Հայաստանի Գիտությունների Ազգային Ակադեմիա
Национальная Академия Наук Армении
National Academy of Sciences of Armenia

Հայաստանի Կենսաբանական Հանդես
Биологический Журнал Армении
Biological Journal of Armenia

• Փորձարարական և տեսական հոդվածներ • Экспериментальные и теоретические статьи •
• Experimental and theoretical articles •

Biolog. Journal of Armenia, 3 (72), 2020

BIOHYDROMETALLURGICAL PROCESSING OF LOW-GRADE COPPER-MOLYBDENUM ORE

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The treatment of low-grade ores which is considered as an important source of non-ferrous and precious metals requires the development of high-efficient technologies for metal extraction ensuring low impact on environment. The goal of the present work was to study the possibilities of application of biohydrometallurgical approach for the processing of Kajaran low-grade copper-molybdenum ore. Sulfide and oxidized ore samples containing 0.63 and 0.77 % of copper, 1.81 and 1.55 % of iron and 0.14 and 0.023 % of molybdenum, respectively were used. The experiments were carried out in 250 ml flasks under shaking conditions as well as glass columns. Indigenous and adapted bacterial consortia "Kajaran" and "Kavart" were used for bioleaching of ore samples. The influence of particle size (PS), pulp density (PD), adaptation of culture on the process of copper extraction was studied.

Sulfide and oxidized ores – bacterial consortia – adaptation – copper extraction – column bioleaching

Ցածրորակ հանքաքարերի մշակումը, որոնք համարվում են գունավոր և թանկարժեք մետաղների կարևոր աղբյուր, պահանջում է մետաղների կորզման բարձրարդյունավետ տեխնոլոգիաների մշակում՝ միաժամանակ ապահովելով շրջակա միջավայրի վրա նվազագույն ազդեցություն: Սույն աշխատանքի նպատակը եղել է Քաջարանի ցածրորակ պղնձամոլիբդենային հանքաքարի մշակման համար կենսաhիդրոմետալուրգիական մոտեցման կիրառման հնարավորությունների ուսումնասիրությունը: Օգտագործվել են սուլֆիդային և օքսիդացած հանքանմուշները՝ պղնձի 0.63 և 0.77 %, երկաթի 1.81 և 1.55 %, մոլիբդենի 0.14 և 0.023 % պարունակությամբ, համապատասխանաբար: Փորձերն իրականացվել են 250 մլ կոլբաներում՝ թափահարման պայմաններում, ինչպես նաև լաբորատոր ապակյա աշտարակներում: Յանքաքարի նմուշների կենսատարրալուծման համար օգտագործվել են «Կաշեն» և «Կավարտ» վայրի և ադապտացված բակտերիալ կոնսորցիումները: Ուսումնասիրվել է մասնիկների չափի, ապարախյուսի խտության, բակտերիաների ադապտացման ազդեցությունը պղնձի կորզման գործընթացի վրա:

Սուլֆիդային և օքսիդացած հանքաքարեր – բակտերիաների կոնսրցիումներ – ադապտացում – պղնձի կորզում – աշտարակային տարրալուծում

Обработка низкосортных руд, которые считаются важным источником цветных и драгоценных металлов, требует разработки высокоэффективных подходов к извлечению металлов, обеспечивающих минимальное воздействие на окружающую среду. Целью настоящей работы было изучение возможностей применения биогидрометаллургического подхода при переработке Каджаранской низкосортной медно-молибденовой руды.

Использовались образцы сульфидной и окисленной руды, содержащие 0,63 и 0,77% меди, 1,81 и 1,55% железа и 0,14 и 0,023% молибдена соответственно. Эксперименты проводились в колбах на 250 мл в условиях встряхивания а также в лабораторных стеклянных колонках. Для биовыщелачивания образцов руды были использованы дикие и адаптированные бактериальные консорциумы "Кашен" и "Каварт". Изучено влияние размера частиц, плотности пульпы, адаптации культур бактерий на процесс извлечения меди.

Сульфидные и окисленные руды – бактериальные консорциумы – адаптация- извлечение меди – биовыщелачивание в колонках

Bioleaching is a biohydrometallurgical process which is mainly applied for the treatment of low-grade ores (eg copper, zinc) with acidic solution and microorganisms [1-3]. Recently, low-grade ores are considered as an important source of copper connected with rapid depletion of high-grade ores [4, 5]. It is important to note that copper in ores mainly exists as primary mineral chalcopyrite ($CuFeS_2$). Chalcopyrite is one of the most difficult minerals to be treated by bioleaching technology. Therefore, the processing of such kind of ores requires the development of high-efficient approaches. It is considered that bioleaching of sulfide minerals occurs by indirect non-contact and contact mechanisms via ferric ion [6, 7]. Oxidation of chalcopyrite by ferric ion (indirect mechanism) resulted in the generation of ferrous ion and elemental sulfur can be presented by the reaction 1:

$$CuFeS_2 + 2Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 5\,FeSO_4 + 2S^0 \quad (1)$$

Thus, the contribution of microorganisms to the bioleaching of chalcopyrite is the regeneration of oxidant – ferric ion (Fe^{3+}) and ensuring low pH condition [8-10]. Iron and/ or sulfur oxidizing bacteria involved in bioleaching processes such as *Acidithiobacillus ferrooxidans, Acidithiobacillius thiooxidans, Leptospirillum ferrooxidans, L. ferriphilum* catalyze oxidation of ferrous ions and sulfur to ferric ions (equation 2) and sulfuric acid (equation 3) respectively, that in turn significantly increases the overall reaction rate of chalcopyrite biooxidation (Equation 1);

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{\text{bacteria}} 4Fe^{3+} + 2H_2O \quad (2)$$

$$2S + 3O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2SO_4^{2-} + 4H^+ \quad (3)$$

The oxidation of pyrite could be served as a source of ferrous ion according to following reaction:

$$FeS_2 + 8H_2O + 14Fe^{3+} \longrightarrow 5Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

Indirect contact mechanism presumes attachment of bacterial cells to mineral surfaces that allows considerably increasing the rate of chalcopyrite bioleaching [11, 12]. The optimal growth and bioleaching activity of bacteria is strongly affected by physico-chemical factors such as pH, substrate concentration, particle size, as well as bacterial cell adhesion, adaptation and other properties [13-17].

The goal of the present work was to study the possibilities and effectiveness of bioleaching for the processing of Kajaran low-grade copper-molybdenum ore. The influence of particle size (PS), pulp density (PD), adaptation of culture on the process of copper extraction from tested ore samples was investigated.

Materials and methods. *Ore samples.* Sulfide and oxidized samples of Kajaran copper-molybdenum ore were used for the present investigation. The chemical composition of the ore samples was determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The results of ICP-MS analysis is shown in tab. 1.

Table 1. Chemical composition of the analyzed ore samples

N	Samples	**Mo** $_{Total}$**, %**	**Cu** $_{Total}$**, %**	**S** $_{Total}$**, %**	**Fe** $_{Total}$**, %**	**SiO$_2$** $_{Total}$**, %**
1	Oxidized ore	0,023	0,77	0,49	0,49	1,55
2	Sulfide ore	0,145	0,63	1,3	1,3	1,51

The mineral composition of ore samples was studied in reflected light by polarizing microscope up to 400 times magnification. Sulfide ore mineral composition was found to be as follows: pyrite (euhedral)>>> chalcopyrite (anhedral) >bornite. Oxidized ore was comprised of chalcopyrite (anhedral, replaced on margins by iron oxihydroxides), pyrite (partly euhedral) and galena embedded in malachite. Malachite is supposed to replace chalcopyrite, while hematite represents a typical replacement of pyrite.

Indigenous consortia of iron oxidizing bacteria. Acidophilic iron oxidizing bacterial consortia “Kashen” and “Kavart” used in this study for the bioleaching of sulfide and oxidized ores were obtained from acid mine drainage water of the appropriate copper ore deposits in Armenia using enrichment technique. The consortia originally contained acidophilic sulfur oxidizing *At.thiooxidans,* iron oxidizing *At. ferrooxidans* and *Leptospirillum* spp. bacteria. The optimum pH and temperature ranges at which suitable growth of the isolated bacterial consortia has been observed, are 1.8-2.0 and 30-35°C, respectively. The bacterial consortia were cultivated and maintained in Mackintosh medium with ferrous iron as the source of energy [18].

Culture preparation. Bacterial consortia were transferred to Mackintosh medium containing additionally 100 mg/L dissolved Cu and grown for 3-5 days prior to ore leaching tests. In the logarithmic phase of growth the cells were collected by centrifugation at 6000g for 15 min. Biomass collected was washed with acidified Mackintosh medium without Fe^{2+} and resuspended in the same medium. Bacterial cell number was determined by phase contrast microscopy using a Thoma counting chamber, as well as by the method of tenfold dilutions. The most probable number (MPN) of cells was calculated using the McCready Tables.

Bioleaching of ore samples. Sulfide and oxidized samples of Kajaran low-grade copper-molybdenum ore were tested for bioleaching. The samples were ground in a porcelain mortar to reach a size range between -3500 + 45μm. The ore samples were passed through sieves to obtain fractions of different sizes. Mineral grains were placed into Erlenmeyer’s flasks (250 ml), moistened with water, and sterilized at 0.5 atm. for 30 min. Then 100 ml Mackintosh medium without Fe^{2+} pH adjusted to 2.0 with 10 N H_2SO_4 was added. Consortia (bacterial suspension - 10^8cells/ml) of “Kashen” and “Kavart” used for the bioleaching of ore samples were added to the flasks. The bioleaching experiments were carried out at 37°C in the periodic mode and under shaking conditions (170 rpm). Bioleaching of sulfide and oxidized ore samples was studied in the range of pulp density from 10 to 20 % and particle sizes of 45-3500 μm. The pulp density was calculated as the ratio between solid and liquid. Sampling was performed at 24 h intervals and pH, iron and copper ions were analyzed. The concentration of dissolved copper in the leaching solution was determined by atomic absorption spectrometry (AAS 1N). The content of Fe^{2+} and Fe^{3+} was determined by the complexometric method with EDTA. The efficiency of bioleaching ore samples was assessed according to dissolved iron and copper.

Column bioleaching. At the next stage of investigation the bioleaching of ore samples was carried out in glass columns (percolators) with 35 mm in diameter and 220-230 mm in height using “Kashen” and “Kavart” microbial consortia. Class columns were loaded with oxidized ore samples with PS varying in the range of 0.8-3.5 mm and 9K medium (1:1). Percolation was supplied by microcompressors. The experiments were performed at two stages. At the end of the first stage pregnant sulutions were replaced with fresh medium.

Results and Discussion. *Influence of particle size.* The influence of particle size of ore samples on the bioleaching of copper by bacterial consortia was studied in the range of 45-3000 μm (fig. 1).

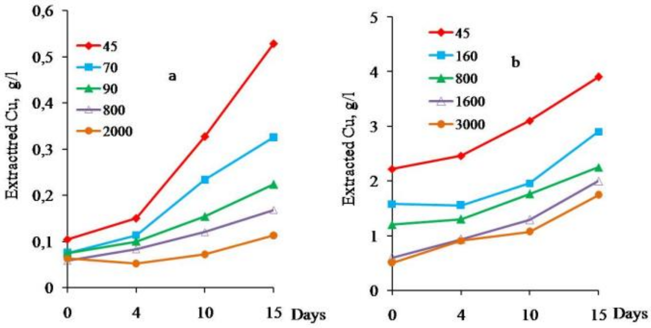

Fig.1. Effect of particle size on bioleaching of copper by "Kashen" consortium from sulfide (a) and oxidized (b) ores of Kajaran deposit (PD – 20%, pH –1.8; t – 35^{0}C, 180 rpm)

As presented in fig. 1, the rates of copper dissolution increased with decreasing particle size from 3000 μm to size fraction of +45 μm. The obtained results showed that the highest efficiency of copper extraction for both sulfide and oxidized ore samples was observed at PS of 45 μm. It can be explained that the decrease in the particle size leads to an increase in the total surface area and consequently, the rate of sulfide mineral oxidation and extent of copper dissolution.

Influence of pulp density (PD). In fig. 2 the effect of pulp density on copper extraction during the bioleaching of sulfide and oxidized ore samples is presented. Pulp densities of 10 and 20 % were tested. Data presented show that the amount of copper transferred into the solution by both bacterial consortia increases about 2-3 times with the increasing of PD from 10 to 20% (fig. 2).

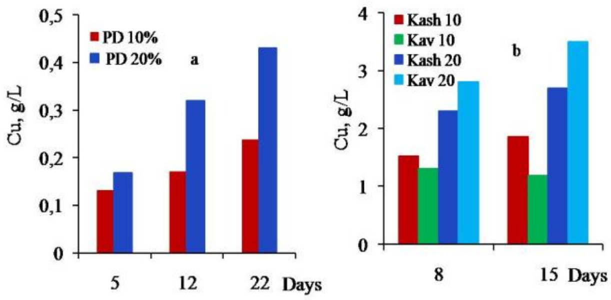

Fig.2. Recovery of copper from sulfide ore by "Kashen" consortium (a) and oxide ore by "Kashen" and "Kavart" consortia at pulp density of 10 (Kash 10, Kav 10) (b) and 20 % (Kash 20, Kav 20) (b) (PS – 63 μm, t – 30 °C , 160 rpm)

However the extent of total copper extraction from sulfide and oxidized ore samples at pulp density of 10 % is higher than at 20 % (tab. 2). It is suggested that the pulp density has an important influence on the dissolution rate of samples because the higher pulp density leads to the higher shearing force while the lower pulp density cannot provide enough energy for the growth of bacteria. Besides, high pulp density can enhance metal extraction but the dissolution of certain compounds which have an enhance metal extraction but the dissolution of certain compounds which have an inhibitory toxic effect on the growth of leaching bacteria will also increase.

Copper extraction by isolated bacterial consortia. Comparative studies of the activities of bacterial consortia "Kashen" and "Kavart" isolated from the corresponding mines in bioleaching of copper from tested ore samples were performed. Testing of different cultures for copper extraction was carried out at pulp densities of 10 and 20 %.

Table 2. Influence of pulp density on bioleaching of copper from Kajaran ore samples by consortia "Kashen" and "Kavart" (PD – 10, 20 %, t – 30^{0}C, 160 rpm)

N	Ore Samples	Pulp density	Bacterial consortia	Extracted Cu		
				mg/L for 15 days	mg/L for 22 days	% 22 days
1	Sulfide ore	10%	"Kashen"	235	261	41,3
2			"Kavart"	202	231	36,5
3		20%	"Kashen"	401	433	34,4
4			"Kavart"	318	334	26,5
5	Oxide ore	10%	"Kashen"	1257	1424	100
6			"Kavart"	1193	1193	100
7		20%	"Kashen"	1732	2677	100
8			"Kavart"	2355	3007	100

As shown in the presented data, "Kashen" consortium indicated higher activity of copper extraction from sulfide ore at 20 % of PD and both tested ore samples at 10 % of PD. (tab. 2). While "Kavart" culture was more active in bioleaching of oxidized ore samples at 20% of PD (fig 2b, tab. 2). It is suggested that the pulp density has an important influence on the dissolution rate of samples because the higher pulp density leads to the higher shearing force while the lower pulp density could not provide enough energy for the growth of bacteria. It is worth mentioning that high pulp density can enhance metal extraction but the dissolution of certain compounds which have an inhibitory toxic effect on the growth of leaching bacteria will also increase.

Copper extraction by adapted bacterial consortia. In the next series of the experiment on bioleaching, "Kashen" and "Kavart" consortia adapted to the tested samples by several passaging in the presence of gradually increasing concentrations of ores were used.

Table 3. Bioleaching of copper from sulfide ore sample by adapted consortia "Kashen" and "Kavart" (PD – 10 and 20 %, t – 30^{0}C, 160 rpm)

N	Ore Samples	Consortia used	Pulp density	Extracted Cu		
				mg/L Initial	mg/L 15 days	% 15 days
1	Sulfide ore	-	10 %	99,2	531	84 %
2		"Kashen"	10 %	111	598	94 %
3		"Kavart"	10 %	99,2	581	91 %
4		-	20 %	81,3	631	50,1 %
5		"Kashen"	20 %	123	1242	98,6 %
6		"Kavart"	20 %	75,4	763	60,5 %

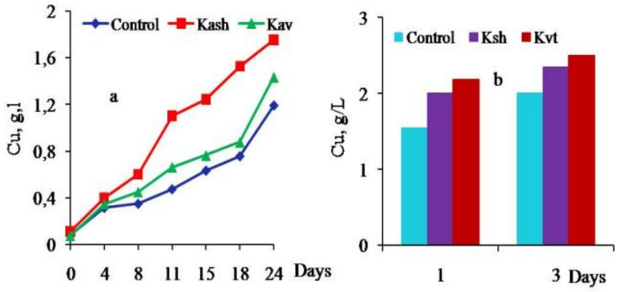

Fig.3. Bioleaching of copper from sulfide (a) and oxidized (b) ore samples by adapted consortia "Kashen" and "Kavart" (PD-20 %, t - 30 ^{o}C, 160 rpm)

The results obtained show that the use of adapted bacterial consortia allows to increase copper extraction from sulfide ore up to 5 times, reaching 91-94 % at a density of 10 % pulp and 98 % at a density of 20 % in 15 days (tab. 3, fig 3a).

In the case of oxidized ore, copper extraction is increased by about 2 times through adapted consortia, reaching 100 % in 2-3 days (fig. 3b). Thus, the extent of copper extraction from tested ore samples significantly increases (up to 94-100 %) when adapted bacterial consortia are used.

Column bioleaching. At the next stage of investigation the bioleaching of ore samples was carried out in glass columns (percolators) using "Kashen" and "Kavart" microbial consortia. The experiments were performed at two stages. At the end of the first stage pregnant sulutions were replaced with fresh medium. The obtained results showed that for 13 days of bioleaching 18 and 26-28 % of copper was extracted in the absence and presence of microbial consortia "Kashen", respectively (fig. 4). At the second stage additional 37-49 % of copper was extracted by microbial consortia.

Investigations showed that the column bioleaching was greatly affected by PS. Thus, the reduction of PS to 0.8-1.6 mm led to the increase of copper extraction from oxidized ores by about 3 times and reached 100 % in 9-12 days compared with that of control without bacteria (84 %). The results suggest that bacterial leaching can be an effective approach for the treatment of low-grade copper-molybdenum ores and is a promising method for copper extraction.

Fig.4. Biolaching of oxidized ore by "Kashen" consortia: 1- control without bacteria, 2, 3-uninoculated by "Kashen" consortium (PD- 150: 120, pH 1.3, at room temperature)

The obtained results showed that the highest efficiency of copper bioleaching by the used bacterial consortia was observed at PS of 45 μm and PD of 20 % for both sulfide and oxidized ore samples. Besides, "Kashen" culture showed higher activity of copper extraction from both tested ore samples at 20 % of PD. "Kavart" culture was more active in bioleaching of oxidized ore samples at 10 % of PD. It was revealed that the use of adapted cultures allowed increasing the extent of copper extraction up to 91-94 % and 98 % from sulfide ore within 15 days at 10 and 20 % of PD. In case of the oxidized ore, the extent of copper extraction by the mentioned adapted cultures was doubled, reaching 100 % in 2-3 days. Experiments carried out in percolators suggested that bacterial leaching can be effectively applied for the processing of Kajaran low-grade copper-molybdenum ore and copper extraction.

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Received on 10.05.2020