ABSTRACT

of thesis on the theme:

“Development of the technology on processing arsenic-bearing materials of lead and copper operations with removal of arsenic in the form of low-hazard waste”

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

TYMBAYEVA AIGERIM ALIBEKOVNA

The aim of the thesis is to develop a technology for processing copper skims of lead production using an alkaline sulfide reagent, which would ensure selective removal of arsenic.

Research Objectives:

- studying thermodynamic behaviors in the process of alkaline sulfide leaching of copper skims from lead production;
- selection and justification of process parameters for copper skims leaching and arsenic precipitation;
- studying the possibility of alkaline sulfide reagent regeneration;
- development of process flowsheet for hydrometallurgical treatment of copper skims from lead production.

Research methods:

The main methods of research and analysis used in the implementation of the thesis include:

- a set of state-of-the-art physical and chemical methods for analyzing raw materials and products of its hydrometallurgical processing: atomic absorption analysis (PinAAcle spectrometer, PerkinElmer company), optical emission analysis (Agilent 710 ES inductively coupled plasma spectrometer), thermogravimetric analysis (Mettler Toledo analyzer), X-ray phase analysis (X'Pert PRO X-ray diffractometer manufactured by PANalytical), microanalysis (scanning electron microscope JSM-6390LV manufactured by JEOL Ltd.), IR spectroscopic analysis (FT-801 IR spectrometer from Simex).
- probabilistic and deterministic method of experiment planning;
- the study of the thermodynamics of hydrometallurgical processes occurring during alkaline sulfide leaching of copper skims and precipitation of arsenic was carried out using the HSC Chemistry program version 5.1;
- statistical analysis of data and their visualization was carried out using the Statistica software version 7.0.

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

- results of physical and chemical studies of the thermodynamics of hydrometallurgical processes occurring during the alkaline sulfide leaching of copper skims;

- results of laboratory studies on leaching, arsenic precipitation and regeneration of alkaline sulfide reagent;

- technology for hydrometallurgical processing of copper skims from lead production using an alkaline sulfide reagent, which ensures selectivity of arsenic removal relative to five valuable metals: lead, zinc, copper, gold and silver.

Description of the key research results:

- For the first time, the regularities of the process on alkaline sulfide leaching of arsenic from copper skims have been experimentally determined. At this:

1) A three-stage mechanism of copper arsenide dissolution in alkaline sulfide solution is proposed. At the first stage, the dissolution of copper arsenide in a polysulfide solution occurs with the formation of a precipitate - copper (I) sulfide and a soluble compound - $NaAsS_2$ by the following reaction:

$$2Cu_3As + Na_2S_x + (x+3)S^0 = 2NaAsS_x + 3Cu_2S \text{ (where x = 2 - 5)}$$

At the second stage, $NaAsS_2$ reacts with sodium sulfide to form - Na_3AsS_3:

$$NaAsS_2 + Na_2S = Na_3AsS_3$$

At the third stage, the oxidation of Na_3AsS_3 with sodium polysulfide proceeds with the formation of Na_3AsS_4:

$$Na_2S_x + (x–1)Na_3AsS_3 = (x–1)Na_3AsS_4 + Na_2S \text{ (where x = 2 - 5)}$$

2) It is shown that under conditions of alkaline sulfide leaching of arsenic from copper skims, the obtained value of the apparent activation energy - 37.5 kJ/mol indicates the possibility of the process in both transient and kinetic modes, that is, the reaction rate largely depends on the composition of the solution.

3) It was found that with a decrease in the proportion of sodium hydroxide in the alkaline sulfide solution from 100 g/dm^3 to 50 g/dm^3, the limiting stage of the process is the interaction of sodium metatioarsenite ($NaAsS_2$) with sodium sulfide to obtain sodium thioarsenite (Na_3AsS_3). The decrease in the share of sulfur in alkaline sulfide solution from 100 g/dm^3 to 25 g/dm^3 leads to the limitation of the process by the oxidation of sodium thioarsenite (Na_3AsS_3) to sodium thioarsenate (Na_3AsS_4).

- For the first time established that the highest degree of deposition of arsenic (>98% As) is achieved in the temperature range 25-85^{0}C at the same pH value of the medium – 1,5-2.

- For the first time, based on experimental data, the possibility of regeneration of alkaline sulfide reagent from a solution, obtained during arsenic precipitation, using a lime-sulfur reagent and thereby creating a closed cycle of the process has been proved.

Justification of the novelty and importance of the results obtained:

The research carried out during the dissertation work made it possible to study in detail and obtain new information about the material and phase composition of copper skims of lead production; theoretically substantiate and experimentally confirm the possibility of processing copper skims by alkaline sulfide leaching and deposition of arsenic into a dump sulfide cake. The principal difference between the proposed technological scheme and the existing modern methods of processing copper skims is the possibility of selective arsenic removal relative to lead, copper, zinc, gold and silver, and the possibility for regeneration of alkaline sulfide reagent.

The proposed method for regeneration of alkaline sulfide reagent from a sodium sulfate solution obtained during the deposition of arsenic will eliminate the accumulation of sodium sulfate solution in a closed water circulation system of metallurgical enterprises, and will reduce the consumption of an expensive reagent - caustic soda.

In general, the scientific novelty of the research is confirmed by the patent of the Republic of Kazakhstan for the "Method of hydrometallurgical processing of arsenic-containing industrial products of non-ferrous metallurgy" No. 34440, published on 03.07.2020.

Compliance with directions of science development or government programs.

Today, the metallurgical industry is increasingly facing the challenge of depletion of the raw material base of non-ferrous metal ores with a low content of impurities, in particular arsenic. Enterprises are receiving more and more materials of complex composition, one of the main harmful impurities in which is arsenic. There are many known ways to remove arsenic from raw materials and industrial products of lead and copper production, however, active work on improving the schemes for obtaining non-ferrous metals leads to a change in the movement of impurity components and the need to develop new schemes for the disposal of arsenic.

This paper analyzes the technology of processing polymetallic raw materials on the example of UKMK "Kazzinc" Ltd. According to the scheme that existed at the enterprise until 2012, the removal of arsenic from the lead plant as part of arsenite-arsenate cakes was 43.65%. However, the modernization of the technological scheme of lead production and starting-up of a copper plant at UKMK Kazzinc Ltd. in 2011-2012 led to a change in the distribution of arsenic and a reduction in the amount of arsenic removed from the technological scheme with arsenate cake to 7.25%. Against this background, there was an increase in the distribution of arsenic to copper skims of lead production. If earlier, according to the classical scheme "sintering – Blast Furnace smelting - refining", 27.65% of arsenic from the total load to the lead plant was transferred to copper skims, then according to the new scheme - 83.72%.

With an increased content of arsenic in lead raw materials, the circulation load of impurities between lead and copper plants increases due to the processing of copper skims, which leads to the risk of low-quality commercial products, wear of the lining of pyrometallurgical units when interacting with aggressive copper arsenide, pollution of the environment with volatile arsenic compounds. To date, at UKMK Kazzinc Ltd.,

copper skims are sent to the electric melting stage, where they are divided into lead- and copper-containing phases. At the same time, arsenic is distributed among the melting products.

Despite the existence of a substantial base of developments devoted to the study of the problem of processing arsenic-containing materials, methods devoted to the problem (task) of selective removal of arsenic from copper skims, relative to lead, copper, zinc, gold and silver, have not been proposed to date.

In this paper, it is proposed to improve the method of opening copper skims of lead production by using an alkaline sulfide reagent that ensures the selectivity of arsenic extraction.

The research work corresponds to the priority direction of science development on “Rational use of natural resources, including water resources, geology, processing, new materials and technologies, safe products and constructions”. The developed process flowsheet on hyrometallurgical treatment of copper skims will improve the environmental safety of production, and will create conditions for the involvement of high impurity ores and concentrates into production.

Description of the contribution of the doctoral student to the preparation of each publication.

1. Tymbayeva A.A., Mamyachenkov S.V., Bannikova S.A., Anisimova O.S. Studying the impact of alkaline sulfide leaching parameters upon the efficiency of arsenic recovery from copper skimmings of lead production // Non-ferrous metals. – 2020. – № 2. – P. 19-24: scientific and theoretical justification, preparation and direct participation in research, analysis and systematization of the results obtained, writing the text of the article;

2. Тымбаева А.А., Куленова Н.А., Мамяченков С.В. Управление отходами процесса осаждения мышьяка в виде сульфидного кека из серощелочных мышьяксодержащих растворов // Вестник Национальной инженерной академии Республики Казахстан. – 2020. – №2. – С. 193-199: scientific and theoretical justification, preparation and direct participation in research, analysis and systematization of the results obtained, writing the text of the article;

3. Тымбаева А.А., Куленова Н.А., Мамяченков С.В. Вопрос накопления сульфата натрия при гидрометаллургической переработке мышьяковых промпродуктов // Вестник ВКТУ. – 2020. – №2. – С. 55-57: scientific and theoretical justification, preparation and direct participation in research, analysis and systematization of the results obtained, writing the text of the article;

4. Набиева А.А., Куленова Н.А., Мамяченков С.В. Термодинамическое моделирование процесса грубого обезмеживания с использованием программного продукта FactSage // Вестник ВКГТУ. – 2019. – № 2. – С. 41-44: simulation the process in the FactSage program, direct participation in the analysis and generalization of the results obtained, writing the text of the article;

5. Пат. 34440 РК. Способ гидрометаллургической переработки мышьяксодержащих промпродуктов цветной металлургии / Набиева А.А., Азекенов Т.А., Банникова С.А., Колтунова Л.Е., патентобладатель ТОО «Казцинк»; опубл. 03.07.2020, Бюл. №26. – 5 с: scientific and theoretical

justification, preparation and direct participation in research, analysis, systematization of the results obtained and in writing the text of the patent;

6. Nabiyeva A.A., Kulenova N.A., Mamyachenkov S.V. Studying Kinetics of Arsenic Recovery from Copper Dross by Alkaline Sulfide Leaching // Materials Science Forum, Trans Tech Publications, Switzerland. – 2019. V. 946. – P. 547-551: scientific and theoretical justification, preparation and direct participation in research, analysis and systematization of the results obtained, writing the text of the article;

7. Набиева А.А., Куленова Н.А. Анализ состояния проблемы переработки мышьяксодержащего сырья цветной промышленности // Материалы V международной научно-технической конференции студентов, магистрантов и молодых ученых «Творчество молодых инновационному развитию Казахстана» посвященный году молодежи в Казахстане. – Усть-Каменогорск, 2019. – С. 75-79: scientific and theoretical justification, direct participation in the search, analysis and systematization of data, writing the text of the article;

8. Набиева А.А., Куленова Н.А. Отечественная база цветной промышленности: проблемы комплексной переработки полиметаллического сырья с высоким содержанием примесей // Инновации в области естественных наук как основа экспортоориентированной индустриализации Казахстана: Материалы Международной научно-практической конференции, посвященной 10-летию Казахстанской национальной академии естественных наук и 25-летию Национального центра по комплексной переработке минерального сырья Республики Казахстан. РГП «НЦ КПМС РК». – Алматы, 2019. – С. 393 – 396: scientific and theoretical justification, direct participation in the search, analysis and systematization of data, writing the text of the article.