuring producing commercial ferrosilicon with maximum extraction of silicon into alloy, zinc and lead into sublimates during electric smelting: a mixture of Shalkiya oxidized and sulfide ores; a mixture of the concentration tailings and Shalkiya sulfide ore.

4. Results of large-scale laboratory tests on the comprehensive processing of the Shalkiya ore's concentration tailings by electric smelting to produce commercial ferrosilicon and Zn-Pb sublimates.

Justification of the need to conduct research work

Currently, the zinc sub-industry lacks a technology for the comprehensive processing of not only stale and current concentration tailings, but also difficult-todress oxidized ores. This, in particular, applies to the Shalkiya deposit ore, because its processing is accompanied by the formation of tailings, the accumulation of oxidized ore in the dumps and a low level of use of raw materials. In this regard, an objective need arose to conduct targeted physicochemical and applied research, the results of which make it possible to create a new technology for the comprehensive processing of oxidized zinc ores and Shalkiya ore's concentration tailings with the simultaneous production of ferrosilicon and zinc and lead containing sublimates in an electric furnace with a partial replacement of steel shavings with magnetite concentrate.

Description of the main results of the study

Using the method of coupling computer thermodynamic modeling and second-order rotatable experiment planning, the conditions were found for producing FeSi25 and FeSi45 grades of ferrosilicon and extracting at least 98% of zinc and 90% of lead in the gas phase from the Shalkiya oxidized ore, concentration tailings and their mixtures.

Based on the experimentally obtained mathematical models, the optimal process parameters for producing FeSi25 and FeSi45 grades of ferrosilicon and sublimates containing 35.5-39.5% of \sum Zn and Pb from the Shalkiya oxidized ore, ore beneficiation tailings and their mixtures were determined, with the extraction of 75-85% of silicon into the alloy and 98-99% of zinc and lead into the sublimates.

The kinetics of silicon extraction into ferrosilicon during the electric smelting of the Shalkiya oxidized ore mixed with its concentration tailings and sulfide ore was investigated. The limiting stage of the process depending on the composition of the charge used was found.

Large-scale laboratory tests of electrothermal processing of the concentration tailings and sulfide ore in the presence of steel shavings, coke, magnetite concentrate and sulfide ore established that the formation of FeSi45 grade ferrosilicon with the extraction of 83-86% of silicon occurs during the smelting of the tailings with magnetite concentrate. Almost all zinc and lead are extracted into sublimates containing up to 31% of Zn and up to 10.1 of Pb.

Estimated economic indicators of the proposed technology for producing ferrosilicon and zinc and lead containing sublimates from a mixture of the oxidized and sulfide ores and their concentration tailings showed that the profit from processing 200,000 tons of the ores and the tailings per year will be 21.6-22.2 million US dollars, the payback period of investments is 3 years, profitability is 31.3-32.1%.

Justification of the novelty and importance of the obtained results

The novelty of the dissertation topic is the development of a technology for comprehensive electrothermal processing of the Shalkiya deposit oxidized ores, the Shalkiya deposit sulfide ore's concentration tailings and their mixtures with the simultaneous production of ferrosilicon and zinc and lead containing sublimates.

The new scientific results are as follows:

- It was established that the carbothermic reduction temperature of zinc sulfide decreases by 414 °C if the process is carried out in the presence of magnetite; in this case, the reactivity series of sulfides changes as follows: PbS> ZnS>FeS₂;

- It was found that the carbothermic reduction of ZnS under equilibrium conditions in the presence of magnetite has a staged nature. At the first stage, Fe₃O₄ is reduced to Fe and FeO. Then, a part (27.3%) of ZnS is reduced with iron. At the last stage (T>1600 °C) it is completed (up to 88.3% at 1800 °C) by the formation of elemental zinc due to the interaction of ZnS with FeO.

- Thermodynamic models of the interaction of the Shalkiya oxidized ore and its concentration tailings and their mixtures with carbon, magnetite, and iron were created, using the established temperature ranges of existence of Fe₃Si, Fe₅Si₃, FeSi, FeSi₂, FeSi_{2.33}, FeSi_{2.43}, Si, SiO_(g), Zn, Zn_(g), Pb, Pb_(g) and ferrosilicon of FeSi25, FeSi45 and FeSi50 grades;

- The constructed 3D images of the electric smelting of the Shalkiya oxidized ore, its beneficiation tailings and their mixtures allowed us to establish the reason for the decrease in the degree of silicon extraction into the alloy with excess carbon – the formation of gaseous SiO and SiC, and also the positive effect of iron on the process due to the fact that it destroys silicon carbide;

- It was established that the electric smelting of the Shalkiya oxidized ore, its beneficiation tailings and sulfide ore mixture in the presence of magnetite is accompanied by the foaming of the melt associated with the presence of gaseous products (CO, SO₂, Zn, Pb) in the melt;

- It was found that the silicon extraction into the alloy during the electric smelting of the Shalkiya oxidized ore and its beneficiation tailings in the presence of magnetite occurs in a transitional mode.

Technological novelty of research:

Based on the experimentally obtained mathematical models, the optimal process parameters (amount of coke, amount of steel shavings, degree of replacement of iron contained in scarce steel shavings with iron contained in the magnetite concentrate) were determined for producing ferrosilicon of FeSi25 and FeSi45 grades and sublimates containing 35.5-39.5% of Σ Zn and Pb from the Shalkiya oxidized ore, its concentration tailings and their mixtures, with extraction of 75-85% of silicon into the alloy and 98-99% of zinc and lead into the sublimates.

The conducted large-scale laboratory tests on the electrothermal processing of the concentration tailings and sulfide ore mixture allowed us to establish that during the formation of FeSi45 ferrosilicon, the maximum degree of silicon extraction into the alloy (83-86%) takes place during the smelting of the tailings and the ore in the presence of magnetite concentrate. At least 98-99% of zinc and lead are extracted in the sublimates containing up to 31% of Zn and 10.1 of Pb.

The economic indicators of the processing the Shalkiya oxidized ore and its concentration tailings were calculated. The profit from the processing 200,000 tons of the ore per year will be 21.6-22.2 million US dollars, the payback period of investments is 3 years.

The importance of the results obtained:

The practical significance and technological novelty of the developed method for processing of the Shalkiya ore was confirmed by Patent for invention of the Republic of Kazakhstan No. 36683 dated 05.04.2024.

Compliance with scientific development directions or state programs

The topic of the dissertation corresponds to the priority direction of scientific development "Ecology, environment and rational nature management"; it

corresponds to the specialized scientific direction "Deep processing of mineral and organic resources" of the National Scientific Council under the Government of the Republic of Kazakhstan.

In accordance with the Classifier of Scientific Directions, the field of the research is "Engineering and technology; Engineering of materials; Metallurgy".

The dissertation work was carried out according to the targeted financing on the topic "Development of a comprehensive technology for processing of the Shalkiya and Zhairem deposits difficult-to-dress polymetallic ores" within the framework of the program BR19777171 "Development of fundamentally new technologies for comprehensive processing of polymetallic raw materials" for 2023-2025 under agreement No. 35 dated June 16, 2023 between the Republican State Enterprise with the Right of Economic Management "National Center for Comprehensive Processing of Mineral Raw Materials of the Republic of Kazakhstan" and the Industry Committee of the Ministry of Industry and Construction of the Republic of Kazakhstan.

The personal contribution of the author consists in setting the goal and objectives of the work, conducting experimental studies, processing and analyzing the results obtained, formulating conclusions, writing articles, patents and abstracts of reports.

Thesis approbation

Based on the results of the dissertation research, 16 printed works were published, including 6 articles in international peer-reviewed scientific journals included in the Scopus/Web of Science database:

1. **Makhanbetova B**., Shevko V., Aitkulov D. Producing A Ferroalloy And Zinc Concentrate From The Shalkiya Deposit Sulfide And Oxidized Ores' Mixture. Journal of Applied Science and Engineering (Taiwan). -2025. - №. 28(1). Journal of Applied Science and Engineering (Taiwan).2025. - №. 28(1).Vol.60 (**Procentile 69**)

2. Shevko V., **Makhanbetova B.**, Aitkulov D., Badikova A. Optimization of joint electric smelting of the Shalkiya sulfide ore and its beneficiation tailings with medium-silicon ferrosilicon production. Complex Use of Mineral Resources, 2025, 334(3), pp. 91–98 (**WoS, Q4**)

3. Shevko V., **Makhanbetova B.**, Aitkulov D., Badikova A., Amanov D. Thermodynamic and Experimental Substantiation of Comprehensive Processing of Zinc Sulfide Ore and Its Concentration Tailings to Extract Non-Ferrous Metals and Produce a Silicon Ferroalloy. Minerals. - 2024. - №. 14(8), 819. (**Procentile 74**)

4. Shevko V., **Makhanbetova B.**, Aitkulov D., Badikova A. Smelting a Zn – Pb Sulfide Ore with Magnetite and Carbon for the Production of a Silicon Alloy and Extraction of Zinc and Lead into Sublimates. Periodica Polytechnica Chemical Engineering. - 2024. - N_{\odot} . 68(1). (**Procentile 53**)

5. Shevko V., **Makhanbetova B.**, Aitkulov D. Theoretical and experimental substantiation of obtaining an alloy from flotation tailings of lead-zinc sulfide ore. Physicochemical Problems of Mineral Processing. - 2023. - №. 59 (1). (**Procentile 52**)

6. **Makhanbetova B.,** Shevko V., Aitkulov D., Lavrov B., Badikova A. Optimization of pyroprocessing of zinc sulfide ore to produce ferroalloy and zinc. E3S Web of Conferences 531, 010 (2024) (**Procentile 23**)

Patent application:

1. Патент РК. Способ переработки высококремнистых сульфидных свинцово – цинковых руд. Патент на изобретение № 36683 КZ. Бюл.14. -опубл. 05.04.2024. (По заявке 2023/0004.1) Айткулов Д.К, Жарменов А.А, Абыкаев Н.А, Шевко В.М, Школьник В.С, Саткалиев С.О, Терликбаева А.Ж, Байсанов С.О, Маханбетова Б.А,Искаков Б.О.

Scientific papers in the materials of domestic and foreign international conferences:

1. Shevko V., Aitkulov D., **Makhanbetova B.,** Badikova A. Creation of a mining and metallurgical complex in the Kyzylorda. Proceeding VII International Conference «Industrial Technologies and Engineering» ICITE – 2021, Volume I. 10-11.11.2021

2. **Makhanbetova B.A.,** Shevko V.M., Aitkulov D.K., Badikova A.D., Lavrov B.A. Oxidative firing of flotation tailings of the Shalkiya deposit enrichment. Science foundations of modern science and practice. Abstracts of X International Scientific and Practical Conference. Athens, Greece. -2021. - pp. 575-581.

3. Шевко В.М., **Маханбетова Б.А.**, Абжанова А.С., Тулеев М.А.Взаимодействие магнетита с сульфидами цинка и железа. Труды МНПК ««Ауэзовские чтения–20: наследие Мухтара Ауэзова - достояние нации». - Шымкент: ЮКГУ им. М. Ауэзова, 2022. -С224-228

4. Маханбетова Б.А., Шевко В.М., Айткулов Д.К. Оптимизация извлечения кремния из руды Шалкия в присутствии углерода и железа. Материалы МНПК «Инновации и комплексная переработка минерального сырья-актуальные составляющие диверсификации экономики» (12-14 октября, Алматы). 2023.Т.1

5. **Makhanbetova B.,** Shevko V., Aitkulov D., Lavrov B. Thermodynamic influence of temperature on the quantitative distribution of sulfur in the Shalkiya sulfide ore -C-Fe system. Proceeding International Conference «Industrial Technologies and Engineering» ICITE – 2023, Shymkent. Pp.223-227

6. **Makhanbetova B.,** Shevko V., Aitkulov D. Thermodynamic model of zinc, lead, and silicon extraction from the Shalkiya-C-Fe sulfide ore system. Proceeding International Conference «Industrial Technologies and Engineering» ICITE – 2023, Shymkent. Pp.216-222

7. Маханбетова Б.А., Шевко В.М., Айткулов Д.К. Поисковые исследования по влиянию углерода и железосодержащего материала при электроплавке руды Шалкия. Труды МНПК «Инновации и комплексная переработка минерального сырья – актуальные составляющие диверсификации экономики» (30 сентября – 1 октября 2024 г.) Алматы, 2024, Том 2, 152-155

8. Шевко В.М., Айткулов Д.К., **Маханбетова Б.А**. Кинетика извлечения кремния из цинксодержащих руд Шалкия и хвостов ее обогащения. Труды V Международной научно-практической конференции «Современные

тенденции в научных исследованиях» Москва: Международный центр «Новые научные исследования». -2025. -С.82-90

9. Шевко В.М., Айткулов Д.К., Маханбетова Б.А. Укрупненнолабораторные испытания электроплавки хвостов обогащения руды месторождения Шалкия с получением ферросилиция и Zn-Pb возгонов. Международная научно-практическая конференция «Вопросы технических и современных физико-математических наук В свете исследований» Новосибирск. Сборник статей по материалом LXXXIV, №2 (75), 2025.-С.55-65.