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Copper Extraction from Complex Waste Dumps by Biochemical Leaching Method

Aigul Koizhanova[1], David Magomedov[1*], Nurgali Abdyldayev[1], Emil Kamalov[1], Maria Yerdenova[1], Akbota Bakrayeva[1]

[1] Institute of Metallurgy and Ore Beneficiation, JSC, Satbyaev University, 29/133, Shevchenko str., Almaty, Kazakhstan, 050010

* Corresponding author's e-mail: davidmag16@mail.ru

ABSTRACT

The article presents the research results for the effectiveness of copper extraction from ores of the Satpayev deposit with complex, mixed composition bacterial leaching. The experiments with pre-acidification of copper samples were performed using biological oxidation by *A. Ferrooxidans* bacterial culture, adapted strain. Biochemical opening moes of mineral raw materials using *A. Ferrooxidans* bacteria of a particular strain adapted to the copper waste composition and capable of oxidizing sulfide and iron-bearing minerals were worked out. The optimal growth conditions for microorganisms in copper mineral pulp medium were established (temperature, pH, S: L.) The highest leaching efficiency, up to 88.65%, was observed in the experiments with preliminary bio-oxidation of samples by *A. Ferrooxidans* bacterial culture.

Keywords: copper dumps, bio-oxidation, *Acidobacillus Ferrooxidans* bacteria, leaching.

INTRODUCTION

Kazakhstan has significant potential reserves of copper-containing mineral raw materials. The Satpayev deposit dumps are an additional source along with ores. The heap leaching method is the most promising for copper raw materials, as it enables to process dumps of old and new pits of deposits, for which the beneficiation method is unprofitable.

The determining factors in the application of heap leaching should include the availability of sufficient metal reserves, climatic conditions of the area of works, the material composition of raw materials, the content of harmful impurities, etc. [Hayes, 2011].

Development of these deposits is made due to reduction of stocks of easily beneficiated sulfide copper ores as well as the arising necessity to involve complex oxidized and mixed hard-to-beneficiate ores in processing. Besides, these ores differ by origin and composition, including, for example, off-balance ores of Benkala, Ayak-Kodzhan deposits. Hydrometallurgical copper extraction from ores and concentrates is a complex and heterogeneous process, the rate of which is determined by the chemical nature of the solvent, its composition, as well as the structure and chemical properties of copper minerals [Mukhanova et al., 2022].

At present, the use of bacteria in the copper extraction from ore is of great importance. The term «bacterial leaching» means an intensified process of metal leaching from ores. The role of *Acidithiobacillus ferrooxidans (At. ferrooxidans*) bacteria in ore bio-oxidation processes is widely known. A number of studies have shown the economic advantages of the bacterial leaching process. It was found that the copper extraction percentage increases by several orders of magnitude, if oxidized ores are pretreated. It was shown that adaptation of bacteria before bioleaching increases the process efficiency [Juan Carlos Gentina et al., 2013].

In most cases, the standard hydrometallurgical technology of copper production is limited to the possibility of using simple composition with low content of divalent iron compounds only on oxidized raw materials. The presence of iron in divalent form, in the form of pyrite, pyrrhotite and other compounds, significantly complicates the leaching process, also increasing the consumption of the main leaching reagent, i.e. sulfuric acid. It results in the need to pretreat raw materials with oxidizing reagents and to convert iron to the oxidized trivalent form. The use of chemical oxidants, such as sodium peroxide, potassium hypochlorite in the process of noble metals leaching, in the case of copper raw material is not cost-effective. The use of bacterial cultures as an oxidizing reagent is known in domestic and world practice, [Abubakriev et al., 2015; Koizhanova et al., 2022; Magomedov et al., 2016]. The main advantages of bacterial oxidation are the high efficiency of divalent iron conversion to trivalent iron, as well as the inexpensive cost of this technology.

Acidophilic bacteria – *Acidobacillus ferrooxidans* – were chosen as the most suitable microorganisms. These microorganisms are characterized by the ability to reduce metals as well as remove sulfur and phosphorus from solutions.

It is required to establish the minimum growth conditions for the use of these microorganisms at both stages of copper extraction and removal of undesirable impurities from working and spent solutions for direct use in work, and optimal conditions – for preparation for use [Patent 2016].

Thus, the preliminary analysis of candidate microbial cultures for use in the proposed technology was based on compliance with such criteria as high lability of physiological and biochemical exchange, ability to grow at pH 0–4 and temperatures ranging from 4 to 35 degrees Celsius, preserving the ability to reduce metals and utilize sulfur, nitrogen and phosphorus, i.e. the ability for phototrophic, heterotrophic and mixotrophic growth. Representatives of thiobacteria – *Acidocillus ferrooxidans* – were chosen as the most suitable microorganisms. Adaptation and growth of *A. ferrooxidans* bacterial culture is usually accompanied by certain changes in the solution parameters [Lin et al., 2021; Santaolalla et al., 2021;], in particular, an active decrease in the Fe^{2+} concentration and increase in Fe^{3+} ions are observed. Copper compounds are often toxic to the standard strain of *A. Ferrooxidans*, which requires additional microbiological selection with cultivation of an adapted culture [Lv, X., et al., 2021]. The *A. Ferrooxidans* strains adapted to the conditions of copper raw materials allow the bioleaching of sulfides with emphasis on copper sulfides [Shenghua et al., 2018; Zhou et al., 2021]. A sample of Acidithiobacillus ferrooxidans-1333 strain bred at the Korean Center for Culture Collection is known to show high results of Fe^{2+} oxidation in chalcopyrite due to high immobilization of the bacteria to the specificity of this mineral [Song et al., 2020].

The aim of the work was to conduct research and develop a biohydrometallurgical technology for copper extraction from waste rock using thionic *At. ferrooxidans* bacteria capable of oxidizing sulfide minerals.

MATERIALS AND METHODS

Different variants of bacterial culture regimes were studied in order to reveal the efficiency of the use of biological agents in the process of copper extraction. Chemolithotrophic microorganisms catalyze the oxidation of inorganic compounds to obtain energy for their vital activity; *A. ferrooxidans* bacteria cause oxidation of iron (II) ions with oxygen.

Media and cultivation conditions

Normal growth and development of bacteria require the presence of mineral salts in the solution, primarily containing nitrogen, phosphorus, and potassium used by cells in energy metabolism. Silverman and Lungren nutrient medium, also called 9K medium that has the following composition per 1 liter of water: 1 ml of 1 n sulfuric acid, $(NH_4)_2SO_4$ – 3 g; KCl –0.1 g; K_2HPO_4 – 0.5 gr; $MgSO_4 \cdot 7H_2O$ – 0.5 g; $Ca(NO_3)_2$ – 0.01 g, $FeSO_4 \cdot 7H_2O$ - to the required concentration, was used for iron (II) oxidation by bacteria of the *Acidithiobacillus ferrooxidans* species. A less concentrated 9K/2 medium was used to reduce the precipitation amount of media elements during immobilization of microorganisms.

The number of microorganisms in the solution was counted by the method of limit tenfold dilutions and by direct cell counting under a microscope with a phase-contrast device. Concentration of dissolved oxygen in solutions was determined by a WTWOxi 3310 oximeter (Germany) with an electrochemical sensor. When analyzing the data on the chemolithoautotrophic bacteria number, the main degree indicators of redox processes, it should be noted that *Acidobacillus ferrooxidans* occurred in solutions in small amounts. The content of *Acidobacillus ferrooxidans* was noted in all samples of the solutions having acidic reaction, and the number of its cells reached from 105 to 106 cells/ml.

Determination of physical and chemical parameters

The values of hydrogen index (pH) and redox potential (Eh) of the solution were determined using I-160MI ionometer. The measuring electrode was used to measure the Eh value of the solution, including platinum ETPL-01M electrodeand auxiliary ESr-10103 chlorosilver electrode.

The moisture of ore and solid leach products (cakes) was determined by drying to constant weight according to the GOST 5180-84 procedure. Sulfuric acid concentration in the solution was determined by the acid-base titration method. The concentration of iron in the solution was determined by means of the trilometric method with a measurement error of 4%.

Perkin Elmer Optima 7000DV (USA) atomic-emission spectrometer with inductively coupled plasma and Ex-Calibur (USA) energy dispersive X-ray fluorescence spectrometer were used to determine the copper concentration in solution and solid phase.

RESULTS AND DISCUSSION

Microorganisms and their adaptation

Selection and optimization of nutrient media are important tasks in microbiological research. *A. Ferrooxidans* bacterial strain adapted to peculiarities of chemical and mineralogical composition of copper raw material was preliminarily selected when a biochemical oxidation solution of ore material was worked out. During the strain adaptation process to the mineral raw material, the number of surviving bacterial cells was analyzed in 10 days, as well as an increase in the iron concentration in oxidation degree 3^+, indicating the active metabolism of microorganisms. Three main adapted strains were selected based on the selection results, with strain 3 showing the greatest activity. The increase in iron concentration is shown in Figure 1.

Thus, an adapted strain of *A. Ferrooxidans* was chosen for further experiment on bacterial oxidation of copper ore. In most cases, the chemical composition of copper ores turns out to be somewhat detrimental for bacterial cells. In particular, Cu^{2+} copper ions and a number of arsenic compounds produced also in the arsenopyrite decomposition have a negative effect on the bacteria growth and metabolism. The flowsheet showing the selection process of the adapated *A. Ferrooxidans* bacterial strain is shown in Figure 2.

The *A. Ferrooxidans* strain adapted to the copper raw material composition was further investigated on the influence of pH factors. For this purpose, an experiment was performed involving agitation leaching of copper-containing

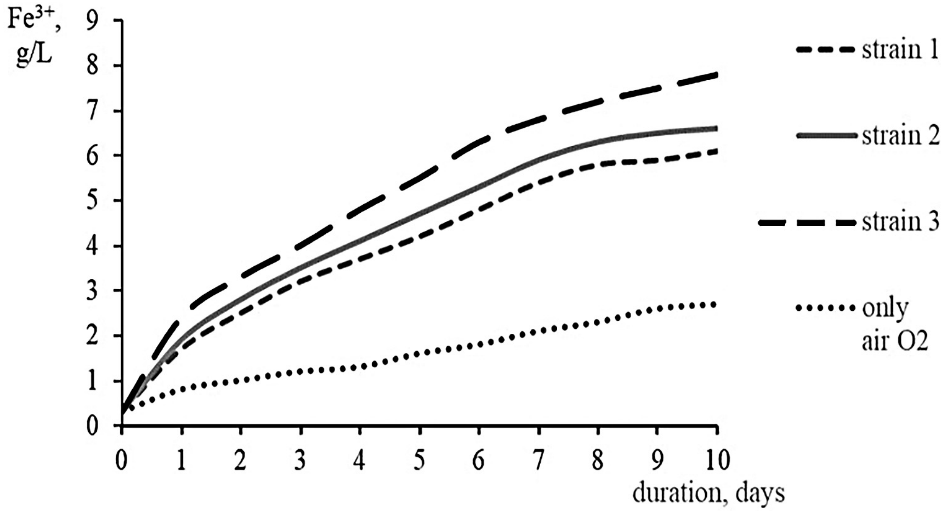


Figure 1. Increase in Fe^{3+} concentration during pulp oxidation by bacterial strains

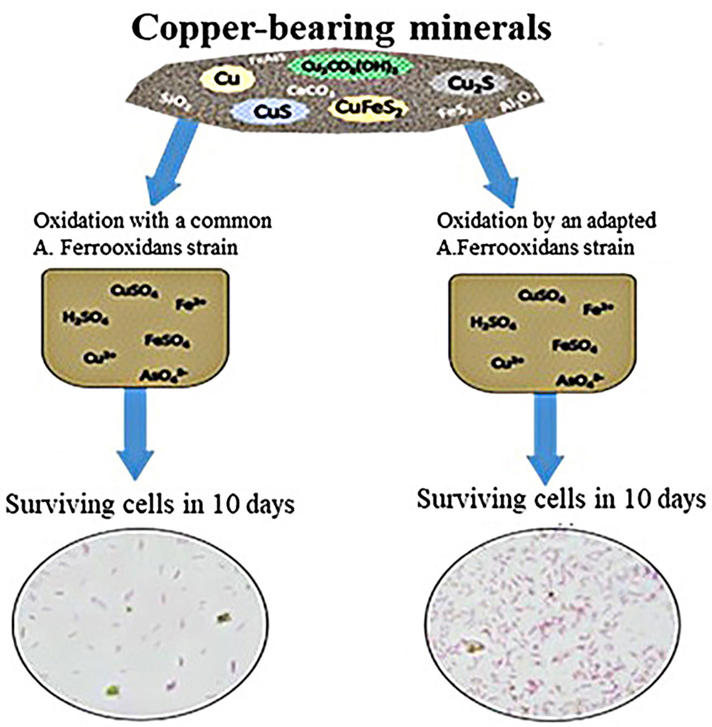


Figure 2. Selection of an adapted *A. Ferrooxidans* strain to the chemical composition of copper minerals

mineral pulp by bacterial culture with different pH variants of the medium. The initial indicators of a bacterial solution were cell concentration 10^5 cells/cm^3 (0.1×10^6), pH = 1.85, Fe^{2+} concentration – 3.1 g/l, and Fe^{3+} concentration – 0.07 g/l. The copper content in the initial mineral raw material is 0.28%, total iron is 2.9%. Total duration of the experiment was 5 days. The obtained solutions were filtered and analyzed for the content of bacterial cells, as well as bivalent and trivalent iron ions. As a result, the following variants of slurry acidity indicators were worked out: pH = 0.8; pH = 1.0; pH = 1.2; pH = 1.5; pH = 1.8; pH = 2.0; pH = 2.3.

It can be seen from the results of Table 1 that the growth of the *A. Ferrooxidans* bacterial culture on the pulp of copper-containing mineral raw materials is observed only at pH values of more than 1.2. Thus, the concentration of bacterial cells in the initial solution at pH = 1.5 increases from 0.1 to 0.4×10^6 cells/cm^3, while the concentration of ferrous ions decreased by 50.0% from 3.1 g/l to 1.55 g/l. At the same time, there is an increase in ferric iron ions that occurs due to the ferrous iron oxidation, as well additional extraction of iron from pulp minerals. The subsequent increase in pH to a level of 1.8 accelerates the growth of bacterial cells already by 9 times, and at pH = 2.0 by 14 times. The maximum growth of bacterial cells, equal to 2.8×10^6 cells/cm^3, was observed at pH = 2.3, which is 28 times higher than the number of cells in the initial solution, while the concentration of Fe^{2+} ions decreased by 92.9% and amounted to 0.22 g /l, and Fe^{3+} ions increased to 4.3 g/l. Three main pH ranges of acidic media that have a different effect on the growth factor of bacterial cells are shown in the graph of Figure 3.

Table 1. Effect of pH values on bacterial cell growth and development

Parameters of bio-solution	Changes of bio-solution parameters at different acidity of slurry						
	pH-0.8	pH-1.0	pH-1.2	pH-1.5	pH-1.8	pH-2.0	pH-2.3
Bacterial cells, c/cm^3 ×10^6	0.01	0.015	0.1	0.4	0.9	1.4	2.8
Changes of bacterial cell	Decrease by 90 %	Decrease by 85 %	Не изм.	Increase by 4 times	Increase by 9 times	Increase by 14 times	Increase by 28 times
Fe^{2+}, g/l	2.5	2.5	1.8	1.55	1.0	0.5	0.22
Fe^{3+}, g/l	1.5	1.6	2.1	2.7	3.3	3.6	4.3
ΔFe^{2+}, %	-19.35 %	-19.35 %	-41.94 %	-50.00 %	-67.74 %	-83.87 %	-92.90 %

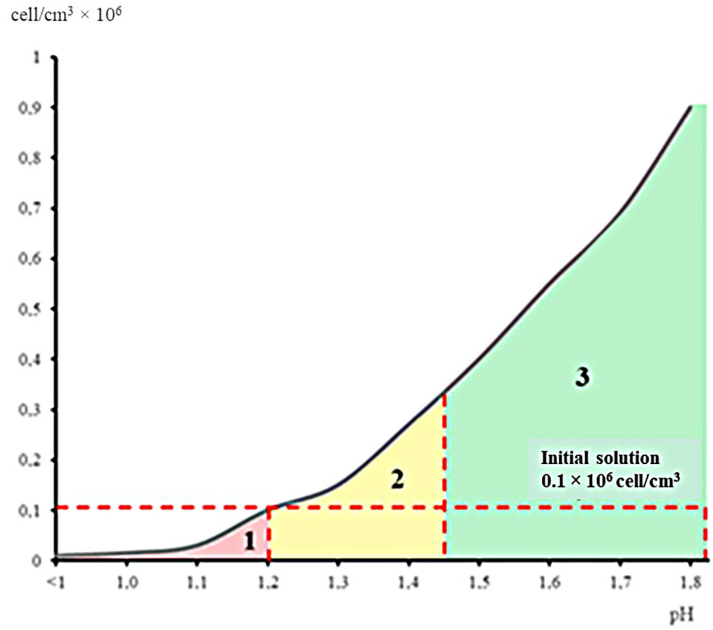


Figure 3. The pH ranges of an acidic environment and their effect on the growth of *A. Ferrooxidans* bacterial cells

Table 2. The content of copper and the main elements of impurities

Element	Content, %				
	1	2	3	4	5
Cu	5.093	0.635	9.895	0.612	1.134
Fe	2.677	2.46	2.205	2.549	1.757
S	0.63	1.12	0.205	0.992	1.2
Ca	2.503	2.902	1.94	2.36	3.087
Al	4.224	6.182	4.396	3.532	5.033

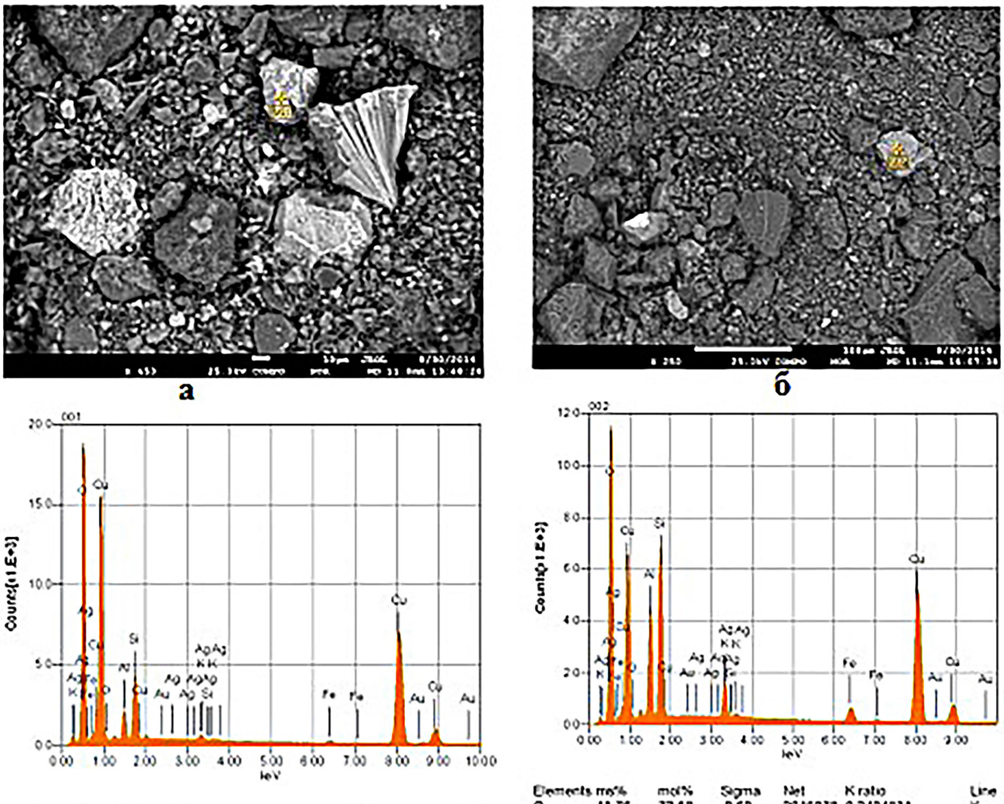
Several samples were taken from different points of the dump to conduct bioleaching experiments by the agitation method. The chemical composition of each point in terms of copper content and impurity elements is presented in Table 2.

From the data in the table, it can be seen that the content of the main component of copper in the ore raw materials of the dump is in the range from 0.612 to 9.895%. The distribution of iron at the occurrence points is relatively homogeneous and ranges from 1.757 to 2.677%. The calcium content is from 1.94 to 3.087%. There is a slight heterogeneity from 0.205 to 1.2% in the distribution of sulfur in the composition of the dump. Aluminum is present in a noticeable amount; on average, its content in the dump area is 4.7%.

Electron microscopic studies were performed on a JEOL JXA-8230 scanning electron microscope (Japan). Point EDS analysis (to determine the structure and relief of the surface of minerals, the elemental composition of the sample) was performed using an energy dispersive spectrometer. Its results are shown in Figure 4.

A detailed mineralogical analysis of the samples enabled to detect the presence of sulfide compounds in the samples, such as pyrite, chalcopyrite, and chalcocite. The samples from different sampling points were studied by mineralogical methods in reflected light using an OLIMPUS-BX 51 microscope. The largest part of the sample is occupied by non-metallic minerals; very small grains of pyrite can be clearly seen from ore minerals, the size of which reaches from 0.01–0.05 mm. Pyrite grains are free but they are also found in intergrowths of non-metallic mass; relatively fine sulfide material retains its detrital and irregular forms inherent in it. There are only single chalcopyrite fragments with grain size up to 0.02 mm. Images of sulfide fragments of samples are shown in Figure 5.

After the optimal concentration of sulfuric acid – 2.5% – was selected, experiments were



Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	56.17	80.66	0.68	3317382	0.3903259	K
Al	2.43	2.11	0.62	396188	0.0083160	K
Si	4.79	3.92	0.55	961009	0.0215669	K
K*	0.40	0.23	0.49	106451	0.0035589	K
Fe*	0.39	0.16	0.90	63745	0.0038717	K
Cu	35.62	12.88	1.88	3341641	0.3026500	K
Ag*	0.14	0.03	1.07	24780	0.0010018	L
Au	nd	nd				M
Total	100.00	100.00				

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	45.76	72.58	0.60	2040078	0.2404831	K
Al	6.47	5.71	0.42	961749	0.0201654	K
Si	9.37	7.94	0.40	1632106	0.0365851	K
K*	2.00	1.22	0.36	451077	0.0153330	K
Fe*	1.80	0.77	0.68	242247	0.0146978	K
Cu	31.19	11.68	1.37	2499617	0.2261438	K
Ag*	0.41	0.09	0.80	59150	0.0024600	L
Au	nd	nd				M
Total	100.00	100.00				

Figure 4. Results of point EDS analysis (a) of the original sample (b) after leaching; a – microstructure of the sample of the original ore sample; b – after ore leaching; c, d – energy dispersive analysis data before (c) and after (d) leaching of copper ore

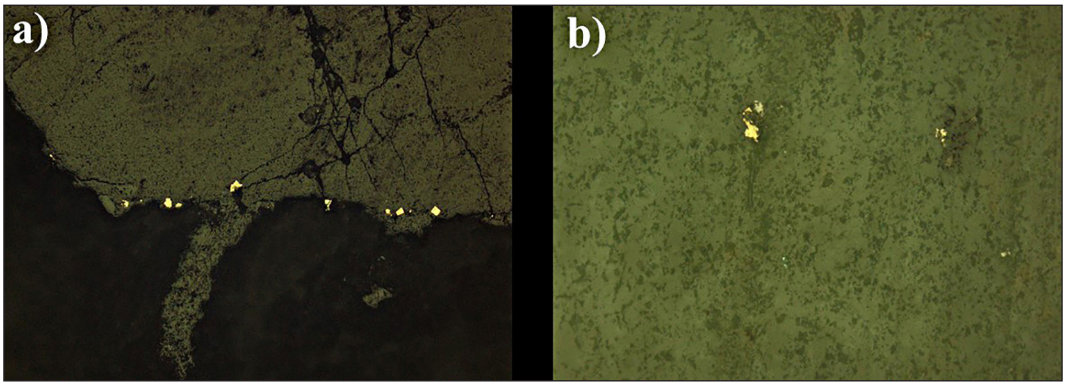


Figure 5. Mineralogical analysis of the sample; a) grains of pyrite; b) chalcopyrite

performed to leach copper from the samples under study, using additional oxidizing reagents. Most often bio-oxidation is considered as an oxidizing compound, and *A. Ferrooxidans* strain 3 bacterial culture previously adapted to the composition of copper-containing raw materials, was used for the hydrometallurgical production of copper. The samples were adapted and subjected to a bacterial solution of *A. Ferrooxidans* at a ratio of S: L = 1:1 for the purpose of preliminary bio-oxidation, followed by leaching by the agitation method. Further leaching of the sample was performed with a

Table 3. Leaching of the original ore sample using bacterial oxidation

Sample	$Cu_{initial}$, %	Extraction, %	
		H_2SO_4 - 2,5%	A.Ferrooxidans / H_2SO_4 - 2,5%
1	5.093	67.6	70.44
2	0.635	26.59	28.58
3	9.895	75.09	88.65
4	0.612	36.24	45.18
5	1.134	73.97	87.3

solution of sulfuric acid with a concentration of 2.5%, with a ratio of S:L = 1:4.

The results of the pre-oxidation leaching experiments presented in Table 3 show a marked increase in copper extraction, compared to conventional sulfuric acid leaching. Thus, the use of preliminary bacterial oxidation on sample 1 enables to extract 70.44% of copper within 6 hours of leaching, while this figure is only 67.6% without oxidation in the first six-hour stage. A noticeable increase in recovery and a halving of the leaching duration with bio-oxidation was also noted at other sampling points.

Studies were performed by the biochemical leaching method for the purpose of a comparative study of the copper extraction from dumps with complex composition. Copper extraction from sample 3 increased from 75.09 to 88.65%; sample 4 – from 36.2 to 45.18%; sample 5 – from 73.97 to 87.3%.

CONCLUSIONS

As a result of microbiological studies, mainly heterotrophic microorganisms adapted to the conditions of the current technological processes of the deposit itself were found in the composition of the microflora of the studied sample. The optimal environment for intensive growth and development of *A. ferrooxidans* thionic iron-oxidizing bacteria is the Silverman and Lundgren 9K medium with a concentration of 5 g/l $FeSO_4 \cdot 7H_2O$. It was established that for more efficient bacterial oxidation of mineral raw materials, it is advisable to pre-treat with a bacterial solution at a pH of at least 1.5. At the same time, an increase of acidity in pulp and a decrease in pH less than 1.2 have an extremely negative effect on the survival of bacterial cells. The optimal temperature regime for the growth and development of *A. Ferrooxidans* culture is the temperature range of 20–30 °C. The use of the most favorable factors for the growth of bacterial cells (pH - 2.3, t = 20–30 °C) ultimately makes it possible to increase their concentration from 0.1×10^6 cells/cm^3 to 2.8×10^6 cells/cm^3.

Copper extraction from dumps with complex composition by biochemical leaching is 88.65%.

A biohydrometallurgical technology has been developed to process waste dumps with a complex composition from the Satpayev deposit. Thus, the use of the catalyzing bacterial culture *A. Ferrooxidans* greatly accelerates oxidative processes and increases the degree of copper extraction by an average of 8–10%.

Acknowledgements

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