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Pilot-scale tank biooxidation of gold bearing arsenopyrite concentrates

This article shows the results of experimental tests of bacterial oxidation of arsenopyrite gold concentrate that contains gold (60 g/t), sulfides (23 %), iron (26 %) and arsenic (11 %). A consortium, consisting of the mesophilic strain *Acidithiobacillus ferrooxidans* AF-2 and moderately thermophilic strains of *Sulfobacillus thermosulfidooxidans* OT-1 and *Sulfobacillus thermosulfidooxidans* SK-4, was used in the test. The tests were carried out on the equipment, consisting of 6 reactors with a volume of 1.5 m³ each. The concentration of solids in the pulp was maintained at 20 % (w/w). In the process of optimizing the parameters of the bacterial oxidation plant, the retention time of the concentrate was reduced from 12 to 6 days. During the test, the destruction of sulfides was over 90 %, which provided gold recovery from biooxidation products by cyanide leaching over 94 %. In addition, the average gold recovery rate reached 95 %. The removal of arsenic from the leaching solutions was carried out by means of two-stage neutralization with calcium carbonate. Due to high oxidation degree maintained throughout the entire operation of the experimental plant, a high ratio of iron to arsenic concentration in the solution was observed, which provided ideal conditions for arsenic precipitation in the form of trivalent iron arsenate. Determination of the stability of precipitate residuals was carried out according to the protocol Toxicity Characteristic Leaching Procedure (TCLP). The precipitate obtained after neutralization of the leaching solution does not require special disposal, since the final concentration of arsenic in the extracts of TCLP tests was 0.14 mg/L.

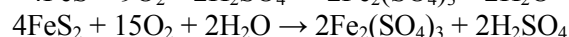
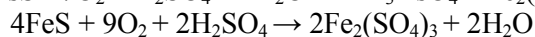
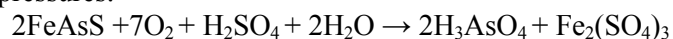
Keywords: arsenopyrite concentrate, biooxidation, tank leaching, *Acidithiobacillus ferrooxidans*, *Sulfobacillus thermosulfidooxidans*, gold, arsenic, pilot-scale.

Introduction

The main problem of gold mining in Kazakhstan is that in most cases (65 %) the gold-bearing ores are classified as refractory ores. The deposits with these stubborn ores are hardly developed in our country [1]. In this regard, a necessity to use additional procedures at the processing of these ores arises. Currently, there are several approaches to «open» the refractory ores; these are physicochemical methods (oxidation under the high temperature and high pressure) and biological method (bioleaching) [2].

Pressure leaching is the method of oxidative decomposition of the sulphide minerals of iron and non-ferrous metals, with which the particles of gold associate in the ore. It occurs in industrial autoclaves under the high pressure (1 MPa or higher) and high temperatures (150–200 °C).

Bacterial leaching (bioleaching) is a relatively new and promising method based on the use of the ability of some natural bacteria (iron- and sulfur-oxidizing) to oxidize sulfide minerals and to produce energy at normal temperatures and pressures:



However, for refractory gold ores and concentrates with a low arsenic content, the choice between the two technologies (the physicochemical and bacterial) has an individual character for each particular deposit, depending on size and physicochemical characteristics of the deposit. Moreover, for arsenopyrite ore with a high arsenic content, the use of physical and chemical methods is limited by both environmental problems and economical issues. It poses a risk of the release of highly toxic arsenic into the surroundings [3].

Tank method of bacterial leaching is a relatively new and promising method for the processing of arsenic-containing ores and concentrates. In this process, the gold extraction occurs by the destruction of the crystal lattice of sulfide minerals which finely disseminate the gold. One of the benefits of this method is that it can be used for the cleaning of the concentrates from the harmful compounds such as arsenic. Finally, the bioleaching is the up-to-date tool for the selective extraction of metals from collective concentrates or industrial products [4].

Methods

The microbial culture, used in this study, were mixed culture of mesophilic and moderately thermophilic microorganisms: *Acidithiobacillus ferrooxidans* AF-2 (B-RKM 0797), *Sulfobacillus thermosulfidooxidans* OT-1 (B-RKM 0794) and SK-4 (B-RKM 0796), which was deposited in the official collection at the RSE «Republican Collection of Microorganisms» of the Committee of Science of Ministry of Education and Science of the Republic of Kazakhstan.

The pH and redox potential (Eh) were determined by the analyzer «Mettler Toledo Seven Multi S47-K». The concentration of metals in solid samples and solutions was determined using atomic emission spectrometry on the spectrometer iCAP 7200 ICP-OES Analyzer of «Thermo Scientific» company and using the method of atomic absorption with atomization in a graphite furnace using the «QUANTUM-2AT» atomic absorption spectrometer [5]. The concentrations of Fe³⁺ and Fe²⁺ ions in the liquid phase were determined spectrophotometrically on «KFK-3-01» colorimeter (at wavelength $\lambda=510$ nm) [6]. The sulfur content in the sulfide concentrate and in the residues of leaching was determined gravimetrically [7].

During the pilot test, the arsenopyrite concentrate was obtained from the Bestobe deposit (JSC «Mining and Metallurgical Complex «Kazakhaltyn»). The average gold content is 60 g/t, the content of sulfides is 23 %, iron is 26 %, arsenic is 11 %. The concentration of solids in the pulp of the pilot plant was maintained at 20 % (w/w).

The pilot plant for bacterial oxidation of arsenopyrite concentrates consisted of 6 reactors with a volume of 1.5 m³ each. The bioreactors are equipped with stirring devices, bubbling rings for air supply and heaters to maintain the temperature at 40 °C. Pulp preparation was carried out in a 2 m³ conditioning tank, provided with a stirring device.

First three bioreactors worked in parallel and formed the first stage. A combined stream from these bioreactors was then cascaded into a series of three bioreactors. The use of the first three bioreactors in parallel had a crucial role in the growth and stability of bacterial populations due to the fact that the retention time at first stage increases threefold. Schematic diagram of the installation is shown in Figure 1.

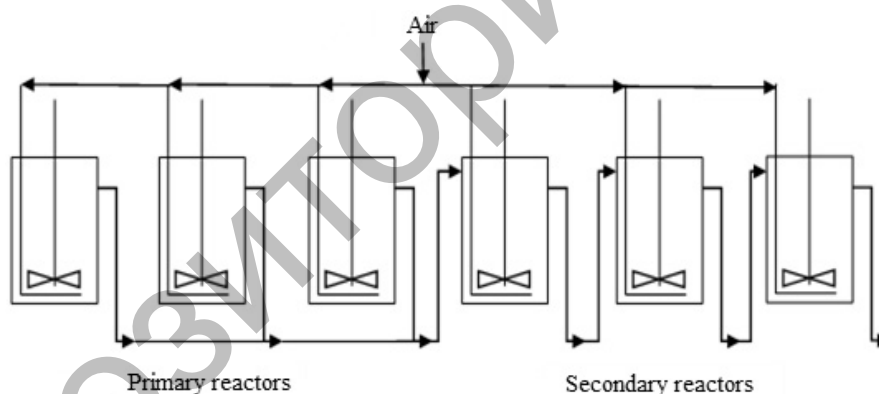


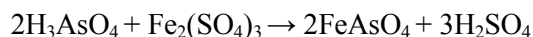
Figure 1. The scheme of pilot-scale plant

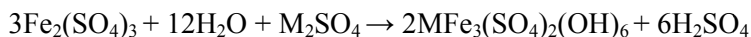
The cyanidation of bacterial leach residues and untreated concentrates was carried out in 100 ml Erlenmeyer flasks at a working volume of 40 ml with 40 % pulp on a shaker at 25 °C and 200 rpm for 24 hours. The pH of the pulp was maintained at pH 10.5–11.0 by the addition of 10N sodium hydroxide.

Results

Initially, the retention time of the concentrate in the plant was 12 days. Due to the slow flow rate into the primary reactor, the feed was supplied hourly from the pre-weighed packages of the concentrate, and the water was added continuously. After the stable operation with a certain retention time was demonstrated, the feed rate had increased.

In the process of bacterial oxidation special attention was accentuated on the maintenance of the optimum acidity of the pulp (pH 1.0–1.5). Controlling the acidity of the pulp is necessary to prevent a decrease in the activity or death of acidophilic bacteria, as well as the precipitation of iron and arsenic compounds with an increase in acidity [8]:





where M^+ — is K^+ , Na^+ , NH_4^+ or H_3O^+ .

Samples were taken from each reactor for chemical analysis on a daily basis. The analysis included the determination of total iron, total sulfur, sulfide sulfur and arsenic in the solid samples and iron, sulfate sulfur and arsenic were analyzed in the solutions. The parameters of the bacterial oxidation process are shown in Table 1.

Table 1

Parameters of bacterial oxidation in a pilot plant

Pulp density, %	20
Retention time, days	6
Temperature, °C	40
Iron, g/L	45–49
Arsenic, g/L	16–19
pH	1.2–1.3
Eh, mV	640–720
The concentration of dissolved oxygen, ppm	2.0–5.0
Weight loss, %	38
Sulfide oxidation, %	90
Removal of As, %	92
Average recovery of Au, %	95

In the process of optimizing the parameters of the pilot bacterial oxidation plant, the retention time of the concentrate was reduced from 12 to 6 days. The recovery of gold was determined by standard bottle tests. Gold recovery, obtained from bacterial oxidation products, is shown in Figure 2.

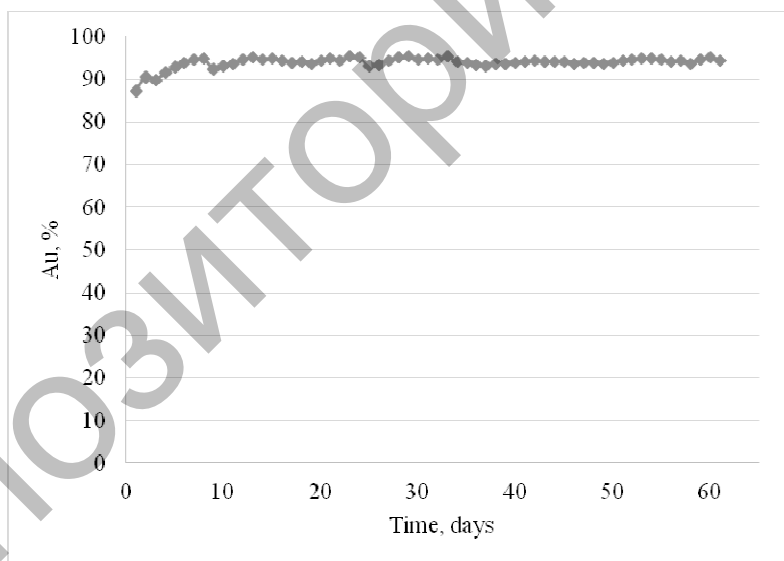


Figure 2. The gold recovery obtained from the bottle tests

According to the data presented in Figure 2, it can be seen that high levels of the gold recovery were observed throughout the test period. Figure 3 shows the graph of the gold recovery, depending on the total oxidation of sulfides.

According to the data presented in Figure 3, it can be seen that during the tests, the destruction of sulphides was over 90 %, which ensured the recovery of gold from biooxidation products over 94 %. The average gold extraction was about 95 %.

Many researchers have shown that in order to effectively remove arsenic from the solution and obtain a stable precipitate of iron (III) arsenate, neutralization should be carried out step by step [8–11].

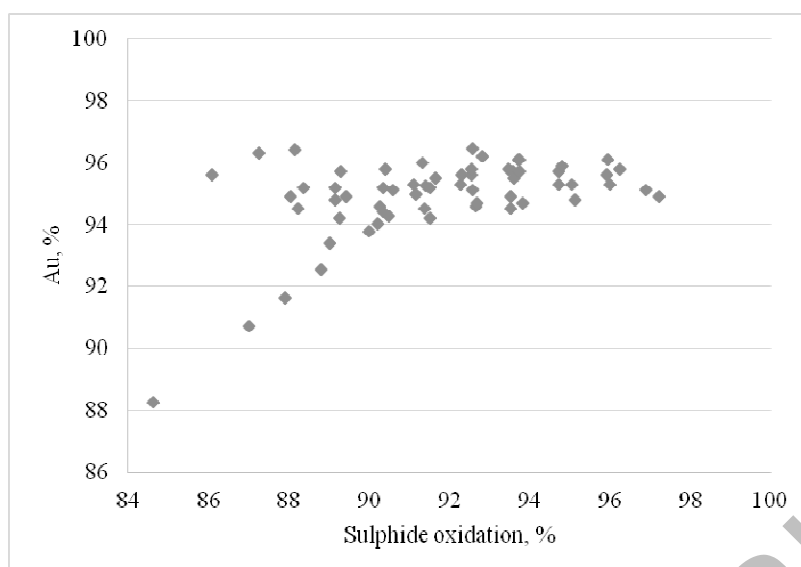
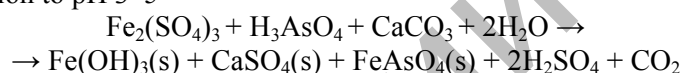


Figure 3. Dependence of the gold recovery on the oxidation state of sulfides

In the first stage, arsenic is deposited in the form of stable iron arsenate at pH 3–5, after that, the pH is raised to 6–8, in order to reach an environmentally acceptable level. The chemical processes that occur in this case can be described by the following equations:

Stage 1: Neutralization to pH 3–5



Stage 2: Neutralization to pH 6–8



The formation of calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$ should be avoided during the neutralization of the arsenic solutions. Calcium arsenate is more soluble than iron (III) arsenate and is not a suitable form for long-term storage due to decomposition to carbonate under the influence of carbon dioxide contained in the air. The formation of calcium arsenate can be prevented with a molar ratio of iron (III): arsenic above 3: 1 and an increase in pH in the first stage of no more than 4–5 [12].

Due to high oxidation degree is maintained throughout the entire operation of the experimental plant, a high ratio of iron to arsenic concentration in the solution was observed, which provided ideal conditions for the arsenic precipitation in the form of trivalent iron arsenate. Determination of residual precipitation stability was carried out according to the protocol U.S. EPA-TCLP. The threshold concentration of TCLP for arsenic is 5 mg/L. The test results are shown in Table 2.

Table 2

Data of solution and residue analysis

Biooxidation solution			In solution after precipitation	In TCLP extract
Fe, g/L	As, g/L	pH	As, mg/L	As, mg/L
47	18	1.2	0.05	0.14

According to Table 2, the precipitate obtained after neutralization of the leaching solutions does not require special disposal, since the final concentration of the arsenic in the extracts of TCLP tests was 0.14 mg/L.

Conclusion

The pilot test have shown a high efficiency of biooxidative pretreatment of the arsenopyrite concentrate using *Acidithiobacillus ferrooxidans* AF-2, *Sulfobacillus thermosulfidooxidans* OT-1 and *Sulfobacillus thermosulfidooxidans* SK-4 for the gold extraction. 92 % of arsenic was recovered in 6 days of treatment. Only 47 % of gold is recovered through the direct cyanidation of the concentrate, while cyanidation after biooxidation has shown 95 % of the gold recovery.

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Арсенпиритті алтын концентратты күбде биототықтырудың тәжірибелі сынағы

Мақалада құрамында алтын 60 г/т, сульфидтер 23 %, темір 26 %, күшәлә 11 % арсенпиритті алтын концентратты күбде биототықтыру сынақтарының нәтижелері көрсетілген. Сынақ кезінде *Acidithiobacillus ferrooxidans* AF-2 мезофилді штамнан және орташа-термофилді штаммдардан тұратын консорциум пайдаланды. Сынақтардың әрбірі 1,5 м³ көлемді 6 реактордан тұратын қондырғыда жүргізілді. Қондырғы қуат көзінде қатты заттар концентрациясын 20 % (мас./мас.) деңгейінде ұстады. Күбде бактериялық тотықтыру қондырғысының оңтайландыру барысында концентратты ұстау уақыты 12-ден 6 тәулікке дейін қысқартылды. Сынақ үстінде сульфидтер бұзылуы 90 % жоғары, бұл биототықтыру өнімнен алтынды алу 94 % жоғары, сынақ ішінде алтынды орташа алуы 95 % құрады. Шаймалау ерітінділерден күшәләні арылту кальций карбонатымен екі кезеңді бейтараптандыру жолымен жүргізілді. Эксперименттік қондырғының бар жұмысы бойы ұсталынатын тотықтырудың жоғары деңгейінен үш валентті темір арсенаты түрінде күшәләнің тұнуына кемшіліксіз жағдайды тудырған ерітіндіде күшәләға үш валентті темір концентратының жоғары қатынасы байқалды. Сонымен бірге темір арсенатының (III) тұрақты тұнбасы пайда болды. Тұну тұнбасының тұрақтылығын анықтау Toxicity Characteristic Leaching Procedure (TCLP) хаттамасы бойынша жүргізілді. Шаймалау ерітіндісін бейтараптандыру нәтижесінде алынған тұнба TCLP тесттер сінділерінде күшәләнің соңғы концентрациясы 0,14 мг/л құрағандықтан, арнайы сақтауды талап етпейді.

Кілт сөздер: арсенпиритті концентрат, биототықтыру, шанда шаймалау, *Acidithiobacillus ferrooxidans*, *Sulfobacillus thermosulfidooxidans*, алтын, күшәлә, сынамалы сынау.

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Опытное испытание чанового биоокисления арсенопиритного золотого концентрата

В статье приведены результаты опытных испытаний чанового бактериального окисления арсенопиритного золотого концентрата: содержание золота 60 г/т, сульфидов 23 %, железа 26 %, мышьяка

11 %. При испытании использовали консорциум, состоящий из мезофильного штамма *Acidithiobacillus ferrooxidans* AF-2 и умеренно-термофильных штаммов *Sulfobacillus thermosulfidooxidans* OT-1 и SK-4. Испытания проводились на установке, состоящей из 6 реакторов, объемом 1,5 м³ каждый. Концентрацию твердых веществ в питании установки поддерживали на уровне 20 % (мас./мас.). В процессе оптимизации параметров установки чанового бактериального окисления время удержания концентрата было сокращено с 12 до 6 суток. В ходе испытания разрушение сульфидов составило свыше 90 %, которое обеспечило извлечение золота из продуктов биоокисления при цианировании свыше 94 %, среднее извлечение золота в течение испытаний составило 95 %. Удаление мышьяка из растворов выщелачивания проводили путем двухстадийной нейтрализации раствора карбонатом кальция. Из-за высокой степени окисления, поддерживаемой на протяжении всей работы экспериментальной установки, наблюдалось высокое отношение концентрации трехвалентного железа к мышьяку в растворе, что обеспечило идеальные условия для осаждения мышьяка в виде арсената трехвалентного железа. Определение стабильности осадков осаждения проводили по протоколу Toxicity Characteristic Leaching Procedure (TCLP). Осадок, полученный в результате нейтрализации раствора выщелачивания, не требует специального захоронения, так как конечная концентрация мышьяка в экстрактах TCLP тестов составила 0,14 мг/л.

Ключевые слова: арсенипиритный концентрат, биоокисление, чановое выщелачивание, *Acidithiobacillus ferrooxidans*, *Sulfobacillus thermosulfidooxidans*, золото, мышьяк, опытное испытание.

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