Study of the bacterial-chemical leaching process using stepwise ultrasonic treatment ofore pulp and bacterial suspension

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Biogeotechnologies occupy an important place in the industrial processing of mineral resources, especially in the extraction of metals from ores. The work investigated the process of bacterial-chemical leaching of nickel, copper and cobalt from sulfide ore using step-by-step ultrasonic treatment of both the bacterial suspension and the ore pulp. Two experiments were carried out. In the first experiment, the ore pulp (28.0 W/cm^2, 22 kHz, 30 min.) and the bacterial suspension (0.5 W/cm^2, 40 kHz, 5, 10, 20 min.) were treated with ultrasound in stages, and then mixed, carried out bacterial-chemical leaching of nickel, copper and cobalt for 18 days. The second experiment was carried out for 7 days to study the effect of ultrasonic exposure on the vital activity of chemolithotrophic microorganisms used in the experiment. Ultrasonic processing of ore pulp took place in the flow chamber of the installed installation. Ultrasonic treatment of the bacterial suspension was carried out in an UltraSonic PS-40 ultrasonic bath. The bacterial-chemical leaching process was carried out in flasks installed in an ES-20/80 Biosan shaker-incubator. The experimental results show that with increasing duration of ultrasonic exposure on a bacterial suspension, the process of bacterial-chemical leaching occurs more intensely, with greater extraction of target metals, which is associated with stimulation of the growth and vital activity of microorganisms by ultrasonic exposure. The extraction of target metals without the use of ultrasonic action on a bacterial suspension has much lower values – 2.07 times less for nickel, 1.1 times less for copper and 2.09 times less for cobalt. Experiments have shown that the chemical treatment of sulfide cobalt-copper-nickel ore of the Shanuch deposit with a $S : L$ ratio of ore pulp of 1 : 5 and a $S : L$ ratio of bacterial suspension pulp of 1 : 8 is appropriate for obtaining polymetallic solutions rich in composition.

Key words: bacterial chemical leaching, sulfide cobalt-copper-nickel ore, bacterial suspension, ultrasonic treatment, radiation intensity, ore pulp, bacterial suspension pulp.

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Introduction

In recent decades, biogeotechnology has become an important part of industrial mineral processing, especially in the extraction of metals from ores. The use of acidophilic chemolithotrophic microorganisms, such as *Acidithiobacillus thiooxidans, A. ferrooxidans, A. caldus, Leptospirillum ferriphillum, L. ferrooxidans, Sulfobacillus thermosulfidooxidans*, and others [1–4], demonstrates high efficiency and environmental sustainability in the process of bacterial chemical leaching (BCL). The function of microorganisms is to biologically regenerate of trivalent iron as a result of the oxidation of divalent iron, the main oxidizing chemical agent in the dissolution of minerals. In addition, they facilitate the formation of sulfuric acid and the maintenance of low pH values in the environment as a consequence of the oxidation of elemental sulfur and its reduced compounds. The iron- and sulfur-oxidizing ability of microorganisms ensures the accelerated conversion of metals from insoluble forms (sulfides) to soluble forms (sulfates) [5–7]. The utilisation of microorganisms in the leaching processing of low-grade ores and man-made waste has been demonstrated to be a viable solution for the expansion of the mineral resource base, whilst concomitantly effecting a reduction in the negative environmental impact [8, 9]. A key aspect of the successful application of these technologies is the optimization of conditions for the growth and activity of microorganisms.

One promising way to improve the kinetic characteristics of BHV is to use different physical fields, like ultrasonic (US) exposure, during the reactor oxidation of mineral components in the pulp. Thanks to the use of phased US exposure with high and low intensities, the oxide films on the surface of ore pulp particles will be destroyed [10–14], surface defects and microcracks will form, and the growth and activity of microorganisms will be stimulated [15–16]. Such energy exposure can significantly reduce the duration of the leaching process and increase the percentage of target metals extracted into the solution [17, 18].

Accordingly, the aim of this work is to study the process of bacterial-chemical leaching of Ni, Cu, and Co from sulfide ore of the Shanuch deposit (Kamchatka) using stepwise ultrasonic treatment of ore pulp and bacterial suspension.

Materials and Methods

The study used oxidized sulfide cobalt-copper-nickel ore from the Shanuch deposit (Kamchatka) with an initial metal content in the ore of 3.73% Ni; 0.5% Cu; 0.11% Co. Sulfide ore minerals: pyrrhotite – 20–30%, pentlandite – 5–10%, chalcopyrite – 3–5%. Pyrrhotite is represented by grains 0.1–0.4 mm in size. Pentlandite is in the form of small (0.1–0.2 mm) grains of irregular, less often isometric shape. Chalcopyrite forms small deposits, gravitating towards intensively altered areas of the host rock.

The dominant species in the autochthonous mixed bacterial culture sample were *Acidithiobacillus thiooxidans, A. ferrooxidans,* and *Sulfobacillus thermosulfidooxidans*. For the ultrasonic treatment of the crushed sulfide ore and distilled water (ore pulp) mixture at a mass ratio of 1 : 5, a flow chamber of a mounted installation and an ultrasonic generator UZTA-0.4/22 were utilised [19, 20]. The mixture of inoculum and iron-free 9K nutrient medium (bacterial suspension) was subjected to ultrasonic treatment in an UltraSonic PS-40 ultrasonic bath. The accumulation of bacterial culture (for a period of 15 days) and the process of bacterial-chemical leaching of the bacterial suspension and ore pulp (bacterial suspension pulp) mixture was carried out in an ES-20/80 Biosan shaker incubator at chamber temperature 30 °C, the platform oscillation frequency at 150 rpm, and by the passive aeration. The pH and redox potential values were measured using a Mettler-Toledo Seven Compact S220 portable pH meter/ionometer. The concentrations of divalent and trivalent iron in the liquid phase of the bacterial suspension pulp were determined by complexometric titration with Trilon B. The determination of Ni^{2+}, Cu^{2+}, and Co^{2+} in the liquid and solid phases was performed by atomic absorption using a Shimadzu 6300 spectrophotometer.

Experimental conditions

First experiment

The experiment was conducted in three stages. The first stage involved ultrasonic treatment of the ore pulp. The second stage involved ultrasonic exposure of the bacterial suspension. The third stage involved bacterial-chemical leaching of nickel, copper, and cobalt from the bacterial suspension pulp.

First stage. Milled ore with a degree of grinding of 100% – 100 μm was weighed (200 g), sterilized in a dry oven at 120 °C for one hour, and after cooling to 20–22 °C, mixed with distilled water. The particle size distribution of the ore was as follows: ≈ 80% – 100 μm; ≈ 17% – 8–100 μm; ≈ 3% – 50–80 μm. The ore pulp was pumped into a chamber with ultrasonic exposure, where it was treated with ultrasound at an intensity of 28 W/cm^2, a frequency of 22.000 Hz, a duration of 30 minutes, and a circulation rate of 6 [19]. The particle size distribution of the ore after ultrasonic treatment at this intensity was as follows: ≈ 32% – 100 μm; ≈ 26% – 80–100 μm; ≈ 22% – 50–80 μm; ≈ 20% < 50 μm.

Second stage. The bacterial suspension was poured into four flasks, with each flask containing 50 g of inoculum and 200 g of nutrient medium (a mass ratio of 1 : 4). The flasks (3 pieces), closed with cotton plugs, were placed in an ultrasonic bath filled to 2/3 of its volume with distilled water at a temperature of 28 °C. The suspension was subjected to ultrasonic exposure with an oscillation intensity of 0.5 W/cm^2 and a frequency of 40.000 Hz for 5, 10, and 20 minutes. A bacterial suspension that was not treated with ultrasound was used as a control.

Third stage. From each flask with a bacterial suspension, 60 g of suspension was taken and poured into separate flasks, to which 120 g of ore pulp treated with ultrasound was added (mass solid-to-liquid $S : L$ – 1 : 8). The flasks were then placed in a shaker incubator and a 10 ml blank sample was taken from each flask. During the experiment, the bacterial suspension pulp was not acidified, and the biomass, pH, Eh, and concentrations of Ni, Cu, Co, Fe^{2+}, and Fe^{3+} were monitored. Samples were taken once a day for 18 days.

Second experiment

A second experiment was conducted to confirm the growth- and activity-stimulating effects of low-intensity ultrasound exposure on microorganisms. The procedure and parameters were identical to those of the second stage of the first experiment. However, this time the duration was seven days. By this point in the experiment, a significant difference had emerged in the number of cells in the bacterial suspensions that had been treated with ultrasound and those that had not.

Results and Discussion

During the first day of the experiment, the pH value in all flasks rose sharply from a minimum value of 2.4 to 3.6, while Eh decreased from a maximum value of 278.3 to 207 mV as a result of the low concentration of iron sulfate Fe^{3+} (a decrease from 1.117 to 0.041 g/l) and the intensive transition of iron sulfate Fe^{2+} into solution (an increase to 0.558 g/l) from the destroyed sulfides. **(Figs. 1, 3).**

Further, during the 2–4 day period of the experiment, the concentration of iron (II) sulfate increased slightly in all flasks, while the concentration of iron (III) sulfate remained low. However, from the 4th day of leaching, there was a gradual increase in the number of planktonic microorganism cells (**Fig. 2**), intensive oxidation of Fe^{2+} to Fe^{3+}, and oxidation of SO to H_2SO_4, which in turn led to a decrease in pH values and an increase in redox potential values. During the period from 4 to 7 days, the concentration of iron (II) sulfate in the pulp of the bacterial suspension of 4 flasks fell from 0.558 to 0 g/l, while the concentration of iron (III) sulfate increased to 0.58 g/l, reflecting an increase in the intensity of redox processes in the pulp of the bacterial suspension.

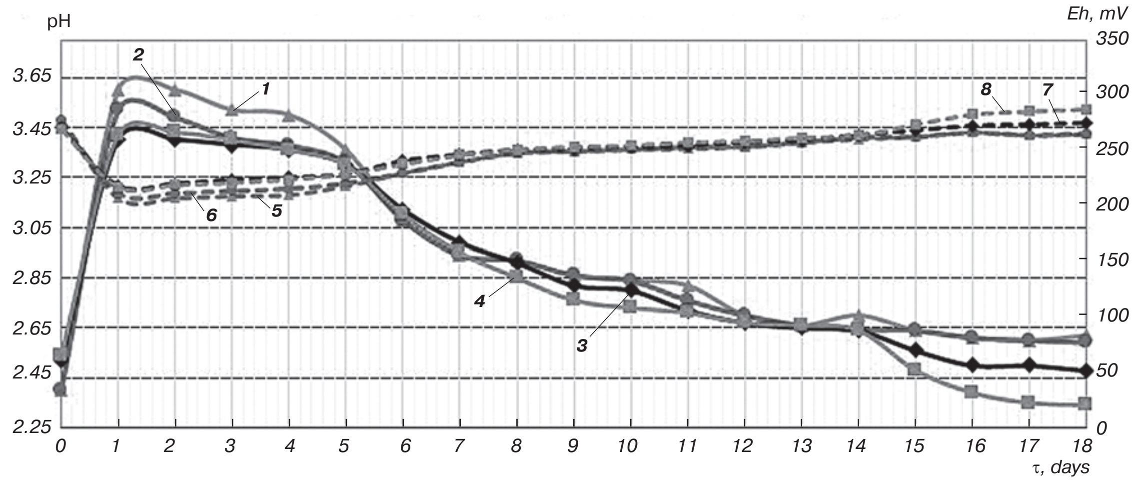

Fig. 1. Change in pH and Eh of the liquid phase of the bacterial suspension pulp during the BCL process:
1 – control flask (pH); *2* – flask with ultrasonic exposure to the bacterial suspension for 5 min (pH); *3* – flask with ultrasonic exposure for 10 min (pH); *4* – flask with ultrasonic exposure for 20 min (pH); *5* – control (Eh); *6* – with ultrasonic exposure for 5 min (Eh); *7* – with ultrasonic exposure for 10 minutes (Eh); *8* – with ultrasonic exposure for 20 minutes (Eh)

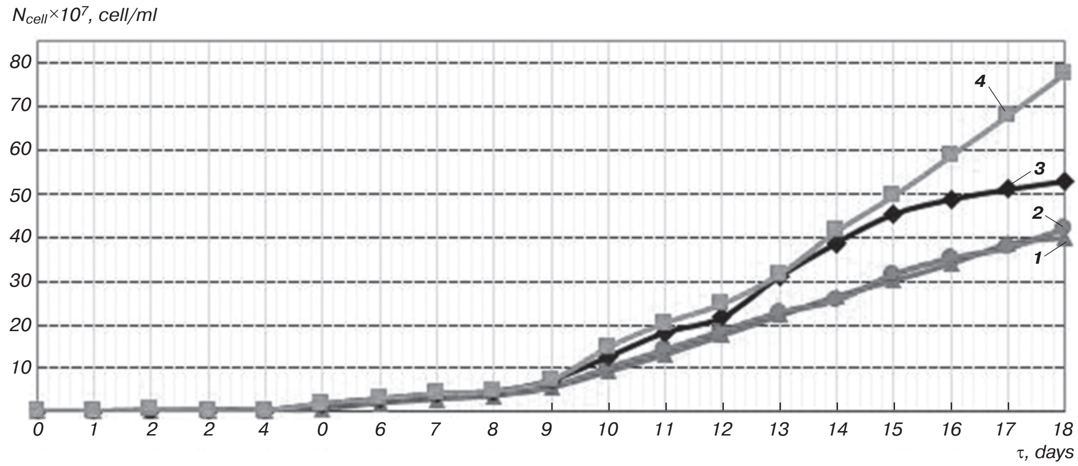

Fig. 2. Change in the number of planktonic cells in the liquid phase of the bacterial suspension pulp during the BCL process:
1 – control flask; *2* – flask with ultrasonic exposure to the bacterial suspension for 5 min; *3* – flask with ultrasonic exposure for 10 min; *4* – flask with ultrasonic exposure for 20 min

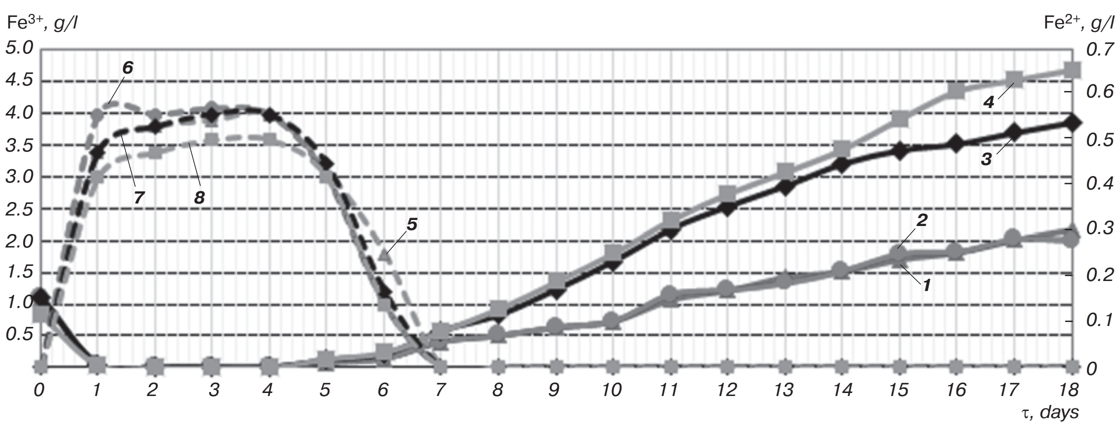

Fig. 3. Change in Fe^{3+} and Fe^{2+} concentrations in the liquid phase of the bacterial suspension pulp during the BCL process:
1 – control flask (Fe^{3+}); *2* – flask with ultrasonic exposure to the bacterial suspension for 5 min (Fe^{3+}); *3* – flask with ultrasonic exposure for 10 min (Fe^{3+}); *4* – flask with ultrasonic exposure for 20 min (Fe^{3+}); *5* – control (Fe^{2+}); *6* – with ultrasonic exposure for 5 min (Fe^{2+}); *7* – with ultrasonic exposure for 10 min. (Fe^{2+}); *8* – with ultrasonic exposure for 20 min. (Fe^{2+})

The increase in Fe^{3+} concentration and the number of microorganisms in all flasks continued from day 7 to day 18 (end of the experiment) at zero Fe^{2+} concentration.

At the same time, in flasks with ultrasonic treatment of the bacterial suspension for 10 and 20 minutes, the growth of Fe^{3+} and N_{cell} was more intense.

The dynamics of the process over time, shown in **Figs. 1–3**, indicate that as the duration of ultrasonic exposure to the bacterial suspension increases (5, 10, 20 min), the process of bacterial-chemical leaching becomes more intense, which is associated with the stimulation of the growth and vital activity of microorganisms **(Fig. 2)**, which contribute to the acceleration of redox processes. This is confirmed by the results of the second experiment, where on day 7, N_{cell}, cell/ml increased by 98.5% after 20 minutes of ultrasonic treatment with an intensity of 0.5 W/cm^2 and a frequency of 40.000 Hz, which is 3.94 times more than in the control sample without ultrasonic exposure. The results of the second experiment are presented in **Table 1**.

The dynamics of changes in pH, Eh, N_{cell}, Fe^{3+}, and Fe^{2+} allow us to divide the BCL process in all flasks into three periods. In the first period, lasting 1 day, the values of pH and Fe^{2+} increase, while the values of Eh and Fe^{3+} decrease. During this period, the concentrations of Ni^{2+}, Cu^{2+}, and Co^{2+} in the bacterial suspension pulp in all flasks increased. The maximum concentration of Ni^{2+} was 380 mg/l, Cu^{2+} was 10.11 mg/l, and Co^{2+} was 8.06 mg/l. In the second period, over 6 days (days 1–7), complete oxidation of iron (II) sulfate to iron (III) sulfate occurred with a simultaneous increase in Eh, a decrease

Table 1
Results of ultrasonic exposure to bacterial suspension in the second experimen

No.	$N_{cell} \times 10^7$, cell/ml	pH	Eh, mV
Start of the experiment (0 days)			
1. Without US exposure	0.91	1.98	301.20
2. US exposure for 5 min	0.75	2.02	304.70
3. US exposure for 10 min	0.71	2.01	305.40
4. US exposure for 20 min	0.71	2.02	306.60
End of the experiment (7 days)			
1. Without US exposure	1,21	2.01	302.00
2. US exposure for 5 min	1.21	2.03	301.20
3. US exposure for 10 min	1.32	2.06	299.90
4. US exposure for 20 min	1.39	2.01	301.40

Table 2
Leaching rate, extraction of Ni^{2+}, Cu^{2+} and Co^{2+} in the BHP process with and without ultrasonic treatment

Duration of periods, days	Ni^{2+}, mg/l·day	Cu^{2+}, mg/l·day	Co^{2+}, mg/l·day
Flask No. 1 (control, without US exposure)			
0–1	22	0.26	1.63
1–7	21.5	3.11	0.39
7–18	66	6.64	1.1
Average value, mg/l·day/extraction, %	36.5/19.41	3.336/15.19	1.04/12.33
Flask No. 2 (US exposure for 5 min)			
0–1	22	0.1	1.61
1–7	27	2.96	0.24
7–18	64	7.46	1.16
Average value, mg/l·day/extraction, %	37.66/19.63	3.5/16.5	1.003/12.2
Flask No. 3 (US exposure for 10 min)			
0–1	30	2.55	1.93
1–7	59	2.98	1.05
7–18	126.5	7.3	1.71
Average value, mg/l·day/extraction, %	73.83/32.23	4.28/16.37	1.57/20.8
Flask No. 4 (US exposure for 20 min)			
0–1	36	2.55	2.18
1–7	65.3	2.98	1.14
7–18	126.45	7.3	2.23
Average value, mg/l·day/extraction, %	75.91/40.26	4.28/16.6	1.85/25.85

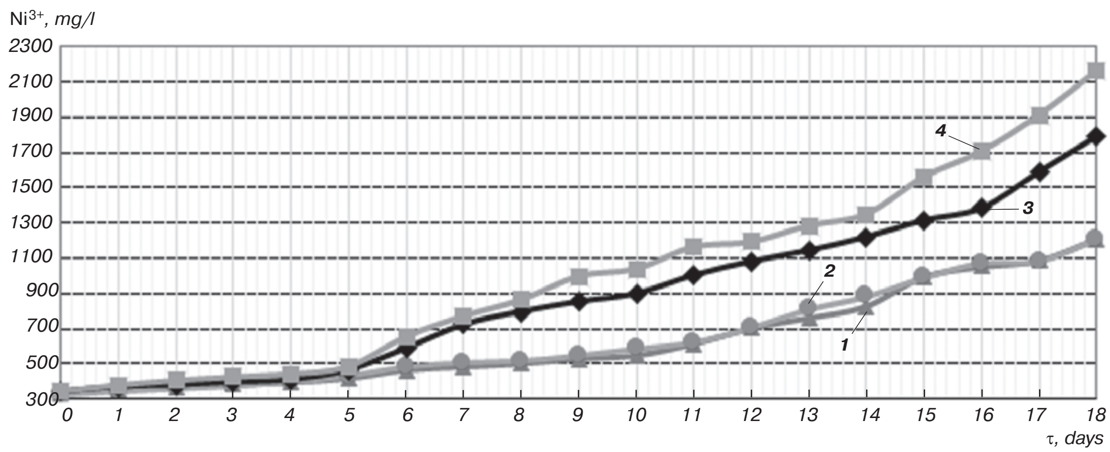

Fig. 4. Change in Ni^{2+} concentrations in the liquid phase of the bacterial suspension pulp during the BCL process: *1* – control flask; *2* – flask with ultrasonic exposure to the bacterial suspension for 5 min; *3* – flask with ultrasonic exposure for 10 min; *4* – flask with ultrasonic exposure for 20 min

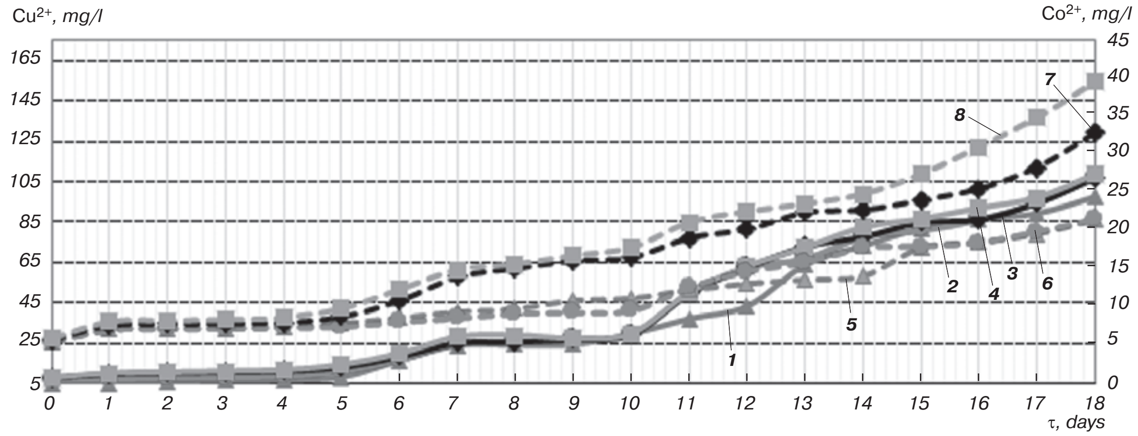

Fig. 5. Change in Cu^{2+} and Co^{2+} concentrations in the liquid phase of the bacterial suspension pulp during the BCL process: *1* – control flask (Cu^{2+}); *2* – flask with ultrasonic exposure to the bacterial suspension for 5 min (Cu^{2+}); *3* – flask with ultrasonic exposure for 10 min (Cu^{2+}); *4* – flask with ultrasonic exposure for 20 min (Cu^{2+}); *5* – control (Co^{2+}); *6* – with ultrasonic exposure for 5 min (Co^{2+}); *7* – with ultrasonic exposure for 10 min (Co^{2+}); *8* – with ultrasonic exposure for 20 min (Co^{2+})

in pH, and an increase in the number of bacterial cells. The concentration of nickel in the flask with ultrasonic exposure for 20 minutes was 772 mg/l, copper – 28 mg/l, and cobalt was 14.9 mg/l, which is 1.59 times higher for nickel, 1.16 times higher for copper, and 1.58 times higher for cobalt than in the control sample (**Figs. 4, 5**).

In the third period, lasting 11 days (days 7–18), there was a decrease in pH values, an increase in redox potential values, and an increase in biomass.

The number of microorganisms in the flask exposed to ultrasound for 20 minutes was 77.7×10^7 cells/ml, which is 1.94 times higher than in the control sample. The concentration of Fe^{2+} also remained at zero, while the concentrations of Fe^{3+}, Ni^{2+}, Cu^{2+}, and Co^{2+} increased **(Figs. 2, 4, 5).**

During the first four days, the leaching of target metals occurred mainly by chemical means due to sulfuric acid initially present in the bacterial culture medium. During this period, the number of bacterial cells was low. No biomass growth was observed. Then, as the number of microorganisms increased, leaching occurred both biologically and chemically, reaching maximum values on days 14–18 (**Figs. 4, 5**). The most intensive extraction of cobalt occurred during the first day of the experiment, and nickel and copper during days 7–18 (see **Table 2**). The low extraction of copper can be explained by its inclusion in the composition of the refractory mineral chalcopyrite, which is difficult to break down with solutions (**Figs. 4, 5; Table 2**).

Summary

The results of the experiments show that with an increase in the duration of ultrasonic treatment (0.5 W/cm^2, 40 kHz) of the bacterial suspension, the process of bacterial-chemical leaching proceeds more intensively, with greater extraction of target metals, which is associated with the stimulation of the growth and vital activity of microorganisms by ultrasonic exposure.

Conclusion

Bacterial-chemical leaching using stepwise ultrasonic treatment of ore pulp and bacterial suspension promotes selective extraction of nickel and cobalt, which is associated with the destruction and removal of oxide films from mineral particles of ore pulp, and the stimulation of microorganism growth by ultrasonic exposure. The extraction of target metals without the use of ultrasonic treatment of bacterial suspension has much lower values – 2.07 times lower for nickel and 2.09 times lower for cobalt. However, the leaching process does not provide a high degree of copper extraction – 16.6%, but with ultrasonic treatment, the copper extraction rate is 1.1 times higher than the copper extraction rate without the use of ultrasound. Experiments have shown that BCHV of sulfide cobalt-copper-nickel ore from the Shanuch deposit with a $S : L$ ratio of ore pulp of 1 : 5 and a $S : L$ ratio of bacterial suspension pulp of 1 : 8 is suitable for obtaining polymetallic solutions of the desired composition. In order to increase the percentage of extraction of target metals – Ni, Cu, Co – it is necessary to continue research into the process of bacterial-chemical leaching at various densities of pulp – ore, bacterial suspension, different durations, intensities of ultrasonic exposure, and different frequencies of radiation.

References

1. Hedrich S., Schippers A. Distribution of Acidophilic Microorganisms in Natural and Man-Made Acidic Environments. *Current Issues in Molecular Biology*. 2021. Vol. 40. pp. 25–48.

2. Hubau A., Guezennec A. G., Joulian C., Falagán C., Dew D., Hudson-Edwards K. A. Bioleaching to Reprocess Sulfidic Polymetallic Primary Mining Residues: Determination of Metal Leaching Mechanisms. *Hydrometallurgy*. 2020. Vol. 197. 105484.

3. Elkina Yu. A., Melamud V. S., Bulaev A. G. Effect of Organic Nutrients on Bioleaching of Low-Grade Copper Concentrate at Different Temperatures. *IOP Conference*

Series Earth and Environmental Science. 2021. Vol. 677, Iss. 4. 042076.

4. Dong Y., Zan J., Lin H. Bioleaching of Heavy Metals from Metal Tailings Utilizing Bacteria and Fungi: Mechanisms, Strengthen Measures, and Development Prospect. *Journal of Environmental Management*. 2023. Vol. 344. 118511.

5. Bobadilla-Fazzini R., Poblete-Castro I. Biofilm Formation is Crucial for Efficient Copper Bioleaching from Bornite under Mesophilic Conditions: Unveiling the Lifestyle and Catalytic Role of Sulfur-Oxidizing Bacteria. *Frontiers in Microbiology*. 2021. Vol. 12. 761997.

6. Khainasova T. S., Levenets O. O., Balykov A. A. Bacterial-Chemical Processes of ore Processing and their Investigation in Kamchatsky Krai. *Mining Informational and Analytical Bulletin*. 2016. Iss. S31. pp. 223–234.

7. Hosseini S. M., Vakilchap F., Baniasadi M., Mousavi S. M., Darban A. K., Farnaud S. Green Recovery of Cerium and Strontium from Gold Mine Tailings Using an Adapted Acidophilic Bacterium in One-Step Bioleaching Approach. *Journal of the Taiwan Institute of Chemical Engineers*. 2022. Vol. 138. 104482.

8. Faramarzi M. A., Mogharabi-Manzari M., Brandl H. Bioleaching of Metals from Wastes and Low-Grade Sources by HCN-Forming Microorganisms. *Hydrometallurgy*. 2020. Vol. 191. 105228.

9. Sun J., Wen J., Wu B., Chen B. Mechanism for the Bio-Oxidation and Decomposition of Pentlandite: Implication for Nickel Bioleaching at Elevated pH. *Minerals*. 2020. Vol. 10, Iss. 3. 289.

10. Iodis V. A., Koydan I. A. Investigation of Oxide Films Removal Process from the Ore Pulp Particle Surface During its Ultrasonic Treatment. *Non-Ferrous Metals*. 2024. No. 1. p. 8–12.

11. Aleksandrova T. N., Litvinova N. M., Rasskazova A. V., Bogomyakov R. V. Influence of Ultrasonic Treatment to Technological Parameters of Carbon-Containing Material Floatation. *Mining Informational and Analytical Bulletin*. 2015. Iss. S1-4. pp. 196–201.

12. Hu Y., Guo P., Wang S., Zhang L. Leaching Kinetics of Antimony from Refractory Gold Ore in Alkaline Sodium Sulfide under Ultrasound. *Chemical Engineering Research and Design*. 2020. Vol. 164. pp. 219–229.

13. Lu J., Wang N., Yuan Z., Zhang Q., Li L., Wang Z. The Effects of Ultrasonic Wave on Heterogeneous Coagulation and Flotation Separation of Pentlandite-Serpentine. *Minerals Engineering*. 2022. Vol. 188. 107828.

14. Kallaev I. T., Kukhtina A. A., Kukhtina P. A., Nikolaeva N. V. Impact of Ultrasound on Grindability of Copper-Molybdenum Ores. *Advances in Current Natural Sciences*. 2024. Iss. 5. pp. 90–97.

15. Swamy K. M., Sukla L. B., Narayana K. L., Kar R. N., Panchanadikar V. V. Use of Ultrasound in Microbial Leaching of Nickel from Laterites. *Ultrasonics Sonochemistry*. 1995. Vol. 2, Iss. 1. pp. S5–S9.

16. Swamy K. M., Narayana K. L., Misra V. N. Bioleaching with Ultrasound. *Ultrasonics Sonochemistry*. 2005. Vol. 12, Iss. 4. pp. 301–306.

17. Trukhin Yu.P., Iodis V.A. Khainasova T.S. Microwave and ultrasound activation of kinetics of bacterial-chemical processes of leaching of cobalt-copper-nickel ores of the Shanuch deposit. *Mining Informational and Analytical Bulletin*. 2021. Iss. 11/S19. pp. 113–123.

18. Iodis V. A. Using Ultrasonic Influence for the Process Bacterial-Chemical Leaching. *Nedropolzovanie XXI vek*. 2024. Iss. 3-4. pp. 114–118.

19. Iodis V. A. Lab-Scale Reactor for Ultrasonic Treatment of Cobalt–Copper–Nickel Ore Pulp. *Gornyi Zhurnal*. No. 12. 2023. pp. 81–87.

20. Khmelev V. N., Barsukov R. V., Barsukov A. R., Tsyganok S. N., Nesterov V. A. Ultrasonic Technological Apparatus with Five Working Tools of Different Diameters for Scientific Research. *South-Siberian Scientific Bulletin*. 2022. Iss. 4. pp. 106–109. NFM