ANNOTATION

dissertation work on the topic:
"PROCESSING OF LOW GRADE, DIFFICULTLY ENRICHABLE COMPLEX LEAD-ZINC ORES AND INDUSTRIAL ENRICHMENT PRODUCTS",

submitted for the degree of Doctor of Philosophy (PhD)
specialty 6D070900 – "Metallurgy"

MERKIBAYEV YERIK SERIKOVICH

Goal of the work.

The purpose of the dissertation work is to improve the technology for processing poor, difficult-to-process complex lead-zinc ores and middling products through the use of preliminary, activating, high-temperature sulfidization of oxidized lead and zinc compounds with pyrite in a fluidized bed furnace in air blast, in a non-oxidizing environment in a fixed bed and industrial enrichment products in a fixed layer.

Research objectives

– conduct a technological assessment of the initial low-grade zinc-oligonite ore of the Zhairem deposit and the lead-zinc tailings of the Ridder concentration plant for the feasibility of processing using preliminary activation by sulfiding roasting;

– conduct a patent information search and literature analysis on the possible use of various sulfidizers and activation methods that intensify the process of extraction of lead and zinc;

– conduct a thermodynamic analysis of possible reactions, justify the choice of pyrite as a sulfidizer; determine optimal firing conditions from a thermodynamic point of view;

– study the technique of sulfiding roasting and conduct a kinetic analysis of the process, determine the stages and speed of chemical reactions of the interaction of oxidized compounds with pyrite; develop recommendations for sulfidation of oxidized lead-zinc ores of carbonate and silicate compositions;

– conduct laboratory and extensive tests of the technology of activating, high-temperature, sulfiding firing in a fluidized bed furnace; determine the properties of pyrrhotines obtained by NMR and ESR methods;

– conduct laboratory tests of thermal activation of industrial lead-zinc enrichment products in a fixed layer containing pyrite in their own composition; conduct extensive tests of magnetic separation of sulfided cinders of lead-zinc middlings;

– perform mathematical modeling and economic assessment of the use of high-temperature activation through sulfidation firing.

Based on the research work carried out, the presented methods and the tasks to be solved in this dissertation work is aimed at achieving the overall goal.

The objects of research are:

The object of the study is zinc-oligonite ore of the Zhairem deposit and lead-zinc tailings from the Ridder concentration plant of Kazzinc LLP.

Methods for modernizing facilities:

– the work has developed a technology for thermal activation of zinc-oligonite ore in a KS furnace;

– results of high-temperature sulfidation of lead and zinc oxide compounds of zinc-oligonite ore in a non-oxidizing atmosphere in a fixed layer were obtained;

– the results of the development of a technology for thermal activation of industrial enrichment products in a fixed bed were obtained.

Methods for studying objects

The work used digital data processing systems for the thermodynamics of the process - the HSC Outocumpu Ou program, for the kinetics of the process - the Thermokinetics NETZSCH program; modern analytical equipment: DSC - thermogravimetric analysis (STA 409, 449 PC/PG NETZSCH), X-ray phase analysis (X-ray diffractometer BRUKER D2), scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS) JEOL-JSM-6010PLLIS / LA, KLY-2 kappameter (Czech Republic), YGR analysis - YAGRS-4 installation in a multichannel analyzer type IP-4840 from Nokia (Finland), ESR analysis was carried out on a JES-FA 200 installation (Jeol, Japan), sorption measurement - SORBTOMETER-M , electrokinetic analysis - macroelectrophoresis method.

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

1. Results of thermodynamic analysis of the sulfidation process.
2. Results of kinetic analysis of the sulfidation process.
3. Results of developing a method for thermal activation of zinc-oligonite ore in a KS furnace.
4. The results of the method of high-temperature sulfidation of oxide compounds of lead and zinc of zinc-oligonite ore in a non-oxidizing atmosphere in a fixed layer.
5. Results of developing a method for thermal activation of lead-zinc industrial enrichment products in a fixed bed.

The work was carried out at the Department of “Metallurgical Processes, Heat Engineering and Technology of Special Materials” KazNRTU named after K.I. Satpayev, Almaty.

Justification of the need for research and work

The decrease in zinc content from 5.0-5.7% and lead from 3.0-3.2% in ores and the liquid content of these metals in enrichment tailings indicate the need to find additional measures and conduct scientific research aimed at increasing the extraction of lead and zinc and improving the quality of the composition of concentrates.

Description of the main results of the study

In the first section, based on a critical analysis of the current state of combined technologies for processing oxidized lead-zinc ores and industrial products, the justification and choice of the direction of scientific research is carried out. The key problems of the mineralogical composition of ores and middling products, the preliminary activation of this type of raw material and the subsequent enrichment of roasting products have been identified.

In the second section, studies of the experimental thermodynamics of the sulfidation process of oxidized compounds of lead and zinc were carried out, the use of various sulfidizers, such as pyrite, elemental sulfur, in which the content of additives in the form of C and Fe_2O_3 was varied, was analyzed, and optimal firing conditions were determined from the point of view of thermodynamics.

In the third section, the results of a kinetic analysis of the sulfidation process were obtained, the stages and rates of chemical reactions of interaction of oxidized compounds with pyrite were determined, microflotation results were obtained, predicting the results of roasting on an enlarged scale, showing the aggregation of ZnS with $Fe_{1-x}S$ and the formation of the compound (Zn, Fe)S in form $Fe_2Zn_3S_5$, recommendations have been developed for the sulfidation of oxidized lead-zinc ores of carbonate and silicate composition.

The fourth section shows the results of the development of technology for activating, high-temperature, sulfiding roasting in a fluidized bed furnace using pyrite concentrate (with a sulfur content of 45.15%) as a sulfidizer. Using NMR and EPR methods, the results of studying the properties of magnetization and structure of a line of magnetic pyrrhotites $Fe_{0.855}S$, $Fe_{0.862}S$, $Fe_{0.877}S$, $Fe_{0.901}S$, $Fe_{0.911}S$, obtained by different methods, were established. A method has been developed for high-temperature sulfidation of lead and zinc oxide compounds in a non-oxidizing atmosphere.

The results of a technical and economic assessment of the processing of zinc-oligonite ore with sulfidation roasting and subsequent enrichment of the cinder are presented. The economic effect is achieved by increasing the extraction of zinc into a non-magnetic product to 88-90%; lead – 100%; increasing the extraction of pyrrhotites into the magnetic product by over 90-92%; increasing the extraction of zinc into the foam product up to 90% (with a content of 23.4%) with a 2:1 ratio of pyrite concentrate and ore during roasting; and also through the use of a cheap sulfidizer, high productivity of the fluidized bed furnace and an increase in the output of commercial products in the form of magnetic pyrrhotites.

The fifth section shows the results of thermal activation of industrial lead-zinc enrichment products in a fixed layer containing pyrite in its own composition of at least 50-54%, used as a sulfidizer, to obtain magnetic pyrrhotite $Fe_{0,855}S$; $Fe_{0,888}S$; $Fe_{0,909}S$. It has been established that preliminary sulfidization of oxidized lead and zinc minerals from enrichment tailings using a pyrometallurgical method helps to increase the efficiency of the flotation enrichment process by more than 20% for zinc and 15% for lead. The results of enlarged tests of magnetic separation of sulfided cinders of lead-zinc enrichment middlings were obtained. The technology of high-temperature activation through sulfidation firing is recommended for pilot testing.

Justification of the novelty and importance of the results obtained

The novelty of the topic lies in the development of technology for intensifying the process of processing poor, difficult-to-process complex lead-zinc ores and middling products through preliminary thermal activation by sulfiding roasting.

The new scientific results are as follows:

- For the first time, the mechanism of sulfidation of oxidized zinc compounds with pyrite was established by the results of thermal analysis TG/DSC and (SEM) and (EDS) spectroscopy: stage 1 - primary formation of ZnS at a temperature of 450 °C; Stage 2 - at the maximum degree of sulfidization at 700-750 °C, a stable film of ZnS is formed with the formation of pyrrhotites of the composition Fe1-xS, which dissolve in ZnS to form the compound (Zn, Fe)S in the form of $Fe_2Zn_3S_5$ at a temperature of 750 °C; 3 – stage at a firing temperature above 750 °C with the formation of the mineral ZnS, which not only aggregates with Fe1-xS to produce the compound (Zn, Fe)S in the form of $Fe_2Zn_3S_5$, but also aggregates with gangue elements, which negatively affects the efficiency flotation.

- For the first time, NMR and ESR methods have established the dependence of the magnetization of pyrrhotites $Fe_{0.855}S$, $Fe_{0.862}S$, $Fe_{0.877}S$, $Fe_{0.901}S$, $Fe_{0.911}S$, on the firing temperature; it has been established that the magnetization increases from 4.5 G cm^3/g at 600 ° From firing to 12.5 Gs cm^3/g at 800 °C with a further decrease to 3.0 Gs cm^3/g and values of 0 Gs cm^3/g at temperatures above 1000 °C due to a decrease in the number of vacancies in even basal planes pyrrhotite structures.

Technological novelty of research:

- for the first time, a method has been developed for the thermal activation of zinc-oligonite ore, including high-temperature, sulfiding roasting in the presence of a high-sulfur sulfidizer in the form of pyrite concentrate at a ratio to ore of 2:1, in a fluidized bed furnace using air blast at a flow rate of 10 to 20 l/min, at temperature 650°C, with the production of maximum magnetic pyrrhotites, the magnetic susceptibility of which is 1020 - 1330 · 10^{-6} Cu/g, with a degree of sulfidization of

88% and their extraction during magnetic separation into the magnetic fraction by more than 90%.

- for the first time, a technological scheme has been developed for activating sulfiding roasting of zinc- and lead-containing industrial enrichment products in a fixed layer containing pyrite in its own composition of at least 50-54%, used as a sulfidizer, to obtain pyrrhotites with a maximum magnetic susceptibility equal to: $Fe_{0,855}S$ = 3,75; $Fe_{0,888}S$ = 5,43; $Fe_{0,909}S$ = 2,18 SI units.

Compliance with areas of scientific development or government programs

The topic of the dissertation work corresponds to the priority direction of the development of science “Ecology, environment and rational use of natural resources”; 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.

Area of research in accordance with the Classifier of scientific fields “Engineering and technology; Materials Engineering; Metallurgy".

The dissertation work was carried out within the framework of a grant funding project for 2020-2022. AP08052829 “Development of a hybrid technology for the complex processing of oxidized, difficult-to-enrich zinc, lead-containing ores and middling products enriched by sulfidation roasting with subsequent enrichment of cinder” and is a continuation of the applicant’s research as a postdoctoral fellow and leader in the project “Zhas Galym” for 2022-2024 AP15473200 “Development of processing technology oxidized ores with preliminary high-temperature sulfidization."

Author's personal contribution

The author's personal contribution is to carry out the experimental research outlined in the dissertation work, including experimental research methods, conducting research, analyzing and processing the results in the form of publications and scientific reports.

Approbation of the work Based on the materials of the dissertation work, 16 printed works were published, of which 4 articles were published in international peer-reviewed scientific journals included in the Scopus/Web of Science database:

1. **Y. Merkibayev,** M Panayotova, Luganov V., Panayotov V.A., Chepushtanova T.A. Sulphidation roasting as means to recover zinc from oxidised ores (article)
Comptes rendus de l’Acad´emie bulgare des Sciences. Tome 71, No 8, 2018, P. 1116-1123., ISSN 13101331, Procentile 32, Q3

2. T.Chepushtanova, **Y. Merkibayev,** I. Motovilov, K. Polyakov, S.Gostu, Flotation studies of the middling product of lead-zinc ores with preliminary sulfidizing roasting of oxidized lead and zinc compounds (article). Kompleksnoe

Ispolzovanie Mineralnogo Syra, 323(4), 2022, P. 77–83, ISSN-L2616-6445, ESCI, JCT (Q3)

3. T.A. Chepushtanova, **Y. S. Merkibayev,** B. Mishra, I.E Kuldeyev.Processing of the Zinc-Lead-Bearing Flotation Middlings by Sulfidizing Roasting with Pyrrhotites Production by Predicted Properties (article). Non-ferrous Metals, 2, 2022, P. 15–24. 2022, DOI10.17580/nfm.2022.02.03. https://rudmet.ru/journal/2173/article/36106/, procentile 53.

4. T.A.Chepushtanova, **Y. S. Merkibayev,** O. S. Baigenzhenov, B. Mishra. Technology of high-temperature sulfidizing roasting of oxidized lead-zinc ore in a fluidized bed furnace (article). Non-ferrous Metals, 2, 2023, P. 3-10. DOI: 10.17580/nfm.2023.01.01.. https://www.rudmet.ru/journal/2217/article/36738/, procentile 53

Articles in publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan:

1. **Е.С. Меркибаев,**В.А. Луганов, Т.А.Чепуштанова, Г.Д.Гусейнова, Б.Мишра Термодинамическое обоснование высокотемпературного сульфидирования оксида цинка (статья). Вестник КазНИТУ, №2, 2020 г, С. 761-765. ISSN 1680-9211

2. В.А. Луганов, Т.А.Чепуштанова, Г.Д.Гусейнова, И.Ю.Мотовилов, **Е.С. Меркибаев**. Установление термодинамических условий процесса обжига пиритно-кобальтового концентрата (статья). Вестник Национальной инженерной академии Республики Казахстан», № 1, 2020 г. С. 82-88. ISSN 1606–416X

3. В.А. Луганов, Т.А.Чепуштанова, Г.Д. Гусейнова, **Е.С. Меркибаев**, И.Ю.Мотовилов . Исследование влияния углерода на показатели сульфидирования золотомышьякового концентрата в условиях «кипящего слоя» (статья) Вестник КазНИТУ 6(136)/2019, с. 888-893, ISSN 1680-9211

4. Т.А.Чепуштанова, **Е.С. Меркибаев,** И.Ю.Мотовилов, К.В. Поляков, Разработка гибридной технологии сульфидирующего обжига цинк, свинецсодержащих промпродуктов обогащения (статья)«Горный журнал Казахстана» № 10 - 2021 г. С. 28-35. ISSN 0017-2278

Articles published in other scientific journals and publications

1.T.A.Chepushtanova, I.Y. Motovilov, **Y. S. Merkibayev**, M.S.Sarsenova, G. Sumedh.Technology of sulfidizing-pyrrhotizing roasting of lead flotation tailings (article). Journal Mining and geological science. Volume 63. P. 31-37. ISSN 2683-0027

Proceedings of international scientific and practical conferences:

1. **Е.С. Меркибаев,** И.Ю. Мотовилов, В.А.Луганов, Ж.И.Ескен Термодинамическое обоснование технологии переработки окисленных полиметаллических руд (доклад). Труды Международных Сатпаевских

чтений «Научное наследие Шахмардана Есенова» −Алматы. 2017. С. 174-179 ISSN:978-601-323-034-4

2. Т.А.Чепуштанова, **Е.С. Меркибаев,** К.В. Поляков. Технология переработка хвостов обогащения свинцово- цинковых руд методом активирующего, сульфидирующего обжига (доклад) 25$^{\text{-ая}}$Международная научно-практическая конференция «ИННОВАЦИЯ-2021». Г.Ташкент, Узбекистан. 26-27 октября 2021 года. *ISSN* 1561-6940

3. Т.А.Чепуштанова, **Е.С. Меркибаев,** И.Ю.Мотовилов В.А.Луганов, С.Г.Темірхан. Термическое сульфидирование поверхности окисленных цинковых и свинцовых минералов пиритом в присутствии восстановителя в трубчатой печи (доклад) ТРУДЫ МЕЖДУНАРОДНОЙ НАУЧНО-ПРАКТИЧЕСКОЙ КОНФЕРЕНЦИИ «САТПАЕВСКИЕ ЧТЕНИЯ – 2022. ТРЕНДЫ СОВРЕМЕННЫХ НАУЧНЫХ ИССЛЕДОВАНИЙ» 12 апреля 2022 г, стр. 139-144, ISBN 978-601-323-291-1

4. Т.А.Чепуштанова, **Е.С. Меркибаев,** М. С. Сарсенова, С.Г.Темірхан. Переработка сложных полиметаллических руд месторождения Жайрем с использованием процесса сульфидирования (доклад) «Перспективы развития науки и образования в условиях новой реальности» Сборник материалов Международных XXI Байконуровских чтений, стр. 317-322, ISBN 978-601-7971-70-8

Patents

Т.А.Чепуштанова, **Е.С. Меркибаев,** В.А.Луганов. Способ переработки окисленной свинцово-цинковой руды . № 36282 от 30.06.2023

Monograph, textbook, books

Т.А.Чепуштанова, **Е.С. Меркибаев**. Переработка окисленных, труднообогатимых цинк, свинецсодержащих руд и промпродуктов обогащения. Монография. – Алматы: 2022. – 100 с. ISBN 978-601-269-133-7.С 100.