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Bacterial oxidation in the hydrometallurgical process of copper extraction from copper-containing ore

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Abstract: Copper extraction technologies are constantly being improved including chemical oxidants. However, chemical oxidants slightly increase the extraction. Thus, this study aims to increase copper extraction using bacterial oxidation as oxidizing reagent. It also compares extraction results between standard leaching with sulfuric acid and Acidithiobacillus ferrooxidans with amino acids nutrient medium. Ore from Zhezkazgan deposit that contains chrysocolla, malachite and iron hydroxide was used as a sample. The ore was dug from a 6m depth. The initial sample was crushed, grinded, mixed, and reduced before preliminary biooxidation by bacterial culture of Acidithiobacillus ferrooxidans. A mineralogical study of ore was conducted to confirm the copper contains, other compounds and phase composition as well. Acidithiobacillus ferrooxidans were cultured within the nutrient medium of amino acid. This study chooses amino acid serine L, glycine, and asparagine to provide optimum bacterial cell of A. Ferrooxidants. Results showed that preliminary biooxidation by bacterial culture of A.Ferrooxidans increased copper extraction significantly. Further, Acidithiobacillus ferrooxidans that grow in the nutrient medium containing L-Serine have the highest effect on copper extraction.

Keywords: Copper-containing technogenic raw materials; Bio-leaching; Bacterial culture of Acidithiobacillus ferrooxidans; Biooxidation

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1. Introduction

Modern production of non-ferrous metals is characterized by an increase in the mass of rocks in the form of dumps and volumes of tailings dumps. As a rule, useful components including non-ferrous metals are found in mining waste mainly in small-size classes and hard-to-recover forms. In addition, man-made waste is environmentally hazardous, especially its sulfide and arsenic-containing components (Dresher, 2004; Gentina & Acevedo, 2013; A. K. Koizhanova et al., 2024; Santaolalla et al., 2021). The current trend of most copper deposits in Kazakhstan decrease in reserves of rich raw materials, as well as the accumulation of significant volumes of off-balance sheet dumps with a low copper content of 0.3-0.5%. This content makes the process of pyrometallurgical melting of such raw materials completely unprofitable. Currently, the practice of flotation enrichment of ores and dumps with a low content of copper, mainly in sulfide form, has become widespread. A standard hydrometallurgical technology for the processing of off-balance copper raw materials that represented mainly by the oxidized form of copper-containing minerals is used. It includes sulfuric acid leaching, followed by liquid extraction and electrolysis.

However, in addition to off-balance ores and dumps having a pronounced sulfide or oxidized form of copper in minerals, there are numerous deposits with complex mineralogical composition, which requires the development of new approaches to solving the problem (Canterford et al., 1985; Kenzhalievich et al., 2024; Lin et al., 2021; Lv et al., 2021; Watling, 2006; Zhou et al., 2021). To achieve better results in the processing of substandard copper-containing raw materials, comprehensive in-depth research including a study of the bioleaching process and the influence of the composition of the culture liquid is necessary. In-depth studies of the physico-chemical characteristics of copper-containing mineral raw materials will become the basis for the development of new technological solutions. In most cases, the standard hydrometallurgical technology for producing copper is limited to the possibility of using only oxidized raw materials of a simple composition with a low content of ferrous compounds.

The presence of iron in divalent form, in the form of minerals pyrite, pyrrhotite and other compounds, significantly complicates the leaching process, also increasing the consumption of the main leaching reagent – sulfuric acid (A. Koizhanova et al., 2022; Liu et al., 2017). This leads to the need for the pretreatment of raw materials with oxidizing reagents and the conversion of iron into an oxidized trivalent form. The use of chemical oxidants such as sodium peroxide, and potassium hypochlorite in the leaching of precious metals insignificantly increases the extraction and not cost-effective in the case of copper raw materials. In domestic and world practice, there are known methods of using bacterial cultures as an oxidizing reagent.

The main advantages of bacterial oxidation are the high efficiency of converting divalent iron to trivalent iron, as well as the inexpensive cost of this technology. For certain changes in the parameters of the biological solution such as an active decrease in the concentration of Fe^{2+} and an increase in Fe^{3+} ions characterize the development and growth of bacterial culture A.Ferrooxidans. In addition to the decomposition of iron-containing minerals, some strains of A.Ferrooxidans adapted to the presence of copper ions in solution. It allows the bioleaching of sulfides with an emphasis on copper sulfides. The novelty of the topic lies in the development of an effective method for extracting copper from substandard raw materials by choosing leaching conditions depending on its physico-mechanical, chemical and mineralogical characteristics. Thus, this study determines the effect of bacterial oxidation as oxidizing reagent to increase copper extraction. Further, it also compares the using of sulfuric acids and A.Ferrooxidans with amino acids nutrient medium in the hydrometallurgical process of copper extraction.

2. Material and methods

This study involved ore of the Zhezkazgan deposit from a depth of 6 meters. The study of the composition of the Zhezkazgan deposit dump included the selection of representative samples, distribution, packing, preparation of samples for analysis, and sample identification before extraction. It used A.Ferrooxidans in preliminary biooxidants and culture in amino acids nutrient medium (L-Serine, glycine, and asparagine).

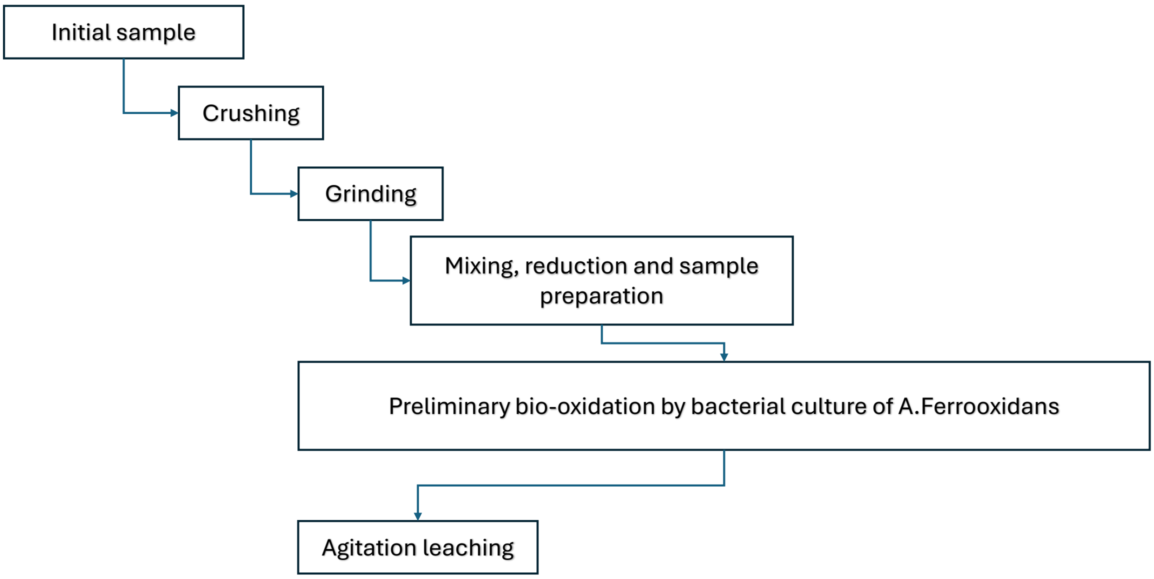

Figure 1. Schematic diagram of the research procedures

Studies on the material composition of the ore included: X-ray fluorescence multi-element analysis, X-ray phase qualitative and quantitative analysis for the content of the main components, and chemical analysis for the content of copper. The chemical compound of the ore samples includes a copper content of 1.027% and Fe of 2.640%, meanwhile, the main compound is Oxygen (53.7%) and Si (27.120%) (Table 1).

Table 1. The components compound of ore samples

Components	Content, %	Components	Content, %	Components	Content, %
O	53.7	Cl	0.012	**Cu**	**1.027**
Na	1.66	K	0.967	Zn	0.013
Mg	1.082	Ca	1.765	Rb	0.006
Al	6.537	Ti	0.579	Sr	0.006
Si	27.120	Cr	0.011	Zr	0.007
P	0.071	Mn	0.090	Pb	0.020
S	0.065	**Fe**	**2.640**	-	-

This study used the Zhezkazgan deposit as a sample. The main phase components of minerals are quartz and albite within mass fractions equal to 51.1 and 29.1%, respectively as figured in Figure 2. The detailed main phase components of initial sample of the Zhezkazgan deposit based on Figure 2 is stated in Table 2. The crushed material was received for the study of the material of the samples. A polished full face was made from the sample, which was studied on an OLYMPUS BX 51 microscope.

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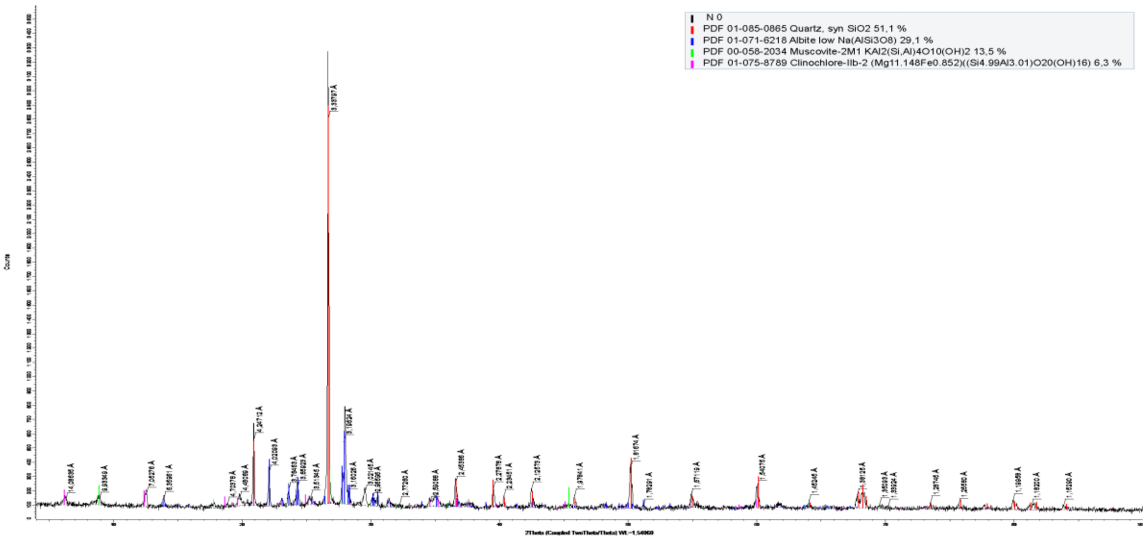


Figure 2. Diffractogram of the initial sample of the Zhezkazgan deposit

The detailed main phase components of initial sample of the Zhezkazgan deposit based on Figure 2 is stated in Table 2. The crushed material was received for the study of the material of the samples. A polished full face was made from the sample, which was studied on an OLYMPUS BX 51 microscope.

Table 2. Phase composition of the initial ore sample

Name	Formula	S-Q, %
Quartz, syn	SiO_2	51.1%
Albite low	$Na(AlSi_3O_8)$	29.1%
Muscovite-2M1	$KAl_2(Si,Al)_4O_{10}(OH)_2$	13.5%
Clinochlore-IIb-2	$(Mg_{11.148}Fe_{0.852})(Si_{4.99}Al_{3.01})O_{20}(OH)_{16}$	6.3%

Sample 1 involved in this study contains chrysocolla, malachite and Iron hydroxides. Chrysocolla $(Cu, Al)_2H_2Si_2O_5(OH)_4.nH_2O$ is a bright green, isotropic mineral. The mineral is presented in the form of anhedral grain shape. Grains of a radially radial structure are also observed. The grain size reaches up to 944.7 microns (Figure 3).

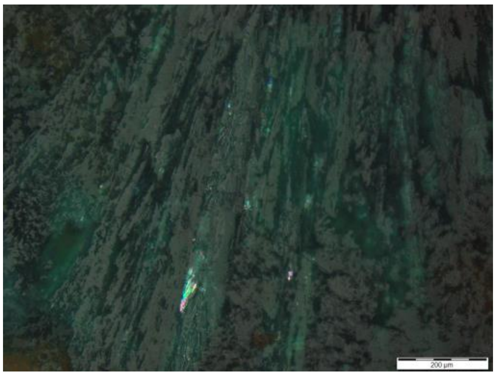
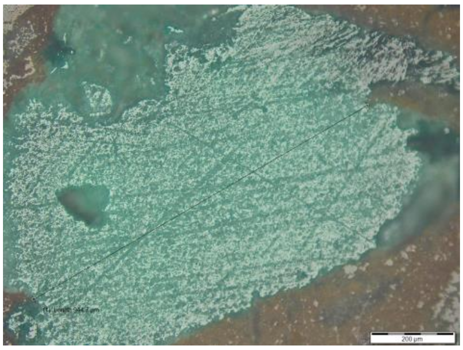
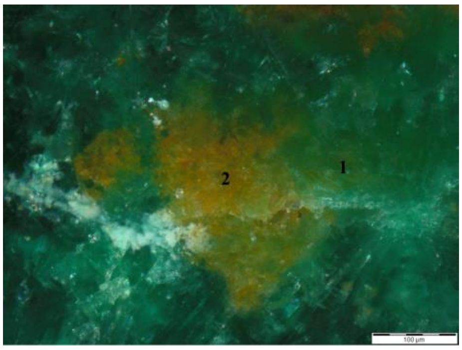


Figure 3. Chrysocolla. Sample 1, uv.100, without analyzer

Malachite $Cu_2(CO_3)(OH)_2$ is a gray highly anisotropic mineral with bright green internal reflexes. The shape is irregular with tortuous constraints. On the surface of the anschlift, about 60% of malachite is noted in combination with iron hydroxides and sometimes with chrysocole. The grain size reaches up to 316.6 microns (Figures 4 a and b).



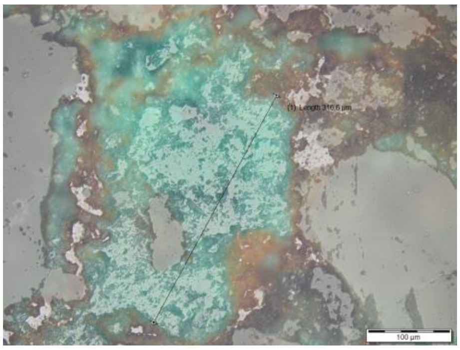
a



b

Figure 4. Mineralogical study of micrographs of minerals: *a* - Chrysocolla. Sample 1, uv.100, without analyzer; *b* - Malachite (1) in fusion with iron hydroxides (2). Sample 1, uv.200

Iron hydroxides (FeOH)$_2$ have a gray color with red internal reflexes. They are observed in the form of xenomorphic grains. They are found in free grains, and also sometimes in fusion with malachite. The grain size of free iron hydroxide grains is 143.3 microns (Figures 5 a, b and c).



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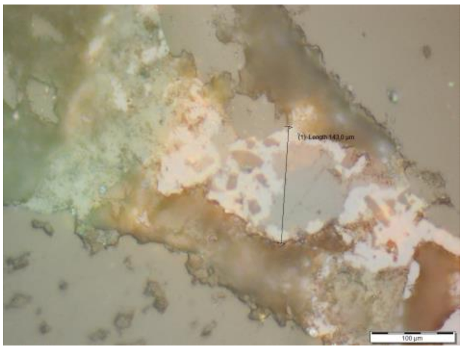

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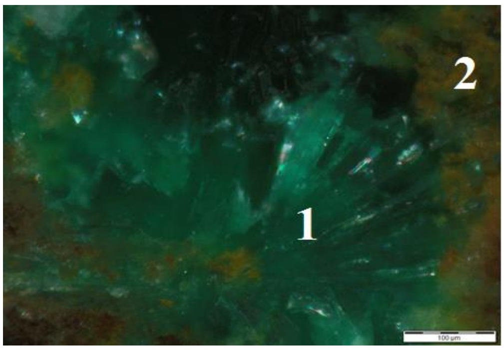
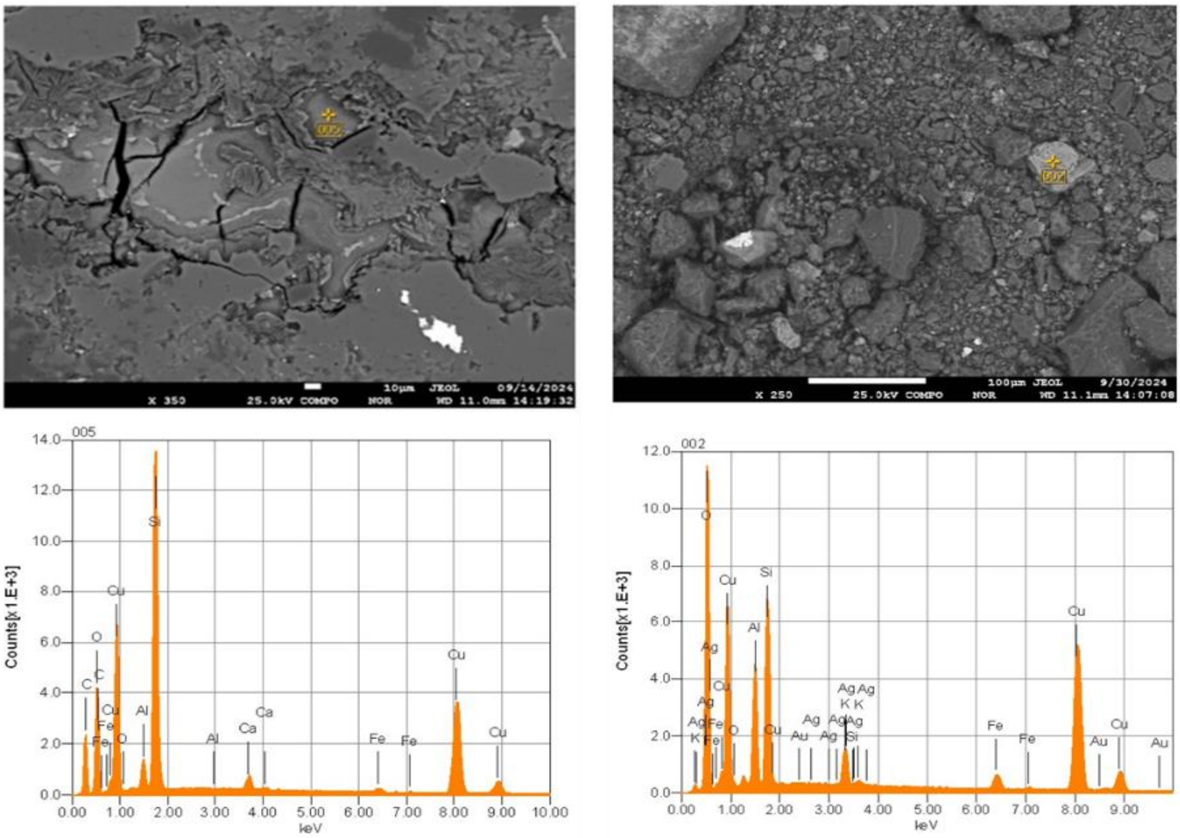


c

Figure 5. Mineralogical study of micrographs of minerals: *a* - Malachite in fusion with iron hydroxides. Sample 1, uv.200, without analyzer; *b* - Iron hydroxides, Sample 1, uv.200, without analyzer; *c* - Malachite (1) in fusion with iron hydroxides (2). Sample 1, uv.200

A detailed study of the forms of copper in minerals was carried out on the JEOL JXA-8230 electron probe microanalyzer. The presence of copper in predominantly oxidized forms of minerals has been confirmed, with concomitant aspects characteristic of carbonate and silicate forms of minerals. Micrographs of oxidized mineral copper-containing fragments, 10-100 microns in size, are shown in Figure 6.



Elements	ms%	mol%	Sigma	Net	K ratio	Line
C	31.66	47.86	0.52	321566	0.0082850	K
O	31.82	36.10	0.74	817219	0.0961439	K
Al	1.28	0.86	0.21	280446	0.0058859	K
Si	13.83	8.94	0.20	3638001	0.0816348	K
Ca	0.73	0.33	0.23	208292	0.0073065	K
Cu	20.68	5.91	0.86	1994449	0.1806154	K
Total	100.00	100.00				

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	48.76	72.58	0.60	2046078	0.2404831	K
Al	6.47	5.71	0.42	961749	0.0201654	K
Si	9.37	7.94	0.40	1632105	0.0365881	K
K*	2.00	1.22	0.36	451077	0.0163339	K
Fe*	1.80	0.77	0.68	242247	0.0146976	K
Cu	31.19	11.69	1.37	2499617	0.2261438	K
Ag*	0.41	0.09	0.80	59150	0.0024603	L
Au	nd	nd				M
Total	100.00	100.00				

A **B**

Figure 6. Electron-raster micrography of fragments of oxidized copper-containing minerals A – 10 microns; B – 100 microns

In addition to the predominant forms of oxidized copper-containing minerals, electron microscopy revealed individual inclusions of sulfide fragments, 1-10 microns in size. In general, the presence of these forms of copper-containing minerals was recorded in insignificant amounts, unlike oxidized ones. Mineral formations with spectra characteristic of copper sulfide minerals are shown in Figure 7.

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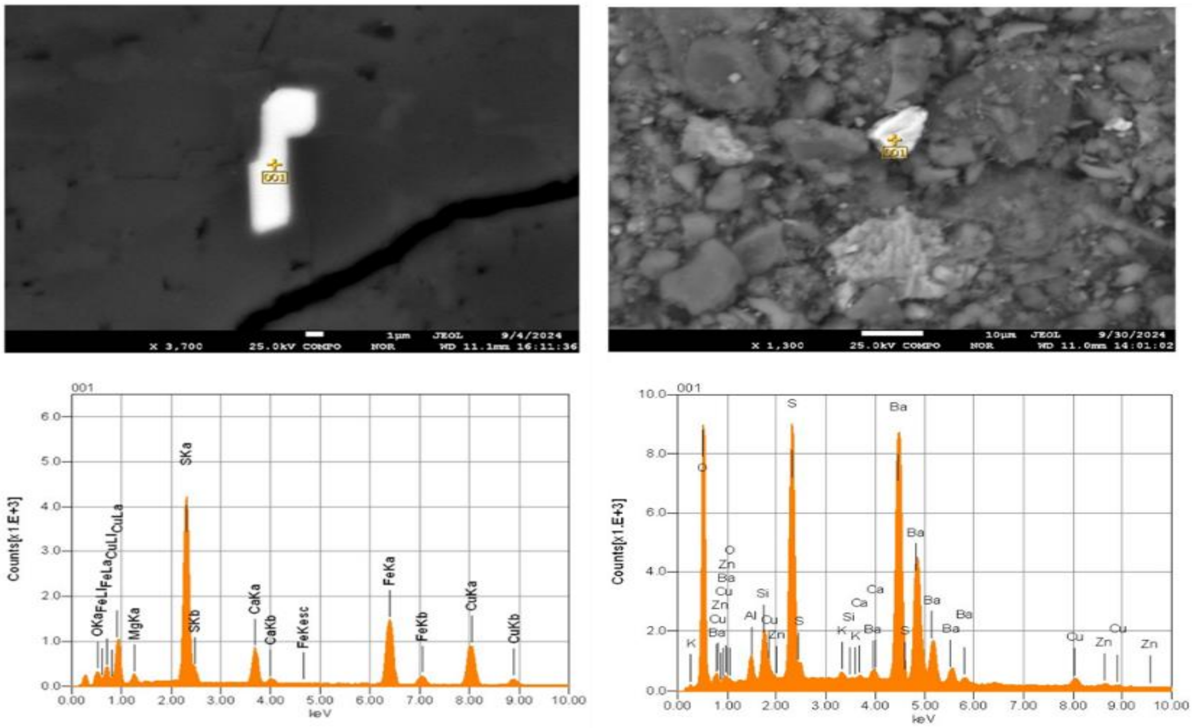

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	8.51	20.93	0.57	47390	0.0244706	K
Mg	2.00	3.24	0.29	46080	0.0043508	K
S	26.37	32.35	0.16	1311837	0.1688380	K
Ca	5.89	5.78	0.22	295478	0.0454923	K
Fe	26.64	18.76	0.39	787531	0.2099183	K
Cu	30.59	18.94	0.76	555433	0.2207689	K
Total	100.00	100.00				

A

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	36.34	72.27	0.60	1526595	0.1793089	K
Al	1.31	1.54	0.43	187297	0.0039246	K
Si	1.65	1.87	0.39	294522	0.0065982	K
S	12.35	12.26	0.29	2621325	0.0767418	K
K*	0.34	0.28	0.36	79707	0.0028844	K
Ca*	0.20	0.16	0.36	48503	0.0016987	K
Cu*	1.44	0.72	1.35	117483	0.0106219	K
Zn*	0.60	0.29	1.64	42729	0.0045188	K
Ba	45.77	10.60	1.04	5807952	0.3698025	L
Total	100.00	100.00				

B

Figure 7. Electron-raster micrograph of fragments of sulfide copper-containing minerals A – 1 micron; B – 10 microns

The build-up of 1 m^3 was carried out within one month with the periodic method of operation of the bioreactor. Unloading the finished product with a high concentration of bacterial cells in a container with a nutrient medium made it possible to maintain the necessary concentration of living cells at a level of at least 2.0 x 10^6 kl/cm^3. The fermenter chan-bio-reactor Selecta was used to increase the bacterial mass with all the necessary components completed following the scheme.

3. Results and discussion

The modern standard technology of heap leaching and liquid extraction of copper is disclosed in detail in a number of works by domestic and foreign researchers (A. Koizhanova et al., 2023). 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. A number of studies have shown the economic advantages of the bacterial leaching process. It was found that during the preliminary bio-treatment of oxidized ores, the percentage of copper extraction increased significantly. It has been shown that the adaptation of bacteria before bioleaching increases the efficiency of the process.

Most often, peptone broths based on protein waste from food production are used as a source of amino acids for the cellular growth of bacterial cultures, in particular A.Ferrooxidans, on an enlarged scale. Adaptation and growth of the strain and the supply of a nutrient medium were carried out at a temperature of 25°C, which is the most favorable for the development of bacterial cells. The influence of the temperature regime factor on the growth and development of bacterial culture A.Ferrooxidans is shown in the diagram in Figure 8.

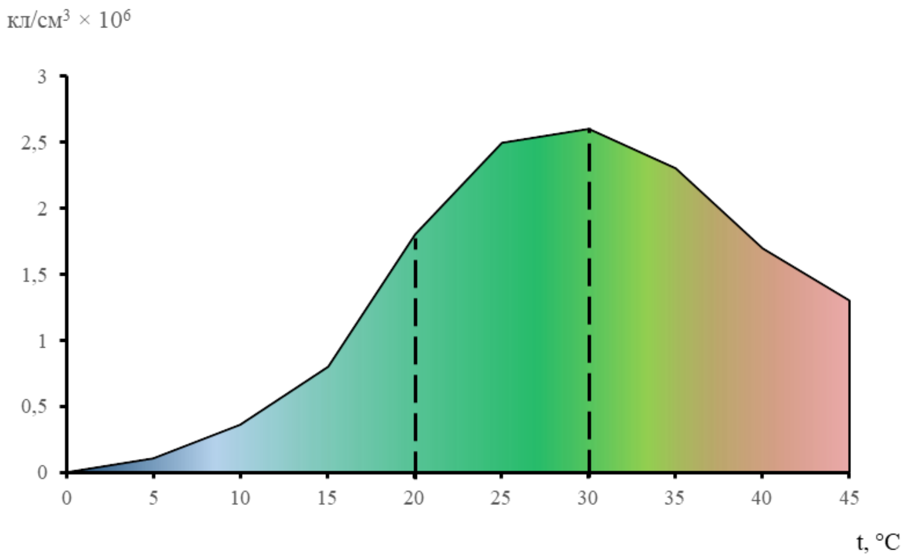

Figure 8. The effect of temperature on the growth of bacterial cells A.Ferrooxidans

The mechanism of biotechnological leaching of metals involves the oxidative treatment of ore material or man-made waste of a mixed type, partially containing metal sulfides. Before treatment with sulfuric acid solutions, viable thionic, iron-oxidizing bacteria are introduced. At the same time, a common problem of hydrometallurgical industries developing copper deposits with a high iron content is the accumulation of excessive concentrations of iron ions in the productive solution. Exceeding the concentration of trivalent iron ions, more than 10 g/l, negatively affects the extraction process, since it reduces the selectivity of the organic extractant for copper, which leads to a deterioration in the quality of the electrolyte and the cathode copper obtained during electrolysis. It is impractical to consider the addition of iron (III) sulfate as an oxidizing reagent in such cases.

Nutrient media for bacterial culture growth included options for the supply of the following amino acids – L-Serine, glycine, asparagine. In the variant with a dosage of sulfanol, its maximum permissible concentration was 1%, in order to exclude active foaming of the pulp. The initial copper content in the ore sample under study was 0.964%. The experiments on the leaching of Zhezkazgan ore included a series of comparative tests, including a standard sulfuric acid solution with a concentration of 2.5%, methods with preliminary biooxidation with a bacterial culture of A.Ferrooxidans grown under various nutrient conditions, as well as a method of processing ore using surfactant sulfanol. The leaching was carried out by the agitation method. The results of agitation leaching of copper off-balance sheet ore from the Zhezkazgan deposit are presented in Table 3.

Table 3. Results of copper leaching from ore deposits

Method	Cake Cu, %	Extraction Cu of cake, %
H_2SO_4 – 2.5 %	0.351	63.59
A. Ferrooxidans + L-Serine, H_2SO_4 – 2.5 %	0.155	83.92
A. Ferrooxidans + glycine, H_2SO_4 – 2.5 %	0.182	81.12
A. Ferrooxidans + asparagine, H_2SO_4 – 2.5 %	0.177	81.64
Sulfanol, H_2SO_4 – 2.5 %	0.321	66.70

The results of experiments on agitation leaching have shown the effectiveness of the use of pre-biooxidation. Thus, with standard leaching with sulfuric acid, only 63.59% of copper was extracted from the ore material, whereas in the method with bacterial oxidation, an increase in extraction was observed by an average of 20.0%. The maximum recovery of 83.92 % was noted during the preliminary oxidation of mineral raw materials by the bacterial culture of A.Ferrooxidans grown with the supply of a nutrient medium containing the amino acids L-Serine. When using amino acid variants such as glycine and asparagine to feed a bio-oxidative culture, the final copper extraction averaged 81.12-81.64%. Processing of the ore material with surfactants allowed a slight increase in copper extraction by 3.11%.

Thus, in order to carry out effective hydrometallurgical processing of off-balance ore from the Zhezkazgan deposit, it is recommended to perform preliminary biooxidation with a bacterial culture of A.Ferrooxidans. To carry out the bio-catalytic process of decomposition of ore minerals represented by sulfides, in particular those containing iron, by the culture of A.Ferrooxidans, it is necessary to select an optimal nutrient medium that provides bacterial cells with amino acids. An experiment conducted in parallel with standard leaching on bacterial oxidation of ore samples showed the possibility of achieving a sufficiently high level of copper extraction – 83.92%. This effect is achieved due to oxidative mechanisms occurring during the associated decomposition of minerals containing sulfur and iron. The sulfide minerals present in the ore sample, in small amounts (pyrite and chalcopyrite), after bacterial oxidative treatment provided partial regeneration of sulfuric acid, which eventually affected the overall level of reagent consumption.

4. Conclusion

Based on the analysis of scientific literature, it has been shown that the role of bacterial methods of opening low-grade ores and man-made raw materials has recently increased. A study of the effect of amino acids on the leaching of copper from low-grade ores has been substantiated. Mineralogical studies of the copper-containing ore of the Zhezkazgan deposit shown that the ore belongs to substandard with a high copper content. In order to carry out effective hydrometallurgical processing of ore from the Zhezkazgan deposit, preliminary biooxidation was performed with a bacterial culture of A.Ferrooxidans. Agitation leaching increases the use of pre-biooxidation effectively. Bacterial oxidation increases the copper extraction significantly compare to standard leaching with sulfuric acid. The maximum recovery of 83.92% was noted during the preliminary oxidation of mineral raw materials by the bacterial culture of A.Ferrooxidans grown with the supply of a nutrient medium containing the amino acids L-Serine.

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Declarations

Author contribution

Kenzhaliyev Bagdaulet Kenzhalievich: Conceptualization, Methodology, and Software. Koizhanova Aigul Kairgeldyevna: Data curation and Writing- Original draft preparation. Bakrayeva Akbota Nurdildakyzy: Visualization and Investigation. Yerdenova Mariya Beisenbekovna: Visualization and Investigation. Magomedov David Rasimovich: Supervision. Abdyldayev Nurgali Nurlanovich: Software and Validation.

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Competing interest

There are no competing interests for all authors.

Ethical Clearance

This research does not involve human subjects.

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