ABSTRACT

of dissertation work for the Doctor of Philosophy (Ph.D.)
6D072000 – «Chemical technology of inorganic substances»

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Technology of hydrometallurgical processing of copper smelter slag

The relevance of the research topic

Exhaustion of the ore base of non-ferrous metals, in particular zinc and copper, makes it necessary to find new sources of these raw materials. Such a source can be copper smelter slag, which is formed in significant quantities during the pyrometallurgical production of copper. The content of copper and zinc in the waste slag reaches 2 and 5 wt. % or more, respectively, which is comparable to the content of the indicated metals in the ore, or even exceeds this value. The main method for recovering copper from waste copper slag is flotation enrichment, with obtaining a concentrate containing about 8-10 % copper. The relatively low content of copper in the concentrate, as well as the almost complete loss of zinc with the tailings, does not allow us to consider flotation enrichment as an acceptable method for processing these slags. Another method that has practical application is slag depletion in electric furnaces; this method is not economically feasible due to high energy consumption. Hydrometallurgical processing of copper smelter slag, which is the processing of material with an aqueous solution of chemical reagents, seems attractive. A significant amount of sulfuric acid produced in copper smelters as a by-product makes it preferable to use this particular reagent for slag leaching. However, sulfuric acid leaching of slag requires the use of elevated (up to 80-90 ˚C) temperatures; besides, a significant amount of iron passes into the solution, which complicates further processing of the pulp. Thus, the development of conditions allowing hydrometallurgical processing of waste copper slag without the use of elevated temperatures, with selective extraction of copper into solution, seems to be a very urgent and important task.

Purpose of the thesis: to find optimum conditions for mechanical activation of copper smelter slag and its subsequent low-temperature sulfuric acid leaching, providing high extraction of copper and zinc into solution.

Research objectives:

- Determination of a model describing the leaching of components of waste copper slag in a sulfuric acid solution. Determination of the main kinetic parameters of the leaching reactions of copper-, zinc- and iron-containing minerals;
- Determination of the effect of potassium dichromate on the copper, zinc and iron recovery into a sulfuric acid solution during leaching. Establishing the influence of the form of copper in the slag on the degree of the mentioned metals recovery into solution;
- Revealing the influence of dry and wet mechanical activation of copper smelter slag in a planetary mill and attrition mill on the change in the specific surface area (SSA) of copper smelter slag. Determination of mechanical activation parameters that

have the greatest impact on SSA. Establishing conditions for the greatest increase in SSA of copper smelter slag;

- Revealing the effect of mechanical activation of copper smelter slag on the copper, zinc and iron recovery into a sulfuric acid solution in the presence of potassium dichromate;

- Optimization of conditions for mechanical activation of copper smelter slag and its subsequent sulfate leaching in the presence of potassium dichromate to maximize the degree and selectivity of copper extraction;

- Development of a schematic diagram of sulfuric acid leaching of copper smelter slag in the presence of potassium dichromate.

The object of the thesis is copper smelter slag samples collected from the «Kazakhmys Smelting» company (Balkhash, Central Kazakhstan).

The subject of the thesis is the processes occurring during dry and wet mechanical activation of dump copper slag, as well as during leaching of initial and mechanically activated slag with sulfuric acid solutions, including in the presence of oxidants.

The research hypothesis was as follows: As known, mechanical activation is accompanied by a change in the internal energy and specific surface area of the processed material. Consequently, it was expected that the mechanical activation of the copper smelter slag would lead to a change in the reactivity of its components during leaching. In turn, the presence of potassium dichromate will not only intensify the process of dissolution of target minerals due to oxidizing ability but also, possibly, will allow to selectively extract one of the components due to the difference in leaching rates of the present metals.

The scientific novelty of the thesis results obtained is ascertained by the fact that for the first time:

-the main kinetic parameters of the reactions of copper, zinc and iron recovery into solution during sulfuric acid leaching of copper smelter slag have been determined;

-the influence of dry and wet mechanical activation of copper smelter slag on the specific surface area, as well as on leachability in a sulfuric acid solution was revealed;

-the possibility has been shown and the reason has been described for the selective extraction of copper into solution during the sulfuric acid leaching of copper smelter slag in the presence of potassium dichromate.

Theoretical significance. The results of the dissertation research expanded the known knowledge in the field of mechanical activation of copper smelter slag and hydrometallurgical leaching of copper, zinc and iron.

Practical significance. The developed technical solutions for sulfuric acid leaching of copper smelter slag have prospects for practical use in industry and will expand the raw material base of copper and zinc.

The main provisions to be defended:

1. Wet mechanical activation of copper smelter slag in a planetary mill and attrition mill leads to a more significant increase in its specific surface area than dry mechanical activation;

2. Dry and wet mechanical activation of copper smelter slag increases the degree of zinc, copper and iron recovery into solution during sulfuric acid leaching;

3. The presence of potassium dichromate increases the degree of copper, zinc and iron recovery from the original and mechanically activated copper smelter slag during sulfuric acid leaching;

4. Leaching of copper smelter slag in sulfuric acid solution in the presence of potassium dichromate makes it possible to selectively extract copper into solution, thereby separating it from zinc and iron. This phenomenon is caused by the higher dissolution rate of copper sulfide minerals, in comparison with the dissolution rate of iron (mainly fayalite) and zinc (mainly zinc ferrite)- containing minerals under the investigated conditions.

The main results of the study:

Based on the data presented in this dissertation work, the following results were obtained:

1) Sulfuric acid leaching of copper, zinc and iron from copper smelter slag is described by a shrinking core model; the rate of leaching of these metals into the solution at 298, 313 and 323 K is controlled by the rate of the chemical reaction. The activation energies of the leaching reactions of copper, zinc and iron were 28.1, 23.1, and 16.5, kJ/mol, respectively. The maximum extractions of the metals achieved at 70 °C, leaching duration of 1hour, final pH of 2.3, the rotation speed of 300 rpm, were, %: Cu 58.7, Zn 84.2, Fe 79.7;

2) The presence of $K_2Cr_2O_7$ in the sulfuric acid allows selectively separating copper from zinc and iron during leaching. Copper recovery is highly dependent on the copper-bearing mineral present in the slag: covellite and chalcocite are more easily leached than chalcopyrite. From chalcopyrite-, covellite- and chalcocite-containing copper slag, under the conditions of the liquid-to-solid ratio of 67, leaching duration 2 hours, T= 298 K, rotation speed 450 rpm, $[H_2SO_4]$ = 0.5 M, $[K_2Cr_2O_7]$ = 0.5 M, the extractions of metals were, %: Cu 68.0, Zn 4.1, Fe 5.0. From chalcopyrite-containing slag, under the same conditions (except for liquid-to-solid ratio, which was 75 in this case), the extractions of metals were, %: Cu 34.2, Zn 2.1, Fe 4.9;

3) Dry and wet mechanical activation of copper smelter slag in both planetary ball mill and attritor resulted in an enhancement of the specific surface area, with the greatest effect in the case of the wet mechanical activation in a planetary ball mill. Under the conditions of 1200 rpm, ball-to-powder ratio 40:1 and 75 min, the SSA of the slag sample increased 68.2 times;

4) Mechanical activation of the slag led to an increase in the degree of extraction of copper into solution during leaching with the sulfuric acid solution in the presence of dichromate ions, whereas that of Fe and Zn only increased marginally. The selectivity for copper is due to the higher dissolution rate of copper minerals compared to iron and zinc minerals;

5) The samples obtained using optimized conditions have been subjected to leaching and the following conditions were found to be optimal for Cu recovery in attrition mill (in parentheses for copper selectivity): $[K_2Cr_2O_7]$ = 0.15 (0.03) M, $[H_2SO_4]$ = 0.5 (0.1) M, leaching duration 120 (30) min, liquid-to-solid ratio 75:1

(75:1). Under these conditions, copper recovery reached 87.31%, and Cu selectivity was 95.44 % upon mechanical activation in the attritor. Upon L: S ratio reduction to value 10, and an only slight decrease in Cu recovery has been evidenced (namely it dropped from 78.2 to 73.7 % upon the use of attrition milling and from 77.5 to 71.9 % for planetary milling), which predetermines the proposed methodology to be potentially applicable in the industry;

6) The technological scheme of hydrometallurgical processing of copper smelter slag is proposed. The scheme includes the crushing of the initial slag, wet mechanical activation of the slag in the attritor, two-stage leaching in sulfuric acid solution in the presence of potassium dichromate, as well as filtration processes. The following conditions are applied at the1st stage: wet mechanical activation in attritor mill (milling duration 75 min; ball-to-powder ratio 40:1, rotation speed 1200 rpm); leaching (L: S = 10, [H_2SO_4] = 0.1M, [$K_2Cr_2O_7$] = 0.03M). The solid residue after copper recovery is subjected to further leaching (2nd stage) under the same leaching conditions as the 1st stage. The scheme makes it possible to selectively extract copper (68.3 % recovery) at the 1st leaching stage, and then extract zinc (65.7 % recovery) from the residue at the 2nd leaching stage.

Relation of the thesis with research and government programs

The dissertation work was carried out as part of the research carried out jointly at the Department of General and Inorganic Chemistry of al-Farabi Kazakh national university and Institute of Geotechnics, Slovak Academy of Sciences, as well as within the framework of the grant funding project of the Science Committee of the Ministry of Education and Science of the Republic Kazakhstan (No. AP08856414).

Description doctoral contribution to the preparation of each publication.

The doctoral student was directly involved in the leaching and mechanical activation, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Selective room-temperature leaching of copper from mechanically activated copper smelter slag» in journal «Journal of Materials Research and Technology» (2021, Vol. 12, P. 2011-2025. IF 5.039. Quartile Q1 https://doi.org/10.1016/j.jmrt.2021.03.090).

The doctoral student was directly involved in the leaching and mechanical activation, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Copper smelter slag leaching by using H_2SO_4 in the presence of dichromate» in journal «Journal of Chemical Technology and Metallurgy» (2019, Vol.54, P.657-662. IF 0.806 Quartile Q3).

The doctoral student was directly involved in the leaching, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Vliyanie mekhanicheskoi aktivatsii na skorost vyshchelachivaniya otvalnogo mednogo shlaka v rastvore sernoi kisloty» (in Russian) in conference materials «Materialy IX nauchnoi konferentsii molodykh uchenykh «Innovatsii v khimii: dostizheniya perspektivy» -(2018.– P.478).

The doctoral student was directly involved in the leaching and mechanical activation, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Mechanical activation and subsequent leaching of copper smelter slag» in conference materials «Proceedings of the 10th International Beremzhanov congress on chemistry and chemical technology» (2019. – C.41-42).

The doctoral student was directly involved in the leaching, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the registration of a patent for a useful model No. 5741 «Method for extracting copper from copper melting production slags» (publ. 12.02.21) and No. 4900 «Method of copper extraction from waste copper slags» (publ. 10.01.20)

The doctoral student was directly involved in the leaching and mechanical activation, obtaining experimental data, processing and interpreting experimental results, and also took part in the implementation of physicochemical studies for the design of the article «Effect of mechanical activation on leachability of fayalite in sulfuric acid solution» in journal «Current Physical Chemistry» (2020. – P.1-6).

Volume and structure of the thesis.

The thesis consists of an introduction, four sections, a conclusion, and a list of references. The work is presented on 100 pages, contains 36 figures, 22 tables, and 124 bibliographical references.