

LEACHING OF GOLD FROM A POLYMETALLIC SULPHIDE ORE

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ABSTRACT. A heap consisting of 5 tons of a rich-in-pyrite copper sulphide ore containing also gold and silver finely disseminated in pyrite and arsenopyrite was leached by means of a mixed culture of acidophilic chemolithotrophic bacteria to solubilize copper and to liberate the precious metals from the sulphide matrix. 70.1% of the copper was leached from the ore within 8 months. The degree of sulphide oxidation at the end of this period reached about 59%. The copper was precipitated from the pregnant heap effluents by cementation with metallic iron. The pretreated ore was washed by water and then was leached by means of alkaline solutions containing amino acids of microbial origin and thiosulphate to solubilize gold and silver. 79.4% of the gold and 59.4% of the silver were leached in this way within 30 days. The pregnant heap effluents were treated by cementation with metallic zinc to precipitate the precious metals as mixed gold-silver concentrates. The waste waters from the different technological stages were treated by means of a constructed wetland located near the heap.

ИЗВЛИЧАНЕ НА ЗЛАТО ОТ ПОЛИМЕТАЛНА СУЛФИДНА РУДА

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РЕЗЮМЕ. Халда, състояща се от 5 тона богата на пирит медна руда, съдържаща също злато и сребро фино впръснати в пирит и арсенопирит, бе излужена посредством смесена култура на ацидофилни хемолитотрофни бактерии, за да се разтвори медта и да се освободят благородните метали от сулфидната матрица. 70,1% от медта бе излужена от рудата за осем месеца. Степента на окисление на сулфидите в края на този период достигна около 59%. Тази предварително окислена руда бе промита с вода, след което бе излужена посредством алкални разтвори, съдържащи аминокиселини от микробен произход и тиосулфат, за да разтворят златото и среброто. 79,4% от златото и 59,4% от среброто бяха излужени по този начин за 30 дни. Набогатените на тези метали разтвори, изтичащи от халдата, бяха обработени чрез циментация с метален цинк (Zn⁰), за да се утаят благородните метали като смесени златно-сребърни концентрати. Отпадните води от различните технологични етапи бяха третираны посредством конструирано мочурище, разположено в близост до халдата.

Introduction

The bacterial pretreatment of gold-bearing sulphide ores is an expanding technology, which has been applied in commercial-scale in several countries (Bonney, 2000; Potts, 2001; Gilbertson, 2004).

The pretreatment is achieved by means of acidophilic chemolithotrophic bacteria, which oxidize the gold-bearing sulphide minerals, mainly pyrite and arsenopyrite, and liberate the gold from the sulphide matrix. The liberated gold is then leached by different chemical reagents, mainly by cyanides. However, the cyanides are highly toxic reagents and, regardless of the presence of several technologies for their efficient degradation, the gold cyanidation is connected with sophisticated and expensive measures to avoid substantial environmental problems. For that reason, at present a great attention is paid to non-toxic reagents, which are able to solubilize gold. A very efficient leaching of gold from different mineral raw materials has been achieved by means of solutions containing amino acids of microbial origin and thiosulphate ions as gold-complexing agents (Groudev and

Groudeva, 1993; Groudev, 1996; Groudev et al., 1996, Spasova and Groudev, 1996).

In this study a rich-in-pyrite copper sulphide ore containing gold encapsulated in sulphide minerals was initially treated by means of acidophilic chemolithotrophic bacteria to leach the copper and to liberate the gold. The ore then was leached by solutions containing microbial amino acids and thiosulphate.

Materials and Methods

Data about the chemical and mineralogical composition of the ore used in this study are shown in Table 1. Chalcopyrite was the main copper-bearing mineral in the ore but secondary copper sulphides such as covellite and bornite were also present. The ore was rich in pyrite and the total content of sulphides was about 10 %. Most of the gold was finely disseminated in pyrite and arsenopyrite. The main portion of the gold particles was less than 1 micron. Quartz was the main mineral of the host rock. Clay minerals and oxidation products (mainly jarosites) were also detected.

Table 1

Data about the chemical and mineralogical analysis of the ore used in this study

Component	Content	Component	Content
Copper	0.80%	Silver	8.2 g/t
Total sulphur	4.1%	Gold	4.6 g/t
Sulphide sulphur	3.7%	Gold phases (in % from the total gold content):	
Iron	6.0%		
Sulphide minerals:		Free gold	2.4%
- pyrite	7.0%	Gold encapsulated in iron hydroxides and oxides	10.7%
- arsenopyrite	1.0%	Gold finely disseminated in sulphides	84.2%
- chalcopyrite	1.0%	Gold finely disseminated in silicates	2.7%
- bornite	0.5%	Total	100%
Other sulphides	0.5%		

The treatment of the ore was carried out by the heap technique. The heap had the shape of a truncated pyramid and was constructed on a slightly steep ground cover by a corrosion-resistant cement to facilitate the collection and to prevent the seepage of solutions. The heap contained 5 tons of ore crushed to minus 10 mm. A system of perforated PVC pipes was installed inside the heap during its construction. The open ends of these pipes stick out outside the ore mass to facilitate the natural aeration of the heap. Solutions containing chemolithotrophic bacteria, iron ions (mainly in the trivalent state), some essential nutrients (mainly ammonium and phosphate ions), sulphuric acid and dissolved oxygen were used to leach copper and to liberate the gold from the sulphide matrix. The solutions were recycled through the heap at a rate of 100 l/ton ore per 24 h. The pregnant heap effluents were treated by cementation with metallic iron (Fe^0) when their copper content exceeded 500 mg/l. The cementation was carried out in reactors with mechanical stirring using fine iron shavings to precipitate the copper. The pH of the recycled solutions was maintained at values lower than 2.5 by addition of sulphuric acid, and the redox potential (Eh) was maintained at values higher than 500 mV by oxidation of the ferrous ions to the ferric state in a BACFOX unit (Groudev et al., 1984). $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 were added to produce concentrations of the NH_4^+ and H_2PO_4^- ions of about 200 and 50 mg/l, respectively. The progress of the bacterial oxidation was followed by analysis of the circulating solution for ferrous, ferric and total iron species, copper and sulphate ions, pH, Eh, and number of the iron-oxidizing chemolithotrophic bacteria.

After the sulphide oxidation and the copper leaching the ore was washed with fresh water and then treated with solutions containing microbial protein hydrolysate – 1.0 g/l, thiosulphate ions (added as ammonium thiosulphate) – 15 g/l, copper ions (added as copper sulphate) – 0.5 g/l and sulphite ions – 0.5 g/l. The pH of the solutions was maintained in the range of 9.5 – 10.0 by addition of ammonia. The protein hydrolysate was a mixture consisting of protein hydrolysates from waste biomass of three different microbial species. The hydrolysates contained

different gold-complexing amino acids and were mixed together in suitable proportions.

The leach solutions were pumped to the top of the heap at a rate of 200 l/ton ore per 24 h. The solutions percolated through the ore mass and dissolved gold and silver. The heap effluents were collected in a collector pond and then were pumped to a stirred reactor where the dissolved precious metals were precipitated by means of cementation reactions with metallic zinc (Zn^0). The depleted solutions from the cementation were collected in a regeneration vessel where make up water and reagents were added to the desired level. The leach solutions adjusted in this way were then recycled to the heap.

The waste waters from the copper and then from the gold leaching stages were treated by means of a constructed wetland located near the heap. The wetland was characterized by an abundant water and emergent vegetation and a diverse microflora. *Typha latifolia* and *Typha angustifolia* were the prevalent plant species in the wetland but representatives of the genera *Juncus*, *Potamogeton*, *Carex* and *Poa* as well as different algae were also present.

Elemental analysis of the ore samples was performed by digestion and measurement of the ion concentration in solution by atomic adsorption spectrometry and induced coupled plasma spectrometry. Gold and silver were determined also by means of the fire assays. These spectrometrical methods were also used to analyse the liquid samples. The amino acid concentrations were determined by an amino acid analyzer. The thiosulphate ions were determined titrimetrically with iodine.

The isolation, identification and enumeration of microorganisms were carried out by methods described elsewhere (Karavaiko et al., 1988; Groudev, 1990). The activity in situ in the heap of the acidophilic chemolithotrophic bacteria was determined by following the rates of ferrous ions oxidation and $^{14}\text{CO}_2$ fixation in samples of heap effluents as well as in 9K nutrient medium (Silverman and Lundgren, 1959) inoculated with freshly collected ore samples. The samples were cultivated in the heaps at the different climatic seasons (Spasova et al., 2005).

Results and Discussion

The treatment of the ore by means of the acidophilic chemolithotrophic bacteria was very efficient. Within a few days following initiation of the treatment, the heap was densely populated with such bacteria. *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* were the prevalent microorganisms in the leach system. The total number of these bacteria in the circulating solutions was higher than 10^8 cells/ml. However, most of these bacteria were firmly attached to the ore and their number exceeded 10^9 cells/g ore in the upper heap layers. *Acidithiobacillus thiooxidans* and some acidophilic heterotrophic bacteria (mainly such related to the genus *Acidiphilium*) were also present but in lower numbers. The bacterial activity in situ was very high and markedly depended on the temperature inside the heap which was higher during the warm summer months (Table 2).

Table 2
Bacterial activity in situ at different temperatures

Sample tested	Fe ²⁺ oxidized for 5 days, g/l	¹⁴ CO ₂ fixed for 5 days, counts/min.ml (g)
Heap effluents with pH of 2.1-2.4 + Fe ²⁺ (9 g/l) at 6–9 °C	0.55 - 2.30	1500 - 7700
Heap effluents with pH of 2.1-2.4 + Fe ²⁺ (9 g/l) at 12–18 °C	1.43 - 6.84	4100 - 20100
Ore suspensions in 9K nutrient medium (with 9 g/l Fe ²⁺ and pH of 2.5) at 6–9 °C	0,59 - 2.75	1500 - 8800
Ore suspensions in 9K nutrient medium (with 9 g/l Fe ²⁺ and pH of 2.5) at 12–18 °C	1.36 - 7.74	4100 - 24200

70.1% of the copper was leached from the ore within 8 months of treatment (from the beginning of March to the end of October) (Fig. 1). The treatment of the copper-bearing pregnant heap effluents by cementation was also efficient and the obtained cement copper concentrates contained about 80 – 82 % copper. The consumption of metallic iron during the cementation amounted to about 2.0–2.5 kg iron/g copper.

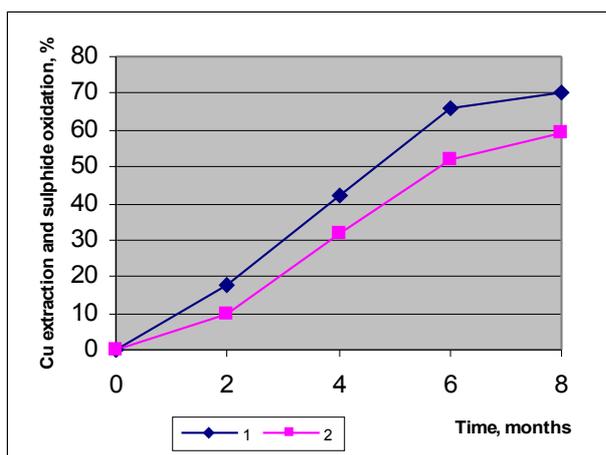


Fig. 1. Leaching of copper (1) and degree of sulphide oxidation (2) during the treatment by means of chemolithotrophic bacteria

The content of sulphide sulphur in the ore at the end of the period of copper leaching was lowered to 2.18% and this reflected a degree of sulphide oxidation of about 59%. Preliminary experiments in small percolation columns (with 10 kg of ore each) revealed that this degree of sulphide oxidation was sufficient to liberate most of the gold from the sulphide matrix. This was probably due to the fact that in the gold-bearing sulphides in the ore the gold was located mainly in the defect sites of their crystal lattices and these sites were preferentially attacked by the chemolithotrophic bacteria (Lazer et al., 1986). During the above-mentioned preliminary experiments it was found that the gold extraction from such pretreated ore samples exceeded 85%, while the extraction from the original, non-pretreated ore was less than 20%.

Control experiments carried out in such columns using cyanide-bearing leach solutions revealed that the gold and silver extractions were similar to those obtained by the combined chemico-biological method used in this study.

The subsequent leaching of precious metals from the pretreated ore heap was also efficient (Fig. 2). The number of undesired microbial contaminants in the leach system was low due to its relatively high pH. The number of chemolithotrophic bacteria growing at the expense of the thiosulphate (mainly such related to the species *Thiobacillus thioparus*) as well as the heterotrophs growing at the expense of the amino acids in the leach solutions were than 10² cells/ml each of these two groups of microorganisms.

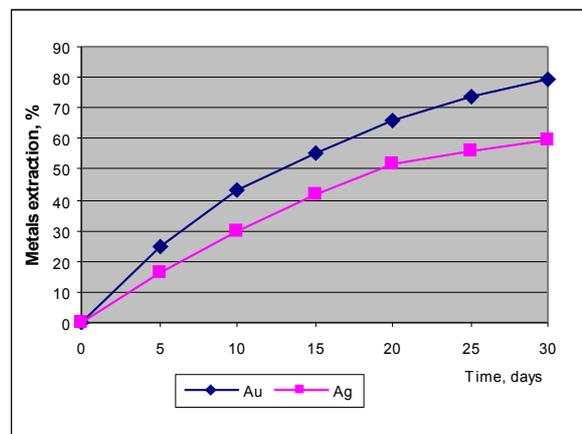


Fig. 2. Leaching of precious from the pretreated ore

The degree of extraction of the precious metals from the pregnant solutions by cementation with Zn⁰ was higher than 97 %. The products from the cementation were mixed gold-silver concentrates, which contained also copper and zinc as valuable components. These concentrates are amenable to processing by the well-known conventional methods for recovering pure gold and silver.

The consumption of reagents during the leaching and cementation of the precious metals amounted to 5.1 kg ammonium thiosulphate, 0.28 kg protein hydrolysate, 0.9 kg copper sulphate and 0.15 kg metallic zinc per ton of ore.

Regardless of the fact that the waste waters from the copper and gold leaching stages differed considerably, these both types of water were cleaned up efficiently by the constructed wetland. The waste waters from the copper leaching stage were acidic, with a very low organic content and contained iron, copper, arsenic and sulphate ions as the main pollutants. The waste waters from the gold leaching stage were alkaline, with a higher organic content and contained different sulphur-bearing ions as the main pollutants. These waters also contained some dissolved heavy metals (mainly copper and zinc) but in relatively low concentrations. The both types of water contained fine solid particles.

The removal of the above-mentioned pollutants in the constructed wetland was due to different processes. The ions of the heavy metals and arsenic were precipitated mainly as the relevant sulphides by the hydrogen sulphide produced by the anaerobic sulphate-reducing bacteria. However, portions of iron and manganese were precipitated as Fe(OH)₃ and MnO₂ after the prior bacterial oxidation of the Fe²⁺ and Mn²⁺ ions, respectively. Some arsenic was removed as a result of its sorption by the iron hydroxides. The different sulphur-bearing ions were transformed to sulphates, which then were reduced

to hydrogen sulphide. Portions of the metal and arsenic ions were adsorbed by the plant and microbial biomass and by the clay minerals present in the wetland. The dissolved organic compounds (mainly residual amino acids and secreted microbial and plant metabolites) were degraded by the heterotrophic microorganisms. The non-dissolved solids were removed mainly by sorption but also by bioagglomeration carried out by secreted microbial metabolites. As a result of the above-mentioned processes, the wetland effluents possessed the qualities of the waters intended for use in the agriculture and/or industry.

The results from this study showed that the consecutive leaching of copper and precious metals from rich-in-pyrite ores by means to microorganisms and non-toxic reagents is technically feasible and environmentally safe way to process such ores.

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