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Study of Copper Leaching Technology from Copper Ores by Biochemical Method

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ABSTRACT

The article presents the research results on the processing of dump ores of copper production from one of the deposits of Kazakhstan. The copper content in various rock formation samples and from different sampling points varies from 0.2 to 0.9%. On average, the calculated copper content on the southern side of the dump was 0.3%, and on the northern side, 0.28%. Phase analysis of the dump samples revealed that the bulk of the rock is represented by quartz, albite, muscovite, clinochlorite, and noticeable amounts of malachite and atacamite were noted from copper dumps in many areas. Detailed mineralogical analysis, in addition to oxidized forms of minerals, also recorded fragments of sulfide mineral formations such as pyrite, chalcopyrite, chalcosine, etc. For this type of deposit, the most effective method of processing will be the use of biohydrometallurgical heap leaching technology. According to percolation leaching, the use of trichloroisocyanuric acid (TCCA) as a chemical oxidant was considered, and an adapted culture of A.Ferrooxidans was also used as a biooxidant. According to percolation leaching, the use of trichloroisocyanuric acid (TCCA) as a chemical oxidant was considered, and an adapted culture of A.Ferrooxidans was also used as a biooxidant. Standard sulfuric acid leaching served as a control option. As a result of the application of the chemical oxidation method using TCCA, an increase in copper extraction into solution compared with other options was observed only during the first 7 cycles. The highest efficiency was observed in the variant of preliminary bacterial oxidation, 76.08% copper was extracted into the productive solution over 28 irrigation cycles. The resulting productive solutions of all variants were subjected to a full technological cycle of hydrometallurgical copper production. As a result of the extraction and re-extraction processes, electrolyte solutions were developed that fully correspond to the qualitative parameters necessary for electrolysis. At the electrolysis stage, 30.8 g of copper was deposited on the cathode from the accumulated electrolyte solutions, which gives a current recovery equal to 94.6%.

Keywords: copper-containing raw materials, biochemical method, leaching, AcidobacillusFerrooxidans, trichloroisocyanuric acid, extraction.

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Introduction

A distinctive feature of most copper deposits in Kazakhstan is the depletion of high-grade ore reserves and the accumulation of off-balance stockpiles containing low copper grades (0.1–0.5%). The processing of such off-balance copper raw materials, predominantly composed of oxidized copper minerals, is typically carried out using conventional hydrometallurgical techniques. These include sulfuric acid leaching, followed by solvent extraction and electrowinning processes.

However, in addition to distinctly sulfide or oxidized copper ores, there exist numerous deposits characterized by complex mineral compositions. In such cases, copper is primarily found in oxidized mineral forms, but the ores also contain significant quantities of pyrite, arsenopyrite, and other iron- and sulfur-bearing compounds. Although oxidized copper minerals dissolve readily in sulfuric acid, the presence of ferrous iron and other sulfides in the ore (or in stockpiles) leads to a substantial increase in acid consumption during hydrometallurgical processing. Moreover, the presence of minerals containing various combinations of iron, calcium, carbonates, and silicates (such as tremolite, clinochlore, calcite, etc.) can also negatively affect the leaching process.

The modern standard technology for copper recovery through heap leaching and solvent extraction has been extensively studied and described by both domestic and international researchers [[1], [2], [3], [4], [5], [6], [7], [8]]. In recent years, increasing attention has been directed toward the use of microorganisms for copper extraction. The term "bacterial leaching" refers to an accelerated biological process for extracting metals from ores.

Numerous studies have demonstrated the economic feasibility of bioleaching. It has been shown that the preliminary bio-treatment of oxidized ores can significantly enhance copper recovery. Furthermore, the pre-adaptation of microorganisms has been found to improve the overall efficiency of the bioleaching process.

The role of *Thiobacillus ferrooxidans* bacteria in the bioleaching of sulfide ores is well established. During biogeotechnological processes, metals are converted from water-insoluble sulfides into water-soluble sulfates. *Thiobacillus ferrooxidans* is capable of oxidizing all metal sulfides. These bacteria obtain the carbon necessary for their growth from carbon dioxide. They thrive in acidic environments (within a pH range of 1.0–4.8) and at temperatures between 3°C and 40°C. The optimal conditions for their growth are a pH of 2–3 and a temperature of 28°C. *Thiobacillus ferrooxidans* can be found in aquatic environments, soils, sulfur deposits, and sulfide ore bodies, but their activity is only observed in the presence of oxygen.

In the biogeotechnological leaching process, sulfide-bearing ore or industrial waste is irrigated with sulfuric acid and ferric salt solutions, followed by the introduction of viable *Thiobacillus ferrooxidans* cultures. To intensify bacterial leaching, oxygen from the air is supplied. As the leaching solution percolates through the sulfide material, metals are transferred into a soluble state. Thus, heap leaching represents an effective method for processing off-balance oxidized copper ores from deposits in the Republic of Kazakhstan. The key parameters of the process are determined experimentally and depend on the chemical and phase composition of the ore.

Both domestic and international practices have demonstrated the use of bacterial cultures as oxidizing agents [[9], [10], [11], [12], [13]]. One of the main advantages of bacterial oxidation is the high efficiency in converting ferrous iron (Fe^{2+}) into ferric iron (Fe^{3+}), along with the relatively low cost of this technology [[14], [15], [16], [17]].

When developing bioleaching technologies, it is essential to consider the sharply continental climate conditions typical of Kazakhstan. Although this technology has been widely adopted in countries such as South Africa, Australia, and Latin American nations, the experience of Finland's Talvivaara company also serves as a notable example. In particular, the implementation of biochemical technology at the Kolmisoppi deposit in 2009–2010 enabled the company to increase production by a factor of 2.7 [[18], [19], [20]].

The object of the study is the bulk ores of copper production at one deposit in Kazakhstan. The purpose of the study is to develop a unique technology that will allow recycling piles, where oxidation minerals are covered with significant inclusions of sulfide minerals and iron–calcium silicates. The use of bacteria as a catalyzing factor for oxidative processes makes it possible to significantly increase the level of transition of copper extraction to a productive solution. Conducting experiments on percolating leaching provides for laboratory simulations of pile leaching. In total, different technological samples were selected, which represent different components of the mound: a rock with significant inclusions of malachite; a sample consisting mainly of a conglomerate; a sample consisting of siltstone; a sample of sandstone, which is more concentrated at the base of the mound.

Experimental Part

Before starting percolation, the main parameters of the leaching process were selected: the concentration of sulfuric acid in the leaching solution was set to 2.5%; the irrigation density was 10 L/m²·h. Additionally, before the main irrigation with sulfuric acid, the sample's moisture saturation and moisture capacity were calculated. The irrigation area is calculated using the following formula: $S = \pi R^2$. After calculating the irrigation surface area and knowing the given irrigation density (L/m²·h), the volume is then calculated.

The loading of ore samples from the waste heap into the percolators was done in the following mass proportions: malachite – 5%, conglomerate – 30%, aleurolite – 40%, sandstone – 25%. All rocks were pre-mixed before loading, and a composite sample was taken. The only exception was sandstone: 10% of the 25% was placed at the bottom of the percolator to simulate the base of the waste heap, and the remaining 15% was evenly mixed with the rest of the ore mass.

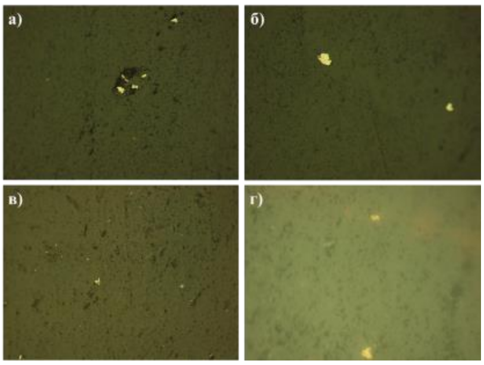
Each rock sample and the composite ore mass for loading were subjected to preliminary X-ray fluorescence analysis. The analysis results are presented in Table 1, where the composition of each individual sample and the composite average sample for the given mass proportions are shown. The theoretical composition of the composite sample was also calculated based on the mass ratios of the samples.

Table 1 – Elemental Composition of Heap Sample Types and Composite Sample for Given Mass Ratios, %

Element	Name of components, %				Mixed sample indicators, %	
	Malachite	Conglomerate	Aleurolite	Sandstone	Actual	Theoretical
O	53.64	50.979	54.209	52.471	50.339	52.777
Na	1.119	1.318	1.802	1.079	1.567	1.4419
Mg	1.246	0.642	1.368	1.331	1.103	1.13485
Al	5.806	3.485	6.789	6.975	4.867	5.79515
Si	22.022	27.846	27.843	25.795	25.708	27.041
P	0.054	0.048	0.062	0.068	0.053	0.0589
S	0.269	0.031	0.116	0.026	0.479	0.07565
Cl	0.012	0.015	0.013	0.015	0.026	0.01405
K	1.147	0.579	1.199	1.662	0.834	1.126
Ca	5.953	5.162	0.855	2.12	3.044	2.718
Ti	0.435	0.239	0.476	0.522	0.312	0.414
V	0.006	0.006	0.007	0.01	0	0.0074
Mn	0.178	0.132	0.066	0.163	0.123	0.116
Fe	2.921	1.38	2.676	3.797	2.289	2.579
Cu	0.448	0.103	0.178	0.028	0.15	0.1315
Zn	0.014	0.007	0.013	0.015	0.024	0.0117
Rb	0.009	0.003	0.007	0.012	0.005	0.00715
Sr	0.011	0.007	0.007	0.014	0.01	0.00895
Zr	0.01	0.006	0.011	0.013	0.01	0.00995
Ba	0	0	0.1	0	0.416	0.04
Pb	0.006	0	0	0.016	0.01	0.0043

The samples were taken from various points and studied using the OLYMPUS BX-51 microscope under reflected light by the mineralogical method. The main part of the sample is composed of gangue minerals. Among the ore minerals, very fine pyrite grains are distinguishable, ranging in size from 0.01–0.05 mm. Pyrite grains are mostly found in their free state, although occasionally they are integrated into the gangue mass. The fine sulfide material retains its characteristic angular and irregular shapes. Chalcopyrite is found in individual grains, with sizes up to 0.02 mm. The images of the sulfide fragments are shown in Figure 1.

After determining the elemental composition, the main phase components, represented by various mineral compounds, were identified in the copper heap samples using X-ray phase analysis. The analysis was carried out on a D8 Advance (BRUKER) diffractometer using Cu – Kα radiation. The results of the X-ray phase analysis are presented in Tables 2 and 3. According to the X-ray phase analysis data, The main part of the rock-forming material in the heap is represented by quartz, which is present in both the northern and southern parts of the heap. Albite, calcite, clinochlore, and muscovite are also found in significant amounts.



a) – Pyrite in gangue material; b) – Free pyrite grains; c) – Very fine pyrite grains;d) – Chalcopyrite grains

Figure 1 – Photographs of the mineralogical analysis of the sample at 400x magnification.

Table 2 – Phase composition results for the northern part of the heap

Name of components	Formula	Proportion in the sample,%		
		Point 1	Point 2	Point 3
Quartz (syn.)	SiO_2	61.5	42.6	63.1
Albit	$Na(AlSi_3O_8)$	18.1	32.5	24.7
Calcite/calcium carbonate	$CaCO_3$	12.2	-	4.4
Muscovite	$H_2KAl_3Si_3O_{12}$	4.9	5.2	3.7
Clinochlor-1MIIb	$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$	3.3	-	4.1
Atakamite	$Cu_2Cl(OH)_3$	-	10.1	-
Hydrosulphate of potassium	$K_3H(SO_4)_2$	-	5.5	-
Potassium sulphite hydrate	$K_2(S_3(SO_3)_2)(H_2O)_{1.5}$	-	4.2	-
hematite (syn)	Fe_2O_3			
thenardite (syn)	Na_2SO_4	-	-	-

Table 3 – Results of the phase composition of the southern side of the mound

Name of components	Formula	Proportion in the sample,%		
		Point 1	Point 2	Point 3
Кварц (syn)	SiO_2	73.9	74.3	64.7
Albit	$NaAl_{0,91}Si_3O_8$	10.2	11.7	14.8
Malachite (syn)	$Cu_2(OH)_2CO_3$	9.1	-	-
Clinochlor -1MIIb, (ferroan)	$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$	4.0	6.7	6.1
Muscovite	$H_4K_2(Al,Fe)_6Si_6O_{24}$	2.7	3.4	5.5
Calcite/calcium carbonate	$CaCO_3$		3.8	8.8

Discussion of Results

As a result, the composite copper ore from the heap was loaded into three percolators, and three percolation leaching variants were studied (Figure 2):

1) Standard sulfuric acid leaching without additional oxidation; 2) Leaching with preliminary bacterial oxidation; 3) Leaching with preliminary chemical oxidation.

Figure 2 – Loaded percolators for three leaching options

The mineral raw material was subjected to oxidation during the moisture conditioning stage. For the bacterial oxidation variant, the percolator was filled with a nutrient solution containing A. ferrooxidans strains, adapted to copper compounds. In the chemical oxidation variant, a 0.5% trichloroisocyanuric acid (TICA) solution was used. In the percolator where leaching was performed without prior oxidation, a 0.5% dilute sulfuric acid solution was used for the conditioning process.

In all three variants, the moisture level was maintained at 10%. After the moisture conditioning and oxidation treatments, the leaching process was initiated. A solution with a 25 g/L concentration of sulfuric acid was supplied via peristaltic pumps at a 10 L/m²·h irrigation rate, by the main leaching density.

After the ore material passed through the percolators, the volume of the resulting pregnant leach solutions was monitored, and the residual sulfuric acid content, along with the copper ion concentration, was analyzed.

The concentration of sulfuric acid in the pregnant solutions was adjusted up to 25 g/L, and their volume was brought to 2 liters, after which they were reused in subsequent leaching cycles.

The first copper extraction was carried out after 17 leaching cycles, at which point the copper concentration in the solution exceeded 3 g/L. Post-extraction leaching was performed using raffinate—the solution remaining after copper was recovered from the pregnant leach solution using an organic extractant.

The second stage of copper extraction occurred during the final phase of the percolation leaching process, specifically after 28 cycles.

The results of the percolation leaching, as well as the copper recovery dynamics from the pregnant leach solution using both conventional and oxidative methods, are presented in Table 4 and Figure 3.

Based on the analysis of the data table and the graphical results, it was found that during the initial stage of leaching (the first seven irrigation cycles), the copper recovery rates remained nearly identical across all systems. In the subsequent days, an increase in the amount of copper transferred into the solution was observed in the chemical oxidation system. However, over time, the efficiency of chemical oxidation began to decline, while the metal recovery rate continued to increase in the bacterial oxidation variant.

When the copper concentration in the solution reached 3–4 g/L, its transfer rate into the secondary pregnant leach solutions temporarily decreased. To restore the intensity of this process, additional experiments on copper extraction and re-extraction were conducted. These methods allowed for the selective separation of dissolved copper from the pregnant solutions and its transfer to the electrolyte phase.

The extraction was carried out using a 10% solution of the copper-selective extractant Lix 984 dissolved in the organic solvent Escaid. During the extraction, the ratio of aqueous to organic phases was 1:1, and during the re-extraction, it was 3:5. Phase separation and settling processes were performed in separatory funnels (Figure 4).

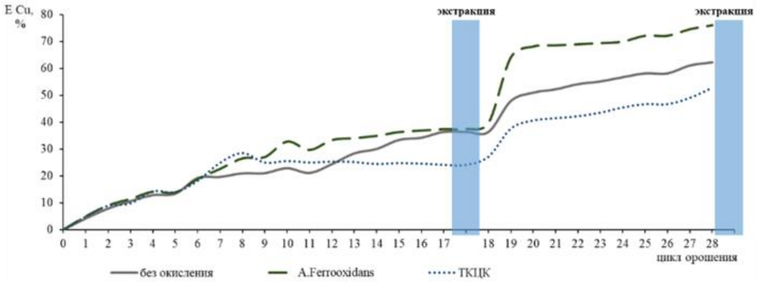


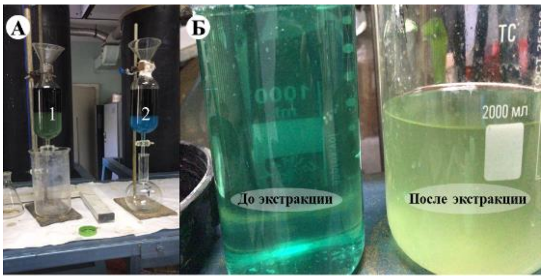
Figure 3 - Dynamics of product release into solution

In the first stage of extraction, 57.45% of the standard sulfuric acid leaching solution was.

From the bacterial oxidation leachate, 66.79% of copper was transferred to the electrolyte, while from the solution treated with the TCIC oxidizing agent (trichloroisocyanuric acid), the transfer reached 69.02%. In addition to the raffinate, a certain amount of copper also remained in the organic phase. This phenomenon is attributed to the one-time copper loss that occurs when freshly prepared organic-phase solutions are used. Such losses are due to the retention of a portion of copper by the organic phase during the extraction process, and this retained copper cannot be completely removed even during the washing stage.

However, no further accumulation of copper in the organic phase was observed – after complete re-extraction, its concentration typically stabilized at 0.2–0.5 g/L.

In the second stage of the extraction process, copper transfer to the electrolyte reached 84.04% for the standard sulfuric acid method, 84.4% for the bacterial oxidation method, and 78.06% for the chemical oxidation method using TCIC. The extraction performance of pregnant leach solutions obtained through different methods is presented in Table 5.



a) separation of aqueous and organic phases
b) in the separation pits:
1– extraction, 2 – re-extraction;
b) color change of the product solution.

Figure 4 - Extraction and re-extraction processes, sedimentation and separation in the funnel

Table 4 – Results of percolation leaching of copper-containing sample

Product solution parameters																				
Cu,g/l	H_2SO_4,g/l	Fe^{3+}, g/l	Fe^{2+}, g/l	V,l	H_2SO_4,ml	E Cu, %	Cu, g/l	H_2SO_4,g/l	Fe^{3+},g/l	Fe^{2+}, g/l	V,l	H_2SO_4, ml	E Cu, %	Cu, g/l	H_2SO_4, g/l	Fe^{3+}, g/l	Fe^{2+},g/l	V,l	H_2SO_4, ml	E Cu, %
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Without oxidation, only H2SO4 25 g/l							A.Ferrooxidans + H2SO4 25 g/							TCCC + H2SO4 25 g/l						
0,5	5.1	1.1	0.2	2.0	22.1	4.17	0.63	3.70	2.3	0.1	2.0	23.67	4.94	0.66	0.00	1.40	0.10	2.0	27.8	4.89
0,94	5.4	1.2	0.2	2.0	21.8	7.83	1.15	5.88	2.5	0.15	2.0	21.24	9.02	1.20	1.08	1.50	0.10	2.0	26.6	8.89
1,41	11.3	1.8	0.2	1.8	16.5	10.58	1.62	11.3	2.7	0.15	1.8	16.48	11.44	1.65	6.80	1.50	0.10	1.6	21.7	9.78
1,54	9.8	2.2	0.2	2.0	16.9	12.83	1.80	10.8	3.3	0.15	2.0	15.78	14.12	1.92	7.35	1.70	0.10	2.0	19.6	14.22
1,78	10.3	2.5	0.3	1.8	17.5	13.35	1.96	12.25	3.3	0.2	1.8	15.53	13.84	2.10	10.10	2.10	0.10	1.8	17.7	14.00
2,3	12.0	2.5	0.3	2.0	14.4	19.17	2.4	16.0	3.3	0.2	2.0	10.00	18.82	2.45	10.80	2.40	0.10	2.0	15.8	18.15
2,35	12.7	2.7	0.3	2.0	13.7	19.58	2.88	14.7	3.5	0.2	2.0	11.44	22.59	3.36	11.20	2.40	0.15	2.0	15.3	24.89
2,51	11.76	3.2	0.3	2.0	14.7	20.92	3.38	13.72	3.5	0.2	2.0	12.53	26.51	3.85	8.82	2.40	0.15	2.0	18.0	28.52
2,65	11.5	3.4	0.3	1.3	19.5	14.35	4.12	16.4	3.6	0.2	1.6	13.20	25.85	3.41	9.80	2.50	0.15	0.8	23.4	10.10
2,74	5.0	3.4	0.3	2.0	22.2	22.83	4.18	12.3	3.6	0.2	2.0	14.11	32.78	3.45	5.00	2.50	0.15	2.0	22.2	25.56
2,81	12.3	3.4	0.3	1.8	15.5	21.08	4.20	13.5	3.6	0.2	1.8	14.28	29.65	3.50	9.00	2.80	0.20	1.3	21.3	16.85
2,92	15.92	3.6	0.3	2.0	10.1	24.33	4.25	17.4	3.8	0.2	2.0	8.44	33.33	3.42	17.60	2.80	0.20	2.0	8.2	25.33
3,4	20.09	3.8	0.3	2.0	5.5	28.33	4.34	19.6	4.3	0.2	2.0	6.00	34.04	3.40	10.29	3.00	0.20	2.0	16.3	25.19
3,6	15.4	4.0	0.3	2.0	10.7	30.0	4.45	16.9	4.3	0.2	2.0	9.00	34.90	3.30	18.40	3.00	0.20	2.0	7.3	24.44
4,0	16.4	4.0	0.3	2.0	9.6	33.33	4.63	15.7	4.5	0.23	2.0	10.33	36.31	3.35	17.40	3.20	0.25	2.0	8.4	24.81
4,1	14.1	4.2	0.3	2.0	12.1	34.17	4.70	16.0	4.5	0.23	2.0	10.00	36.86	3.32	14.50	3.20	0.25	2.0	11.7	24.59
4,36	13.47	4.2	0.33	2.0	12.8	36.33	4.77	16.66	4.5	0.23	2.0	9.27	37.41	3.26	13.72	3.20	0.28	2.0	12.5	24.15
Extraction: 10 % Lix984 / 90 % Escaid							Extraction: 10 % Lix984 / 90 % Escaid							Extraction: 10 % Lix984 / 90 % Escaid						
1,35	25.0	4.5	0.4	2.0	0.0	36.33	1.09	25.0	4.8	0.25	2.0	0.0	39.75	0.52	25.0	3.5	0.3	2.0	0.0	27.17
3,03	12.74	4.5	0.4	1.8	15.0	47.81	4.46	15.2	4.8	0.25	1.8	12.58	64.12	2.03	11.5	3.5	0.3	1.75	16.6	37.64
3,1	19.1	4.5	0.4	2.0	6.6	50.92	4.5	17.64	4.9	0.25	2.0	8.18	68.17	2.14	15.4	3.5	0.32	2.0	10.67	40.67
3.25	19.6	4.7	0.5	2.0	0.0	52.17	4.55	26.95	4.9	0.25	2.0	0.0	68.58	2.24	26.0	3.5	0.3	2.0	0.0	41.5
3.48	10.3	4.7	0.5	2.0	16.3	54.08	4.6	17.15	5.0	0.25	2.0	8.72	69.0	2.33	12.25	3.5	0.3	2.0	14.17	42.25
3.79	14.2	4.75	0.5	2.0	12.0	56.67	4.72	18.4	5.1	0.25	2.0	7.33	70.0	2.72	14.7	3.7	0.35	2.0	11.44	45.5
3.6	14.7	4.7	0.5	2.0	11.4	55.08	4.65	17.15	5.0	0.25	2.0	8.72	69.42	2.49	15.2	3.55	0.3	2.0	10.89	43.58
3.96	17.2	4.9	0.5	2.0	0.0	58.08	4.98	17.2	5.1	0.25	2.0	0.0	72.17	2.87	17.2	3.7	0.35	2.0	0.0	46.75
4.2	18.86	4.9	0.55	1.8	8.9	56.58	5.11	20.3	5.2	0.28	1.8	7.48	68.99	3.02	18.4	3.7	0.35	1.8	9.38	45.48
4.31	15.93	4.95	0.55	2.0	0.0	61.0	5.27	18.13	5.2	0.28	2.0	0.0	74.58	3.15	14.7	3.9	0.35	2.0	0.0	49.08
4.45	10.29	5.09	0.6	2.0	16.3	62.17	5.45	17.15	5.2	0.28	2.0	8.72	76.08	3.6	10.29	3.9	0.38	2.0	16.34	52.83

Table 5 – Copper balance during extraction and re-extraction process

	Solution parameters								
	Without oxidation, only H2SO4 25 g/l			A.Ferrooxidans + H2SO4 25 g/			TCCC + H2SO4 25 g/l		
Өнім атауы	Cu, g/l	V, l	%	Cu, g/l	V, l	%	Cu, g/l	V, l	%
Extraction 1									
PLS (productive solution)	4.36	2.0	100.00	4.77	2.0	100.00	3.26	2.0	100.00
Raf (mixed solution)	1.35	2.0	31.0	1.09	2.0	22.9	0.52	2.0	16.0
Organic	2.02	0.5	11.6	1.976	0.5	10.4	1.96	0.5	15.0
Electrolyte	16.7	0.3	57.45	21.24	0.3	66.79	15.0	0.3	69.02
Cu from circulation, g	6.02			7.36			5.48		
Extraction 2									
PLS (productive solution)	4.45	2.0	100.00	5.45	2.0	100.00	3.6	2.0	100.00
Raf (mixed solution)	0.6	2.0	13.5	0.8	2.0	14.7	0.7	2.0	19.4
Organic	0.44	0.5	2.5	0.2	0.5	0.9	0.36	0.5	2.5
Electrolyte	45.0	0.3	84.04	55.2	0.3	84.40	37.0	0.3	78.06
Cu from circulation,gr	13.72			16.66			11.28		

The copper concentration in the obtained electrolytes met the required parameters (at least 30 g/L, not exceeding 60 g/L). All produced electrolytes were used in the next technological stage – copper electrowinning in an electrolytic cell. For the deposition process, a copper cathode with an initial mass of 94.2 g was used, while insoluble lead plates served as anodes. The electrochemical equivalent of copper is A = 0.329 mg / (A·s). The electrolysis process lasted for 11 hours. The theoretical yield of metal during electrolysis was calculated using the following formula:

$$G = A \cdot I \cdot t \qquad (1)$$

where:
G – the mass of the deposited substance,
I – electric current, A,
t – time, s.

$$G = 0.329\ \text{mg/(A·s)} \times 2.5\ \text{A} \times 11 \times 60 \times 60 = 32{,}571\ \text{mg} = 32.571\ \text{g} \qquad (2)$$

After the electrolysis process was completed, the cathode mass increased to 125 g (Figure 4). Thus, 30.8 g of copper was deposited on the cathode. The current efficiency of copper deposition was calculated as:

$$E_{Cu} = G\_actual / G\_theoretical \times 100\% = 30.8 / 32.571 \times 100\% = 94.6\%$$

Conclusion

Thus, the material composition of copper-bearing mineral raw materials was studied, and sampling from the heap was carried out. The bulk of the heap rock consists of conglomerates, siltstone, and sandstone, while the copper minerals identified include malachite, chalcopyrite, and atacamite. The copper content in various lithological samples and samples taken from different points of the heap ranged from 0.2% to 0.9%. On average, the estimated copper content was 0.3% in the southern part of the heap and 0.28% in the northern part.

Phase analysis of the heap samples showed that the primary mass of the rock is composed of quartz, albite, muscovite, and clinochlore. In certain zones, a significant presence of malachite and atacamite was found as copper-bearing minerals. Detailed mineralogical analysis revealed the presence of both oxidized copper minerals and sulfide mineral formations such as pyrite, chalcopyrite, chalcocite, and other compounds. Hence, the study of the chemical, phase, and mineralogical composition of copper-bearing materials from the heap revealed the heterogeneous distribution of copper in various mineral forms, as well as the presence of associated impurity elements.

In the percolation leaching process, trichloroisocyanuric acid (TCCA) was used as a chemical oxidant, while an adapted culture of *A. ferrooxidans* bacteria was used as a bio-oxidant. The standard sulfuric acid leaching method served as a control. The use of the TCCA-based chemical oxidation method resulted in a higher copper recovery during the first seven leaching cycles compared to the other methods. However, over time, the effectiveness of chemical oxidation gradually declined, and by the end of 28 leaching cycles, the copper recovery reached 52.83%. During the same period, sulfuric acid leaching yielded 62.17% copper recovery. The highest efficiency was observed in the bio-oxidation method using bacteria, where 76.08% of copper was transferred to the pregnant leach solution after 28 irrigation cycles.

The pregnant leach solutions obtained from all three methods were subjected to the complete hydrometallurgical processing cycle. As a result of the extraction and re-extraction stages, electrolyte solutions that fully met the quality parameters required for electrowinning were obtained. During the electrolysis stage, 30.8 g of copper was deposited on the cathode from the electrolyte solution, corresponding to a current efficiency of 94.6%.

During the experiments, the optimal conditions for the growth of *A. ferrooxidans* bacterial culture, adapted to the chemical composition of copper-containing mineral raw materials, were determined. The results showed that for effective bio-oxidation of mineral raw materials, the initial bacterial solution used in the pretreatment should maintain a pH level not lower than 1.5. An increase in pulp acidity and a drop in pH below 1.2 negatively affect the viability of bacterial cells.

The optimal temperature range for the growth and development of *A. ferrooxidans* culture was found to be between 20–30 °C. Under the most favorable conditions (pH = 2.3, temperature = 20–30 °C), the concentration of bacterial cells increased from 0.1×10^6 cells/cm^3 to 2.8×10^6 cells/cm^3.

The catalytic mechanisms by which microorganisms influence the oxidation of sulfide minerals in copper-bearing raw materials were also identified. The presence of the bacterial culture as a catalytic factor significantly accelerates the decomposition rate of sulfide minerals, particularly those containing copper (e.g., chalcopyrite, chalcocite, etc.).

The best selectivity results were observed when using an extractant from the LIX984 series:

The highest copper extraction from solution was 94.0%; The lowest iron co-extraction was 0.83%.

Based on the evaluation of copper-loading capacity of the organic phase, the optimal flow ratio between the pregnant leach solution and the organic phase was determined to be O:A = 1:2. If the ratio exceeds O:A > 1:5, the viscosity of the organic phase increases due to oversaturation, which in some cases may lead to the formation of stable emulsions or phase separation issues.

Conflict of interest. On behalf of all the authors, the correspondent author declares that there is no conflict of interest.

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Мыс кендерінен мысты биохимиялық әдіспен шаймалау технологиясын зерттеу

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ТҮЙІНДЕМЕ

Мақалада Қазақстанның бір кен орнында мыс өндірісінің үйінді кендерін қайта өңдеу бойынша зерттеу нәтижелері ұсынылған. Әртүрлі жыныстардан алынған сынамалардағы мыстың мөлшері 0,2-0,9 % аралығында өзгереді. Орташа есеппен үйіндінің оңтүстік жағында мыс мөлшері 0,3 %, солтүстік жағында – 0,28 % құрайды. Үйінді сынамаларын фазалық талдау жыныстың негізгі массасы кварц, альбит, мусковит, клинохлордан тұратынын көрсетті, ал кейбір учаскелерде мыс минералдары – малахит және атакамиттің айтарлықтай мөлшері анықталды. Минералогиялық зерттеу барысында тотығу түрлерімен қатар, сульфидті минералдардың (пирит, халькопирит, халькозин және т.б.) бөлшектері де табылды. Бұл кен орындары үшін ең тиімді қайта өңдеу әдісі ретінде үйінділік шаймалаудың биогидрометаллургиялық технологиясын қолдану ұсынылады. Перколяциялық шаймалау барысында химиялық тотықтырғыш ретінде трихлоризоцианур қышқылын (ТХЦҚ) қолдану мүмкіндігі зерттелді, ал биооксидант ретінде A. Ferrooxidans бейімделген дақылы пайдаланылды. Бақылау нұсқасы ретінде стандартты күкіртқышқылды шаймалау жүргізілді. ТХЦҚ негізінде химиялық тотықтыру әдісі қолданылған кезде, мыс алу көрсеткіші басқа нұсқалармен салыстырғанда тек алғашқы 7 цикл ішінде жоғары болды. Ең жақсы нәтиже алдын ала бактериялық тотықтыру кезінде байқалды, 28 сулау циклының ішінде өнімді ерітіндіге мыстың 76,08 %-ы өтті. Барлық нұсқалардың алынған өнімді ерітінділері мыс гидрометаллургиясының толық технологиялық циклынан өтті. Экстракция және реэкстракция процестері нәтижесінде электролиз жүргізуге қажетті сапалық параметрлерге толық сәйкес келетін электролит ерітінділері алынды. Электролиз сатысында алынған электролит ерітінділерінен катодта 30,8 г мыс тұндырылды, бұл ток бойынша бөліп алу дәрежесін 94,6 % жеткізді.

Түйін сөздер: құрамында мыс бар шикізат, биохимиялық әдіс, шаймалау, Acidobacillus Ferrooxidans, трихлоризоцианур қышқылы, экстракция.

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Исследование технологии выщелачивания меди из медных руд биохимическим методом

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АННОТАЦИЯ

В статье представлены результаты исследований по переработке отвальных руд медного производства одной из месторождений Казахстана. Содержание меди в пробах различного породообразования и взятых из разных точек отбора варьируется от 0,2 до 0,9 %. В среднем по южной стороне отвала расчетное содержание меди составило 0,3 %, по северной – 0,28

%. Фазовым анализом проб отвала установлено, что основная масса породы представлена кварцем, альбитом, мусковитом, клинохлором, из медных отвалов в ряде участков отмечены заметные количества малахита и атакамита. Подробным минералогическим анализом, помимо окисленных форм минералов, зафиксированы также фрагменты сульфидных минеральных образований, таких как пирит, халькопирит, халькозин и др. Для данного типа месторождений наиболее эффективным методом переработки будет использование биогидрометаллургической технологии кучного выщелачивания. По перколяционному выщелачиванию в качестве химического окислителя был рассмотрен вариант применения трихлоризоциануровой кислоты (ТХЦК), в качестве биоокислителя также использовалась адаптированная культура A.Ferrooxidans. По перколяционному выщелачиванию в качестве химического окислителя был рассмотрен вариант применения трихлоризоциануровой кислоты (ТХЦК), в качестве биоокислителя также использовалась адаптированная культура A.Ferrooxidans. Стандартное сернокислотное выщелачивание служило в качестве контрольного варианта. В результате применения химического метода окисления с использованием ТХЦК рост извлечения меди в раствор по сравнению с другими вариантами, наблюдался только в течение первых 7 циклов. Наибольшая результативность наблюдалась в варианте предварительного бактериального окисления, за 28 циклов орошения в продуктивный раствор было извлечено 76,08% меди. Полученные продуктивные растворы всех вариантов подвергались полному технологическому циклу гидрометаллургического производства меди. В результате процессов экстракции и ре-экстракции были наработаны растворы электролитов, полностью соответствующие качественным параметрам необходимым для проведения электролиза. На стадии электролиза из наработанных растворов электролитов было осаждено на катоде 30,8 г меди, что дает извлечение по току равное 94,6 %.

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