ABSTRACT

to the thesis on **"Development of a comprehensive innovative technology for the joint processing of lead intermediates, recycled materials and high-sulfur copper-zinc concentrate"**, submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D070900 - "Metallurgy"

ZHOLDASBAY ERZHAN YESENBAYULY

The purpose of the dissertation is to develop a new resource-saving, environmentally friendly redox bubbling technology adapted to wide variations of the type and composition of the feedstock, for the joint processing of accumulated substandard intermediates, recycled materials, slags and hard-to-process copper-zinc concentrate with high extraction of valuable metals from them into target products.

The object of research is substandard intermediates and recycled materials of lead production, difficult-to-process copper-zinc concentrate.

The subject of the study is the initial charge, including substandard intermediates and recycled materials of lead production, as well as a multicomponent slag system saturated with copper oxide: Cu_2O-FeO-SiO_2-CaO-Al_2O_3.

Research objectives:

- establishment of the distribution of copper, lead, arsenic and antimony between the products of mine contractile smelting in the conditions of Kazzinc LLP. Determination of the forms of copper, lead, zinc, arsenic and antimony in the products of mine contractile smelting;

- study of the thermodynamics of equilibrium of a complex system of copper-lead matte - iron-silicate slag - gas phase under controlled partial pressure values of oxygen (P_{O2}) and sulfur (P_{S2}). Determination of solubility of copper, lead, arsenic and antimony in a complex multicomponent oxide system Cu_2O–FeO–SiO_2–CaO-Al_2O_3;

- selection and justification of the optimal slag composition, which ensures minimal losses of copper and lead with slag. The composition of ash, mass%: SiO_2 26-28, CaO 8-10, $FeO/SiO_2 = 0.8 \div 0.9$;

– study of the liquidus temperature, viscosity and solubility of copper oxide in complex multicomponent slag system Cu_2O–FeO–SiO_2–CaO-Al_2O_3.

– selection and justification of the optimal composition of the initial charge with the establishment of the distribution of non-ferrous metals and related co-smelting of lead intermediates, working hard recyclable materials and copper-zinc concentrate.

Research methods. The equipment used in conducting experimental studies: a 75T-DR vibrating crusher, an electronic scale for weighing the mass of components Shimadzu ELB 1200, a high-temperature electric furnace SNOL, an inert gas supply system.

Equipment used in the study of chemical and mineralogical composition, microstructure: scanning electron microscope JSM 5910 and X–ray powder

diffraction (XRD, Rigaku TTRAXIII), optical microscope "Neophot 32" and X-ray analytical microprobe microscope "PAM 30-g", chromatograph Crystal 2000M.

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

- a new installation and dynamic gas flow method for studying the thermodynamic equilibrium of a complex multicomponent system of copper-lead matte - slag - gas phase with determination of the solubility of copper, lead, arsenic and antimony in the slag at controlled values of P_{O2} and P_{S2};

- selection and justification of a new slag composition, which ensures the minimum solubility of copper and lead in it, depending on the change in the composition of copper-lead matte;

- new results on liquidus temperature, viscosity and solubility of copper oxide in a complex multicomponent slag system $Cu_2O–FeO–SiO_2–CaO-Al_2O_3$;

- selection and justification of the optimal composition of the new initial charge of mine contractile melting;

- new results on the distribution of non-ferrous and related metals in the joint processing of substandard intermediates and recycled materials of lead production with hard-to-process copper-zinc concentrate.

Description of the main results of the study.

- a new installation and methodology has been developed to study the equilibrium of complex multicomponent systems: copper-lead matte - slag - gas phase, metal-slag -gas under controlled values of P_{O2}, P_{S2}. The mechanism of the transition of copper and lead from a complex copper-lead matte to slag has been studied, the solubility values of copper and lead from copper-lead matte to slag have been determined depending on the change in the composition of the matte;

– new data on liquidus temperatures, viscosity and solubility of copper oxide in a multicomponent $Cu_2O–FeO–SiO_2–CaO-Al_2O_3$ system saturated with copper oxide were obtained for the first time. The optimal slag composition, % by weight, was determined: 26-28 SiO_2, CaO 8-10, FeO/SiO_2 = 0.8÷0.9, providing minimal losses of copper and lead. It was found that when melting a new charge for the optimal slag composition, an increase in zinc extraction into slag is achieved from 80% according to the existing technology to 95%, with a decrease in the solubility of copper and lead in the slag from 0.8 to 0.3% and from 1.8 to 0.5%, respectively;

- new data have been obtained on the distribution of Cu, Pb, Zn, As, Sb and their compounds between melting products during the joint melting of high-sulfur copper-zinc concentrate with intermediates and recycled materials of lead production. It has been established that the best results for the extraction of non-ferrous metals into target products are achieved at a concentrate consumption equal to 30% (of the weight of the charge). The selective extraction of metals into the target products was: copper in matte - up to 96%, against 88% compared to the existing technology; lead in rough lead - 94%, against 60.8%; zinc in slag - 94.7%, against 80.7%; arsenic and antimony in dust - 92.3 and 91%, against 69.5% and 59.8%, respectively.

- based on the enlarged laboratory tests, the main optimal parameters of the technology were established and technological recommendations for practice were given. High rates of lead extraction in rough lead – 92.0%; copper in commercial matte – 96.0%; arsenic, antimony in dust – 91 and 89%, respectively.

Substantiation of the novelty and importance of the results obtained.

Currently, when processing substandard intermediates and recycled materials, no high extraction of valuable metals into target products is achieved in any of the existing technological processes. There is not enough deep sublimation of arsenic and antimony into dust, which reduces their withdrawal from the main production. Their accumulation in the main production is increasing, as a result of which the material and energy costs for the production of lead and copper are increasing, the quality of the products obtained is decreasing, and the negative load on the environment is increasing.

The new resource-saving technology developed in the work, adapted to wide variations in the type and composition of the feedstock, environmentally friendly redox technology for the joint processing of accumulated substandard intermediates, recycled materials, slags and hard-to-process copper-zinc concentrate allows achieving high recovery of valuable metals into target products. At the same time, the simultaneous removal of arsenic and antimony from the main technological chain is ensured due to their deep sublimation into dust.

The use of the developed technology, along with the direct processing of hard-to-process copper-zinc concentrate, provides additional high extraction of copper into matte and zinc into slag. The use of copper-zinc concentrate as a sulfidizer improves the quality of the products obtained and reduces the consumption of expensive coke during melting by two times compared to the existing technology.

Compliance with the direction of science development or state programs.

The current state of processing of lead intermediates and recycled materials does not ensure the achievement of high technological indicators. The existing technology of processing substandard intermediates and recycled materials at Kazzinc Ltd is based on mine contractile melting. During the melting of the initial charge of mine contractile melting, significant volumes of non-ferrous, noble and related harmful metals-impurities (As, Sb) circulate in the technological chain "melting-conversion". As a result, valuable metals are smeared on the melting products, and related metals-impurities (As, Sb) accumulate in the technological chain, which reduces the quality of the products obtained, increases the negative impact on the environment and the safety of workers ' life. The technology is aimed at extracting the main metals-copper and lead. At the same time, the extraction of copper into the matte is low, and is ~ 83%. The extraction of lead into rough lead barely reaches the level of 60%. The low extraction of lead is explained by its high content in matte (up to 30%) and slag (up to 1.7%). The process is accompanied by a large consumption of expensive coke and slag yield (up to 60% of the weight of the loaded charge), high energy and material costs. The dust yield is ~15% of the weight of the loaded charge and is characterized by a high content of non-ferrous

metals,%: Pb-20; Cu-6-7; Zn-up to 10. Due to the lack of favorable conditions for deep sublimation of arsenic and antimony, their extraction into dust is low and amounts to 70% and 57%, respectively. The complex composition of the resulting matte, characterized by a high content of Pb up to 25%, As-up to 2% and Sb ~1.5%, complicates their further processing by conversion and increases the energy and material costs of the process. The key task of the dissertation work is to solve the issue of complex use of raw materials with the establishment of optimal technological solutions and approaches of a new technology that ensures high extraction of valuable metals into target products.

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Contribution of the doctoral student to the preparation of each publication.

The author's personal contribution consists in setting the goals and objectives of the work, conducting research, processing and analyzing the results, formulating conclusions, writing articles and abstracts.

21 publications were published on the topic of the dissertation work, including 3 articles in scientific journals included in the Web of Science database, 2 articles in scientific journals included in the Scopus database, 2 articles in scientific journals included in the RSCI database, 5 articles in scientific journals recommended by the KOKSON of the Ministry of Education and Science of the Republic of Kazakhstan and 2 patents of the Republic of Kazakhstan were obtained.

The main results of the dissertation work have been published in 5 international scientific and practical conferences, including:

1. Жолдасбай Е.Е., Досмұхамедов Н.Қ. Шахталық қысқартып балқыту процесінің математикалық моделі // «Индустрия 4.0 жағдайында минералды және техногенді шикізатты тиімді пайдалану» Халықаралық ғылыми-тәжірибелік конференциясының Еңбектер жинағы. 14-15 наурыз, 2019. Алматы. – 478-493 б.

2. Жолдасбай Е.Е., Досмухамедов Н.К. Влияние состава шлака на потери меди, свинца при плавке медь-, свинец содержащего сырья // Тр. Международной научной конференции «Наука и инновации – современные концепции». 21 февраля, 2019. Москва. – С. 139-154.

3. N. Dosmukhamedov, E. Zholdasbay, V. Kaplan Partitioning of Cu, Pb, Zn and As following high temperature treatment of smelter slag // IX International

science conference The latest research in modern science: experience, traditions and innovations. 20-21 June, 2019, Morrisville, North Caroline, USA. – P. 34-42

4. Dosmukhamedov N., Zholdasbay E. Model of oxide solubility of copper and lead in slag of reduction smelting of copper -, lead-containing raw materials // The 5th International scientific and practical conference Dynamics of the development of world science. January 22-24, 2020. Vancouver, Canada. –P.78-90.

5. Dosmukhamedov N., Kaplan V., Zholdasbay E. Cu, Pb, Zn And As Distribution in the Slag Treatment Process // 11th International Conference on Molten Slags, Fluxes and Salts. 21-25 February 2021, Seoul, Korea.