ABSTRACT of
thesis on subject:
"PHYSICAL AND CHEMICAL RESEARCH AND DEVELOPMENT OF HYDROMETALLURGICAL TECHNOLOGY FOR PROCESSING HARD-TO-ENRICH OXIDIZED ZINC ORES".
submitted for the degree of Doctor of Philosophy (PhD)
on speciality 6D070900 - "Metallurgy"
RAMAZANOVA RAIGUL AMANGELDINOVNA

The purpose of this dissertation work is to develop the technology of hydrometallurgical processing of hard-to-enrich oxidized zinc ores in order to expand the raw material base of zinc hydrometallurgy by involving oxidized zinc minerals in the processing.

Research objectives:

1) Study of the material composition of oxidized zinc ore;
2) Determination of thermodynamic characteristics of oxidized zinc minerals and comparative assessment of their reactivity;
3) Performance of theoretical researches on thermodynamic estimation of process of sulfuric acid leaching of investigated ore;
4) Research of kinetics of sulfuric acid leaching of zinc from oxidized zinc minerals – calamine and smithsonite;
5) Experimental studies of stage-by-stage sulfuric acid leaching of the investigated ore;
6) Development of the technological scheme of hydrometallurgical processing of oxidized zinc ore.

Research Methods:

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

– complex of modern physical and chemical methods of analysis of raw materials and products of their hydrometallurgical processing: Atomic absorption analysis (PinAAcle spectrometer by PerkinElmer), optical emission analysis (inductively coupled plasma spectrometer by Agilent 710 ES), thermogravimetric analysis (analyzer by Mettler Toledo), X-ray phase analysis (X'Pert PRO X-ray diffractometer by PANalytical), structural analysis (scanning electron microscope JSM-6390LV by JEOL Ltd. "Ltd.), infrared spectroscopic analysis (FT-801 infrared spectrometer by Simex);

– packages of specially developed computer programs for calculation of thermodynamic characteristics of reactions (HSC Chemistry 5.1);

– software package for statistical data analysis, data management, data mining and visualization (Statistica 7.0);

– methodology of kinetic studies of Waldman-Zelikman;

– methodology of thermodynamic research of academician Ospanov H.K;

– use of Excel table processor for processing the obtained results.

Defended main provisions (proven scientific hypotheses and other conclusions, which are new knowledge):

The following provisions are presented for the defense of the dissertation work:

1) results of thermodynamic characteristics of oxidized zinc minerals and series of increases in their reactivity;

2) Results of kinetic dependences of sulfuric acid leaching of zinc from calamine and smithsonite;

3) technology of hydrometallurgical processing of oxidized zinc ore using sulfuric acid four-stage countercurrent leaching.

Description of the main results of the study:

The analysis of the current state and prospects of development of hydrometallurgy of zinc was carried out and it was established that a number of deposits of rich oxidized zinc ores with commercial reserves of zinc were discovered in Kazakhstan and other countries of the world. However, quite a small part of these deposits is involved in processing, which leads to reduction of raw material base of zinc production. It was defined, that a rather large quantity of oxidized zinc minerals contains 52,15÷80,30% wt. % of zinc, that is comparable with its content in the main mineral, used in zinc metallurgy - sphalerite. Even more oxidized zinc minerals contain over 20 wt. % zinc. For further development of raw material base of zinc the involving of oxidized zinc raw material into processing makes it attractive from the point of view of cheaper zinc hydrometallurgy.

The study of material composition of the investigated ore showed that zinc content in it is 21,07 % wt. Different fractions of the given ore are characterized by zinc content of 22,23±2,15 % wt. By results of spectral and chemical analyses it was defined that elemental composition of the initial ore is mainly zinc (21,07 % wt.), silica (20,70 % wt.) and calcium (13,30 % wt.). Carbon, iron and sulfur are present in the ore in insignificant amounts (0,97÷3,27 % wt.).

The results of X-ray phase analysis and scanning electron microscopy of the studied ore confirm the presence of zinc silicate - calamine in the ore, taking into account the high content of zinc (13,59÷47,91%), silicon (11,05÷18,70%) and oxygen (37,85÷47,10 %) in it. According to the results of immersion analysis of the initial ore, it was found that the main zinc-bearing minerals in this ore are calamine and smithsonite. The content of calamine (24,60%) prevails over the content of smithsonite (11,42%), sphalerite is present in the initial ore in an insignificant quantity – 2,65%.

The values of the average atomic Gibbs energy $\Delta_f \overline{G}^o$ of formation for more oxidized zinc minerals were calculated. The Gibbs energies $\Delta_r G^o_т$ of chemical reaction of sphalerite (ZnS), smithsonite ($ZnCO_3$) and calamine ($Zn_4(Si_2O_7)(OH)_2$-H_2O) with sulfuric acid were determined: sphalerite – 13,27 kJ/mol, smithsonite – 75,46 kJ/mol, calamine – 154,07 kJ/mol. A series of changes of standard values of Gibbs energies $\Delta_r G^o_T$: $ZnS>ZnCO_3>Zn_4(Si_2O_7)(OH)2H_2O$ has been established, which confirms the reactivity of the minerals studied.

On the basis of the analysis of the thermodynamic calculations obtained it was established that the involvement into processing of oxidized zinc minerals with commercially acceptable zinc content, such as hydrozincite ($Zn_5(CO_3)2(OH)_6$), zincrosazite ($Zn_2(CO_3)(OH)_2$), smithsonite ($ZnCO_3$), calamine ($Zn_4(Si_2O_7)(OH)_2$-H_2O), adamine ($Zn_2AsO_4(OH)$), villemite ($Zn_2(SiO_4)$), will increase the economical efficiency of oxidized zinc ores processing.

According to the Purbe diagrams the existence of new low-soluble phases-products of reactions, which can screen the surface of soluble particles, causing intra-diffusion difficulties, is revealed. For the system Zn-Si-S-H_2O the region of zinc cations stability was determined at 25 ^oC which is limited by pH 5,4-5,5, and at 60 ^oC processes of hydrate formation begin in a more acidic region (pH 4,7-4,8). For the system Zn-Si-S-H_2O it was found that with increasing pH the following transition sequence is observed: $SiO_2 \rightarrow HSiO_3^- \rightarrow Si(OH)_3^- \rightarrow SiO_3OH^{3-}$. It was determined that a pH shift to the neutral region (pH 4-8) leads to the formation of silicic acid sols. Their adsorption on the surface of dissolving particles leads to the formation of a low-permeable film, i.e. to the intradiffusion inhibition of leaching.

In the study of kinetics of sulfuric acid leaching of zinc from calamine and smithsonite, the values of E_q. were calculated equal to 3,075 kJ/mol and 2,633 kJ/mol, respectively. The values found confirm that the dissolution reactions of calamine and smithsonite in sulfuric acid proceed in the diffusion region. It can be assumed that these reactions are limited by the diffusion rate of acid molecules to the reaction surface through the layer of formed reaction products - soluble zinc sulfate and carbon dioxide.

The possibility of increasing the degree of zinc extraction from calamine and smithsonite by updating the reaction surface of these minerals in the process of zinc leaching from them, at the expense of a staged leaching process which will lead to intensive removal of reaction products from the reaction surface has been proved.

It has been established that the method of sulfuric acid four-stage direct leaching of rich oxidized zinc ore in comparison with the classical zinc sulfide ore processing allows to increase the through zinc extraction from ore into the sulfate solution from ~75,00 to 94,65%, with zinc content of 40-45 g/dm^3 in the target sulfate solution.

The technological scheme of 4-stage countercurrent leaching of oxidized zinc ore is developed, it allows extracting zinc from ore into sulfate solution ~95,00 %, with zinc content of 61,55 g/dm^3 in the target sulfate solution. This does not require expensive processes of ore enrichment with obtaining zinc concentrate and oxidizing roasting of the concentrate.

Substantiation of novelty and importance of the obtained results:

The novelty lies in the development of technology for processing of oxidized zinc ores by expanding the raw material base of zinc hydrometallurgical production, increasing their economic efficiency and environmental safety.

New scientific results were obtained:

– the main thermodynamic characteristics of oxidized zinc minerals and series of increasing of their reactivity were determined for justified involvement of these minerals in hydrometallurgical processing;

– kinetic dependences of sulfuric acid leaching of zinc from calamine and smithsonite for calculation of value of "apparent" activation energy of reaction of these minerals with sulfuric acid and identification of limiting stage of the mentioned reactions were established;

– the technology of hydrometallurgical processing of oxidized zinc ore using sulfuric acid four-stage countercurrent leaching was developed.

The developed hydrometallurgical technology of oxidized zinc ore processing can be applied at enterprises specializing in zinc production and having a problem with stocks of processed raw materials. When zinc-containing oxidized ore is directly involved in hydrometallurgical processing, it can be considered as a raw material for processing, bypassing enrichment at the stages of sulfuric acid leaching of the cinder obtained from the sulfide zinc concentrate and/or waelz-oxide. The use of the above raw materials does not require the cost of their enrichment, as well as the oxidizing roasting and waelz-process of zinc extraction from the cakes of sulfuric acid leaching of cinder in zinc hydrometallurgy.

In general, the scientific novelty of the research, is confirmed by the patent for the invention of the Russian Federation "Method of oxidized zinc ore processing" RU2767385, published on 17.03.2022 Bulletin № 8 and the patent of the Republic of Kazakhstan for the useful model "Method of oxidized zinc ore processing" № 2062, published on 15.03.2017 Bulletin № 8.

Compliance with the directions of science development or state programs.

Today in spite of the growing demand for zinc products, its consumption is restrained both by the limited mineral and raw material base of zinc, and by the high cost of zinc. In hydrometallurgy of zinc the raw-material base is limited practically by a single mineral - zinc sulfide (sphalerite). But other minerals of zinc can also be of industrial interest in case they are found to have high reactivity and increased content of a valuable component. Some oxidized minerals, such as zinc silicate (calamine), zinc carbonate (smithsonite) and others, can be attributed to such zinc minerals.

A number of deposits of rich oxidized zinc ores with commercial reserves of zinc are discovered in Kazakhstan and other countries of the world. However, insignificant part of these deposits is involved into processing, which reduces the raw material base of zinc manufactures. And in separate deposits zinc content in ore is comparable with its content in sphalerite concentrates consumed by zinc hydrometallurgy. This circumstance allows speaking about expediency of using rich oxidized zinc ores without their expensive enrichment. Directly in zinc hydrometallurgy at the stage of sulfuric acid leaching, i.e. bypassing the energy-intensive stage of oxidizing roasting of raw materials. Thus, involving oxidized zinc raw material in processing makes it attractive in terms of cheaper zinc hydrometallurgy.

Despite the existence of a significant base of developments devoted to the study of the problem of oxidized zinc ore processing, to date, no cost-effective technology has been proposed that makes it possible to involve oxidized zinc minerals with commercially acceptable zinc content in the processing.

This work analyzes the technology of processing hard-to-enrich oxidized zinc ores and establishes the problem of expensive enrichment of mineral raw materials, associated with significant losses of zinc with tailings, as well as the application (energy intensive processes) of expensive oxidizing roasting of initial concentrate and waelz-process of cake processing. This work proposes to solve this problem by processing oxidized zinc ores according to the following scheme: sulfuric acid leaching of oxidized zinc ore in a four-stage counter-current mode. This scheme does not require ore enrichment and waelz-processing of cakes for zinc extraction.

The developed technological scheme of oxidized zinc ore processing by hydrometallurgical method will improve the environmental safety of production and will create conditions for involving oxidized zinc minerals with commercially acceptable zinc content into processing.

The research work corresponds to the priority direction of development of science of RK "Rational use of natural, including water resources, geology, processing, new materials and technologies, safe products and constructions". In 2022, Ramazanova R.A. received support from the state for further development and continuation of research work in the form of grant funding for research of young scientists on the project "Zhas galym" on the topic AP14972774 "Development of new promising hydrometallurgical technology for processing of oxidized zinc ores".

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

The author's personal contribution consists in setting the goal and objectives of the work, conducting experimental studies, processing and analysis of the results, formulating conclusions, writing articles, patents and abstracts.

According to the results of the dissertation research, 12 papers have been published, which are 5 articles in journals indexed in Scopus and Web of Science databases (CiteScore percentile of more than 35%), 2 articles in publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan and 3 papers in the collections of International and Republican scientific and practical conferences. Also published 2 patents - 1 patent for invention of the Russian Federation and 1 patent of the Republic of Kazakhstan for a useful model.

Articles in international peer-reviewed scientific journals included in the Scopus and Web of Science databases:

1) Ramazanova R.A., Mamyachenkov S.V., Seraya N.V., Daumova G.K., Aubakirova R.A., Bagasharova Z.T. Research of kinetics of zinc leaching with sulfuric acid from smithsonite // Metalurgija, Vol. 60, Nos. 3-4, 2021, p. 407–410.

2) Ramazanova R.A., Samoilov V.I., Seraya N.V., Daumova G.K., Azbanbayev E.M., Aubakirova R.A. Investigation of the kinetics of sulphuric acid leaching of zinc from calamine // Metalurgija, Vol. 60, Nos. 1-2, 2021, p. 113-116.

3) Ramazanova R.A., Zhussupova A.K., Mamyachenkov S.V., Seraya N.V., Daumova G.K., Azbanbayev E.M. Thermodynamic Description of Oxidized Zinc Minerals and Comparative Analysis of Their Reactivity // Chemical engineering transactions. 2021, Vol. 88, pp. 1159-1164.

4) Ramazanova R.A., Seraya N.V., Samoilov V.I., Daumova G.K., Azbanbayev E.M. New Method of Rich Oxidized Zinc Ore Sulfuric Acid Leaching // Metallurgist, 2020, Vol. 64, Nos. 1-2, pp. 169-175.

5) Ramazanova R.A., Seraya N.V., Bykov R.A., Mamyachenkov S.V., Anisimova O.S. Features of Shaimerden deposit Oxidized zinc ore leaching // Metallurgist. 2016, Vol. 60, Nos. 5-6, pp. 629-634.

Articles in journals recommended by the Committee for Quality Assurance in the Field of Science and Higher Education MS and HE RK:

1) Рамазанова Р.А., Самойлов В.И., Быков Р.А., Серая Н.В. Исследование минералогического состава окисленной цинковой руды месторождения Шаймерден // Вестник Национальной инженерной академии Республики Казахстан. 2018. № 4 (70) – С. 61-67.

2) Рамазанова Р.А., Самойлов В.И., Быков Р.А., Серая Н.В. Физико-химические исследования окисленной цинковой руды месторождения Шаймерден // Труды университета. 2019. – №3 (76). – С. 164-167.

Patents:

1) Пат. RU2767385. Способ переработки окисленной цинковой руды / Е.Ю. Ван, Р.А. Рамазанова, В.И. Самойлов, Н.В. Серая, Г.К. Даумова, Р.А. Аубакирова, Э.М. Азбанбаев; опубл. 17.03.2022, Бюл. № 8.

2) Пат. РК 2062. Способ переработки окисленной цинковой руды / Р.А. Быков, Р.А. Рамазанова, Е.Ю. Ван, Н.В. Серая, С.В. Мамяченков; опубл. 15.03.2017, Бюл. 8.

Scientific papers in the materials of domestic and foreign international conferences:

1) Рамазанова Р.А., Самойлов В.И., Серая Н.В., Мамяченков С.В. Способы сернокислотного выщелачивания окисленных цинковых руд различных месторождений // Materials of the XIII International scientific and practical Conference Scientific horizons – 2018. SHEFFIELD. Science and Education LTD, 2018. – С. 58-67.

2) Самойлов В.И., Рамазанова Р.А., Рыспаев Т.А. Современное состояние технологий производства цинка из минерального сырья и пути их развития // Материалы XV Международной научно-практической телеконференции «Advances in Science and Technology», Москва, 2018. – 124-130 С.

3) Рамазанова Р.А., Серая Н.В., Быков Р.А. Проблема переработки низкосортных окисленных и смешанных цинковых руд // Материалы Международной научно-практической конференции «Инновационные технологии и проекты в горно-металлургическом комплексе, их научное и кадровое сопровождение» г. Алматы, КазНТУ, 2014. – С. 507-509.