ANNOTATION

dissertation work on the topic:
“DEVELOPMENT OF SLAG DEPLETION TECHNOLOGY FOR AUTOGENOUS SMELTING OF COPPER SULFIDE CONCENTRATES”

submitted for the degree of Doctor of Philosophy (PhD)
specialty 8D07204 - "Metallurgical Engineering"

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Goal of the work.

The purpose of the dissertation work is to develop measures to optimize the complex processing of raw materials at the Balkhash copper smelting plant (BCP), with the possibility of using existing equipment, without expensive capital costs.

Research objectives

– conduct a patent information search and literature analysis on existing methods for depleting copper slag;

– conduct a study of the physical and chemical characteristics of the charge, fluxes and slags of copper production to identify possible reasons for the loss of copper with slags;

– conduct a thermodynamic analysis of the interaction of slag components with carbon;

– perform mathematical planning of experiments to assess the influence of various indicators on copper losses with slag;

– conduct laboratory experiments on slag depletion under deeply reducing conditions;

– conduct industrial experiments to study the behavior of an additional heat source;

– improve the design of the two-zone Vanyukov furnace for effective slag depletion;

– carry out preliminary technical and economic calculations of slag depletion indicators in a two-zone Vanyukov furnace.

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

The objects of research are:

The object of the study is concentrates, fluxes and slags from autogenous smelting of copper sulfide concentrates of the Kazakhmys Smelting LLP corporation.

Methods for modernizing facilities:

– using X-ray phase analysis and scanning electron microscopy (SEM), it has been established that the flux ores used at the BCP contain a high content of Al_2O_3,

which binds silica into various aluminosilicates: Al_2SiO_5; $(K,Na)AlSi_3O_8$, $Al_2Si_4O_{10}(OH)_2$; $KAl_2[Si_3AlO_{10}](OH)_2$; and significantly reduces the fluxing ability of these ores;

- new data were obtained on the behavior of an additional heat source (coal) during smelting at the BCP;

- new data on slag recovery under deeply reducing conditions at $P_{O2} < 10^{-10}$ atm were obtained.

Methods for studying objects

The main methods of research and analysis used in the dissertation work include:

- critical analysis of patent information sources;

- a set of modern analysis methods, such as:

1. Chemical methods of analysis (on an optical emission spectrometer with inductively coupled plasma Optima 8300 DV, USA, PerkinElmer; titrimetric method);

2. Semi-quantitative X-ray phase diffractometer (D8 Advance diffractometer (Bruker AXS GmbH);

3. Thermal analysis of slags on the STA 449 F3 Jupiter device, processing of the results obtained was carried out using the NETZSCH Proteus software;

4. Electron probe micro analyzer JEOL JXA 8230;

5. petrographic analysis on a direct industrial microscope OLYMPUS BX-51 polarizing “Olympus” (Japan);

6. Thermodynamic calculations were performed using the HSC – 5 software package (Outocumpu Ou).

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

–results of studies on the physical and chemical characteristics of the charge, fluxes and slags of copper production;

–results of thermodynamic analysis of the interaction of slag components with coal carbon;

–the influence of various factors on the copper content in slags was determined;

–results of laboratory tests on slag depletion;

–results of industrial tests;

–an improved design of a two-zone Vanyukov furnace was proposed;

–results of technical and economic calculations.

The work was carried out in the laboratory “Pyrometallurgy of heavy and non-ferrous metals” of JSC “IMiO”, Almaty.

Justification of the need for research and work

Currently, more than 24.6 million tons of waste containing copper have accumulated on Earth as a result of anthropogenic activities. This is due to the fact that the production of non-ferrous metals by pyrometallurgy is characterized by significant slag formation compared to the amount of metal extracted during the

smelting process. Sometimes the amount of slag produced during smelting exceeds the output of valuable industrial products by more than ten times. It is reported that more than 20 million tons of copper smelting slag are generated annually, and slag reserves in Kazakhstan reach 130 million tons. For every ton of matte produced, about 2.2 tons of slag are generated. The solid waste of mining and metallurgical enterprises contains about 2 million tons of copper, which is already comparable to the proven and estimated world copper reserves of 650 million tons. The average content of zinc in them is 2%, copper 0.5%, iron 35%, and lead 0.8%.

To solve the problem of processing metallurgical slags and obtaining a metallized phase and a metal-depleted silicate part, it is necessary to create a process with deep reduction of slag melts. However, to date, this task has not been fully resolved. To create new technologies for processing non-ferrous metallurgy slags, it is necessary to conduct a set of physicochemical studies using modern scientific equipment.

In light of the above, it is necessary to conduct scientific research aimed at studying the main reasons for the loss of copper with slags, as well as developing effective methods that allow for more complete extraction of valuable components.

Description of the main results of the study

In the first section, the main reasons for the loss of copper with slag are identified. Also, based on the current state of copper production, a brief analysis of autogenous smelting processes of sulfide copper-containing raw materials, and a deep analysis of existing methods for depleting slag, the justification and choice of direction for scientific research have been conducted.

The second section studies the characteristics of the chemical composition of the charge, slag samples, the calorific value of additional heat sources, the distribution of copper and precious metals, as well as the reasons and factors influencing the formation of liquid phases and the loss of copper with slag.

In the third section, the physico-chemical characteristics of flux ore are investigated, revealing a high content of Al_2O_3, which binds silica into various aluminosilicates: Al_2SiO_5; $(K,Na)AlSi_3O_8$, $Al_2Si_4O_{10}(OH)_2$; $KAl_2[Si_3AlO_{10}](OH)_2$; significantly reducing the fluxing ability of these ores.

The fourth section presents a thermodynamic analysis of the interaction of slag components with coal. Mathematical planning of experiments was conducted, resulting in a regression equation:

$$Y = 0.769 + 0.058X1 - 0.033X2 - 0.158X3 + 0.031X1X2X3,$$

showing that the most significant factor is temperature. Laboratory experiments have shown that depleting slags under deeply reductive conditions leads to a decrease in the content of copper and magnetite in slags. The optimal temperature of the process is 1300°C.

The fifth section presents the results of pilot industrial trials, indicating that not all coal burns with heat release; part of it enters into endothermic reactions interacting with metal oxides: $C+MeO=CO+Me -\Delta H$ and reducing them.

In the sixth section, a design of a two-zone Vanyukov furnace with an electrically heated reduction zone is proposed. The results of laboratory experiments

confirm the feasibility of this improved design. Reduction processing significantly depletes copper from 0.81% to 0.043%. Also, the reduction of Fe_3O_4 and Fe_2O_3 by carbon to metallic iron occurs. The degree of iron reduction and its transition to a metallized phase in this experiment was 30-50%.

A specialized device for the delivery of the reductant ensures its even distribution and effective interaction with the slag. This method also prevents the process of reoxidation, reduces dust emissions, and binds excess oxygen from the blast.

In the seventh section, calculations of the technical and economic indicators of slag depletion using these innovations are presented. The results of these calculations showed that the reduction method in the proposed two-zone furnace could contribute to improving the extraction of valuable metals and increasing profitability compared to current extraction methods, which will amount to more than 40 million US dollars.

Justification of the novelty and importance of the results obtained

The novelty of the topic lies in the development of a technology for depleting slags from autogenous smelting of copper sulfide concentrates, using the current type of raw materials (concentrates, fluxes, coal) at the BCP, with minimal costs for reconstructing the existing equipment.

The new scientific results are as follows:

–For the first time, X-ray phase analysis and Scanning Electron Microscopy (SEM) have established that the flux ores used at the Copper Smelting Plant contain a high level of Al_2O_3, which binds silica into various aluminosilicates: Al_2SiO_5; $(K,Na)AlSi_3O_8$, $Al_2Si_4O_{10}(OH)_2$; $KAl_2[Si_3AlO_{10}](OH)_2$; significantly reducing the fluxing ability of these ores.

–New data have been obtained on the behavior of an additional heat source (coal) during smelting at the Copper Smelting Plant.

–New data have been obtained on slag reduction under deeply reductive conditions at $P_{O2} < 10^{-10}$ atm.

Technological novelty of research:

An improved fundamental design of the Vanyukov furnace has been proposed, featuring two main zones: a melting zone and a reduction zone. The reduction zone, in turn, is equipped with a system for feeding reductants through tuyeres. A key aspect is ensuring low PO2 values at which deep reduction occurs and control over the temperature regime, which will allow for achieving a high degree of copper extraction from the slag.

Compliance with areas of scientific development or government programs

The dissertation work's theme aligns with the priority direction for the development of science "Ecology, environment, and rational natural resource 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. The research area is in accordance with the Classifier of scientific directions "Engineering and technology; Materials engineering; Metallurgy". The dissertation work was carried out within the framework of the project for program-targeted financing of scientific research for the years 2019-2021 "Development of technology for autogenous smelting of sulfide copper raw materials in conditions combining in the melt zones of charge loading, oxidizer introduction, and heat release" on the topic: "Study of the thermal regime of autogenous smelting in the Vanyukov furnace using additional fuel when it is fed through tuyeres into the liquid bath of the melt" (AR08855511).

Author's personal contribution

The author's personal contribution consists in the study of raw materials used in autogenous smelting, conducting laboratory experiments described in the dissertation work, including experimental research methods, participation in industrial trials, analysis, and presentation of results in the form of publications, scientific reports at international conferences, and a patent.

Approbation of the work

Based on the materials of the dissertation work, 8 printed works have been published, of which 3 articles are in international peer-reviewed scientific journals included in the Scopus/Web of Science databases:

1. M.Dyussebekova, B. Kenzhaliyev, S. Kvyatkovskiy, E. Sit'ko, D.Nurkhadianto. The main reasons for increased copper losses with slags from Vanyukov Furnace. Metalurgija. Vol 60. 2021. P. 309-312, Procentile 37%.
2. Dyussebekova, M.; Kenzhaliyev, B.; Kvyatkovskiy, S.; Kozhakhmetov, S.; Semenova, A.; Sukurov, B. Study of the Effect of Fluxing Ability of Flux Ores on Minimizing of Copper Losses with Slags during Copper Concentrate Smelting. Metals 2022, 12, 1240. https://doi.org/10.3390/met12081240, Procentile 75%, Q2.
3. Ye. A. Ospanov, S. A. Kvyatkovskiy, S. M. Kozhakhmetov, L. V. Sokolovskaya, A. S. Semenova, M. Dyussebekova & A. A. Shakhalov. Slag heterogeneity of autogenous copper concentrates smelting. Canadian Metallurgical Quarterly 2022, DOI: 10.1080/00084433.2022.2119495, Procentile 47%, Q 4.

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

1. Kenzhaliyev B.K., Kvyatkovskiy S.A., Dyussebekova M.A., Semenova A.S., Nurhadiyanto D. Analysis of Existing Technologies for Depletion of Dump Slags ofAutogenous Melting. Complex Use of Mineral Resources 2022, 4, 323. DOI: 10.31643/2022/6445.36

Proceedings of international scientific and practical conferences:

1. M.Dyussebekova «Processing of Various Copper Sulfide Concentrates by Vanyukov Smelting». Proceedings of the International Conference on Engineering, Technology and Vocational Education (ICETVE 2020), Malaysia, 7-th November 2020. P.70-71

2. Dyussebekova M.A., Kvyatkovskiy S.A., Kenzhaliyev B.K. & Didik Nurhadiyanto. «Dependence of the increased content of copper and magnetite in the slags on the composition of the smelting products». Proceedings of the International Innovation Arsvot Malaysia (IAM2021), 10-th of April 2021.P. 387

3. M.A. Dyussebekova, S.A. Kvyatkovskiy, L.V. Sokolovskaya, A.S. Semenova. «Effective methods of depletion of liquid slags of autogenous smelting of copper sulfide concentrates». Proceedings of the international scientific and practical conference "Satpayev Readings - 2022. Trends in modern scientific research" April 12, 2022, pp. 1325-1329, ISBN 978-601-323-291-1.

4. M.A. Dyussebekova «The process of Depletion of Copper Smelting Slag in a Two-zone PV Furnace». Presentation Materials of VI International Practical Conference "Challenges of Science" 15-16 November, 2023, pp. 532-541, ISBN 978-601-323-356-7.

Patents:

Dyusebekova M.A., Kenzhaliyev B.K., Kozhakhmetov S.M., Kvyatkovskiy S.A., Sitko E.A., Semenova A.S. Furnace for continuous smelting of sulfide materials in a liquid bath. No. 8335 dated 05.05.2023.

The total personal participation of the author amounted to 100%.