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Bacterial and chemical leaching of copper containing ores with the possibility of subsequent recovery of trace silver

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Abstract

This investigation compares bacterial leaching to chemical leaching to solubilize copper from a copper containing ore of the new site *Northern Qarashoshaq* in *Zhylandy* (Kazakhstan) which is currently under commercial development. From ICP-OES analysis the bulk ore sample contains 1.5% of Cu and a trace level at 0.0024 % of Ag. Phase analysis shows the main copper containing minerals are covellite, chalcocite, malachite, chrysocolla and chalcopyrite. According to X-ray diffraction analysis silver is mainly presented as jalpaite (Ag_3CuS_2) minerals. Copper leaching was carried out by acidophilic bioleaching for comparison with extraction by chemical methods involving the addition of sulfuric acid and Fe^{3+} or only sulfuric acid in flasks, as well as column leaching tests to simulate heap leaching. Ag was extracted by cyanidation methods again in flasks as well as column leaching tests. Results showed that copper extraction is up to 95% when using bioleaching in the flask, 83% in the case of Fe^{3+} with sulfuric acid and 76% for sulfuric acid. Furthermore, subsequent extraction of Ag reaches 97% for bioleaching and 92% for chemical leaching. Column bioleaching tests showed an 82.3% yield of copper after 70 days of the experiment and a 70% of silver, whereas for chemical leaching the yield of copper is 66.8% and silver is 51%. In conclusion this investigation demonstrated higher extraction for both copper and silver from the primary ore in the bioleaching sample compared to the chemical leaching sample. More silver was extracted in the bioleaching case as there was less copper remaining to compete for the cyanide anions.

Keywords: Copper, silver, heap leaching, bioleaching, low-grade ore.

1. Introduction

The development of reserves of placer deposits with a free-milling ore increases the proportion of copper deposits which are characterized with refractory raw materials. Due to this issue, many technological advances have taken place with the bioleaching of refractory mineral ores (Wen et al. 2016).

Depending on the composition and amount of the material, the leaching of low-grade ore is conditionally divided into two methods. Dump leaching is designed for dumps of poor copper ores ($\text{Cu} < 0.3\text{-}0.5\%$) with a sulfuric acid solution. Generally, the ore material, which has the large particle size, is treated for a long time by spraying with an acid solution on the

surface of the heap (Brierley and Brierley, 2001; Wu et al., 2007). The second method is heap leaching which is similar to the dump leaching. The main difference of the heap leaching is that the ore is pre-crushed and stored on specially equipped sites (Petersen, 2016). Most mining companies prefer heap leaching due to its economic advantages and it is currently the best alternative to conventional treatment techniques (for example, flotation, autoclave and tank leaching). However, the use of the heap leaching also has significant drawbacks, such as a slow rate of extraction and an incomplete recovery of metals. These problems can be handled by the heap bioleaching technology using various microorganisms, like acidophilic bacteria or fungi. The most familiar representatives of acidophilic bacteria, which are commonly used as bioleaching bacteria to solubilize metals from mine tailings, are bacteria from species *Acidithiobacillus*, *Leptospirillum*, *Acidimicrobium*, *Sulfobacillus* and *Sulfolobus* (Rawlings and Johnson, 2007). Even though bioleaching mainly relies on chemolithotrophic bacteria, several species of fungi also can be utilized for bioleaching purposes. Likewise, strains of *Aspergillus niger* and *Penicillium simplicissimum* were used for the bioleaching of valuable metals from electronic scrap and fuel ash from power plant (Kolencik et al. 2013, Rasoulnia et al. 2016).

Nowadays, heap bioleaching technology is a promising method of processing for poor, low-grade and refractory ores along with wastes from mining industries (Johnson, 2014). Utilizing acidophilic bacteria increases recovery levels of metals and it can also be used in waste disposal purposes (Drobíková et al., 2015; Jerez, 2017). In comparison with conventional methods, it is more advantageous due to its technological simplicity, low energy and material costs. It provides efficient processing of ores with a high recovery of precious metals contained within them and does not cause secondary pollution of the environment (Jerez and Moo-Young, 2011). However, up-scaling of the process also needs processing developments (Boufard and Dixon, 2009) due to the intrinsic complexity of the process. Other challenges are related to the bio-dissolution kinetics and temperature control (Liu and Granata, 2018).

From a geological perspective, copper ores are divided into copper oxide ores and copper sulfide ores (Cao et al, 2009). Oxide minerals such as malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), chrysocolla ($(\text{Cu},\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O}$) and bobkingite ($(\text{Cu}_5\text{Cl}_2(\text{OH})_8 \cdot 2\text{H}_2\text{O})$) are easily dissolved in acidic or alkaline media (Bingole and Canbazoglu, 2004; Kokes et al., 2014):

Copper sulfide minerals like covellite (CuS) and bornite (Cu_2FeS_2) require the addition of an oxidant for complete dissolution. In the case of bioleaching, it happens by an

88 “indirect” mechanism. Indirect leaching occurs due to the oxidation of sulfide by Fe^{3+} ions
 89 formed during the enzymatic (re)oxidation of Fe^{2+} ions (Watling, 2006). Thus, Fe^{3+} ions leach
 90 copper sulfide minerals by the following reaction:

92 Domic (2001) very thoroughly described the technology at the *Quebrada Blanca Mine*
 93 in Chile and conducted studies on improving the copper extraction efficiency. The deposit
 94 contains copper sulfide ore of the chalcocite variety with a content of about 1% copper. A
 95 large number of studies have also been conducted on the *Zijinshan* copper mine (Liu et al.,
 96 2016; Wu et al., 2016; Zou et al., 2015). The *Zijinshan* copper mine is the largest secondary
 97 copper-sulfide mine in China. It has an ore reserve of more than 400 million tons with an
 98 average copper content of 0.43% (Renman et al., 2006). Heap bioleaching has also been
 99 demonstrated for the pre-oxidation of refractory gold ores prior to cyanide leaching. *Newmont*
 100 *Mining Corporation* successfully applies a two-stage process of gold extraction from
 101 refractory sulfide ores. It has been demonstrated that low-grade refractory ores (Au 1-3g/t)
 102 with high sulfide content can be subjected to heap bioleaching followed by gold cyanidation
 103 (Roberto, 2017). For example gold recovery in May 2005 was 53.6 % (Rawlings and Johnson,
 104 2007).

105 Comparative analysis with available data in the literature is difficult due to the variety
 106 of ore composition. Nevertheless, the analysis of literature showed that Mwase et al. (2012)
 107 were able to get fruitful results using a two-stage heap leaching technology for low-grade
 108 concentrate at various temperatures. Firstly, recovery of 91.1% Cu, 98.5% Ni and 83.5% Co
 109 was obtained with the use of bench-scale columns in 88 days at 65 °C. Further leaching with
 110 cyanide solution permitted an increased extraction up to 96.5% Pd, 97.5% Au and 35% Pt in
 111 45 days at 50 °C. Norris et al. (2017) reported another application of two-stage leaching
 112 technology for copper-silver concentrate (Cu 13.2%, Ag 849 g/t). Bioleaching in a stirred
 113 reactor demonstrated copper extraction over 90% at 30, 48 and 76 °C. In the next stage, the
 114 highest silver recovery was observed when thiosulfate was used as extractant with a high
 115 temperature bioleach residue.

116 At the present time, a new site *Northern Qarashoshaq* in the *Zhylandy* deposit in
 117 Central Kazakhstan (48°09'34.8"N 67°32'37.9"E) is under development and the search for an
 118 effective technology and optimized parameters for the heap leaching of these ores is of great
 119 interest. The ore reserves are about 2 million tons and classified as mixed sulfide oxide ores
 120 based on geological studies. Copper in the samples is in sulfide and soluble forms as well as

121 in the form of copper silicates. The contents of copper and silver are 1.5% and 0.0024 %,
122 respectively.

123 This work investigates both the chemical and bacterial leaching of copper containing
124 ores of a new site of the *Zhylandy* deposit which also contains silver. The aim of the research
125 was to compare the efficiencies of biotechnological and chemical approaches, as the sulfuric
126 acid leaching process is going to be used in the site.

127

128

2. Experimental

129 All chemical analyses of ore samples and solutions were performed by the
130 Biomedpreparat Scientific Analytical Center, which is an accredited laboratory (ISO
131 17025:2009).

132 All presented data were based on triplicate experiments and is presented in the form of
133 confidence interval ($P = 0.95$).

134

135 2.1 Materials

136 Ore samples were obtained from the new site *Northern Qarashoshaq* in what is known
137 as the *Zhylandy* deposit in Central Kazakhstan (48°09'34.8"N 67°32'37.9"E). Unless
138 otherwise stated, all chemicals utilized were of analytical grade.

139

140 2.2 Bacteria and culture condition

141 In order to achieve efficient bioleaching, it is reasonable to use a consortium of
142 acidophilic bacteria rather than a pure culture (Akcil et al., 2007; Fu et al., 2008; Nguyen et
143 al., 2015). Consequently, *Acidithiobacillus ferrooxidans* FT-22, *Acidithiobacillus*
144 *ferrooxidans* FT-23, *Acidithiobacillus ferrooxidans* BF and *Acidithiobacillus ferrivorans* SU-
145 8, which has been previously isolated from sulfide ore sites, were used in the present work
146 (Ten et al. 2015). These cultures were deposited in the official collections at RSE Republican
147 Collection of Microorganisms SC MES RK (<http://rcm.kz/>) as B-RKM-0627, B-RKM-0628,
148 B-RKM-0630 and B-RKM-0644, respectively. 9K medium (Silverman and Lundgren, 1959)
149 which contains $(\text{NH}_4)_2\text{SO}_4 - 3.0 \text{ g/l}$, $\text{K}_2\text{HPO}_4 - 0.5 \text{ g/l}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} - 0.5 \text{ g/l}$, $\text{KCl} - 0.1 \text{ g/l}$
150 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} - 44.2 \text{ g/l}$, was used for the growth of microorganisms. The cultures were
151 incubated in Erlenmeyer flasks at 28 °C and 180 rpm so this was a dynamic cultivation.

152

153 2.3 Ore analysis

154 2.3.1 Bulk chemical analysis of the ore

The total content of the elements was determined by stirring 0.25 g of the ore with 8.00 ml of 35% HCl, 2.00 ml of 45% HF and 0.50 ml of 65% HNO₃, then heating at ~150 °C on a hot plate for 1 hour. The suspension was then cooled to room temperature and diluted before analysing for target elements using an ICP-OES (Thermo Scientific iCAP 7200 ICP Duo, USA).

160

2.3.2 Mineralogical analysis of the ore

Mineral composition of the ore was analysed in diffractometers D2 Phaser (Bruker AXS GmbH, Germany) and MiniFlex 600 (Rigaku, Japan) using the X-ray diffraction method. Mineralogical phases of elements were identified in SEM Hitachi S-3400N with EDS Bruker XFlash 4010 for X-ray spectroscopic analysis. The samples were investigated at low vacuum using electron backscatter diffraction to determine the crystallographic structure of the minerals. These analyzes were carried out in the Uranium Geology International Center at the Department of Geoecology and Geochemistry of the National Research Tomsk Polytechnic University.

To determine copper containing ores minerographic and phase analysis of the ore samples has been conducted in the Tsentrgeolanalit LLP (Qaraghandy, Kazakhstan). Preparation of polished samples for ore microscopy was conducted according to the Manual of mineragraphy (Vakhromeyev, 1950). The study of thin and briquetted polished sections was carried out using inverted microscope Axiovert 200 MAT (Carl Zeiss, Finland). The main mineragraphic features of copper containing minerals and their associations (concretions) like composition, structure and texture have been investigated in detail. The photo of them was taken on digital camera Pixera Pro 150ES. The grain size was determined by comparison with reference scales. Phase analysis is conducted in accordance with the national standard № KZ.07.00.01301-2011 (<https://kazinmetr.kz/bd/reestr/mvi/6432/>) for determination of copper phases in ores.

181

2.4 Ore leaching tests

2.4.1 Experiments in Erlenmeyer flasks

To evaluate the suitability of the ore for leaching tests experiments were conducted in Erlenmeyer flasks. In order to reduce the duration of the experiments, ore with a particle size of less than 72 µm was used. Copper extraction was carried out in 750 ml Erlenmeyer flasks containing 10% ore (w/v) in thermostatically controlled shakers at 180 rpm and 28°C. The initial pH in the medium was set to 1.5 using 10 N sulfuric acid solution (H₂SO₄). Chemical

189 extraction of copper was conducted with the addition of Fe^{3+} (as added $\text{Fe}_2(\text{SO}_4)_3$) in the
 190 amounts of 1, 3, 5, 7 g/l (Fig. 3 Flasks 1-4). In bacterial extraction experiments, the 10% (v/v)
 191 inoculum was immersed without Fe^{3+} addition in solution (Fig. 3 Flask 5). A typical method
 192 of copper extraction by sulfuric acid leaching was tested for comparison (Fig. 3 Flask 6). All
 193 clean flasks were sterilized by autoclaving using Steam Autoclave VK-75 at 1 atm and 121 °C
 194 for 20 min before inoculation. In order to prevent growth of indigenous bacteria in flasks 1-4,
 195 6, benzoic acid (50 mg/l) was immersed to un-inoculated medium (Norris et al., 2015).

196

197 2.4.2 Cyanide leaching of Ag in Erlenmeyer flasks

198 After flask experiments, cyanide leaching of Ag was performed for treated and
 199 untreated ore material. The cyanidation experiments were carried out in 250 ml Erlenmeyer
 200 flasks with a working volume of 40 ml and concentration of 40% (w/v) solids in
 201 thermostatically controlled shakers at 25 °C and 180 rpm for 48 hours. The pH of the pulp
 202 was maintained between 10.5 and 11.0 using NaOH solution. The concentration of CN^- was
 203 set to 1 g/l in solution using NaCN.

204

205 2.4.3 Column leaching tests

206 To evaluate the extraction of copper, tests were carried out in columns (height 1 m,
 207 diameter 70 mm) which simulate heap leaching. (Karavaiko et al., 1989) writes that the
 208 maximum particle size should not exceed 20% of the diameter of the columns during the
 209 column leaching tests. Consequently, 2 kg of representative ore from the *Northern*
 210 *Qarashoshaq* deposit was crushed to the size less than 10 mm. The ore material was
 211 agglomerated using a rotating drum agglomerator (316 stainless steel, 0.25 m in diameter,
 212 0.35 m in length) at 25-30 rpm. H_2SO_4 was used as a binding agent at a concentration of 1.02
 213 mol/L. To obtain stable agglomerates with the size of less than 10 mm, the agglomeration was
 214 carried out for 15 minutes. Prior to the loading into the columns, all agglomerates were kept
 215 for 24 hours at room temperature (~ 25°C). The final moisture of the pellets was 15-20%; the
 216 consumption of sulfuric acid was 50 kg/ton of ore. The first column was irrigated with 0.08
 217 mol/l sulfuric acid solution. The second column was irrigated with solution containing
 218 bacterial consortium, 1.5 g/l Fe^{3+} and 0.08 mol/l sulfuric acid solution. The irrigation rate was
 219 $10 \text{ l m}^{-2} \text{ h}^{-1}$ without recycle. The concentration of sulfuric acid solution and the irrigation rate
 220 for both columns were in the same values as used in the *Northern Qarashoshaq* site now.
 221 These column tests were performed at room temperature ~ 25°C which is a slightly lower
 222 temperature than the experiments in Erlenmeyer flasks.

2.4.4 Bottle Roll Cyanidation Test

Bottle roll cyanidation tests were carried out after column leaching experiments. Samples, which have been irrigated using sulfuric acid or bacterial solutions, were leached using 1 g/l CN^- solution. The content of the solids was 40% (w/v) and the pH was maintained between 10.5-11.0 by the addition of lime. Samples of the solution were taken every 2, 4, 8, 24 and 48 hours to measure the concentration of CN^- and the concentrations of dissolved silver and copper. After 48 hours the residues were washed with water and air dried for subsequent Ag and Cu analysis.

2.5 Other analytical methods

At the beginning of the flask experiments, the sample solutions for analysis (2 ml) were collected each day under sterile conditions. Then the sampling frequency was changed to each 48 hours. In the column leaching, the samples (50 ml) were taken daily. The pH, redox potential, bacterial cells and the concentrations of Ag, Cu and Fe were measured for each sample. The pH was measured using a SevenMulti-A pH-meter (Mettler Toledo, Switzerland). The redox potentials were measured using a universal ionomer EV-74 (Russia) with a Pt electrode which is relative to Ag, AgCl reference electrode.

The concentration of bacteria in the solutions was measured both by direct counting using optical microscopy Standard 25 (Carl Zeiss, Germany) with phase contrast and by serial dilutions. The concentrations of the metal ions were measured by the method of atomic absorption spectroscopy with the AAS Kvant-2AT (Russia) (Mendham et al. 2000). The spectrophotometric method by BioMate 3S UV-Visible spectrophotometer (Thermo Scientific, USA) was used to determine the concentration of ferric and ferrous ions in the liquid phase (Mendham et al. 2000). Cyanide concentration in the aqueous solution was measured by titration using AgNO_3 as titrant and rhodamine as indicator.

Total sulfuric acid consumption of the ore sample was determined by bottle roll tests. A solution of sulfuric acid with various concentrations (0.05; 0.1; 0.2 M) was added to the ore material. Then the bottles were agitated for 3 days. After that, the amount of the remaining acid was determined using the acid-base titration method and the acid consumption of the ore was calculated.

3. Results and discussion

3.1 Ore sample characterization

1000 kg of the primary ore samples were collected from the site *Northern Qarashoshaq* in the *Zhylandy* copper containing ore deposit of Qazaqmys Corporation LLP (Kazakhstan). Results of the chemical analysis using ICP-OES of the ore sample are shown in Table 1. The total content of Cu is 1.5 % while Ag was observed in trace amounts (0.0024%). According to X-ray diffraction analysis (Fig. 1), the major minerals in the sample are albite ($\text{NaAlSi}_3\text{O}_8$), quartz (SiO_2), clinochlore-1MIIb ($(\text{Mg,Al,Fe})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$), muscovite-2M1 $\text{KAl}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$, illite-2M2 ($(\text{KH}_{30})\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$).

Table 1. The major elemental content of ore samples obtained by ICP-OES analysis

Elements	Cu	As	Fe	S	Ag	Au
Composition (%)	1.5 ± 0.27	0.017 ± 0.005	1.80 ± 0.36	0.50 ± 0.03	0.0024 ± 0.0005	ND ^a

^aNot detected

Fig. 1. XRD pattern of ore sample, obtained by using D2 Phaser diffractometer

Since the detection limit of X-ray diffractometric analysis is 1% of the total amount of minerals, to determine the copper containing minerals, phase analysis of copper was

performed. It has been determined that the copper is mainly represented by sulfide minerals. The major copper-containing minerals are covellite, chalcocite, malachite, chrysocolla and chalcopyrite. The results are shown in Table 2. Moreover, the trace level of silver is mainly present in jalpaite (Ag_3CuS_2) minerals according to XRD analysis using a MiniFlex 600 diffractometer (Rigaku, Japan) (the spectrum is not shown).

Table 2. The results of the chemical phase analysis of copper in the ore

Cu phases	Mass fraction (%)	Distribution (%)
Cu in malachite, azurite, atacamite	0.285	17.66
Cu in chrysocolla	0.165	10.22
Total "Free" Cu as oxide	0.450	27.88
"Trapped" Cu as oxide	0.011	0.68
Total Cu as oxide	0.461	28.56
Cu in covellite, chalcocite	1.053	65.24
Cu in bornite	0.026	1.61
Cu in chalcopyrite	0.074	4.58
Total Cu as sulfide	1.153	71.43
Total Cu as oxide and sulfide	1.614	100

To characterize the main copper containing minerals mineragraphical and SEM-EDX analyzes were performed. It has been determined that all minerals have a fragmented form and their surfaces are non-corroded. The SEM images of some minerals are shown in the supplementary material.

Mineragraphical analysis was conducted using optical microscopy. Sample of polished ore is represented by cupriferous sandstone. The images taken of the minerals are shown in Fig. 2.

Ore mineralization is represented by finely disseminated chalcocite (Cu_2S), confined to the cementation zone of the rock, partially, rarely completely replacing it, with the formation of its irregular and elongated parts. Grain size of chalcocite is characterized by a wide range from 0.001-0.01 mm to 0.1-0.25 mm. The cracks of the twinning, cleavage and desiccation are distinctly shown in the grains. The boundaries of the grains are uneven and serrated. Numerous relics of non-metallic minerals are developed inside the grains.

Covellite (CuS) was found in the irregular forms with particle size from 0.001mm to 0.25 mm, which is explained by the early, partial, often complete metasomatic replacement of chalcocite and bornite.

295 Malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) forms, predominantly finely disseminated, rarely cement
 296 inherited microtextures of its fibrous aggregates ranging in size from 0.02 mm to 0.15 mm,
 297 confined to intergranular space, to the cementation zone of non-metallic ores, taking the shape
 298 and size of their interstitium. The minor part of the malachite contains residual micro relics of
 299 thin-plate covellite, whose grains size barely reach 0.025-0.030 mm.

300 Chalcopyrite (CuFeS_2) is noted in the amount of single grains with particle size of
 301 0.001-0.01 mm.

Fig. 2a. x200
Emerges of chalcocite (Ch)

Fig. 2b. x200
Residual micro relics of covellite (Cv)
encapsulated in malachite (Mh)

Fig. 2c. x500
Single micro grain of chalcopyrite (Cp) and
small agglomeration of hematite Fe_2O_3 (Gm)

Fig. 2d. x500
Hypogenic chalcocite (Ch) is being
replaced by covellite (Cv)

Fig. 2. Optical microscopy images of the minerals

3.2 Ore leaching tests

3.2.1 Experiments in Erlenmeyer flasks

Due to the complexity of the extraction process, the effects of the ferrous and ferric iron concentration, the use of bacteria and the sulfuric acid on the copper extraction are important to investigate.

Initially, the pH values of the flask solutions were set to 1.5, because the reaction of the ores in the leaching solution occurs with acid consumption (as demonstrated in equation 1). After that, the acidity in the leaching solutions was within the range of 1.5-1.6. Total sulfuric acid consumption of the ore sample was determined by bottle roll tests and was 50-60 kg H₂SO₄/t. Stirred experiments in Erlenmeyer flasks were conducted without adding mineral salts, as a consequence the ore was the only source of energy for the bacterial culture in this dynamic cultivation.

Copper recovery and changes in the Eh, Fe³⁺, Fe²⁺ over time are shown in Figure 3. By the end of these stirred chemical extraction experiment, the copper extraction in Flask 1 was 79% and it was in the same range of 82-83% in Flasks 2-4. Consequently, the addition of Fe³⁺ of more than 3 g/l does not have a significant impact on the copper yield. In the Flask 6 (currently used in copper leaching by Qazaqmys Corporation LLP), copper recovery into the solution was 76% after 16 days of this sulfuric acid leaching experiment. It is noteworthy that a higher recovery of 95% was achieved using a bacterial consortium (Flask 5).

The Eh and the ferric and ferrous iron content were approximately the same for 4 days in the chemical extraction with 1 g/l Fe³⁺ and bacterial extraction (Flasks 1 and 5). Although, the copper recovery data differed by 3% in favor of Flask 5. Most likely this is due to the presence of biogenic Fe³⁺, which contributed to the better yield of copper (Abhilash and Pandey, 2013; Mathur et al., 2000).

A further sharp increase in copper yield of 4% in Flask 5 is explained by the oxidation of ferrous iron by bacteria, where the Eh value was 630 mV. In support of this it is observed that the amount of Fe³⁺ rises (Fig. 3C) and Fe²⁺ falls (Fig. 3D) in flask 5 after 4 days. The Eh in the flasks with the chemical extraction of copper did not exceed 600 mV even with a content of 7 g/l Fe³⁺. In the control flask, the Eh was around 380 mV throughout the experiment. Data on the yield of copper and Eh are directly correlated in all the flasks.

Fig. 3. Degree of copper extraction (A), Eh (B), Fe^{3+} (C), Fe^{2+} (D) depends on the time in the Erlenmeyer flask experiments. The legend is presented in (A) and applies to all the graphs.

3.2.2 Cyanide leaching of Ag in Erlenmeyer flasks

An addition of $\text{Fe}_2(\text{SO}_4)_3$ in the amount of 7 g/l led to increasing the copper extraction only up to 83%. This is not sufficient from an economic point of view. Therefore, only the bacterial extraction and sulfuric acid extraction for comparison were further investigated. After the copper recovery experiments in the flasks, the residues from the flasks 5 and 6 were cyanidated for extraction of the trace level of silver. Additionally, direct cyanidation without preliminary treatment of the ore was carried out. No silver was detected in the solution during the direct cyanidation, since copper leaching occurred in preference. Moreover, the cyanide consumption was more than 20 kg/t. Consequently, direct cyanidation for the extraction of silver is pointless.

The results of cyanidation of the ore residues after sulfuric acid (SAL) and bacterial leaching (BL) of copper showed a yield of silver in the solution of 92% and 97% respectively

(Fig. 4). Data on the yield of silver were relatively equal. This may be due to the grinding of the ore material to the size of less than 72 μm . Cyanide consumption was 1.71 kg per ton of ore. In the course of the experiment, the copper yield was analyzed during the cyanidation. The results after sulfuric acid extraction showed an additional copper yield of 1.16%, while the additional yield after bacterial extraction was only 0.04% (Fig. 5). This can be explained as due to the low extraction yield of copper at the first stage in the case of sulfuric acid leaching, resulting in a higher copper content remaining. Consequently, the higher content of copper at the stage of cyanidation can consume an extra amount of the sodium cyanide.

Fig. 4. Silver and copper extraction from cyanidation after sulfuric acid leaching (SAL, flask 6) and bacterial leaching (BL, flask 5)

3.2.3 Column leaching tests

The copper recovery from the ore of the *Northern Qarashoshaq* site was assessed by column tests which simulated heap leaching. Usually, the results of the column tests are close to the results of the pilot and industrial heap leaching processes. Before the leaching tests, the ore was pre-agglomerated. The agglomeration results showed that stable agglomerates were obtained using H_2SO_4 as a binding agent at a concentration of 1.02 mol/l. Experiments in the columns were carried out with a concentration of sulfuric acid of 0.08 mol/l. The results of the copper recovery, based on the concentration of metal in the solution and in the ore remains, are shown in Figure 5. The yield of copper was 66.8% at sulfuric acid leaching, whereas for bacterial leaching, the yield of copper was 82.3% after 70 days of the experiment. In

comparison, the recovery rate in C2 was considerably high, for example, the yield of copper in the solution was 66.8% for 22 days, while this result in C1 was achieved at the end of the experiment. This factor has an importance for heap leaching for the northern and central regions of Kazakhstan, where the warm climate lasts 5-6 months. It was also noted in both experiments that intensive copper recovery into the solution was observed during the first 17 days and then slowed down.

During the first 10 days, changes in the pH indicated abundant acid consumption by the ore sample, and then the pH was kept at 1.4-1.6 throughout the entire experiment. Eh increased from 380 mV to 700 mV over 25 days and gradually began to decrease within 1 week and after that remained constant in C2 due to the bacterial oxidation of ferrous iron. In the column with sulfuric acid leaching, Eh remained constant at ~ 420 mV (the data is not presented).

Fig. 5. Copper extraction in C1 leached with sulfuric acid and C2 leached with the bacterial consortium

Residues after the column tests were analyzed by SEM-EDX. Data from SEM-EDX of C2 residues indicate that any chlorine-containing copper oxide in the sample was not detected, and all the copper minerals in the sample are corroded. Minerals, where sulfur atoms outnumber copper atoms, are frequently observed (unidentified mineral) (Fig. 6a). In addition, minerals of silver are mainly presented by silver iodide with copper sulfide shown in Figure 6b-c.

Fig. 6. SEM images and EDX spectra of unidentified mineral (a) and silver iodide with copper sulfide (b-c)

In addition to the SEM-EDX, copper phase analysis was conducted with some residues after column leaching tests. The results of these analyses are depicted in Table 3.

Table 3. The results of the chemical phase analysis of copper and copper recovery in the residual ore after sulfuric acid and bacterial leaching.

Cu phases	Sulfuric acid leaching		Bacterial leaching	
	Mass fraction (%)	Distribution (%)	Mass fraction (%)	Distribution (%)
Cu in malachite, azurite, atacamite	0.072	14.46	0.087	37.34
Cu in chrysocolla	0.009	1.81	0.038	7.73
Total "Free" Cu as oxide	0.081	16.27	0.125	45.06
"Trapped" Cu as oxide	0.002	0.40	0.005	2.15
Total Cu as oxide	0.083	16.67	0.130	47.21
Cu in covellite, chalcocite	0.32	64.26	0.098	42.06
Cu in bornite	0.023	4.62	0.007	3.00
Cu in chalcopyrite	0.072	14.46	0.018	7.73

Total Cu as sulfide	0.415	83.33	0.123	52.79
Total Cu as oxide and sulfide	0.498	100	0.253	100
Cu recovery from oxide minerals (%)*	82.1		71.9	
Cu recovery from sulfide minerals (%)*	64		89.3	
Total Cu recovery (%)*	69.1		84.3	

* Based on the values reported in Table 2

As you can see from the table 3, both methods successfully leached copper from copper oxide minerals. However, sulfuric acid leaching of copper sulfide minerals wasn't as much efficient as bacterial leaching, having respective 64% and 89.3% copper recovery from the copper as sulfide minerals. According to phase analysis, total yield of copper was 69.1% at sulfuric acid leaching, whereas for bacterial leaching, the yield of copper was 84.3% after 70 days of the experiment. These results correlate with the previously obtained data using the method of atomic absorption spectroscopy (Fig.5.).

3.2.4 Bottle Roll Cyanidation Test

After the column tests, the remains of the ore sample were cyanidated in a bottle roll. The purpose of this experiment was to estimate the maximum possible yield of silver after heap leaching of copper at a particle size of less than 10 mm. The results of silver and copper cyanidation after sulfuric acid leaching (SAL (Ag) and (Cu)) and bacterial leaching (BL (Ag) and (Cu)) are shown in Fig. 7. The cyanidation results show that silver recovery after sulfuric acid leaching and bacterial leaching for 48 hours was 51% and 70%, respectively. A low degree of silver recovery indicates that the samples of this ore are resistant to extraction.

Furthermore, an additional copper yield was monitored during the experiment. The results for the extraction of additional copper after 48 hours were 5.4% and 3% after sulfuric acid leaching and bacterial leaching, respectively. Again this reflects that more copper was extracted before this cyanidation step in the case of bacterial leaching sample. The reaction of cyanidation of copper after bacterial leaching occurred in the first 4 hours and further extraction did not occur. Most likely, this is due to the high sulfur content in the ore residues, as evidenced by the SEM-EDX data (Fig. 6.).

Fig. 7. Silver extraction and copper extraction after cyanidation of residues after sulfuric acid leaching (SAL) and bacterial leaching (BL) versus time

Conclusions

Thus, copper leaching of the new site *Northern Qarashoshaq* in *Zhylandy* (Kazakhstan) was carried out by bioleaching and chemical methods both in Erlenmeyer flasks and column leaching tests. Different parameters were tested to see the influence on the degree of extraction. The use of the bacterial leaching in the flasks showed a greater recovery of copper (95%) compared to the chemical leaching (76%). A similar trend in the extraction of copper was obtained during the column experiments and a lower recovery was also observed. On the other hand, the extraction of the trace level of silver from the leaching residues after the shake flask experiments did not show much difference (92% for chemical and 97% for bacterial leaching). Nevertheless, cyanidation of the leaching residues in the columns showed an increase in the yield of silver after bacterial treatment by nearly 1.4 times compared to chemical treatment, having respective 70% and 51% recovery levels. The results showed a good prospect for the bioleaching with a new, promising ore material and can be used as a basis for the development of technology for copper and silver recovery from the studied raw materials.

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