

RESEARCH PAPER

The pre-bio-oxidation and its effect on the leaching process of low-grade copper ore in percolation columns*Bagdaulet Kenzhaliyev, Aigul Koizhanova, Gulnar Abdykirova, David Magomedov, Nurgali Abdyladayev, Akbota Bakrayeva, Ainur Mukhanova**JSC Institute of Metallurgy and Ore Beneficiation, Satbayev University, Shevchenko 29/33, Almaty 050010, Kazakhstan; imio@imio.kz*Corresponding author: ainura-muhanova@mail.ru, tel.: +7 778 931-12-89, JSC Institute of Metallurgy and Ore Beneficiation, Satbayev University, Shevchenko 29/33, Almaty 050010, Kazakhstan

Received: 30.04.2025

Accepted: 19.05.2025

ABSTRACT

The results of laboratory studies aimed at extracting copper from standard copper raw materials using percolators are presented in this work. The results of chemical elemental analysis, X-ray phase analysis and chemical phase analysis for the copper and iron forms in the ore are also presented herein. The efficiency of sulfuric acid and bacterial leaching in percolation columns was compared. When standard sulfuric acid leaching was used, copper extraction into the solution was 49.85%. In contrast, bacterial oxidation (using chemolithotrophic bacteria, *Thiobacillus thiooxidans*, which oxidise sulfur and iron compounds) achieved 74.81% copper extraction during a 60-day experiment. The redox potential values for standard sulfuric acid and bacterial leaching of copper ore are presented, which correlate with copper yield. As a result of the research, it was found that the use of bacterial technology provides deeper processing of copper ore due to the oxidation of copper sulfide minerals.

Keywords: low-grade copper ore, *Thiobacillus thiooxidans*, bacterial culture, leaching.**INTRODUCTION**

Global demand for copper is growing, and the mining industry in the Republic of Kazakhstan is increasingly faced with the need to process low-grade ores, overburden rocks and waste from current mining operations. Economically feasible extraction of copper from low-grade ores requires low-cost treatment methods, such as in-situ leaching, leaching into a disposal area, and heap leaching [1,2].

A large number of hydrometallurgical methods have been developed along with the pyrometallurgical method. They differ in the reagents used to convert copper into the solution.

The hydrometallurgical method involves the extraction of copper through leaching (for example, with weak sulfuric acid solutions) and subsequent separation of metallic copper from the solution [3-5]. They include chloride leaching, ammonia leaching, autoclave leaching, and biological leaching [6,7].

One of the pressing problems worldwide is the leaching of copper from low-grade ores. The main components of copper ores are sulfide minerals, mainly chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), chalcocite (Cu_2S) and covellite (CuS) and oxidized minerals - azurite, malachite, tenorite, etc. Chalcopyrite is generally considered the most difficult to leach using conventional hydrometallurgical methods among the minerals, as mentioned earlier. This is due to its complex crystal structure and the presence of iron in the mineral lattice. The leaching resistance of chalcopyrite is a significant problem in the extraction of copper from some ore deposits. Various methods are employed to address this issue, including high-temperature pressure leaching [5-7], bioleaching [8-10], chemical pretreatment [11], and a combination of leaching methods [12-13].

Several methods are employed to intensify the leaching processes of copper sulphide ores, including high-temperature pressure leaching, bioleaching, chemical pretreatment, and a combination of leaching methods.

Copper oxides are readily soluble in a diluted solution of sulfuric acid. Still, primary refractory sulfides require high temperatures and pressures, and secondary sulfides require additional oxidizing agents to dissolve effectively.

Copper ore leaching is done differently depending on the minerals present in the ore. Oxide ores containing chrysocolla, malachite, azurite, cuprite, and other minerals are easily subject to acid leaching [12-13].

Copper oxide minerals containing copper in a divalent state, such as azurite, malachite, tenorite and chrysocolla, are highly soluble in both acidic and alkaline environments at room temperature. It is well known that sulphuric acid is the most common leaching agent for oxidised copper ore, and the acid consumption

ranges from 0.4 to 0.7 tons of H_2SO_4 per ton of copper recovered, depending on the nature of the ore. The leaching chemistry of oxidised copper ore in sulfuric acid and the extraction of copper from raffinate by solvent extraction (SX) has been intensively studied [14]. The kinetics of leaching of malachite in ammonia solutions was investigated in the work [15]. It has been observed that the leaching rate increases with an increase in ammonia concentration, reaction temperature, solid/liquid ratio and particle size.

Works [3,4] consider options for using sulfuric acid or ammonium carbonate solutions for oxidised copper ores; ferric solutions (especially sulfate) as an oxidiser of copper sulfides in a sulphate medium; mineral acids, including hydrochloric, nitric, and concentrated sulfuric; chloride solutions of iron (III) ions and copper (II) ions; and oxygen as an oxidiser of sulfides in autoclaves. Preliminary bacterial oxidation is also used for low-grade ores [8,9].

It is known that various additives have been proposed to intensify the leaching of sulfide copper ores and concentrates with acidic solutions, including sulfur and nitric acid salts of iron(III) and ammonium, fluoride ions, surfactants, oxygen, ozone, sodium chloride, nitrates, and chlorides of alkali and alkaline earth metals. [16] Bacterial leaching is used for low-grade ores and wastes. After leaching, the solutions are concentrated by copper, for example, by solvent extraction or sorption with ion exchangers, followed by electrowinning of copper, or copper is separated from them by carbonisation with iron turnings.

Secondary sulphide ores containing chalcocite and covellite are also leachable, but the chemical mechanism is more complex. Iron ions easily leach secondary sulfides. As copper minerals dissolve, iron is reduced to iron. Iron must be oxidized back to iron to increase the leaching rate. This process is facilitated by natural microorganisms, making bacterial leaching, also known as biohydrometallurgy, a viable option.

Heap and dump biological leaching are generally the most suitable technologies for processing low-grade secondary copper sulphide ores, and to a lesser extent, primary copper sulphides such as chalcopyrite.

In recent decades, bacterial heap leaching of low-grade copper ores has been successfully applied to extract copper from secondary sulphide minerals worldwide. One of the advantages of bioleaching is the potentially lower capital and operating costs, which have become increasingly important as ore grades decline [2,6].

The modern standard technology of heap leaching and liquid extraction of copper is described in detail in several works by domestic and foreign researchers [1-8]. Currently, great importance is attached to the use of bacteria in the extraction of

copper from ore. The term “bacterial leaching” refers to the intensified process of leaching metals from ores.

Bacterial heap leaching of low-grade copper sulphides is a technology successfully used to extract copper from such secondary sulphide minerals as chalcocite in many facilities around the world. [17]. It is known that heap bioleaching of refractory primary copper sulfide, chalcopyrite, has not yet been implemented on an industrial scale. Traditionally, the benefits of bacterial leaching have been compatible with the following requirements:

- moderate capital investments with low operating costs;
- appropriate extraction of metals from low-grade ores and wastes;
- main equipment and simple operating procedures.

The role of the Thiobacillus ferrooxidans bacteria in the leaching of sulfide ores is widely known. During the biogeotechnological process, metals are transferred from water-insoluble sulfides to soluble sulfates. Thionic Thiobacillus ferrooxidans bacteria oxidize all metal sulfides. They obtain the carbon required for bacterial growth from carbon dioxide. These bacteria grow in an acidic environment (pH range 1.0-4.8) at temperatures from 3 to 40 °C. The optimal parameters for the development of bacteria are the pH value within 2-3, temperature 28 °C. Thionic bacteria are found in water bodies, soil, and deposits of sulfur and sulfide ores. But they are active in the presence of oxygen [18-22].

A special role in these processes is played by the Thiobacillus ferrooxidans bacteria, which are involved in the leaching of sulfide ores. These bacteria convert insoluble metal sulfides into soluble sulfates in a biogeotechnological process. Thiobacillus ferrooxidans oxidize all metal sulfides and obtain the carbon required for their growth from carbon dioxide. These bacteria develop in an acidic environment with a pH of 1.0 to 4.8 and a temperature of 3 to 40 °C, with optimal pH conditions of 2.3 and a temperature of 28 °C.

Ore material or man-made waste containing metal sulfides is irrigated with sulfuric acid solutions and iron salts in the process of biogeotechnological leaching of metals, and viable thionic bacteria are introduced. The leaching process is intensified by the use of oxygen in the air. As a result of filtration of the solution through a material containing metal sulfides, the metals are transformed into a soluble state. Thus, heap leaching is an effective method intended to process oxide copper off-balance ores from deposits in the Republic of Kazakhstan with the parameters determined experimentally depending on the chemical and phase composition of ores.

In most cases, standard hydrometallurgical technology for copper production is limited to the possibility to use only oxidized raw materials of simple composition, with a low content of divalent iron compounds. The presence of iron in divalent form, in the form of minerals such as pyrite and pyrrhotite, and other compounds, significantly complicates the leaching process, also increasing the consumption of the main leaching reagent, sulfuric acid. It results in the need to pre-treat raw materials with oxidizing reagents and convert iron into an oxidized trivalent form. The application of chemical oxidizers, for example, such as sodium peroxide, potassium hypochlorite, used in the process of leaching precious metals, is not cost-effective in the case of copper raw materials. There are known methods to use bacterial cultures as an oxidizing reagent in domestic and world practice [23]. The main advantages of bacterial oxidation include the high efficiency of converting divalent iron into ferric iron, as well as the low cost of this technology.

Bioleaching is the bacterial catalytic dissolution of metals from sulphide minerals [4]. The main bacteria in biological leaching processes are Acidithiobacillus ferrooxidans. They live in acidic environments, obtaining energy for growth from the oxidation of reduced sulfur and iron compounds [5].

The technological novelty is in the use of bacteria as a factor catalyzing oxidative processes, and it will significantly increase the degree of copper extraction into the productive solution.

The purpose of this work is to simulate the heap leaching process of substandard copper raw materials in percolation columns using preliminary bacterial oxidation and to compare the efficiency of chemical leaching and the bacterial method.

MATERIALS AND METHODS

The object of the research was a sample of substandard copper-bearing ore of the Republic of Kazakhstan.

Sample preparation for physical and chemical analyses included pre-crushing, pulverization, quartering and averaging, according to the sites and sampling points. The entire sample was crushed in stages on a roller mill to a size of 25+0 mm to prepare it for the studies. It was then combined and reduced using normal

procedures, allocating suspensions for technological research and material composition analysis.

Studies of the ore material composition included: X-ray fluorescence multi-element analysis, X-ray phase qualitative and quantitative analysis for the content of major components, chemical analysis for copper content. The chemical composition of ore samples from different layers of occurrence was made using the Shimadzu 7000 atomic absorption spectrometer

R-ray fluorescence elemental analysis was performed with the use of the Axios “PANalytical” wavelength dispersive combined spectrometer (Holland). X-ray phase analysis was performed on a D8-ADVANCE diffractometer made by Bruker Elemental GmbH (Germany). Electron microscopic analysis was performed with a “JEOLJXA-8230” microprobe analyzer made by JEOL (Japan).

Comparison of sulfuric acid and bacterial leaching performance in columns. Samples of ore material, weighing 225 kg and having a particle size of 25.0 + 0 mm, were added to percolation columns with a height of 2.0 m and a diameter of 0.35 m. The first column was irrigated according to the traditional technology - with a solution with sulfuric acid concentration of 10 g/dm³. The second column was irrigated with a bacterial solution for 15 days and then with a sulfuric acid solution of 10 g/dm³. The irrigation density was 6 dm³/m² · h.

The bacterial biomass adapted to the mineral composition of the copper waste was grown in a specialized bioreactor/fermenter, adhering to previously defined parameters. The development and growth of the Thiobacillus thiooxidans bacterial culture are marked by specific alterations in the biosolution parameters [20,21], including a significant reduction in Fe²⁺ concentration and an elevation in Fe³⁺ ion levels. Alongside the decomposition of iron-bearing minerals, certain strains of Thiobacillus thiooxidans, acclimated to copper ions in solution, facilitate the bioleaching of sulfides, particularly copper sulfides [23].

When a solution for the biochemical oxidation of ore material is produced, a previously bred Thiobacillus thiooxidans bacterial strain was used, adapted to the characteristics of the chemical and mineralogical composition of copper raw materials. During the adaptation of strains to mineral raw materials, the number of surviving bacterial cells as well as an increase in the concentration of iron in the oxidation state of 3+, indicating the active metabolism of microorganisms was analyzed in 10 days.

The equipment for the vat-bioreactor for biomass included the installation of air and nutrient supply systems, a sensor for monitoring pH and temperature, a “jacket” covering the fermenter tank to maintain optimal temperature, a mixing system, areas for removing gases and the finished product—the culture fluid of the Thiobacillus thiooxidans strain. The body of the bio-reactor fermenter tank was made of stainless steel. The set temperature for the nutrient medium in the fermenter container is most often maintained by circulating water in a sealed “jacket” layer around the fermenter body.

RESULTS AND DISCUSSION

The copper content in the studied low-grade copper-bearing ore was -0.71%. According to mineralogical analysis, the main ore minerals are malachite, chalcopyrite, pyrite, chrysocolla, covellite. The results of the chemical analysis are presented in **Table 1**.

Table 1 Results of X-ray fluorescence analysis of the initial ore sample

Element name	Content in samples, %	Element name	Content in samples, %
O	50.2	Ti	0.135
Na	1.755	Mo	0.006
Mg	1.123	Mn	0.038
Al	6.63	Fe	2.436
Si	27.595	Cu	0.3
P	0.053	Zn	0.009
S	0.413	Rb	0.001
Cl	0.026	Sr	0.003
K	1.001	Zr	0.006
Ca	1.742	Pb	0.012

The results of the chemical analysis (**Table 1**) indicate that the main elements are silicon, oxygen, aluminum and sodium. They form the basis of quartz and albite. It is confirmed by X-ray phase analysis (**Table 2**)

Table 2 Phase composition of the initial sample of low-grade ore

Name	Formula	S-Q, %
Quartz, syn	SiO ₂	53.3
Albite low	Na(AlSi ₃ O ₈)	14.6
Clinocllore, ferroan	(Mg,Fe) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	12.4
Microcline	K(AlSi ₃ O ₈)	10.5%
Muscovite, ferrian	K _{0.94} Na _{0.06} Al _{1.83} Fe _{0.17} Mg _{0.03} (Al _{0.91} Si _{3.09} O ₁₀) (OH) _{1.65} O _{0.12} F _{0.23}	7.3%
Cordierite	Mg _{1.772} Fe _{0.136} Al _{3.830} Si _{4.792} O ₁₈ (H ₂ O) _{0.85}	1.8%

The results of the phase analysis for the forms of copper are presented in **Table 3** and the phase analysis for the forms of iron are presented in **Table 4**.

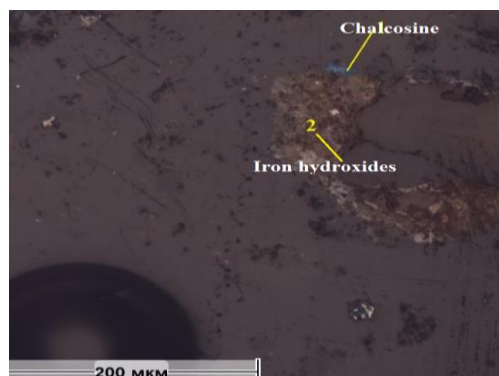
Table 3 Results of chemical phase analysis for the forms of copper in the ore

Forms of copper	Content, %	
	absolute	relative
Oxygen-containing compounds (malachite, chrysocolla, etc.)	0.026	8.9
Primary sulfides (chalcopyrite)	0.19	63.3
Secondary sulfides (covellite, chalcocite, etc.)	0.083	27.8
Total copper content	0.3	100.0

Table 4 Results of chemical phase analysis for iron forms in ore

Iron forms	Content, %	
	absolute	relative
Oxygen-containing compounds (hematite, iron hydroxyls, siderite, etc.)	0.64	26.5
Sulfide forms (pyrite, pyrrhotite, bornite, etc.)	1.796	73.50
Total content	2.436	100.0

In the surface section (**Fig. 1**), the following minerals were determined in the sample: chalcocine (a), chalcopyrite (b), malachite (c), chrysocolla d).



(a)



(b)



(c)



(d)

Fig. 1 Mineralogical study of mineral microphotography. Magnification x200: chalcocine (a), chalcopyrite (b), malachite (c), chrysocolla d).

Chalcopyrite (CuFeS₂) has an exceptionally characteristic brassy yellow color that makes it easily distinguishable from all other ore minerals. It has high reflectivity and barely noticeable anisotropy. There are no internal reflections. Fragments of irregularly shaped grains, measuring 34 μm in size, represent it. Chalcocite (Cu₂S) is a light gray with a bluish tint, an isotropic mineral. It is noted in aggregation with chalcopyrite and individual grains with the size of 0.03 mm. The shape is anhedral.

Malachite (CuCO₃·Cu(OH)₂) is a copper carbonate, a mineral. The syngony is monoclinic, the color is green with different shades; the luster is different. It is characterized by solubility in acids with the release of carbon dioxide, as well as in ammonia that is stained in a beautiful blue color.

Chrysocolla (Cu, Al)₂H₂Si₂O₅(OH)₄·nH₂O is a mineral of the silicate class, an aqueous copper silicate, very light. The color is blue or bluish-green.

Conducting research on the extraction of copper from low-grade copper ore through preliminary bio-oxidation.

The essence of the column test lies in laboratory tests to leach copper from raw materials using drip irrigation. The volume of the solution entering the tank is measured and analyzed for copper content, pH level, concentration of leaching reagent (sulfuric acid). These determinations are made for each portion of the collected productive solution. The leaching procedure continues until the copper content in the productive solution is stabilized at low concentrations. When the complete extraction of copper into solution is achieved, the loaded raw material is washed and then removed from the column and dried. After drying, the material is analyzed for copper content.

Percolation leaching of low-grade copper-containing raw materials was conducted in a solution of sulfuric acid with a concentration of 10 g/dm³. Figure 3 shows the process of copper leaching in percolators. Ore leaching was studied in columns (percolators) with a diameter of 0.5 m and a height of 1.7 m. The solution for ore leaching was supplied using LS-301 LS peristaltic dosing pump. Percolation leaching mode: ore – 225 kg. Cu is 0.3 % Copper weight in 225 kg of ore is 292.5 g. Irrigation density is 10 l/m² per hour. S = πR² Percolator = 25cm = 0.25m S = 3.14×0.25² = 0.2 m². Irrigation solution is 48 l, consumption is 2 l per hour.

Solutions emerging from the columns were collected in receiving tanks. Samples were taken from the obtained solutions for analysis for copper and residual acid. The pH is measured. For further use of the solution (leaching with a recycled solution), the concentration of sulfuric acid was strengthened to the initially specified one.

The results of percolation, chemical and biochemical leaching of copper from ore are presented in Fig. 2.

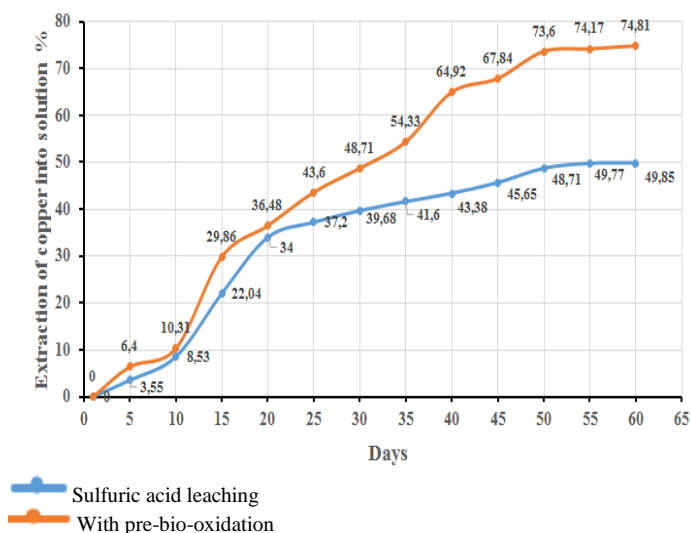


Fig. 2 Copper extraction dynamics

Percolation leaching of copper with pre-biooxidation is significantly superior to leaching without pre-biooxidation. For example, the copper content in the

solution after 60 days is 7.01 g/l without oxidation and 10.52 g/l with preliminary bio-oxidation, with recoveries of 49.85% and 74.81%, respectively.

The data in Fig. 3 indicate that biooxidation contributes to a more complete extraction of copper from low-grade ore, making this method more efficient and productive.

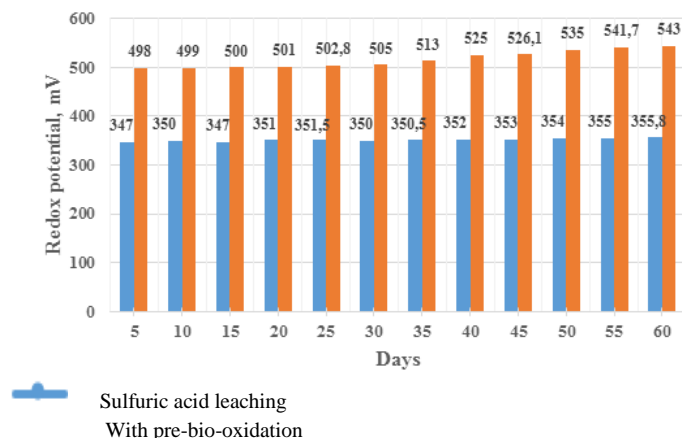


Fig. 3 Dynamics of changes in the redox potential of the solution during copper leaching

These changes in the redox potential of the leaching solution shown in Fig. 4 correlate with copper yield.

The research results indicate that the use of bacterial technology enables a deeper processing of copper ore through the oxidation of copper sulphide minerals.

CONCLUSION

Thus, the results of large-scaled laboratory experiments showed the efficiency of leaching copper from substandard raw materials with the preliminary bacterial method of oxidation compared to the chemical method.

The extraction of copper into solution was 49.85% with the use of standard sulfuric acid leaching while it was 74.81% with bacterial oxidation (chemolithotrophic bacteria Thiobacillus thiooxidans, oxidizing sulfur and iron compounds) during the 60 days of the experiment.

The redox potential values are presented for standard sulfuric acid and bacterial leaching of copper ore, which correlate with copper yield.

Acknowledgements: This research was supported by a grant project of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan, project No BR24992757.

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