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Flotation extraction of elemental sulfur from gold-bearing cakes

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Currently, in the development of the raw materials base of the gold mining industry, there is a tendency to reduce the quality of the initial mineral raw materials due to the depletion of reserves of rich gold-bearing ores. The article discusses the technology of extraction of refractory gold-bearing concentrates based on low-temperature leaching of pyrite concentrate. A decrease in the parameters of the autoclave oxidation of sulfide minerals, such as pyrite and arsenopyrite, leads to the incomplete extraction of gold into the solution and, consequently, its losses during subsequent cyanidation. As a possible option for a more complete extraction of gold using low-temperature oxidation technology, a method of flotation separation of elemental sulfur from leaching cakes is proposed. According to the basic process flow chart, the flotation process designed for gold extraction is carried out after autoclave oxidation, but before cyanidation. A series of experiments were carried out with varying reagent conditions and the dependence of gold losses on the extraction of elemental sulfur in the flotation tailings was established. As determining factors, pH and solid content in the initial pulp were considered. The paper justifies the separation of elemental sulfur from autoclave cake to enriched sulfur concentrate. The cake flotation modes after autoclave oxidative leaching of pyrite concentrate are investigated. The distribution of elemental sulfur and gold by flotation products makes it possible to conduct the tailings cyanidation process with acceptable indicators.

Key words: gold-bearing pyrite concentrate; finely disseminated gold; low-temperature leaching; elemental sulfur; flotation

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Introduction. In recent decades, in the gold mining industry, there has been a tendency to process low-grade and hard to recover refractory gold-bearing raw materials, including pyrite concentrates. The processing of ores and concentrates in which finely disseminated gold is associated with sulfide minerals, such as pyrite or arsenopyrite, requires much more complex technological flows, since during grinding such gold is extracted only partially, the main mass remains in sulfides, while cyanidation it is not dissolved, in the processes of gravitational and flotation concentration it is extracted together with carrier minerals. Due to the lack of gas emissions of highly toxic arsenic and sulfur compounds, and higher gold extraction compared to other methods, hydrometallurgical autoclave technologies are the most preferred. Such technologies are distinguished by the use of high temperatures and pressure of reaction gases, which allows not only to intensify the process of direct extraction of non-ferrous and noble metals but also to ensure their easier separation during pulp processing and elutriation [6].

The promising technologies for extraction of gold from sulfide concentrates include the method of hydrometallurgical autoclave oxidation of concentrates in an acidic medium, based on high-temperature leaching, where the process temperature reaches 200-220 °C. However, this technology has several disadvantages – high capital costs in the implementation of the process (since according to existing technologies and industrial production based on autoclave oxidative leaching of gold-containing sulfide raw materials, oxidative processes require harsh physical and chemical conditions), as well as the difficulty in that the gold-containing sulfides should be completely oxidized to sulfate ions [4].

Problem statement. The main factor determining the technological refractory of gold-bearing ores is the close association of finely disseminated gold with sulfides, iron hydroxides, and carbonates. Besides, the “persistence” associated with gold sulfides is due to its presence in sulfides not only in the form of finely dispersed particles of native metal but also in the form of a solid solution, colloidal particles, and the so-called “surface” gold [1, 11]. The autoclave technology for processing gold-bearing concentrates enables higher gold extraction compared to oxidative calcination methods

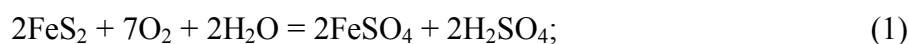
and eliminates the loss of gold with dust, thereby eliminating the need for complex dust collection systems, since this mode provides not only the quantitative oxidation of sulfides and the recovery of the associated gold but also the conversion of most of the arsenic to insoluble iron arsenate, which is the most environmentally acceptable form of arsenic [5, 6, 9, 17].

Since high costs along with complex flow process make the technology based on high-temperature leaching of concentrates seldom applicable for use, especially in remote areas and small enterprises, currently the possibility of using technology based on low-temperature leaching is considered to be used to reduce the oxidation parameters of sulfide materials, which consists in heating the pulp in the autoclave to a temperature of 120 °C in an atmosphere of air or oxygen at a pressure of 0.8-1.0 MPa. The advantages of this technology are due to the low cost of autoclave equipment and increased gold extraction. Besides, the relatively low temperature of autoclave leaching will favorably affect the extraction of gold in the hydrometallurgical cycle by reducing the harmful effects of chlorides, organic carbon, and its decomposition products in the autoclave. However, a decrease in the parameters of the autoclave process entails an increase in the requirements for the particle size distribution of raw materials [8]; therefore, it is advisable to use ultrafine grinding of the feedstock, where 80 % of the particles have a particle size of fewer than 10-12 microns [3, 4].

The basic flow chart for the autoclave processing of refractory gold-bearing concentrate at relatively low parameters includes the stages of fine grinding, decarbonization, autoclave oxidative leaching, dehydration (filtration, washing, thickening), and sorption cyanidation.

The chemistry of the leaching of sulfide minerals (pyrite, arsenopyrite) in an acidic medium can be represented by two competing reactions – with the formation of sulfate ion or elemental sulfur.

Autoclave oxidation of pyrite in an acidic medium to a sulfate ion [2, 3, 7, 8]:



to elemental sulfur:



However, the process of low-temperature leaching (110-120 °C) is accompanied by the formation of a significant amount of elemental sulfur, which envelops particles of gold sulfide minerals finely disseminated in the crystal lattice, not allowing them to completely undergo the oxidation process, forming an insoluble residue. If enough amount of gold is bound to sulfides, it will not be recovered at the leaching stage and will not be extracted further into the cyanide solution. Incomplete oxidation of sulfur compounds leads to losses of gold with solutions and cyanide cakes. Also, sulfur entering the cyanidation cycle is accompanied by its interaction with cyanide, which greatly increases the consumption of the latter.

The main objective of the study is to justify the possibility of using flotation separation of elemental sulfur from autoclave cakes of low-temperature leaching of pyrite concentrate for more complete extraction of gold into solution. The purpose of the flotation process is to recover gold and obtain tailings for elemental sulfur content, which will contribute to reducing the amount of equipment in subsequent operations and increasing the efficiency of the technology based on low-temperature leaching.

Research methodology. The flotation process and, accordingly, its results largely depend on the reagent mode, mineralogical composition, dissemination fineness, particle size distribution of solids, density, temperature, and composition of the pulp aqueous phase [2]. It is important to note the design parameters of the flotation machine. The optimal value of each of the factors is determined experimentally and should be constant since the violation of at least one of them can completely reduce the efficiency of the flotation process.



Quality of the mineral. The characteristic of a mineral means its mineralogical composition, i.e. the properties of individual minerals and their quantitative ratio, the nature of their intergrowth, the presence of isomorphic impurities, and secondary changes [10, 12, 14-16]. Leaching cake is characterized by the presence of metallic and non-metallic minerals mainly with a particle size of fewer than 40 microns.

The mineralogical composition of the initial cakes calculated by the authors is presented below:

Component	Quartz	Hydrojarosites	Clay substance	Sulphide minerals	Non-sulfide minerals	S ⁰
Content, %	44	17	13-14	2-3	0.5-0.8	6-7

The cakes were obtained after low-temperature autoclave leaching of a pyrite concentrate, the main ore mineral of which is pyrite (the content of 44.5 %), arsenopyrite (1.5 %) and pyrrhotite (1 %) are present. The autoclave leaching of pyrite flotation concentrate was carried out under the following conditions: grinding to the size of 10-12 microns not less than 80 %, temperature – 130 °C, and oxygen pressure – 10 atm.

Sulfide minerals are represented mainly by chalcopyrite, galena, stibnite, single grains of pyrite, muscovite, and kaolinite. The presence of non-sulfide ore minerals such as titanium and rutile was detected in cakes. Elemental sulfur is partially represented by rounded granules of 15-40 microns in size and lumpy precipitates of up to 50 microns in size, some part is in a submicroscopic state and mixed with jarosite, clay, and residual sulfides.

Grain size of the feedstock. Milling fineness has a decisive effect on the flotation process. The presence of slime in the pulp worsens flotation, reducing its speed, and leads to an increase in reagent consumption. For autoclave oxidative leaching pulps of pyrite concentrate, the cake is highly dispersed, 80 % of the particles have a particle size of not more than 10-15 microns.

Reagent mode. In a series of flotation experiments, methyl isobutyl carbinol (MIBC) was used as a collecting and frothing agent. The depressor of the major non-metallic minerals was water glass; in the case of rutile, titanium, and stibnite it is a solution of potassium permanganate (KMnO₄). Activators (and depressors) regulate the actions of collecting agents on particles of minerals, increasing the selectivity of flotation [13].

Operation of flotation machines. The volume of pulp entering the flotation machine should provide the optimal time for the process while maintaining the density and volume of the pulp at a constant level is a prerequisite. Flotation studies were carried out in a laboratory flotation machine of the mechanical-air type of the FMZ brand with air supply to the chamber according to a unified technological scheme (Fig.1) with varying process parameters and solid content of 15 % in the initial pulp [3].

The basic process of laboratory research includes four operations of sulfur flotation to produce three sulfur concentrates, different in elemental sulfur content, and flotation tailings [4, 15]. Before the process, the autoclave cake was subjected to a short washing.

Technological parameters of a series of experiments on the flotation of elemental sulfur from autoclave cakes were the following:

- flotation reagents – methyl isobutyl carbinol (MIBC), water glass, a solution of potassium permanganate KMnO₄, a mixture of lime CaO and sodium sulfide Na₂S (in the 2:1 ratio);
- total reagent consumption in the flotation cycle – 200-600 g/t methyl isobutyl carbinol, 250-525 g/t water glass;
- pH of the initial pulp is 2-12.

Main characteristics of the FMZ flotation machine:

- 0.75-liter camera;
- rotor speed – about 2000 rpm.

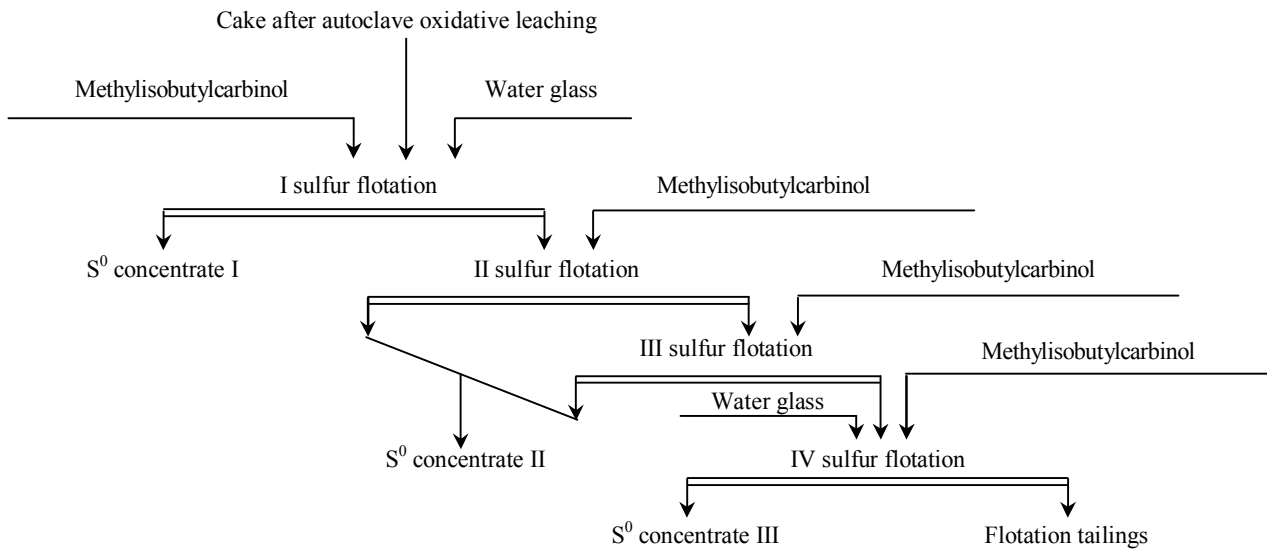


Fig.1. Process flow of an experimental study of the process of flotation of elemental sulfur from autoclave cakes after low temperature oxidative leaching of pyrite concentrate

Reagents were supplied portion-wise before each flotation operation. After each experiment, frothing flotation products were sent for filtration and drying, then for chemical analysis to determine the sulfur and gold content. After filtration, a sample was separated from the flotation tailings to determine the moisture, sulfur, and gold contents, and the rest of the tailings in the raw state was sent to cyanidation of gold.

Discussion. As the studies showed, gold is distributed among the flotation products in proportion to the distribution of elemental sulfur, although its extraction into the total concentrate is less important than elemental sulfur. Technological indicators of a series of flotation experiments are presented in Table 1.

Table 1

Material balance of a series of flotation experiments

Flotation products	Output, %	Elemental sulfur		Gold	
		Content, %	Extraction, %	Content, g/t	Extraction, %
Sulfur concentrate	17.1-37.2	11.8-23.32	59.5-90.12	54.9-94.2	47.5-77.6
Tailings	62.8-82.9	1.13-3.68	10.92-44.4	12.8-24.4	24.8-54.1
Total	100.0	6.5	100.0	34.0	100.0

The discrepancy in elemental sulfur amounted to 1-3.9 %, in gold – to 1.6-2.4 %. The extraction of total sulfur in flotation tailings raised to 53 %.

During the first two experiments of flotation studies, the pH of the initial pulp was maintained at level 2. In the first experiment, the total consumption of the flotation reagent methylisobutylcarbinol was 200 g/t, while the reagent was fractionally fed into the chamber of the flotation machine. As a result of the first experiment, the elemental sulfur content in the total flotation concentrate was 22.58 %, the recovery was 59.5 % from the operation, the gold content in the concentrate was at the level of 94.2 g/t (gold recovery 47.5 % from the operation). When the content of elemental sulfur in the flotation tailings was 3.48 %, the gold content in cyanidation tailings was 2.52 g/t.

In the second experiment, in addition to MIBC, water glass was supplied to the pulp as flotation reagent, the total consumption of which was 250 g/t. This made it possible to reduce the elemental sulfur content in the flotation tailings to 2.02 %, while the extraction of elemental sulfur in the total flotation concentrate increased to 74.6 % of the operation. As a result, the extraction of gold amounted to 55.49 % of the operation, the gold content – to 73.18 g/t. The gold content in cyanidation tails is 1.29 g/t.

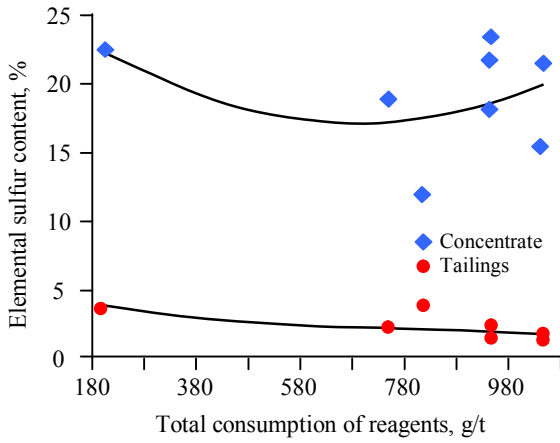


Fig.2. Elemental sulfur content in flotation products

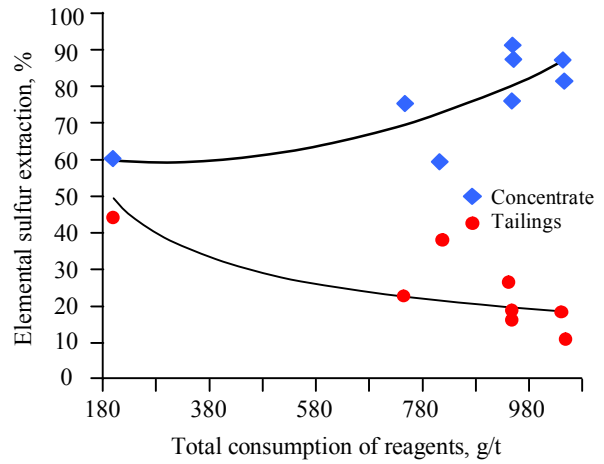


Fig.3. Extraction of elemental sulfur in products flotation

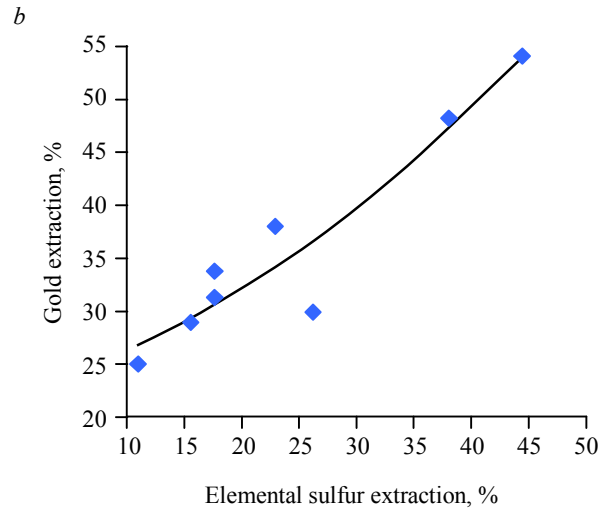
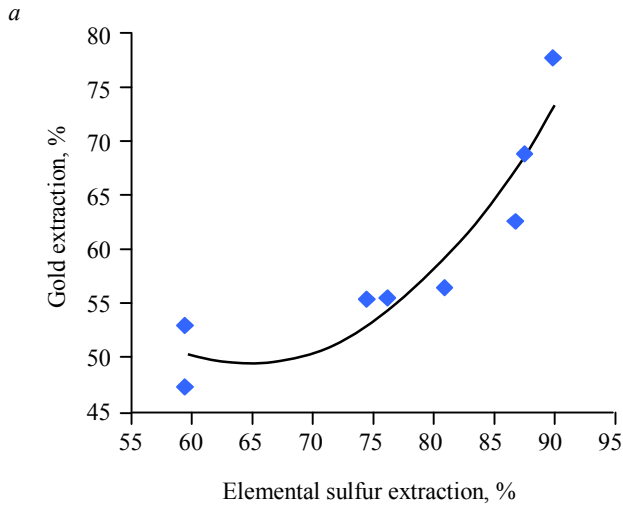


Fig.4. Dependence of gold recovery on elemental sulfur extraction; a – concentrate; b – tails

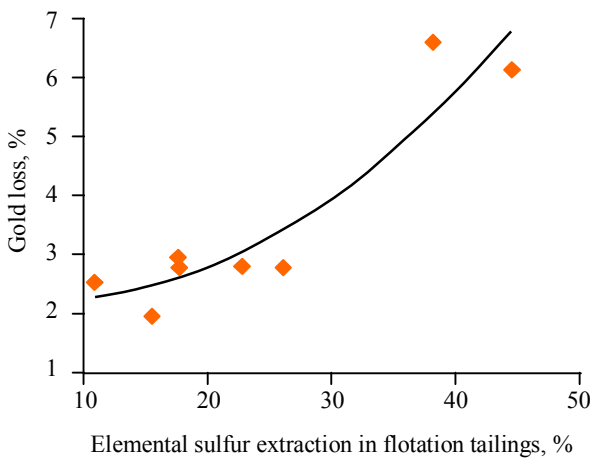


Fig.5. Dependence of gold losses with cyanidation tails on the extraction of elemental sulfur in flotation tailings

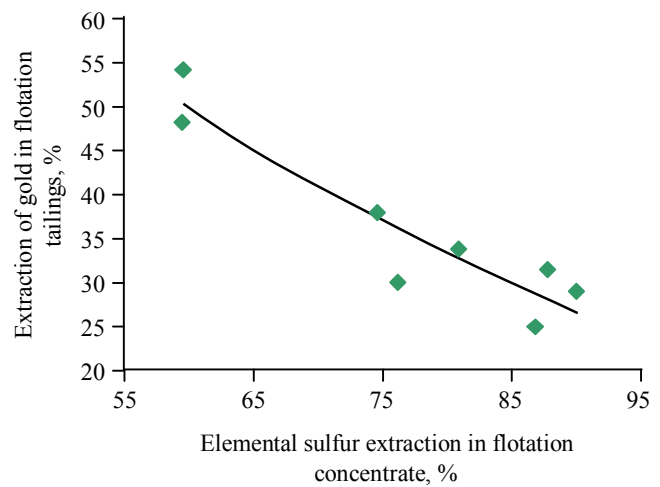


Fig.6. Dependence of gold recovery in flotation tails from the extraction of elemental sulfur in flotation concentrate



In the third experiment, the pH value of 12 was taken as the initial one. Such a high pH value was achieved by feeding a mixture of reagents (lime and sodium sulfide) before the first flotation. The consumption of lime amounted to 14 kg/t. In the course of the experiment, the formation of rich foam was observed, which is explained by the presence of clay substance and hydrojarozite in it, which could serve as a decrease in enrichment indices for both elemental sulfur and gold. The elemental sulfur content in the total concentrate was only 11.8 %, gold – 54.92 g/t, recovery rate – 59.5, and 52.96 %. The gold content in the flotation tailings increased slightly – to 24.4 g/t, and in the cyanidation tailings – 3.35 g/t.

In a subsequent series of experiments, the initial pH of the pulp ranged from 3 to 4.41. The use of water glass reduced the elemental sulfur content in the flotation tailings to 1.13-2.16 %, and in the total concentrate, this value was 15.2-23.3 % (Fig.2). The gold content in the concentrate reached the level of 78.5-89.2 g/t (Fig.3), while the extraction of elemental sulfur in the total concentrate increased to 76-90 %, gold to 55-78 % of the operation. The gold content in cyanidation tails ranged from 1 to 1.4 g/t.

The distribution of elemental sulfur by flotation products in a series of experiments is shown in Fig.2, 3.

The dependences of gold extraction on the distribution of elemental sulfur by flotation products (concentrate, tails) are shown in Fig.4.

Technological indicators of the cyanidation process of flotation tailings are presented in Table 2.

Table 2

Flotation tailings cyanidation process indicators

Flotation products	Elemental sulfur	
	Content, %	Extraction, %
Sulfur concentrate	11.8-23.32	59.5-90.12
Tailings	1.13-3.68	10.92-44.4

The gold content in the tailings after cyanidation was 1-3.35 g/t, gold losses were up to 6 %. The dependences of gold losses on the extraction of elemental sulfur in the flotation tailings are shown in Fig.5.

If a sufficient amount of elemental sulfur, as well as its compounds, passes into the concentrate during the flotation process, the gold associated with sulfur will be released and remain in the flotation tailings. Then it is advisable to send sulfur flotation tailings to cyanidation. Therefore, the additional recovery of gold at the cyanidation stage is directly related to the extraction of elemental sulfur in the flotation concentrate (Fig.6).

The inefficient flotation process can lead to significant gold losses at the cyanidation stage (see Fig.5). The more sulfur remains in the flotation tailings, the more gold will be associated with it, and the loss of gold with cyanidation tailings can reach 6-7 %.

Conclusion. Laboratory studies have shown an increase in reagent consumption at a higher pH of the pulp, which leads to a decrease in the elemental sulfur content in the flotation tailings to 1.13 %, but at the same time the sulfur content in the total flotation concentrate is low and amounts to only 15.2 %.

As a result of the flotation of the autoclave cake, it was possible to reduce the elemental sulfur content in the flotation tailings from 6 to 3.5 %, which makes it possible to carry out the subsequent cyanidation process with acceptable indicators, while the gold content in the tailings after the cyanidation process is about 1-1.4 g/t.

REFERENCES

1. Naboichenko S.S., Shneerson Ya.M., Kalashnikova M.I., Chugaev L.V. Autoclave hydrometallurgy of non-ferrous metals. Vol. 2. Ekaterinburg: UGTU – UPI, 2009, p. 611 (in Russian).
2. Naboichenko C.S., Ni L.P., Shneerson Ya.M., Chugaev L.V. Autoclave hydrometallurgy of non-ferrous metals. Ekaterinburg: UGTU – UPI, 2002, p. 940 (in Russian).



3. Ivanik S.A. Separation and dehydration of ultrafine phases in autoclave leaching technology of refractory gold-bearing concentrates: Avtoref. dis. ... kand. tekhn. nauk. Natsionalnyi mineralno-syrevoi universitet "Gornyi". St. Petersburg, 2012, p. 20 (in Russian).
4. Lapin A.Yu., Bitkov G.A., Shneerson Ya.M. Autoclave-hydrometallurgical processing of refractory gold-bearing sulfide materials at low temperatures. *Tsvetnye metally*. 2011. N 12. p. 39-44 (in Russian).
5. Lodeishchikov V.V. Technology for the extraction of gold and silver from refractory ores. Irkutsk: OAO "Irgiredmet", 1999, p. 342 (in Russian).
6. Modestova S.A. Investigation of the extraction of non-disintegrated electrolyte sludge of copper production. *Zapiski Gornogo instituta*. 2010. Vol. 186, p. 191-193 (in Russian).
7. Naboichenko S.S. Autoclave hydrometallurgy in Russia (history, experience, problems). Sbornik dokladov mezhdunarodnogo kongressa "Tsvetnye metally – 2009". Krasnoyarsk, 2009, p. 521-526 (in Russian).
8. Sizyakov V.M., Ivanik S.A., Boginskaya A.S., Bitkov G.A. Pulp dehydration after autoclave leaching of finely ground sulfide concentrates. *Estestvennye i tekhnicheskie nauki*. 2012. N 1 (57), p. 369-375 (in Russian).
9. Shneerson Ya.M., Naboichenko S.S. Trends in the development of autoclave hydrometallurgy of non-ferrous metals. *Tsvetnye metally*. 2011. N 3. p. 15-20 (in Russian).
10. Petrov G.V., Fokina S.B., Boduen A.Ya., Fidarov B.F., Zotova I.E. Aspects of electrochemical reaction mechanism of magnetite reductive leaching in sulfuric acid medium. *International Journal of Mechanical Engineering and Technology*. 2019. Vol. 10(1), p. 1595-1601.
11. Boduen A.Ya., Fokina S.B., Polezhaev S.Y. The hydrometallurgical pretreatment of a refractory gold sulfide concentrate. Innovation-Based Development of the Mineral Resources Sector: Challenges and Prospects: Proceedings of the 11th conference of the Russian-German Raw Materials, 2018. Germany, 2019, p. 331-340.
12. Jia Y., Huang K. The selective flotation behavior and adsorption mechanism of thiohexanamide to chalcopyrite. *Minerals Engineering*. 2019. Vol. 137, p. 187-199.
13. Jorjani E., Ghahreman A. Challenges with elemental sulfur removal during the leaching of copper and zinc sulfides, and from the residues; a review. *Hydrometallurgy*. 2017. Vol. 171, p. 333-343.
14. Long G., Peng Y., Bradshaw D. Flotation separation of copper sulphides from arsenic minerals at Rosebery copper concentrator. *Minerals Engineering*. 2014. Vol. 66, p. 207-214.
15. Medina Tripodi E.E., Rueda Gamboa J.A. Characterization and geostatistical modelling of contaminants and added value metals from an abandoned Cu–Au tailing dam in Taltal (Chili). *Journal of South American Earth Sciences*. 2019. N 93, p. 183-202.
16. Corrans Ian J., Angove John E. Patent US 5232491A. Activation of a mineral species. Date of Patent: Aug. 3, 1993, p. 5.
17. Sun W., Zhang Y. Activated flotation of pyrite once depressed by lime. *Journal of Central South University (Science and Technology)*. 2010. N 41, p. 813-818.

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