ABSTRACT

to thesis research on:

«MECHANOCHEMICAL SYNTHESIS OF SULFIDIZER FOR PROCESSING OF COPPER ORES»,

Submitted for the Degree of Doctor of Philosophy Ph.D. Majoring in "Metallurgy" - 6D070900

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Assessment of the current state of solved scientific or technological problems. Among the variety of methods for increasing the reactivity of solids, a special place is occupied by the methods of mechanochemical activation, which are a simple, affordable and effective way to influence the energy state of a substance. Pulsed force loads on material particles during mechanical processing lead to surface and volume structural deformation of bodies, and repeatedly repeated deformations create a wide range of metastable states that accumulate excess energy and provide the system with a tendency to subsequent physical and chemical processes. Understanding the mechanisms of solid-phase interaction at the stage of preliminary preparation of materials can contribute to the targeted synthesis of substances with a given set of properties. The industrial development of the principles and methods of mechanochemistry and solid-phase synthesis will undoubtedly reveal new areas of their application in various fields of metallurgy, chemical catalysis, and materials science.

Currently, easily-concentrated copper-containing ores in the Republic are becoming less and less, while the number of difficult-to-concentrate oxidized and mixed ores is increasing. The well-known technologies for the oxidation of mixed and oxidized ores are based on the sulfidization of oxidized copper minerals, where sodium sulfide (Na_2S) is used as a surface sulfidizer, which, unfortunately, Kazakhstan and the CIS countries do not produce, but purchase from China, moreover, the classical method of production sodium sulfide is a multi-stage and expensive process. Purchased sulfidizer does not always give the desired result. In this regard, the basis for the development of the theme is the possibility of synthesizing a new sulfidizing agent by a mechanochemical method that could replace traditional sodium sulfide at the stage of enrichment of copper-containing raw materials, and the method itself would be less energy-consuming and economically feasible. In addition, a number of scientific studies are known where the mechanical activation of mineral raw materials facilitated the transition from some schemes of processing raw materials to other technological schemes, in particular from pyrometallurgy to hydrometallurgical processes [1-3]. Considering the fact that the processes of mechanochemical processing have not yet found wide application in metallurgy, the aim of this work is to develop the scientific foundations for controlling mechanical activation processes for their further application in various fields of metallurgical production.

The basis and initial data for the development of the topic.

The basis for the development of the topic is the need and the possibility of organizing the production of sodium polysulfides in Kazakhstan on the basis of

caustic soda and industrial sulfur produced in the country - waste from the oil refining industry, for use in enrichment processes in metallurgical industries.

In the work, methods for producing sodium sulfides are considered and a technological scheme for the synthesis of polysulfides by means of a joint mechanochemical treatment of alkali with sulfur is proposed.

Based on a critical analysis of the literary material, a technological operation is proposed for preliminary mechanical activation of the initial concentrate of the processing plant of «Kazakhmys» JSC in order to replace the pyrometallurgical production scheme with the hydrometallurgical one.

Justification of the need for research work.

The need for this research work is dictated by the State Program of industrial and innovative development of the Republic of Kazakhstan for 2015-2019. In particular, the Program says that one of the key problems of the non-ferrous metallurgy sector is "... depletion of the reserves of rich and easily accessible non-ferrous metal ores and the difficulty of beneficiation due to the multicomponent mineral composition ...". The list of tasks of the Program includes: "... expanding existing production and mastering the production of new products from base metals for related sectors; reducing the volume of imports of metal products due to the development of domestic competitive production ..." [4]. In this regard, expanding the possibilities of processing refractory ores.

Information about the planned scientific and technical level of development, about patent research and conclusions from them.

In the course of the research, it was planned to study the possibility of synthesizing sodium polysulfide by the mechanochemical method, and using synthetic polysulfide as a flotation reagent for enriching refractory copper ore.

The research level meets modern requirements: modern research and analysis methods are used, the research results are processed in accordance with the basic laws of mechanochemistry and enrichment, the modern thermodynamic calculation program HSC Chemistry of Outokumpu Technology Engineering is used. The level of research is confirmed by scientific publications on the topic of research.

Patent studies are performed in accordance with ST RK GOST R 15.011-2005 - Patent studies. As a result of the patent Studies made the following conclusions:

– the selected objects (elemental sulfur and caustic soda, hard-to-ore ore) and the subject (the process of synthesis of sodium polysulfide and its use for processing polymetallic copper ore) studies are promising and most representative for study;

– the selected research methods can reliably and fully reflect the results obtained;

– the results of patent research are fully reflected in this dissertation in the form of an analytical review of the literature.

Information about metrological support.

All the results obtained in this work are based on known theoretical information or are proved using modern physicochemical methods of analysis and research.

Analytical equipment and instruments used in the research have the necessary metrological support.

Relevance of work.

In recent decades, an increasing number of refractory polymetallic ores has been involved in the country's metallurgical sector, which is associated with a decrease in the reserves of easily refractory ores. As a rule, refractory copper ores are mainly present in oxidized and mixed oxidized-sulfide forms, and as a result, have a complex mineralogical composition. Today there is a situation in which it is difficult to manage only with traditional flotation schemes, so there is a need to develop new schemes, including various methods of neutralizing the adverse features of the structure and composition of such ores, and developing new reagents that can increase the extraction of valuable components. In addition, the concentrates of mixed ores after flotation concentration must be processed to extract copper using hydrometallurgical operations using new technological elements. These and many other developments allow us to involve in the process of hydrometallurgy available types of raw materials and operations.

The novelty of the topic. The novelty of the topic and the tasks to be solved is to establish the conditions for the synthesis of sodium polysulfide and to study the effect of the mechanical activation of the concentrate on the acid leaching process.

Scientific novelty of the results:

− a method for mechanochemical synthesis was developed for the first time sodium polysulfides from a mixture of elemental sulfur (S0) and sodium hydroxide (NaOH);

− results of modeling and optimization of slurry output at mechanical activation of copper ore;

− a comparative analysis of the results of flotation enrichment of copper-containing raw materials using sodium sulfide and sodium polysulfides;

− The results of thermodynamic analysis and kinetics are presented leaching copper concentrate with nitric acid;

− experimentally shown the effect of mechanochemical activation for leaching of copper concentrate;

− it was found that using mechanochemical activation direct reduction of copper from sulfur-containing mineral - chalcopyrite is possible.

Communication with the scientific and research work.

The work was carried out in the laboratory "Mechanochemical processes" of the «Institute Combustion of Problems», at the department "Metallurgical processes, heat engineering and technology of special materials" KazNITU them. K.I. Satpayev and at the Rheinvestfal University of Technology (Germany), in accordance with international research projects identified in the Strategy "Kazakhstan-2050", the concept of innovative development of the Republic of Kazakhstan until 2020 and plans for research work of the department "Metallurgical processes, heat engineering and technology of special materials" KazNITU named after K.I. Satpayev.

The purpose of the thesis is the development of scientific and practical principles for managing mechanical activation processes with the aim of their application in various fields of metallurgical production.

The objects of study are copper-containing ore of the Irtysh and Shatyrkol deposits, elemental sulfur and sodium hydroxide.

Subject of research - thermodynamics of the synthesis of sodium polysulfide, the possibility of its use as a sulfidizing agent for processing polymetallic copper ore, the kinetics of flotation concentration using a new sulfidizing agent, leaching of copper concentrate with nitric acid solution.

The objectives of the study, their place in the implementation of research work as a whole. The main task of the dissertation: - to synthesize sodium polysulfide by the mechanochemical method and use it as a flotation reagent for the enrichment of sulfide-oxidized copper ore, followed by mechanochemical treatment of the resulting concentrate and its further leaching.

The main research objectives include:

− analysis of scientific literature;

− calculation and analysis of thermodynamics of obtaining sodium polysulfide mechanochemically;

− synthesis of sodium polysulfide in a planetary centrifugal mill with identification of synthesis products;

− development of the optimal flotation regime of polymetallic ores with using a new sulfidizer;

− modeling and optimization of slurry output at mechanical activation of copper ore;

− conducting research on the processing of ore by mechanical activation;

− conducting research on the use of the received sulphide copper concentrate after using synthesized sodium polysulphide for copper leaching;

− technical and economic assessment for the production of sodium polysulfide.

The methodological base of research

When performing the thesis, the following basic research and analysis methods were used:

– thermodynamic calculation of the possibility of a reaction between elemental sulfur and sodium hydroxide was carried out using Outokumpu Technology Engineering's HSC Chemistry program;

– the obtained samples of sodium polysulfide were investigated on Solver Spectrum Raman spectrometer when exposed to a blue laser with a wavelength of 473 nm, as well as an X-ray diffractometer and electron microscopy;

– modeling and optimization of slurry output during mechanical activation of copper ore was carried out using the programming language DELPHI 7.0;

– construction of diagrams indicating the possibility the reaction between nitric acid and chalcopyrite was carried out using Outokumpu Technology Engineering's HSC Chemistry program;

– determination of the kinetics of the leaching of copper concentrate in nitric acid;

The practical significance of the results of the work lies in the synthesis of sodium polysulfide by the mechanochemical method and its use as a flotation reagent for the processing of copper-containing ore, with further leaching of the

obtained copper concentrate using nitric acid. All this can be used by industrial enterprises in scientific research conducted in the field of copper ore processing.

The main provisions to be defended.

The following provisions are made to defend the thesis:

− ore composition research results;

− the results of the study of the grinding process of the studied ores in a planetary centrifugal mill;

− the results of a thermodynamic analysis of the synthesis of sodium polysulfide mechanochemically;

− results of Raman spectroscopy and x-ray phase analysis of the obtained samples of sodium polysulfide;

− simulation and optimization results of slurry yield during mechanical activation of copper ore;

− comparative analysis of experimental results on the effect of sodium sulfide and sodium polysulfide on copper recovery;

− kinetics of the flotation process using Na_2S and Na_2S_n as sulfidizers;

− results of thermodynamic analysis of leaching of copper concentrate with nitric acid;

− results of the kinetics of leaching of copper concentrate with nitric acid.

Work approbation:

The main provisions of the work were reported and discussed at 3 scientific and practical conferences, including the Joint IX International Conference «Physics and Chemistry of Carbon Materials / Nanoengineering» (Kazakhstan, Almaty, 2016), 9th International Conference on Mechanochemistry and Mechanical Alloying «INCOME 2017» (Slovakia, Kosice, 2017), V International Conference «Fundamental Bases of Mechanochemical Technologies» (Russia, Novosibirsk, 2018). As a result of the work, 3 articles were published in journals recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan: «Industry of Kazakhstan », «Bulletin of the National Engineering Academy of the Republic of Kazakhstan », and 2 articles in an international rating journal included in the database Scopus: «Non-ferrous Metals», «Acta Physica Polonica A».

The structure and scope of the dissertation.

The composition of the dissertation includes the following elements: «Normative references», «Designations and abbreviations», «Introduction», literature review, experimental part, «Conclusion», «List of references» and "Appendices". The dissertation is contains 51 tables, 53 figures, 116 literary sources.