ANNOTATION

of the dissertation on the topic:

«RECYCLING OF METALLURGICAL SLAGS FROM LEAD AND COPPER PRODUCTION IN THE CONTEXT OF TRANSITION TO SUSTAINABLE DEVELOPMENT OF THE METALLURGICAL INDUSTRY»,

submitted for the degree of Doctor of Philosophy (PhD) in the specialty «8D07202 – Metallurgy»

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The aim of the dissertation research is to develop a technology aimed at optimizing the complex processing of metallurgical slags from lead and copper production, including additional extraction of residual concentrations of valuable components (Pb, Cu, Zn) and subsequent use of the slag residue in the synthesis of new multi-purpose ceramic materials for the transition to sustainable development of the metallurgical industry.

Research objectives:

- conduct an analysis of literary data on the current state and prospects for processing metallurgical slags within the framework of the concept of a circular economy and the transition to sustainable development of the metallurgical industry;
- conduct a study of the composition and structure of metallurgical slags from copper and lead production at enterprises in Eastern Kazakhstan to assess the possibility of involving metallurgical slags in the synthesis of ceramic materials in a mixture with natural aluminosilicates;
- conduct laboratory experiments on hydrometallurgical processing of metallurgical slags for additional extraction of residual amounts of heavy non-ferrous metals (Pb, Cu, Zn);
- develop slag-containing batch compositions (based on slag residue after hydrometallurgical processing) for obtaining new multi-purpose ceramic materials using powder metallurgy methods;
- manufacture a pilot batch of new multi-purpose slag-containing ceramic materials with specified properties of various configurations (in the form of granules, tablets, blocks, etc.);
- conduct pilot tests of the obtained slag-containing ceramic materials to determine their strength characteristics;
- use digital technologies to assess the influence of various indicators and visualize individual stages of the synthesis process of new slag-containing ceramic materials;
- test the obtained slag-containing ceramic materials in ecological catalysis;
- perform a preliminary technical and economic assessment of the developed technology for the complex processing of metallurgical slags using the example of catalyst carriers and/or catalysts.

The objects of the study are metallurgical slags from lead and copper production in the East Kazakhstan region.

Research methods

To conduct research on the creation of a technology for the production of composite materials from a mixture of metallurgical slags and natural raw materials, the following were used:
- a set of physical and chemical methods (XRD, TGA / DTA, OM, SEM);
- HSC 9 software for calculating thermodynamic reactions and constructing diagrams of metallurgical processes;
- SolidWorks Flow Simulation software for modeling the extrusion process.

The main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense:
- results of the study of the composition and structure of metallurgical slags of lead and copper production in Eastern Kazakhstan and domestic natural aluminosilicates (zeolites and bentonites);
- results of laboratory tests of hydrometallurgical processing of metallurgical slags;
- results of the influence of varying the content of batch components, studying phase transformations, humidity and sintering temperature on the structure and properties of slag-containing ceramic materials;
- results of a pilot test of the strength characteristics of slag-containing ceramic materials;
- results of mathematical and computer modeling of the synthesis process of slag-containing ceramic materials;
- a technology is proposed to optimize the complex processing of metallurgical slags of lead and copper production;
- results of testing and technical and economic assessment of the obtained slag-containing ceramic materials in environmental catalysis.

Justification of the need to conduct this research work. The work was carried out within the framework of the priority areas of scientific development of the Republic of Kazakhstan - "rational use of natural resources, including water resources, geology, processing, new materials and technologies, safe products and structures." The need for a systematic study and processing of metallurgical slags is due to their significant volume and potential value as secondary raw materials. This makes research and development of technologies in this area particularly relevant.

Description of the main results of the study:

The first section analyzes the prospects and feasibility of using metallurgical slags for involving them in processing within the concept of a circular economy. Hydrometallurgical processing of slags for additional extraction of valuable components is described. An analysis of existing studies in the field of powder metallurgy is conducted. Methods of mathematical and computer modeling are considered as a way to optimize the technological process.

The second section describes the objects of study and develops methods of research and conducting experiments. Methods of analysis of physical, chemical and mechanical characteristics of composite materials are described.

The third section presents the studies on the composition and structure of the starting materials. The results of hydrochloric acid leaching of metallurgical slags from lead and copper production are presented. The thermodynamic and kinetic regularities of the leaching process of Pb, Cu and Zn from lead and copper slags in

HCl are studied and the degree of extraction into the productive solution of Zn 73-89%, Pb 24 - 31%, Cu 76-77% is ensured. The studies of the synthesized new composite materials are conducted. The effect of heat treatment temperature on the mechanical strength of the samples is studied. The linear dependence models, heat map and three-dimensional response surface are presented, illustrating the effect of slag content on mechanical strength. The analysis showed that the mechanical strength depends on the proportion of slag in the composition, with the optimum slag content being about 20% of the total batch weight. The results of testing the obtained samples are presented. It was determined that in a series of granulated samples, with oxidative conversion of CO at a temperature of 600 °C, the conversion is - 74.2%, with oxidative conversion of CH_4 it is 61%. Among the block samples, the conversion for CO is 84.5% and for CH_4 - 99.8%. A process flow chart is presented that provides for the initial leaching of residual concentrations of valuable components to obtain an inert material from metallurgical slags suitable for subsequent processing and synthesis of new multi-purpose composite materials from a mixture of metallurgical slags and natural raw materials in the form of granules, tablets, blocks, refractory tiles and lego bricks. The economic efficiency of the developed technology for obtaining new composite materials is presented.

Justification of the novelty and importance of the obtained results

The new scientific results are as follows:

– for the first time a comprehensive study was conducted (using X-ray phase analysis, scanning electron microscopy, differential thermal analysis, optical electron microscopy, etc.) of the composition, structure and properties of metallurgical slags from lead and copper production in Eastern Kazakhstan in combination with the analysis of natural aluminosilicates to assess their potential in the synthesis of ceramic materials;

technological regulations for plasticizing slag-containing molding masses have been established, providing the required rheological properties for molding ceramic products by pressing and extrusion methods. It has been revealed that metallurgical slags, unlike clay components, do not have plasticity and binding capacity, therefore, knowledge of the patterns of formation of the matrix structure of the molding mixture under the influence of various factors (temperature, composition of the initial charge, etc.), the sequence of thermal destruction of materials and the composition of volatile components are required for the synthesis of slag-containing ceramic materials;

- the applicability and efficiency of preliminary leaching of metallurgical slags from lead and copper production in Eastern Kazakhstan in hydrochloric acid for additional extraction of residual amounts of heavy metals (Pb, Zn, Cu) and the prospects of involving slag residue from leaching in the process of obtaining products with high added value by synthesizing multi-purpose ceramic materials in the context of the transition to sustainable development of the metallurgical industry in contrast to the current long-term storage or use for cement production are shown;

- for the first time, the patterns of change in the chemical and mineralogical compositions of technogenic and natural raw materials, as well as synthesized ceramic materials based on them, depending on the sintering temperature were

identified. It was determined that in order to obtain a thermally stable and durable slag-containing ceramic material, the amount of metallurgical slag in the batch can be varied in the range from 10 to 30 wt.%. It was found that in order to obtain a thermally stable and durable slag-containing ceramic material, the optimal ratio of components in the batch are 2 options: 20-60-20 and 20-50-30 (where 20 is the slag content, 60 or 50 is the zeolite content and bentonite is the rest). It was shown that an increase in the proportion of bentonite (up to 30 wt.%) while reducing the proportion of zeolite contributes to an increase in the strength of the slag-containing ceramic material, which is due to improved plasticity and uniform distribution of particles during molding. It was found that the optimal compositions in terms of strength and resistance to heat treatment are those based on Taizhuzgen zeolite, Dinosaur bentonite and IMZ copper slag at a firing temperature of 1000°C and a composition of 20-50-30;

- for the first time a technology has been developed for the synthesis of slag-containing ceramic materials from a mixture of domestic technogenic and natural raw materials suitable for efficient use in ecological catalysis. Regularities have been revealed in the interaction of slag residue components (SiO_2, Al_2O_3, Fe_xO_y, etc.) from lead and copper slag leaching with natural aluminosilicates under temperature treatment conditions (up to 1000 °C) with the formation of durable (45-75 MPa), thermally stable ceramic systems suitable for use as catalyst carriers and/or catalysts. It has been established that the studied metallurgical slags can be used as an additional component to the zeolite-bentonite base to create a slag-containing ceramic carrier for a catalyst and/or a catalyst efficient for the oxidative conversion of CO and/or CH_4 to CO_2 and H_2O (α conversion 50-90%);

- the prospects of using digital technologies for modeling, visualization and forecasting the properties of synthesized slag-containing ceramic materials have been substantiated, allowing to reduce the number of practical experiments on ceramic synthesis and to determine the optimal parameters for the synthesis of slag-containing ceramic materials with specified properties;

- a new technological scheme for the complex processing of metallurgical slags from lead and copper production has been substantiated, providing for the initial leaching of residual concentrations of valuable components, with subsequent processing and synthesis of new multi-purpose ceramic materials from a mixture of metallurgical slags and natural raw materials in the form of granules, tablets, blocks, Lego bricks, tiles.

Technological novelty of research

A new technological scheme for the complex processing of metallurgical slags of lead and copper production is proposed, which provides for the initial leaching of residual concentrations of valuable components, followed by processing and synthesis of new multi-purpose ceramic materials from a mixture of metallurgical slags and natural raw materials in the form of granules, tablets, blocks, Lego bricks, tiles. This technology not only promotes the efficient use of metallurgical waste, but also significantly reduces the environmental burden by reducing the volume of slag burials and preventing pollution of land resources. As a result of the scheme implementation, land plots are freed from accumulated industrial waste, which

allows them to be used for agricultural purposes, construction or recreational areas. In addition, the introduction of such technology contributes to the creation of a closed cycle of resource processing and increased environmental safety of the industrial complex.

Importance of the results obtained

The results of the study make a significant contribution to the development of technologies for processing metallurgical slags and synthesizing new composite materials. The data obtained are of practical value for the industrial sector of Kazakhstan and can be used to implement the proposed solutions at East Mineral Resources LLP for the purpose of hydrometallurgical extraction of valuable components from IMZ waste slags, as well as at Kazzinc LLP for the implementation of methods for recycling technogenic waste.

Compliance with scientific development directions or state programs. The topic of the dissertation was carried out within the framework of:

- GF scientific research "Development of technology for obtaining new ceramic materials based on domestic natural raw materials and man-made waste of metallurgical enterprises of Kazakhstan" for 2018 - 2020;
- GF of young scientists "Zhas Galym" "Development of digital production of advanced ceramic materials synthesized from natural raw materials and semi-finished products of non-ferrous metallurgy" for 2024 - 2026.

The author's personal contribution consists of carrying out experimental studies presented in the dissertation, including work on studying the composition and structure of metallurgical slags, developing compositions and varying parameters according to the proposed technological scheme, and presenting the results in the form of publications and scientific reports.

Testing the work: The main scientific results of the dissertation are presented in 3 articles included in the Scopus database and in 6 publications published in the Republic of Kazakhstan:

- Sadenova M.A., Utegenova M.E., Klemeš J.J. Synthesis of new materials based on metallurgical slags as a contribution to the circular economy // Clean Technologies and Environmental Policy. – 2019. – V.21. - P. 2047–2059. Q1, percentile 87;
- Utegenova M.E., Sadenova M.A., Klemeš J.J. Features of the synthesis of block ceramic materials based on natural and technogenic raw materials // Chemical Engineering Transaction. – 2019. − V. 76. − P. 151-156. Q3, percentile 31;
- Utegenova M.E., Sadenova M.A., Klemeš J.J. Physico-mechanical properties of ceramics based on aluminosilicates modified by metallurgical waste // Chemical Engineering Transaction. – 2020. − V. 81. − P. 1339-1344. Q3, percentile 31;
- Utegenova M., Sadenova M., P.Varbanov. Creation of Prototypes of Slag-Containing Composite Materials by Powder Metallurgy Methods // Metallurgical Research & Technology (in print) Q2, percentile 56;
- Utegenova M., Sadenova M., Azamatov B., Dogadkin D. Optimizatsiya tekhnologicheskoy osnastki dlya sinteza keramicheskikh materialov na osnove modelirovaniya // Vestnik KazNITU. - 2019. - No. 4. - P. 112-118;

- Sadenova M.A., Utegenova M.E., Anuarbekov T.B. Kharakteristika nekotorykh prirodnykh i tekhnogennykh syr'yevykh resursov Respubliki Kazakhstan // Vestnik VKGTU. - 2018. –№4. C. 38-45;

- Sapinov R.V., Utegenova M., Sadenova M., Varbanov P. S. Gidrometallurgicheskaya pererabotka shlakov svintsovogo proizvodstva / Nauka i tekhnika Kazakhstana. - 2025. - No. 2. In print (reference).

- 1 patent for utility model of the Republic of Kazakhstan No. 5394 of the Republic of Kazakhstan dated September 25, 2020 was received «Sposob polucheniya granulirovannogo nositelya dlya katalizatora»;

- patent for invention reg. application number 2024/0968.1, dated 11/11/2024 «Sposob uvelicheniya mekhanicheskoy prochnosti keramiki». Submitted at the stage of examination on the merits.