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Intensification of Bacterial-Chemical Leaching of Nickel, Copper and Cobalt from Sulfide Ores Using Microwave Radiation

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Currently, Russia and other countries display a steady tendency to decrease the amount of high grade and free-milling ore reserves. In this regard, the attention is being paid to the technology of bacterial-chemical leaching (BCL), which, unlike traditional pyrometallurgical enrichment methods, is well applicable for processing low-grade mineral raw materials. However, this technology has a significant drawback, which is the inability of microorganisms to create sufficiently aggressive conditions for the effective destruction of mineral complexes, which negatively affects the duration of the processes. The article presents the results of an experiment, the purpose of which was to study the multiple short-term effects of microwave radiation on the efficiency of extraction of nickel, copper, and cobalt in the process of bacterial-chemical leaching of sulfide ore. A microwave oven with a power of 900 W and a radiation frequency of 2.45 GHz was used as a source of microwave radiation. Irradiation was carried out every day throughout the experiment. The exposure time was 5 and 10 s; the flux density was 0.7 W/cm^2. It was found that for all the studied microwave irradiation modes, a significant increase in the efficiency of biomass accumulation and the oxidizing ability of the medium was observed in comparison with the control that was not exposed to microwave radiation. Irradiation for 5 s twice a day increased the reduction of nickel by 16 %, cobalt by 15 % and copper by 6 %. The results of the study allow us to assess the prospects for the application of new biotechnology methods in the industrial practice of ore processing with an improvement in quality indicators.

Keywords: bioleaching; microwave radiation; microwave radiation; enrichment; intensification; chemolithotrophs

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Introduction. Currently, Russia and other countries display a steady tendency to decrease the amount of high grade and free-milling ore reserves. At the same time, the demand for metals is growing steadily. In this regard, the usage of rebellious complex raw materials, as well as tailings with a low content of valuable components, becomes relevant [13].

The use of traditional pyrometallurgical methods for processing low-grade raw materials is economically disadvantageous. Also, high-temperature processes are associated with the risk of environmental pollution by production waste (CO, SO_2) [11].

In recent years, the technology of vat bacterial-chemical leaching (BCL) of ores, which is non-waste and environmentally friendly, has become increasingly popular. Low capital costs and technical simplicity of the equipment can dramatically reduce the cost of processing. This technology is applicable to processing low-grade mineral raw materials [8].

Bioleaching is based on the process of selective extraction of chemical elements from multicomponent compounds due to their dissolution by microorganisms in an aqueous medium. Leaching is carried out by bacteria belonging to the *Thiohacillus* genus, as well as the archaea of the *Sulfolobus* genus. Thiobacilli is autotrophic types of bacteria that oxidize inorganic substances (Fe^{2+}, S^0); the released energy is used to absorb carbon from CO_2. Common types of microorganisms that are used in industry are *Acidithiobacillus caldus*, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus ferrivorans*, *Leptospirillum ferrooxidans u Acidithiobacillus thiooxidans* [6].

The dissolution of metal compounds as a result of bacterial activity occurs due to two main mechanisms: direct and indirect. A direct mechanism is the oxidation of the substrate due to enzymatically catalyzed reactions during the adhesion of bacteria on the surface of a mineral. The indirect one involves the chemical oxidation of minerals by ferric iron, which is produced in the reactions of biological oxidation of Fe^{2+} ions [3].

Despite the advantages over traditional enrichment methods, bioleaching technology has a significant drawback, which consists of the high duration of the process due to the weak kinetics of redox reactions. In this regard, an urgent task today is the search and development of methods for intensification of bacterial-chemical leaching [12].

Different papers describe the ways to increase bacterial activity based on usage of wave radiation, such as ultrasound, microwave, and ionizing radiation. They are also used in the extraction and processing of mineral raw materials [9, 16].

The purpose of this paper is to study the multiple effects of microwave radiation on the efficiency of metal extraction during bacterial-chemical leaching.

For a long time, it was believed that the cause of the biological response to microwave radiation is local heating caused by the friction of polar molecules that change their orientation in the electromagnetic field. However, recently it has been established that the biological effect is manifested at ultra-low intensities of microwave radiation when tissue heating is not decisive or negligible. Such effects are called «specific» or non-thermal [1].

The technical literature contains information about changes in the structure of DNA when exposed to microwave radiation. DNA disorders, the so-called chromosomal aberrations, are manifested in various genes, which is causes a malfunction in the production of functional and structural elements of the cell, which are RNA and proteins. It is also known that the primary target of microwave radiation in a living cell is a biological membrane, changes in which lead to a violation of the transport of substances between the cell and the environment [10].

In addition to the biological component of bacterial-chemical leaching, microwave radiation causes changes in the structure of the ore. Under the influence of microwave radiation, many physical, chemical and mechanical transformations occur – formation of thermomechanical stress, relaxation of residual stresses with the formation of micro- and macro cracks, polymorphic and phase transformations. The formation of thermally induced micro- and macrocracks in the ore due to the action of microwave waves creates an additional surface front of potential attachment sites for chemolithotrophic microorganisms and provides access of the leach solution to the mineral grains, thereby improving the extraction of target components during bacterial-chemical leaching [5].

Paper [9] presented an improved release of copper sulfide, iron sulfide, and natural gold-bearing ores after microwave treatment and subsequent grinding.

Other studies have also demonstrated increased metal reduction efficiency due to the increased opening of mineral grains due to induced destruction of copper, lead-zinc, and nickel sulfide ores [14, 15].

Materials and methods. ***Bacterial culture.*** The tests were performed using a mixed culture of chemolithic autotrophic microorganisms isolated from a sample of sulfide copper-nickel ore from the Shanuch deposit (Kamchatka). According to PCR diagnostics, it included *Acidithiobacillus ferrooxidans*, *A. thiooxidans*, *Sulfobacillus sp.* [7].

Ore. In our work, we used sulfide ore of the Shanuch cobalt-copper-nickel deposit with a sulfide mineral content of 60-90 %, of which 65-75 % is pyrrhotite, 20-25 % – pentlandite, 10 % – violarite, 2-5 % – chalcopyrite. The initial concentration of metals in percentage was the following: Ni – 7.68; Cu – 0.6; Co – 0.15. For tests, the ore sample was ground and sieved through a sieve with a mesh size of 100 μm.

Irradiation process. Irradiation was carried out in a 900 W household microwave oven. The radiation frequency is 2.45 GHz. The radiation flux density is 0.7 W/cm^2. Three experimental groups were formed depending on the duration and the frequency of exposure:

- 5-1 – microwave exposure (5 s) once a day;
- 5-2 – microwave exposure (5 s) twice a day;
- 10 – microwave exposure (10 s) once a day.

Control samples were those not exposed to microwave radiation. The choice of exposure modes is based on previous experiments [2].

Accumulation of bacterial culture. Isolation and accumulation of biomass necessary for the experiment were carried out in a bioreactor containing sulfide polymetallic ore and Silverman and Lundgren nutrient medium (T : L = 1 : 8). The process took place at a constant temperature of 30 °C, with continuous stirring and forced aeration. The concentration of free-floating microorganisms was 10^9 cells in 1 ml of solution.

Assessment of the oxidizing activity of microorganisms depending on the selected microwave irradiation mode. The ferrous iron was used to evaluate the oxidative activity of a mixed culture of chemolithotrophic organisms, which is a key link in their electron transport chain.

Bacterial oxidation of Fe^{2+} was carried out in 250 ml Erlenmeyer flasks containing sterile Silverman-Lundgren mineral medium (9 K) with the addition of ferrous iron. The process was carried out at a constant temperature of 22 °C without additional aeration and mixing. The initial concentration of microorganisms is 10^7 ml^{-1}. Throughout the experiment, cell counting was performed, and pH and Eh parameters were measured. The concentration of ferrous and ferric iron was determined by visual colorimetric titration.

Bacterial-chemical leaching. Bacterial chemical leaching was carried out periodically in 250 ml Erlenmeyer flasks containing 10 g of cobalt-copper-nickel ore and 100 ml of Silverman and Lundgren medium supplemented with iron (3 g/l). The flasks were located on a nutator (90 rpm) in a thermostat at a constant temperature of 22 °C. The initial number of cells was 10^6 in 1 ml of solution.

Throughout the experiment, the number of free-floating microorganisms was determined daily by direct counting under a microscope, and the degree of oxidation of ferrous iron was determined by visual colorimetric titration. The concentration of metals (Ni, Cu, Co) transferred to the solution was identified by atomic absorption spectrometry on a 6300 Shimadzu instrument in an acetylene-air flame.

Discussion and results. 1. *Assessment of oxidative activity.* Analysis of the results showed that exposure to microwave radiation leads to a significant increase in the number of planktonic forms of microorganisms. Figure 1 shows a graph of the change in the number of planktonic forms of microorganisms in different experimental groups.

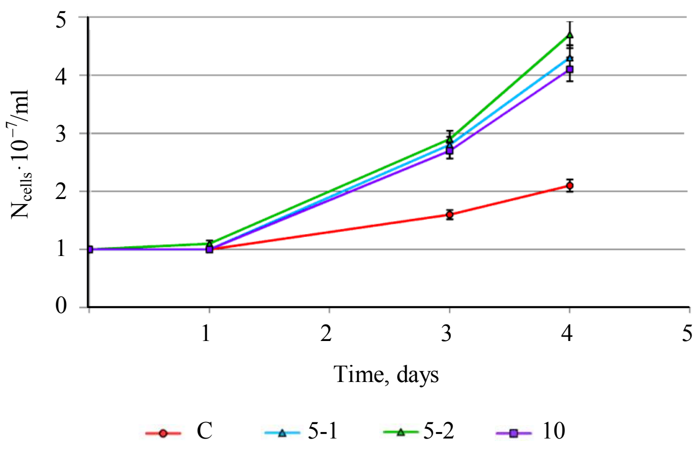

Fig. 1. Change in the number of free-floating cells in 1 ml of solution in various experimental groups: C – control; 5-1 – microwave exposure (5 s) once a day; 5-2 – exposure to microwave (5 s) twice a day; 10 – microwave exposure (10 s) once a day

In the experimental group «5-2», the highest concentration of microorganisms was recorded in 1 ml of solution, which was equal to $(4.7\pm0.2)\cdot10^7$, which exceeds the values in the control sample by more than 2 times. The number of cells in the control sample was $(2.1\pm0.1)\cdot10^7$ ml^{-1}.

The number of microorganisms in 1 ml of solution in the groups «5-1» and «10» was $(4.1\pm0.2)\cdot10^7$ and $(4.3\pm0.2)\cdot10^7$, respectively.

During the experiment, it was also found that exposure to microwave radiation increases the iron-oxidizing activity

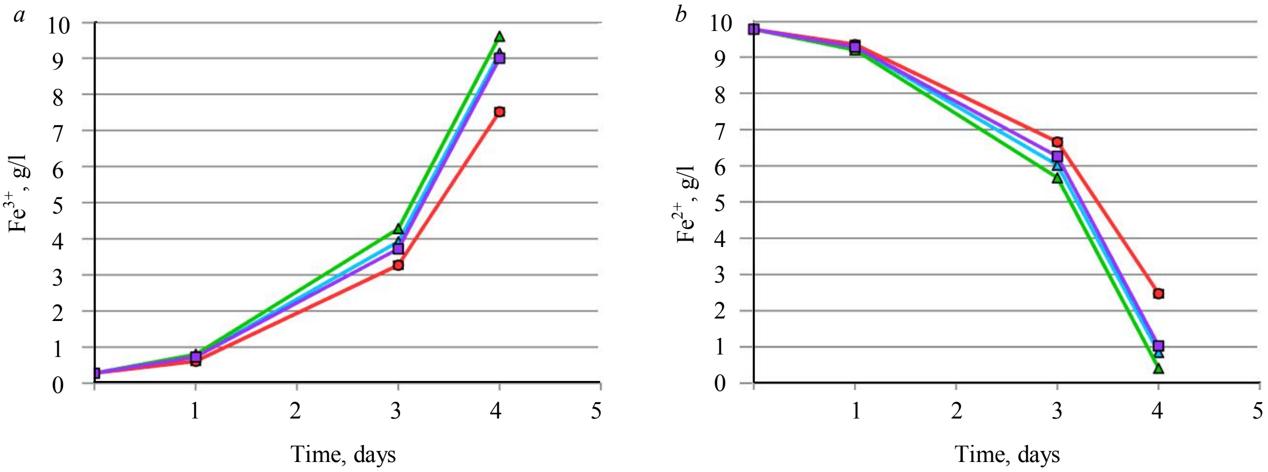

Fig.2. Change in trivalent concentration (a); and bivalent (b) iron.
See legend in Fig. 1

of chemolithotrophic microorganisms. The highest rates of iron oxidation were recorded in 5-2 flasks, which were irradiated for 5 s twice a day at 12-hour intervals. During the experiment, 96 % Fe^{2+} was oxidized in this experimental group, while in control only 81 %.

The exposure to microwave radiation lasting 10 s once a day throughout the experiment also contributed to an increase in the efficiency of oxidation of ferrous iron by microorganisms, but was less pronounced than in the «5-2» group: by the end of the experiment, 89 % of Fe^{2+} in the «10» flasks was oxidized. A 10-second exposure contributes to the occurrence of damage in the cells of microorganisms that exceed the capabilities of their reparative processes (Fig.2).

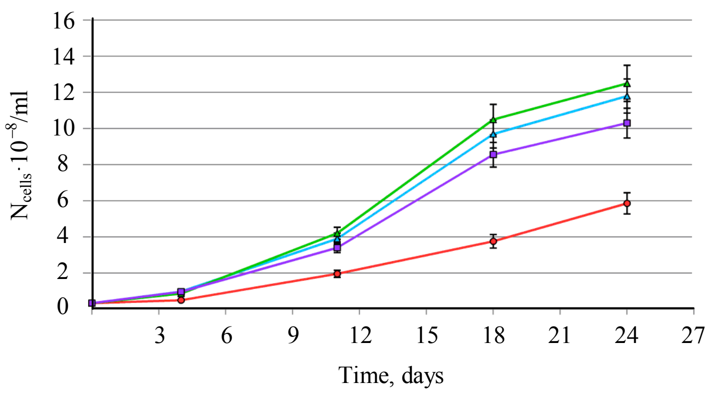

Fig. 3. Change in the concentration of planktonic forms microorganisms in various experimental groups.
See legend in Fig. 1

2. *Bacterial-chemical leaching.* An experiment to study the effect of various microwave radiation modes on the processes of bacterial-chemical leaching of sulfide ore lasted 25 s. The study revealed that daily exposure to microwave radiation increases the rate of biomass accumulation in flasks (Fig.3).

The best growth rates of the number of microorganisms were observed in the experimental group «5-2», where the maximum concentration of free-floating cells, which was recorded at the end of the experiment, was $(1.2\pm0.1)\cdot10^8$ cells/ml. In the control group, which was not exposed to microwave radiation, this indicator reached a value of $(0.6\pm0.1)\cdot10^8$ cells/ml, which is 2 times lower than in the «5-2» group.

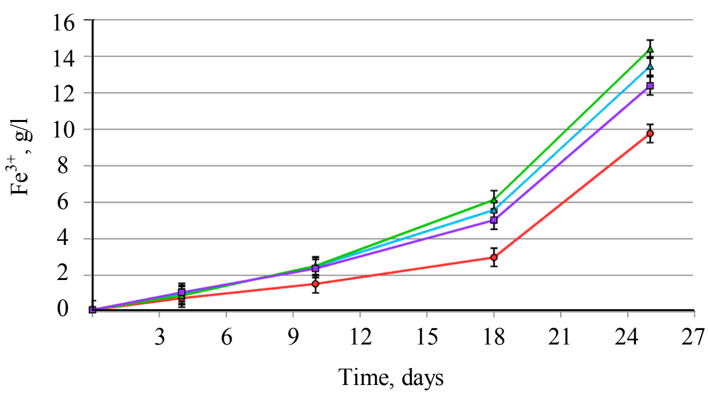

Fig. 4. Changes in the concentration of ferric iron
See legend in Fig.1

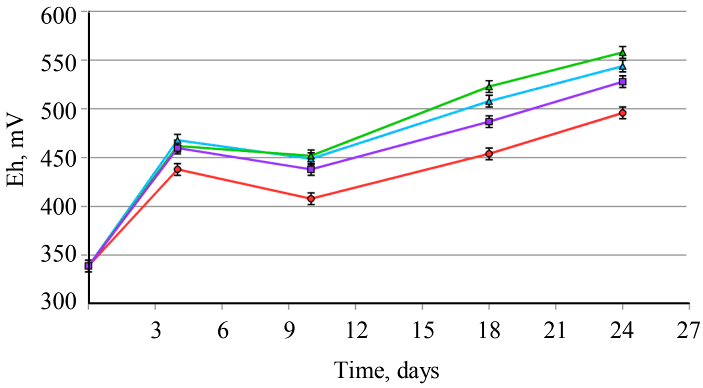

Fig. 5. Change in the redox potential.
See legend in Fig. 1

In the groups «5-1» and «10» the number of cells in 1 ml of the solution was $(1.1\pm0.1)\cdot10^8$ and $(1.0\pm0.1)\cdot10^8$, respectively.

Evaluation of the efficiency of Fe^{3+} generation by chemolithotrophic microorganisms in the BCL process is important since ferric ions are the main component of the indirect oxidation pathway of sulfide ore. The dissolution of the metal can be described by the following equation:

$$MeS + Fe_2(SO_4)_3 = $$
$$= MeSO_4 + 2FeSO_4 + S^0.$$

During the experiment, a significant increase in the concentration of ferric iron in flasks that were exposed to microwave radiation was recorded. This effect may be associated with a better, compared with the control, an indicator of an increase in the number of microorganisms and with an increase in their oxidative activity (Fig.4).

The highest concentration of ferric iron throughout the experiment was recorded in flasks of the experimental group «5-2», which were exposed to microwave radiation for 5 s twice a day throughout the experiment. The maximum concentration in these flasks was fixed at the end of the experiment and was equal to 14.0±0.5 g/l. By this time, in flasks that were not exposed to radiation, this indicator was 9.8±0.5 g/l.

In groups «5-1» and «10» the amount of Fe^{3+} in 1 liter of the solution was 13.5±0.5 and 12.4±0.5 g, respectively.

The Eh (redox potential) in flasks that were exposed to daily microwave radiation was significantly higher than in control ones (Fig.5). At the beginning of the experiment, all flasks had Eh = 339±5 mV. By the end of the experiment in the «5-2» group, this indicator increased to 558±5 mV. In control flasks, the Eh value reached only 496±5 mV and was the smallest in comparison with other experimental groups. In the flasks, the irradiation of which was 10 s, the Eh index was slightly lower (528±5 mV) than in the groups «5-1» and «5-2», but significantly higher than in the flasks that were not exposed to irradiation. These results are consistent with the overall picture of the entire study.

The redox potential (Eh) is a measure of the intensity of the loss or attachment of electrons in redox reactions, represented by the electromotive force, expressed in millivolts. A high Eh indicates that this system has a high oxidative ability.

Figure 6, *a* shows a graph of changes in nickel concentration in the liquid phase of the pulp in the control group, which was not exposed to microwave radiation, and the experimental group «5-2», where the dissolution rates of nickel were the highest among all the others. The diagram (Fig.6, *b*) shows the changes in the concentration of nickel in solution in all experimental groups, including the control, at various stages of the experiment. It can be seen that the effective transition of nickel occurred in all groups from 18 days, which is most likely due to the time of adaptation of microorganisms to aggressive environmental conditions, which are represented by high concentrations of heavy metals and high-frequency microwave radiation. The highest concentration of nickel transferred to the solution was recorded in «5-2» flasks and at the end of the experiment was 6.0±0.4 g/l. By this time, in control flasks, this indicator was 5.1±0.4 g/l. The maximum concentration of dissolved nickel in the «5-1» experimental group was 5.7±0.5 g/l, and in the «10» group – 5.6±0.5 g/l, respectively.

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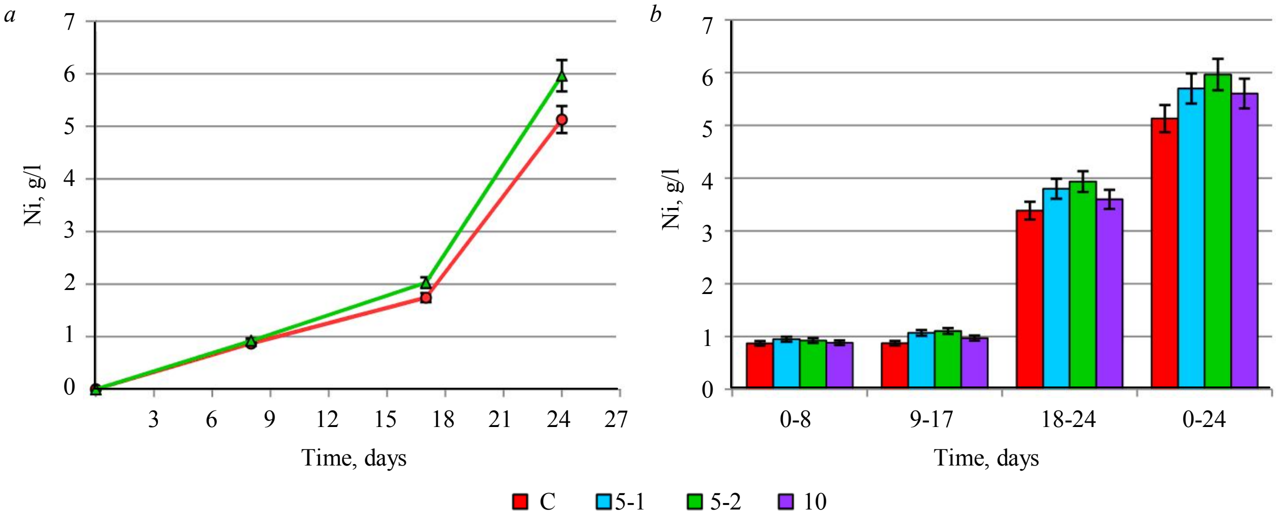

Fig.6. Change in the concentration of nickel ions in the liquid phase of the pulp (*a*) and the concentration of nickel in solution (*b*)at various stages of the experiment
C – control; 5-1 – microwave exposure (5 s) once a day; 5-2 – exposure to microwave (5 s) 2 times a day; 10 – microwave exposure (10 s) once a day

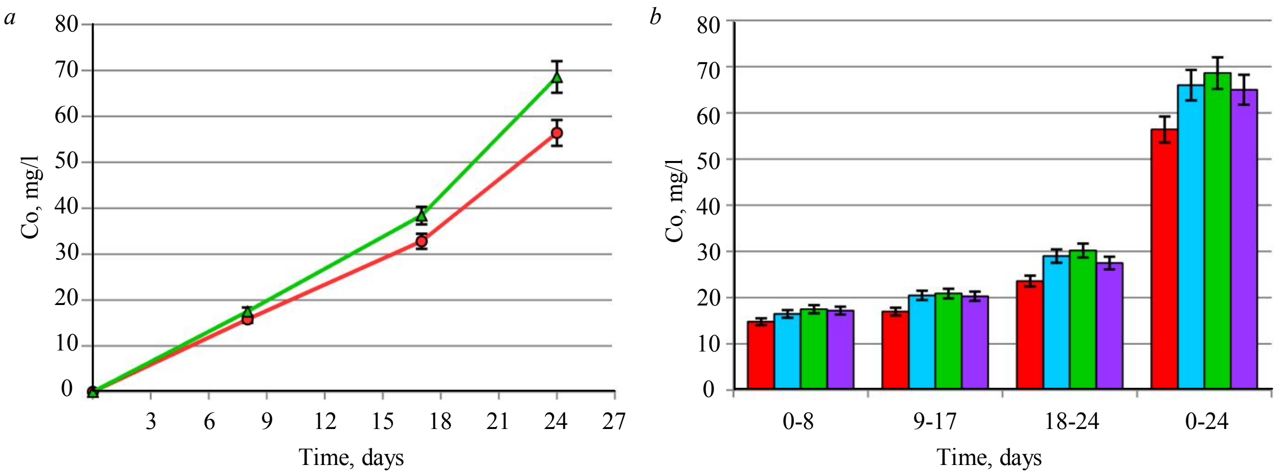

Fig. 7. Change in the concentration of cobalt ions in the liquid phase of the pulp (*a*) and the concentration of cobalt in solution (*b*) at various stages of the experiment
See legend in Fig.6

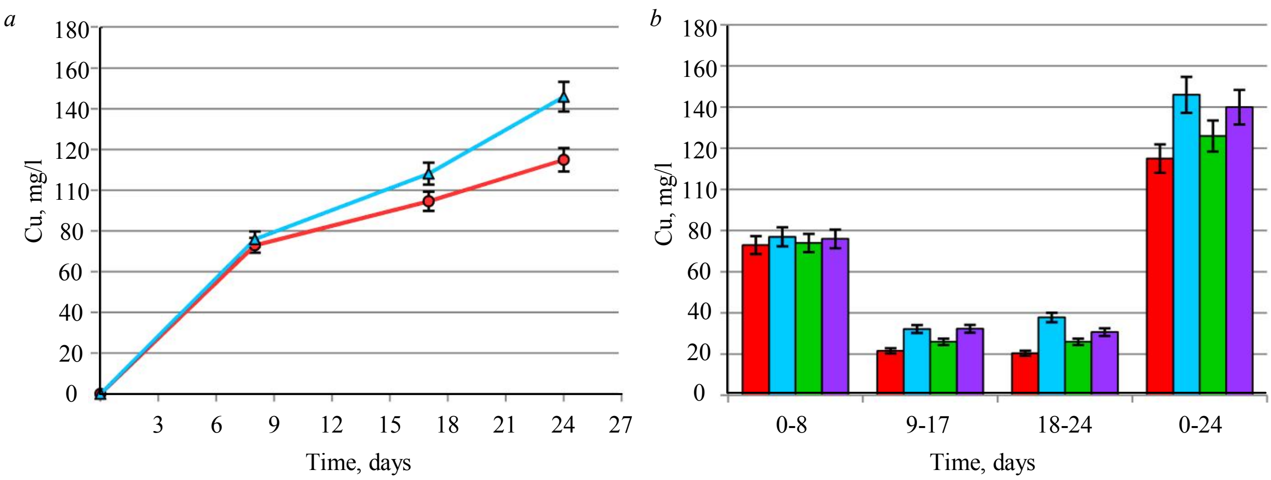

Fig. 8. Change in the concentration of copper ions in the liquid phase of the pulp (*a*) and the concentration of copper in solution (*b*) at various stages of the experiment
See legend in Fig.6

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The electrochemical properties of nickel and cobalt are close; therefore, the general picture of the leaching of these metals is similar (Fig.7). As in the case with nickel, the best indicators of cobalt transition to solution were observed in the «5-2» group, which by the end of the experiment had the concentration of this metal in the liquid phase was 68.6±4.8 mg/l. In the control, this indicator was 56.4±3.9 mg/l. In group «10», the cobalt concentration in the solution (65±4.5 mg/l) was higher than in the control, but lower than in groups «5-1» and «5-2».

The pattern of copper reduction (Fig.8), in contrast to nickel and cobalt, is somewhat different. Here, the highest concentration of copper in solution throughout the experiment was observed in the experimental group «5-1», which by the end of the experiment was equal to 145.9±10.2 mg/l. In control flasks, this indicator was 115.1±8.3 mg/l. In the «10» group, the concentration of the copper extracted from the ore by the end of the experiment was 140.0±9.5 g/l, and in the «5-2» – 122.0±8.5 mg/l.

The metal reduction was calculated as the ratio of the amount of this element in the liquid phase of the pulp to the total mass of the element in the entire sample according to the formula:

$$X = \frac{m(\mathrm{Me})_{\mathrm{sol}}}{m(\mathrm{Me})_{\mathrm{sample}}} 100,$$

where X – metal reduction ratio; $m(\mathrm{Me})_{\mathrm{sol}}$ – mass of metal in solution; $m(\mathrm{Me})_{\mathrm{sample}}$ – total mass of metal in the liquid and solid phases of the pulp.

Metal reduction ratio

Group code	Reduction, %		
	Ni	Co	Cu
C	60	31	14
5–1	72	42	20
5–2	76	46	17
10	69	40	18

The calculation results (see table) showed that in the control sample nickel reduction ratio was 60 %, in the «5-1» group – 72 %, in the «5-2» group – 76 %, in the «10» group – 69 %. The best cobalt reduction ratio was also in the «5-2» group (46 %), which is 15 % more than in the control. The situation with copper extraction is somewhat different: the maximum percentage of extraction is recorded in the «5-1» group (20 %), in the control 14 %.

Thus, during the experiment, it was found that repeated short-term exposure to microwave radiation to the components of bacterial-chemical leaching contributes to the improvement of the extraction of metals from sulfide ore.

Apparently, the reason for this is the increased growth rate of the number of chemolithotrophic microorganisms, as well as the formation of defects induced by microwave radiation in the ore structure, creating an additional surface front of potential attachment of microorganisms and providing access of the leaching solution to the mineral grains, thereby improving the extraction of target components.

Conclusions

1. Multiple short-term exposure to microwave radiation increases the rate of accumulation of biomass of chemolithotrophic microorganisms and increases their oxidative activity.

2. Repeated exposure to microwave radiation (0.7 W/cm^2) for 5 s allows achieving an increase in nickel reduction by 16 %, cobalt by 15 %, and copper by 6 %.

REFERENCES

1. Betskii O.V., Lebedeva N.N. Millimeter waves and living systems. *Nauka v Rossii*. 2005. N 6, p. 13-19 (in Russian).

2. Kioresku A.V. The influence of the duration of preliminary irradiation with microwave waves of a culture of chemolithotrophic microorganisms on the efficiency of bioleaching processes. *Gornyi informatsionno-analiticheskii byulleten'*. 2017. N S32, p. 237-247 (in Russian).

3. Kioresku A.V. Change in the oxidative activity of chemolithotrophic microorganisms under the influence of microwave radiation. *Uspekhi sovremennogo estestvoznaniya*. 2018. N 11(2), p. 343-347 (in Russian).

4. Kioresku A.V. Study of the influence of microwave radiation on acidophilic chemolithotrophic bacteria. *Gornyi informatsionno-analiticheskii byulleten'*. 2016. N S31, p. 86-191 (in Russian).

5. Kioresku A.V. The mechanisms of microwave radiation influence on the leaching of mineral raw materials. *Gornyi informatsionno-analiticheskii byulleten'*. 2015. N 63, p. 335-340 (in Russian).

6. Kuzyakina T.I., Khainasova T.S., Levenets O.O. Biotechnology for the extraction of metals from sulfide ores. *Vestnik Kamchatskoi regional'noi organizatsii*. Seriya: Nauki o Zemle. 2008. N 12, p. 76-86 (in Russian).

7. Rogatykh S.V., Dokshukina A.A., Levenets O.O., Muradov S.V., Kofiadi I.A. Evaluation of the qualitative and quantitative composition of communities of cultured acidophilic microorganisms by PCR-RV and clone library analysis. *Mikrobiologiya*. 2013. Vol. 82. N 2, p. 212-212 (in Russian).

8. Khainasova T.S. Factors affecting bacterial and chemical processes of sulphide ores processing. *Zapiski Gornogo instituta*. 2019. Vol. 235, p. 47-54. DOI: 10.31897/PMI.2019.1.47

9. Amankwah R.K., Ofori-Sarpon G. Microwave heating of gold ores for enhanced grindability and cyanide amenability. *Minerals Engineering*. 2011. Vol. 24. N 6, p. 541-544.

10. Apollonio F., Liberti M., Paffi A., Merla C., Marracino P., Denzi A. Feasibility for microwaves energy to affect biological systems via nonthermal mechanisms: a systematic approach. *IEEE Transactions on microwave theory and techniques*. 2013. Vol. 61. N 5, p. 2031-2045.

11. Johnson D.B. Development and application of biotechnologies in the metal mining industry. *Environmental Science and Pollution Research International*. 2013. Vol. 20. N 11, p. 7768-7776.

12. Litvinenko V. Preface. Innovation-Based Development of the Mineral Resources Sector: Challenges and Prospects – XI Russian-German Raw Materials Conference. Potsdam, Germany, 7-8 November 2018. London: Taylor and Francis Group, 2019, p. 9-11.

13. Mudd G.M., Weng Z., Jowitt S.M. A detailed assessment of global Cu resource trends and endowments. *Economic Geology*. 2013. Vol. 108. N 5, p. 1163-1183.

14. Orumwense O.A., Negeri T., Lastra R. Effect of microwave pretreatment on the liberation characteristics of a massive sulfide ore. *Mining, Metallurgy & Exploration*. 2004. Vol. 21. N 2, p. 77-85.

15. Vorster W., Rowson N.A., Kingman S.W. The effect of microwave radiation upon the processing of Neves Corvo copper ore. *International journal of mineral processing*. 2001. Vol. 63. N 1, p. 29-44.

16. Xia L. Comparison of three induced mutation methods for Acidiothiobacillus caldus in processing sphalerite. *Minerals Engineering*. 2007. Vol. 20. N 14, p. 1323-1326.

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