BIOLEACHING OF METALS FROM A WASTE ORE IN CONNECTION WITH COPPER RECOVERY, ENVIRONMENT PROTECTION AND ELECTRICITY GENERATION

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ABSTRACT. A waste ore dump located in central Bulgaria, near Sredna Gora Mountain, after a long period of industrial and then spontaneous bioleaching process, still contained about 0.14 % residual copper and was inhabited by different acidophilic chemolithotrophic bacteria. After rainfall, as a result of spontaneous bacterial activity, acid drainage waters were generated and polluted the environment. To solve this problem, an experimental laboratory installation to treat samples of such waters was constructed. The installation consisted of percolation columns containing samples from the dump, a collector pool for the drainage waters, a cementation unit for copper precipitation and a BACFOX (BACterial Film OXidation) unit for bacterial oxidation of the ferrous ions to the ferric state. The solutions treated in this way were recycled to the ore subjected to leaching. Another portion of the barren solutions from the cementation unit were treated by means of a permeable reactive multibarrier. The effluents from this multibarrier were enriched in biodegradable organic substrates and were characterized with a pH close to the neutral point, absence of dissolved oxygen and low electrochemical potential and were inhabited by anaerobic heterotrophic microorganisms, including some electrochemically active bacteria possessing iron or sulphate anoxic respiration. It was found that these effluents were suitable for generation of electricity in microbial fuel cells. The treatment of the effluents from these cells in the BACFOX unit made these effluents suitable for leaching copper from the waste ore.

Keywords: waste ore, metal bioleaching, electricity generation, environmental protection

БИОЛОГИЧНО ИЗЛУГВАНЕ НА МЕТАЛИ ОТ ОТРАБОТЕНА РУДА, СВЪРЗАНО С ДОБИВ НА МЕД, ОПАЗВАНЕ НА ОКОЛНАТА СРЕДА И ГЕНЕРИРАНЕ НА ЕЛЕКТРИЧЕСТВО

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РЕЗЮМЕ. Насипище от отработена руда, разположено в България, близо до Средна Гора, след дълъг период на процеси на промишлено и спонтанно биологично излугване, все още съдържаше около 0.14 % остатъчна мед и беше обитавано от различни ацидофилни хемолитотрофни бактерии. След дъжд, в резултат на спонтанната бактериална активност, се генерираха кисели дренажни води, замърсяващи околоната среда. За решаване на този проблеч, беше конструирана лабораторна инсталация за преработване на част от тези води. Инсталацията се състоеше от перколационни колони, съдържащи проби от насипището, колекторен басейн за дренажните води, структура за утаяване на медта и структура за бактериално окисление наферойоните до ферийони. Разворите, третирани по този начин, се рециклираха към излугваната руда. Друга част от обезмедените разтвори след циментацията се третираха чрез пропусклива реактивна мултибариера. Водите, изтичащи от тази мултибариера, бяха набогатени на биологично разградими органични субстрати и се характеризираха с pH близко до неутралния пункт, отсъствие на разтворен кислород и нисък електрохимичен потенциал и бяха обитавани от анаеробни хетеротрофни микроорганизми, включително от някои електрохимично активни бактерии, притежаващи желязо или сулфатно анаеробно дишане. Установено беше, че изтичащите от мултибариерата води бяха подходящи за генериране на електричеството в микробни горивни клетки. Третирането на изтичащите от тези клетки води в структурата BACFOX ги превърна във води, подходящи за излугване на мед от отработената руда.

Ключови думи: бедна руда, извличане на метали, генериране на електричество, опазване на околната среда

Introduction

The ore piles located at the Tsar Asen copper mine, located near the Sredna Gora mountain, in Central Bulgaria, initially (in 1983) contained about five million tons of copper oxide ores from the open cut mining. The initial copper content was about 0.30 %. Malachite was the main copper-bearing mineral but about 20 % of the copper was contained in sulphide minerals, mainly in chalcocite. The lost rock consisted of granite-diorite porphyrites.

The piles containing such low-grade copper oxide ore were subjected to commercial-scale bioleaching by using the classical, at that time, flowsheet of such operations. The leach solution containing bacteria (mainly native acidophilic chemolithotrophs), dissolved oxygen, sulphuric acid and iron ions was pumped to the top of the ore-bearing dumps constructed by transformations of the existed ore piles. The solution percolated through the dumps and dissolved copper. Most copper was solubilized from the oxide minerals by means of the sulphuric acid which was added to the effluents from the cementation unit before their recycling to the dumps. The sulphur content of this ore was too low to permit the formation of sufficient amounts of sulphuric acid during the bacterial oxidation of sulphide minerals.

It must be noted, however, that the role of acidophilic chemolithotrophic bacteria present in the ore dumps was also essential and a considerable amount of the copper present in the ore (mainly the copper in the sulphide minerals) was leached as a result of the bacterial activity (mainly of *Acidithiobacillus ferrooxidans* and Acidithiobacillus thiooxidans but also of *Leptospirillum ferrooxidans* which presence in the ore was established later). The role of these bacteria in the leaching of the ore steadily increased in the course of time which was connected with the much faster leaching of copper from the oxide minerals in comparison with the much more difficult leaching from the sulphides, especially from the chalcopyrite, which was connected with the oxidation of these minerals. The leaching of copper oxide minerals by means of sulphuric acid can be performed as a chemical process using sulphuric acid added to the system from outside. However, the chemolithotrophic bacteria inhabiting the ore facilitate this process and make it economically more attractive by generating sulphuric acid in situ by the oxidation of sulphide minerals (mainly of pyrite and chalcopyrite) present in the relevant ore. The bacterial oxidation of these sulphides can be a direct process carried out by bacteria attached on the mineral surface or to be carried out by means of ferric ions produced as a result of the preliminary bacterial oxidation of ferrous ions (Groudev, 1994; Groudev and Groudeva, 1993; Groudev et al., 2014; Groudeva et al. 1987).

The different amenability of the copper minerals to leaching results step by step to changes of the residual mineralogical and chemical compositions of the relevant copper ores. In general, these changes consist in the decrease of the total content of copper in the partially leached ores and in the increase of the relative portion of the sulphidic copper in these ores. In some cases, these changes are connected with the generation of acid drainage waters as a result of the bacterial oxidation of the residual sulphides, mainly of the pyrite, still present in such ores.

The generation of acid drainage waters in principle is a very serious environmental problem since in most cases these waters contain different toxic elements, such as heavy metals, radionuclides and arsenic. The prevention of this process is usually much more desirable than the subsequent treatment of such waters. Unfortunately, the efficient prevention of acid generation in the huge dumps of rich-in-sulphides waste ores or other mineral wastes is usually an extremely difficult and costly process. In some cases is necessary, even after the total remediation of the environment, to treat polluted drainage waters arising mainly as a result of the activity of some of the indigenous microorganisms inhabiting the relevant territory. Such treatment can be connected with the extraction of some valuable components such as some non-ferrous metals and rare earth elements, and even with the production of electricity by means of especially constructed microbial fuel cells (Groudev et al., 2014).

This paper contains some data about the possibility to combine the bioleaching of copper from an waste ore with the subsequent processing of the copper-bearing pregnant solutions for recovery of cement copper, enrichment of the barren solutions from the cementation in biodegradable organic substrates, followed by the recovery of electricity from the treatment of these solutions in a microbial fuel cell.

Materials and Methods

The ore in the real dump was subjected to a periodic control including the parameters essential for the bioleaching processes (humidity, chemical and mineralogical composition of selected ore samples, presence and numbers of chemolithotrophic bacteria attached on the ore particles, as well as pH, Eh, chemical and microbiological composition of the liquid phase in contact with the ore and of the dump effluents.

The laboratory installation for studying the bioleaching processes consisted of a system of percolation columns containing samples from the waste ore, collector ponds for the pregnant column effluents, cementation units for copper precipitation and BACFOX (BACterial Film OXidation) units for bacterial oxidation of the ferrous ions to the ferric state.

The system for leaching of the ore consisted of four identical plastic percolation columns 80 cm high and with an internal diameter of 20 cm. Each of the columns contained 80 kg of waste ore, with a particle size minus 20 mm. The ore was inhabited by its natural consortium of chemolithotrophic bacteria. The ore in two of the columns was irrigated by solutions from the cementation unit, and in the other two columns – by solutions from the BACFOX unit. Ammonium and phosphate ions were added to these solutions as nutrients for bacteria.

The cementation unit consisted of four plastic cylindrical columns also 80 cm high and with an internal diameter of 20 cm. The columns were filled with iron shavings characterized by large free surfaces to facilitate the precipitation of the cement copper. Each of these columns was connected to receive the pregnant copper-bearing effluent from the relevant percolation ore-containing column.

A portion of the barren solution from the cementation unit was treated by means of a permeable reactive multibarrier. The multibarrier was a plastic cylindrical column 80 cm high, with an internal diameter of 30 cm. The column was filled with a mixture of limestone (crushed to minus 10 mm particle size) and organic matter consisting of spent mushroom compost, fresh leaf compost, animal manure and saw dust. These components contained their own viable indigenous microflora consisting of different anaerobic microorganisms, mainly sulphate-reducing bacteria and other interconnected microorganisms. Apart from the natural microflora of the organic substrates, inoculum containing selected electrochemically active microorganisms was also added to the multibarrier effluents, together with a nutrient solution containing biologically essential elements. Such solutions were subjected to continuous-flow circulation from the inlet and outlet of a membrane-less microbial fuel cell. This fuel cell was a plexiglas column 50 cm high, with an internal diameter of 10 cm, with corrugated slab graphite anode and cathode electrodes located in the bottom and in the top sections of the column, respectively. The treatment of the effluents from the fuel cell in the BACFOX unit made these effluents suitable for leaching copper from the waste ore.

The BACFOX unit consisted of nine plastic columns 80 cm high and with an internal diameter of 3.0 cm each, installed together in a vertical position on the false bottom of a larger plastic column also 80 cm high and with an internal diameter of 20 cm. The surface of the plastic columns was corrugated for increasing the total area for the formation of the biofilms able to oxidize the ferrous iron to the ferric state. These biofilms consisted of ammonium and potassium jarosites densely populated by acidophilic chemolithtrophic bacteria mainly of the species *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*. The numbers and activity of these bacteria were maintained by keeping the whole unit operating during the solutions circulation or submerged in a nutrient solution containing biologically essential elements (usually the 9K nutrient medium was used, with a pH in the range of about 1.8 – 2.3 and with ferrous iron added as ferrous sulphate as a source of energy). The growth and activity of the bacterial films were stimulated by the aeration of the unit with air enriched in carbon dioxide (to about 0.2 %).

The composition of the circulating solutions was monitored at different sampling points located at the inlet and outlet of the units included in the system described above. Elemental analysis was done by atomic adsorption spectrometry and induced coupled plasma spectrometry in the laboratory. The analysis of the elements in solid samples from the ore and precipitates was carried out by decomposition of the samples and measurements of the concentrations of the relevant ions in solution. Mineralogical analysis was carried out by X-ray diffraction techniques. The isolation, identification and enumeration of the microorganisms was carried out by the methods described elsewhere (Karavaiko et al., 1988; Bergey's Manual of Determinative Bacteriology, 1994; Sanz and Köchling, 2007; Escobar et al., 2008; Johnson and Hallberg, 2003).

Results and Discussions

The bioleaching of the initial low-grade copper ore in the real dump to a great extent was connected with the chemical solubilization of the copper oxide and carbonate minerals by the sulphuric acid added to the leach solutions from the outside (Table 1).

The copper extraction from the sulphide minerals, especially from the chalcopyrite, was connected with the oxidation of these minerals, mainly by the chemolithotrophic bacteria inhabiting the dump (Table 2).

This first stage of the leaching turned the initial susceptible to chemical leaching low-grade copper ore (with 59.4 % from the copper present in oxide and carbonate minerals) into a much more refractory low-grade ore with copper predominantly present in sulphides, mainly in chalcopyrite and covellite. A representative sample of this ore was taken from the dump and was tested under laboratory conditions to obtain a stable information about the possibility to continue further the treatment of this ore. The initial experiments revealed that the deep changes in the mineral and chemical compositions of the ore resulted in a quite different efficiency of the copper extraction during the subsequent leaching tests. The leaching by means of sulphuric acid was efficient only towards the residual copper present in oxide and carbonate minerals. However, the stimulation of the chemolithotrophic bacteria still present in the ore by adding nutrients (mainly ammonium and phosphate ions) and maintaining the pH of the leach solutions within the range optimal for these bacteria (from 1.70 to 1.90) resulted in a very efficient bioleaching of sulphides, even of chalcopyrite. The content of copper in sulphides was decreased from the initial 112 mg/100 g ore to 49.6 mg/100 g (i.e. extraction of 55.72 %) for a period of 180 days by leaching in the percolation columns mentioned in this paper. A very positive effect on this leaching was connected with the maintaining of a relatively high Eh potential of the leach solution (higher than 550 mV) by the bacterial oxidation of the ferrous ions after the cementation process to the ferric state in the BACFOX unit. The continuous irrigation of the ore in the columns was very efficient when the leach solutions treated in the BACFOX unit, apart from the predominantly ferric ions, were aerated and contained some dissolved oxygen.

Portions of the barren solutions from the cementation unit (Table 3), instead to be treated for ferrous ions oxidation by the BACFOX unit, were subjected to treatment by means of the permeable reactive multibarrier (Table 4). This treatment was connected with the removal of the toxic components dissolved in these solutions (mainly of the heavy metals and sulphates). The microbial dissimilatory sulphate reduction and the sorption of dissolved metals by the dead plant biomass in the multibarrier were the main mechanisms participating in the water cleaning. The sulphate-reducing bacteria and some metabolically connected microorganisms, mainly cellulose-degrading and sugar-fermenting bacteria, were the prevalent members of the microbial consortium inhabiting the multibarrier.

Table 1.
Data about the bioleaching of a typical low-grade copper ore under different conditions

I. The initial ore sample was subjected to industrial and then spontaneous natural dump bioleaching for a period of about eight years					
Copper content and phase distribution in the ore					
	Before leaching		After leaching		Cu extraction %
	mg Cu/100 g	%	mg Cu/100 g	%	
Cu in oxide and carbonate minerals	243.5	59.4	28.0	20.0	88.5
Cu in secondary sulphide	116.5	28.4	71.0	50.7	39.1
Cu in chalcopyrite	50.0	12.2	41.0	29.3	18.0
Total Cu content	410.0	100.0	140.0	100.0	65.85
II. A sample taken from the ore treated in the first stage and with the composition mentioned for the sample after the above leaching was subjected to new bioleaching in percolation columns for a period of 180 days					
	Before leaching		After leaching		Cu extraction %
	mg Cu/100 g	%	mg Cu/100 g	%	
Cu in oxide and carbonate minerals	28.0	20.0	7.4	13.0	73.6
Cu in secondary sulphide	71.0	50.7	27.6	48.4	61.2
Cu in chalcopyrite	41.0	29.3	22.0	38.6	46.3
Total Cu content	140	100.0	57.0	100.0	59.3

Table 2.
Microflora of the effluents from the real ore dump in Tsar Asen and from the ore-containing laboratory percolation columns

Microorganisms	Cells in the effluents from:	
	Real ore dump	Lab percolation columns
	Cells/ml	
Acidithiobacillus ferrooxidans	$10^3 – 10^6$	$10^6 – 10^8$
Acidithiobacillus thiooxidans	$10^2 – 10^4$	$10^4 – 10^6$
Leptospirillum ferrooxidans	$10^2 – 10^5$	$10^5 – 10^7$
Thiobacillus thioparus	$0 – 10^2$	$0 – 10^1$
Thiobacillus denitrificans	$0 – 10^1$	0
Sulfobacillus thermosulfidooxidans	0	$0 – 10^4$
Acidithiobacillus caldus	0	$0 – 10^3$
Heterotrophic bacteria	$10^1 – 10^3$	$0 – 10^2$
Fungi	$10^1 – 10^3$	$0 – 10^2$
Algae	$0 – 10^2$	0
Protozoa	$0 – 10^2$	0

Table 3.
Data about the recovery of copper by means of cementation of the pregnant leach solutions from the ore dump and from the percolation column

Parameters	Pregnant solutions from	
	Dump	Percolation column
Content of the copper in the pregnant solutions, g/l	0.5 – 1.2	0.8 – 1.7
Recovery of copper from the pregnant solutions, %	86 – 92	92 – 95
Retention time, min	75 – 90	70 – 80
Iron consumed per kg of copper precipitated, kg	2.9 – 3.4	2.8 – 3.2
Copper content in the cement copper, %	60 – 68	80 – 84
Copper content in the effluents from the cementation unit, mg/l	37 – 131	32 – 97

Note: The effluents from the cementation unit were acidified and recycled to the dump or to the BACFOX unit.

It was possible to decrease further the concentrations of dissolved organic compounds and sulphates in the multibarrier effluents by increasing the residence time. However, the efficient reduction of sulphates to hydrogen sulphide followed by precipitation of the dissolved metals as the relevant insoluble sulphides was connected with the presence of relatively higher concentrations of dissolved organic compounds as donors of electrons for the sulphate-reducing bacteria. This usually resulted in high residual concentrations of dissolved organics in the multibarrier effluents at a moment when the metal concentrations in these effluents were decreased below the relevant permissible levels. This made possible the connection of the removal of these organics with the generation of electricity by the microbial fuel cells (MFC). In addition, it was possible to increase the efficiency of electricity generation by such cells by involving some electrochemically active microorganisms from outside to these systems.

Table 4.
Data about the treatment of barren solutions from the cementation unit of the laboratory installation by the permeable reactive multibarrier

Parameters	Before treatment	After treatment	Permissible levels
pH	2.60 – 3.25	7.12 – 7.52	6 – 9
Eh, mV	(+405) - (+563)	(-104) - (-235)	–
Diss. O_2, mg/l	0.3 – 1.0	0.1 – 0.2	2
Solids, mg/l	53 – 125	25 – 95	100
COD, mg/l	32 – 71	345 – 684	40
SO_4^{2-}, mg/l	415 – 1926	198 – 590	400
Cu, mg/l	32 – 53	< 0.5	0.5
Zn, mg/l	8.2 – 23	< 0.5	10
Cd, mg/l	0.03 – 0.14	< 0.01	0.02
Fe, mg/l	307 – 1440	1.4 – 8.2	5
Mn, mg/l	6.2 – 41	< 0.5 – 1.7	0.8

The microorganisms used in this study, apart from the sulphate-reducing bacteria, which transferred electrons from the organic substrates to the anode electrode located in the anoxic section of the MFC by means of the hydrogen sulphide acting as mediator, included also bacteria of the genera *Geobacter* and *Shewanella*. These bacteria formed biofilms on the anode and were able to transfer electrons from the organic substartes via the bacterial respiratory chains directly to the anode. It must be noted, however, that the formation of active and stable biofilms of this type was a slow process and about five months were needed for obtaining the maximum current density generation. Data about the optimum conditions for the connection of the water treatment with the electricity generation in this study are shown in Table 5.

Table 5.
Data about the optimum conditions for the combined wastewater treatment and electricity generation

Parameters	Values
Characteristics of the feeding wastewater:	
COD, mg O_2/l.h	170 – 680
SO_4^{2-}, mg/l.h	147 – 590
COD/SO_4^{2-}, ratio	2.3 – 3.5
pH	7.12 – 7.52
Eh, mV	(-104) - (-235)
Temperature, ^oC	30 – 35
Heavy metal concentrations	Bellow permis-sible levels
Optimum conditions in the MFC:	
Voltage of the open circuit, mV	260 – 280
Current density, mA/cm^2	0.32 – 0.35
O_2 dissolved in the cathodic section, mg/l	7.5 – 8.0
Power, mW/m^2	750 – 800

The continuous treatment of the effluents from the permeable multibarrier by the MFC was connected with a gradual increase of the maximum COD and sulphate removal rates to 248 mg O_2/l.h and 114 mg/l/h, respectively. It was possible to decrease the residual concentrations of dissolved organic carbon and sulphates in the effluents below the relevant permissible levels for waters intended for use in industry, i.e. less than 20 and 400 mg/l, respectively. It must be noted, however, that the treatment of the polluted waters at relatively lower concentrations of the organic donors of electrons (less than 150 mg O_2/l.h) decreased considerably the efficiency of water cleaning and electricity generation. The decrease was connected with the impossibility of these concentrations to satisfy the needs of the microorganisms forming the biofilm on the anode. It was also found that the species composition of the biofilm gradually changed in the course of time.

Comparative experiments for treatment of the multibarrier effluents by means of conventional aerated bioreactor revealed that it was also possible to decrease the concentration of dissolved organic carbon below the relevant permissible level. However, the concentration of sulphates during the treatment was increased and the amount of sludge was much higher (by about one third) than that generated during the anaerobic treatment by the MFC.

Conclusions

The waste ore used in this study and containing only 0.14 % copper was efficiently leached in percolation columns by means of a mixed population of acidophilic chemolithotrophic bacteria. 59.3 % of the copper was leached for a period of 180 days. The pregnant copper-bearing effluents from the columns were efficiently treated by cementation with zero-valent iron and a cement copper containing from 80 to 84 % copper was produced at a very high recovery of 92 – 95 % from the pregnant solutions. The barren solutions from the cementation unit were a subjected to cleaning by means of a permeable reactive multibarrier and the levels of most essential parameters of the effluents with exception of the dissolved organic carbon and sulphates were decreased below the relevant permissible levels for waters intended for use in agriculture and industry. The effluents from the multibarrier were efficiency used for generation of electricity with power of 750 – 800 mW/m^2 by means of MFC.

The results obtained during this study are a solid base for the testing of this research approach under pilot-scale conditions.

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