

TWO-STAGE COMBINED BIOLOGICAL AND CHEMICAL LEACHING OF A REFRACTORY GOLD-BEARING SULPHIDE ORE

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ABSTRACT. A sulphide ore containing 4.1 g/t gold most of which finely disseminated in pyrite, was subjected to two-stage processing for extracting these precious metals. The first stage was connected with liberation of the gold and silver from the sulphide matrix as a result of the sulphide oxidation by means of acidophilic chemolithotrophic bacteria. The liberated gold and silver were solubilised during the second stage by solutions containing thiosulphate and amino acids as complexing agents. About 90 % of the gold and 65 % of the silver were extracted in this way for 15 days from 10 kg samples leached in percolation columns.

Keywords: sulphide ore, gold, combine leaching

ДВУСТАДИАЛНО ХИМИКО-БИОЛОГИЧНО ИЗЛУГВАНЕ НА ТРУДНО ДОСТЪПНА, ЗЛАТО-СЪДЪРЖАЩА СУЛФИДНА РУДА

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РЕЗЮМЕ. Сулфидна руда съдържаща 4.1 g/t злато, по-голяма част от което финно впръснато в пирита, бе подложена на двустадиална обработка за извличане на благородните метали. Първата фаза беше свързана с окисление на сулфидите чрез ацидофилни хемолитотрофни бактерии и разкриване на златото и среброто от сулфидната матрица. През втората фаза се извършваше разтваряне на разкритите злато и сребро чрез разтвори съдържащи тиосулфат и аминокиселини като комплексиращи агенти. За 15 дни бяха извлечени около 90% от златото и 65% от среброто от 10 кг проба в перколационни колонии.

Introduction

Gold finely disseminated in sulphide minerals is refractory to leaching since the leachants can not penetrate inside these minerals to solubilize the enclosed gold. Different acidophilic chemolithotrophic bacteria are able to oxidize the sulphides to soluble sulphates and to liberate this gold. The oxidation is carried out in diluted sulphuric acid solutions in which the exposed gold is practically not soluble. This gold remains in the solid residues after the bacterial oxidation and is susceptible to the subsequent leaching by suitable reagents such as cyanide, thiosulphite and thiourea (Livesey-Goldblatt et al., 1983; Groudev and Groudeva, 1993; Neale et al., 2011). The bacterial pretreatment of gold-bearing sulphides is applied in commercial scale mainly towards sulphide concentrates as a continuous-flow process in units consisting of several reactors with mechanical stirring and enhanced aeration arranged in a series. In some cases, however, e.g. with low-grade sulphide ores, the bacterial oxidative pretreatment is carried out in heaps especially constructed for this purpose. The pretreated ore heaps are then leached for recovering the liberated precious metals.

Various types of chemolithotrophic bacteria can be used in the bacterial oxidation process, where these show differences in the reactions that they catalyze and in the conditions under which they operate. At present, most industrial operations for bacterial pretreatment of gold-bearing sulphide concentrates

use mixed cultures of mesophilic chemolithotrophic bacteria, mainly of the species *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*, which operate optimally at 35 – 41°C. Some moderately thermophilic bacteria, mainly of the species *Acidithiobacillus caldus* and of some species of the genus *Sulfobacillus*, operating at 45 – 55°C, as well as some extremely thermophilic bacteria of the genera *Sulfolobus* and *Acidianus* able to oxidize sulphide minerals at 75 – 80°C have been also used. The bacterial pretreatment in heaps proceeds at lower temperatures and is based mainly on the activity of mixed populations of mesophilic chemolithotrophic bacteria (Olson et al., 2003; Watling, 2006; Rawlings and Johnson, 2007).

Usually, pyrite and arsenopyrite are the main gold-bearing sulphide minerals. It has been found that in some cases the final extraction of gold and silver from bacterially pretreated concentrates depends on the degree of pyrite oxidation. In some other cases, however, it is necessary to oxidize only a relatively small amount of the pyrite for achieving high gold and silver extractions. This is due to the fact that in some pyrite specimens these precious metals are located mainly in the defect sites of the pyrite crystal lattice and these sites are preferentially attacked by the chemolithotrophic bacteria. Similar data are available also for the location of precious metals in other sulphide minerals, e.g. gold in chalcopyrite and silver in galena.

In most industrial operations the leaching of gold is carried out by means of cyanide solutions. Cyanides, however, are highly toxic reagents and can cause serious environmental problems. At the same time, it has been shown that gold and silver are leached efficiently by means of ammoniacal solutions of thiosulphate. In some cases amino acids have been added to these solutions (Groudev et al., 1996). Amino acids have the ability to complex precious and heavy metals (Gillard et al., 1973) and to stabilize thiosulphate. It has been found that the addition of some amino acids to the thiosulphate solutions increases the gold and silver extraction and decreases the thiosulphate consumption (Groudev et al., 1993; Michel and Frenay, 1998; Freg and van Deventer, 2011). The source of the amino acids being used in such leach systems can be different. The most attractive from an economical point of view is the utilization of protein hydrolysates obtained from different rich-in-protein waste products, including microbial biomass, and containing mixtures of different amino acids in suitable proportions.

This paper contains some data from a study on the processing of a low-grade sulphide ore containing gold, silver and some non-ferrous metals (copper, zinc, lead), by means of a two-stage process including the bacterial oxidation of the metal-bearing sulphides as a first stage of the process, followed by the alkaline leaching of the exposed precious metals by means of solutions containing thiosulphate and amino acids as a second stage.

Materials and Methods

The gold-bearing sulphide ore from the Zlata deposit consisted mainly of quartz (84%) and sericite (8%). Clay minerals, carbonates (mainly calcite) and oxidation products (mainly jarosites) were also detected. Pyrite was the main sulphide mineral in the ore but galena, chalcopyrite and sphalerite were also present. The total content of sulphides in the ore was about 2%. The pyrite was the main gold-bearing mineral. The main portion of the gold particles was less than 1 micron in size. Galena was the main silver-bearing mineral in the ore but silver was present also in the pyrite. Data about the chemical and mineralogical composition of the ore are shown in Tables 1 - 3.

Table 1
Data about the chemical and mineralogical composition of the ore used in this study

Component	Content, %	Component	Content, %
Total sulphur	1.40	Quartz	84.2
Sulphide sulphur	1.25	Sericite	8.0
Sulphate sulphur	0.15	Sulphides	2.3
Iron	1.94	Iron oxides and hydroxides	1.4
Copper	0.12	Clay minerals (alumosilicates)	2.5
Zinc	0.05	Carbonates	1.0
Lead	0.19	Others	0.6
Gold	4.1 g/t		
Silver	17.0 g/t		

A large number of pure and mixed cultures of chemolithotrophic bacteria were tested initially to evaluate their ability to oxidize the pyritic ore and to liberate the gold and silver encapsulated in the sulphide crystal lattices. Some of these cultures were isolated from liquid or solid samples collected in the deposit from piles consisting of the pyritic ore and mining wastes and exposed to processes of spontaneous natural leaching. The other cultures were isolated from such samples but collected in other rich-in-pyrite ore deposits.

Table 2
Gold and silver phases in the ore

Phases of the precious metals	Distribution (in % from the relevant total content)	
	Au	Ag
Free metal	6.4	-
Metal encapsulated in iron oxides and hydroxides	18.5	16.1
Metal disseminated finely in sulphides	71.6	78.6
Metal disseminated finely in silicates	3.5	5.3
Total	100.0	100.0

Table 3
Content and distribution of the precious metals in the different particle size fractions of the ore

Particle size fraction, mm	Yield, %	Content, g/t		Distribution, %	
		Au	Ag	Au	Ag
-1	21.2	6.0	26	31.1	32.5
+1 -5	30.1	4.2	18	30.9	32.0
+5 -10	28.4	3.7	14	25.6	23.4
+10 -15	20.3	2.5	10	12.4	12.1
Total	100.0	4.1	17	100.0	100.0

The testing was carried out by the shake-flask technique using nutrient medium of Macintosh without Fe²⁺ but containing finely ground (less than 0.074 mm) pyritic ore at 20% (w/v) pulp density. The flasks were inoculated with 10% (v/v) late-log-phase bacterial culture containing ~ 5.10⁸ cells/ml grown on Fe²⁺ or pyrite as energy sources. The cultivation was carried out on a rotary shaker (180 rpm) at 30°C for 14 days

The five most active cultures from the above-mentioned testing were used in leaching experiments using small PVC columns with an effective height of 1000 mm and a 110 mm internal diameter. Each column was charged with 10 kg of ore crushed to minus 15 mm. Initially diluted sulphuric acid solutions (with a pH of 1.9) containing chemolithotrophic bacteria (about 5.10⁸ cells/ml), (NH₄)₂SO₄ and KH₂PO₄ in concentrations of about 0.2 and 0.1 g/l, respectively, ferric ions (~ 3 g/l, most in the trivalent state) and dissolved oxygen were recycled through the columns in a mixed open-lock mode for about 5 days to inoculate the ore with active bacteria. Then the leaching was proceeded by the lock cycle mode using solutions containing 5 g/l sulphuric acid and applied at an irrigation rate of 8 - 10 l/24 h. Ammonium and phosphate ions were added periodically to maintain their concentrations at

levels higher than 0.05 g/l. Air was injected from the down end of the columns to maintain the dissolved oxygen in the ore pore solution at concentrations higher than 5 mg/l. The duration of leaching was 160 days and the temperature inside the ore mass in the columns varied within the range of 20 – 24°C. The progress of the bacterial oxidation was followed by analyses of the circulating solutions for ferrous, ferric and total iron species, non-ferrous metals, sulphate ions, pH, Eh, and number of iron-oxidizing chemolithotrophic bacteria. Triplicate experiments were conducted with each culture and the standard deviations were within 5%.

After the bacterial pretreatment the ores were washed several times with fresh water to remove the residual acid and then were subjected to leaching by solutions containing thiosulphate and amino acids as complexing agents towards the precious metals and copper. The optimal composition of this solution towards the pretreated ore was established by experiments carried out by the shake-flask technique and in the small columns. Then the ore pretreated to the desired degree of oxidation in a large column was subjected to leaching by solution containing 150 mM $S_2O_3^{2-}$, total amino acids concentration of 50 mM, 10 mM sulphite ions, 15 mM copper ions, with a pH maintained within the range of 9.5 – 10.0 by ammonia. The leaching was carried out at 21 – 23°C for 14 days.

The leach solutions were pumped to the tops of the columns at a rate of 100 l/t ore per 24 h. The pregnant column effluents containing the dissolved gold and silver periodically were treated by cementation with metallic zinc to precipitate these metals as mixed gold-silver concentrates. The depleted solutions from the concentration units were collected in regeneration vessels where make up water and reagents were added to the desired levels. The leach solutions adjusted in this way were then recycled to the columns.

Elemental analysis of the liquid samples from the bacterial pretreatment and gold leaching was carried out by means of atomic absorption spectrometry and inductively coupled plasma spectrometry. Elemental analysis of the solid samples was carried out by digestion and measurement of the ion concentrations in solution by the above-mentioned methods. Control analyses of gold and silver in the solid samples before and after the leaching were carried out by cupellation (fire assay). The amino acids concentrations were determined by an amino acid analyzer. The thiosulphate concentration was determined titrimetrically with iodine.

The isolation, identification and enumeration of microorganisms were carried out by methods described elsewhere (Karavaiko et al., 1988; Hallberg and Johnson, 2001).

Results and Discussion

Bacterial pretreatment of the ore

The testing of different cultures of chemolithotrophic bacteria by the shake-flask technique resulted in the obtaining of degrees of sulphide oxidation within a broad range (from 44.2 to 92.7% for 14 days). The highest degree of oxidation was achieved by a pure strain of *Acidithiobacillus ferrooxidans*. This strain was isolated many years ago from an ore sample from a dump consisting of a low-grade copper sulphide ore.

Chalcopyrite and covellite were the main copper-bearing minerals in this ore but bornite and chalcocite were also present. However, the pyrite was the main sulphide mineral in the ore. The culture used in the present study consisted of a line of this strain adapted to the gold-bearing ore from the Zlata deposit by consecutive transfers during a long period of time.

Some mixed cultures consisting of two or more different species of acidophilic chemolithotrophic bacteria were also active (with a degree of sulphide oxidation within the range of about 80 – 90%). Most of these cultures contained *At. ferrooxidans* and *Leptospirillum ferrooxidans* as the prevalent species. *At. thiooxidans* was also present in most of the cultures, although in lower numbers than the iron-oxidizing species. It is interesting to be mentioned that a pure strain of *L. ferrooxidans* was also very active (with 85.1% of sulphide oxidation), although these bacteria possess no sulphur-oxidizing ability. Two cultures of *Ferroplasma spp.* showed a poor sulphide oxidation.

Some cultures, apart from the mesophiles, contained also some moderately thermophilic species, mainly *At. caldus* and bacteria related to the genus *Sulfobacillus*. The testing of these cultures at higher temperatures (45 – 55°C) resulted in domination of the moderately thermophilic species but the degrees of sulphide oxidation were lower than the best results achieved by the mesophilic cultures. Facultative autotrophs related to the genus *Acidiphilium* were also present in some of the cultures but in low numbers (less than 10^3 cells/ml).

The pH of the leach solutions decreased during the oxidative pretreatment of the ore and in most cases at the end of pretreatment reached values lower than 1.3 as a result of the generation of sulphuric acid. At these low pH values the precipitation of iron (as jarosites) was minimized. However, some jarosites were detected on the surface of the ore particles. The final concentrations of dissolved iron in the most active cultures reached about 3.50 g/l. Most of this iron was in the ferric state and this reflected in Eh values higher than 500 mV.

Apart from the pyrite, the other sulphides present in the ore were also oxidized during the pretreatment. Copper and zinc were solubilized and their maximal concentrations in the leach solution reached 150.7 and 96.0 mg/l, respectively, reflecting maximal copper extraction of 62.8% and a maximal zinc extraction of 96.0%. Most of the galena was oxidized to $PbSO_4$ which is not soluble under the experimental conditions.

Four from the five most active cultures selected of the basis of the shake-flask tests had similar species composition consisting of *At. ferrooxidans*, *At. thiooxidans*, *L. ferrooxidans* and *Acidiphilium sp.* The initial quantitative ratios between these species were to some extent different in the different cultures. However, in all cultures the iron-oxidizing species *At. ferrooxidans* and *L. ferrooxidans* were the prevalent microorganism and their number in the column effluents exceeded 10^7 cells/ml during almost the whole pretreatment period. *At. thiooxidans* was present in lower numbers, usually in concentrations 10^3 - 10^5 cells/ml in the column effluents. *Acidiphilium* was present in small numbers, less than 10^2 cells/ml. The degree of sulphide oxidation achieved by each of these four cultures exceeded 85%, with a maximum of 93.2% achieved by the most active among them.

The pretreatment in the columns was carried out in open systems and it was not possible to prevent the contaminations of the leach systems from microorganisms penetrating from outside. For that reason, the initially pure culture of the very active strain of *At. ferrooxidans* soon since the start of the experiment was turned into a mixed culture with a species composition similar to that of the other four cultures. The introduction of the new members to the bacterial culture consisting only of this strain had not a positive effect on its activity as the final degree of the sulphide oxidation by the new mixed culture was 87.1%

Leaching of precious metals from the pretreated ore

The leaching of precious metals from the original, non-pretreated ore was not efficient and only about 25% of the gold and about 20% of the silver were extracted by thiosulphate (with and without amino acids) or by cyanidation.

The initial experiments on the effect of the degree of sulphide oxidation on the extraction of precious metals during the subsequent leaching carried out by the shake-flask technique and in the small columns revealed that the dissemination of the precious metals in the sulphides, especially in the pyrite, was not homogeneous and that bacteria were able to oxidize preferentially just these sites in the crystal lattices of the sulphides in which the precious metals were located. It was found that a degree of sulphide oxidation of about 75 – 80% was sufficient to extract about 90% of the gold and about 65% of the silver (Figure 1).

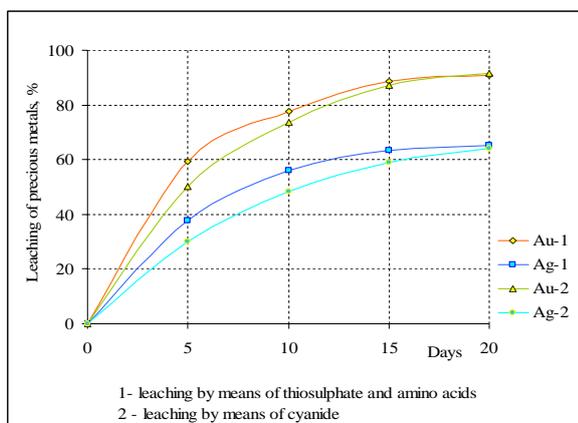


Fig. 1. Leaching of precious metals from the sulphide ore pretreated by means of bacterial oxidation

The consumption of reagents during the leaching of the precious metals amounted to 12.0 kg ammonium thiosulphate, 3.5 kg protein hydrolysate, 0.71 kg copper sulphate, 0.68 kg ammonium sulphite and 5.0 kg ammonia per ton of pre. The degree of extraction of the dissolved precious metals from the pregnant solutions by cementation was higher than 98%. The products from the cementation unit were mixed gold-silver concentrates which contained also copper and zinc as valuable components. The leaching of these concentrates by sulphuric acid at 75 – 80°C and in the presence of oxygen resulted in the selective dissolution of the copper and zinc. These non-ferrous metals can be recovered from the pregnant solutions after leaching by means of different methods, e.g. by solvent extraction plus electrowinning.

Further oxidation of the sulphides resulted in a relatively small increase of the extraction of the precious metals.

Control experiments by cyanidation gave similar results.

Conclusion

The results from this study revealed that the prior bacterial oxidation of refractory gold-bearing sulphide ores containing also non-ferrous metals can be combined with the leaching and recovery of these non-ferrous metals. Only lead is not soluble in the diluted sulphuric acid solutions which are used in such operations. These processes can be performed in heaps with a construction very similar to that of the heaps which are currently used for bacterial leaching of copper. The ores pretreated in this way can be efficiently leached by relatively non-toxic solutions containing thiosulphate and amino acids as metal-complexing reagents. The extractions of precious metals by such solutions in most cases are similar to those obtained by cyanidation.

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