INSTITUT ZA RUDARSTVO I METALURGIJU BOR | YU ISSN: 1451-0162
KOMITET ZA PODZEMNU EKSPLOATACIJU MINERALNIH SIROVINA | UDK: 622

UDK: 579.6:628.4.038:546.56(045)=861 doi:10.5937/rudrad1204079A

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MOGUĆNOST PRIMENE MIKROORGANIZAMA U CILJU DOBIJANJA BAKRA IZ OTPADNIH MINERALNIH SIROVINA**

Izvod

Mikrobiološko luženje predstavlja u svetu priznat metod za izdvajanja korisnih komponenti iz siromašnih ruda i sekundarnih sirovina.

Prednost mikrobiološkog luženja mineralnih sirovina predstavlja malo ulaganje, odnosno ekonomska opravdanostog luženja, vrlo jednostavna primena i pogodnost ovakvog luženja sa aspekta zaštite životne sredine.

U ovom radu je ispitivanja mogućnost mikrobiološkog luženje bakra iz jalovine (raskrivke starog kopa u Boru) u laboratorijskim uslovima, korišćenjem kulture Acidithiobacillus ferrooxidans.

Izveden je eksperiment luženja u erlenmajerima uz mućkanje. Eksperiment je trajao tri nedelje, na prosečnoj temperaturi od 28^{0}C. Procenat izluženog bakra na kraju eksperimenta je iznosio 34%.

Dobijeni rezultati bi trebalo da posluže kao osnova za ponovno uvođenje ove, u svetu prihvaćene tehnologije u eksploataciji mineralnih sirovina, u cilju dobijanja korisnih komponenata iz siromašnih ruda kao i za remedijaciju kontaminiranog zemljišta.

Ključne reči: *bakar, luženje, Acidithiobacillus ferrooxidans*

UVOD

Intenzivna urbanizacija, brzi razvoj tehnologije u savremenom svetu, posebno u poslednjih trideset godina dovodi do sve većeg nagomilavanja otpadnog materijala različitog porekla i do sve većeg zagađivanja životne sredine. Mikroorganizmi imaju izuzetno važnu ulogu u prirodi i očuvanju životne sredine razgrađujući različite otpadne supstrate. Njihova heterogena metabolička aktivnost omogućava ne samo razgradnju većine organskih molekula i recikliranje biogenih elemenata, već i mnogobrojne transformacije neorganskih jedinjenja.

Transformacije, kruženje, migracije i koncentrovanje hemijskih elemenata u

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** *Ova ispitivanja su finansirana od strane Ministrastva prosvete, nauke i tehnološkog razvoja Republike Srbije u okviru projekta TR 33007 "Implementacija savremenijih tehničko-tehnoloških i ekoloških rešenja u postojećim proizvodnim sistemima RBB i RBM".*

atmosferi, hidrosferi, litosferi i čitavoj biosferi mogu da se vrše istovremeno kako abiogenim, tako i biogenim putem. Među mikroorganizmima koji učestvuju u transformacijama i kruženju elemenata u prirodi poseban značaj se pridaje litotrofnim mikroorganizmima (mikroorganizmima koji se hrane kamenom). Uloga ovih mikroorganizama u prirodi upotrebljena je za njihovu primenu u dobijanju metala, zapravo prevođenje u rastvor (ili koncentrovanje) njihovih teško rastvornih jedinjenja (prvenstveno sulfida). Dakle, procesi koji u prirodi teku spontano, usmereni su i pojačani kako bi se dobili korisni metali, prvenstveno iz metalom siromašnih ruda i otpadnih materijala (vanbilansne rude, raskrivke, jalovine itd.) [1].

Mikrobiološko luženje mineralnih sirovina danas ima široku primenu u svetu, što ukazuje da je ova metoda teorijski i praktično dobro razrađena i da se ovim postupkom dobijaju značajne količine metala. Međutim, treba napomenuti da se parametri razlikuju za svaki slučaj posebno i da zavise od karakteristika podneblja i vrste mineralne sirovine. Za svaki konkretan slučaj primene bakterija u sistemu luženja potrebna su detaljna izučavanja sirovine koja se želi tretirati, ekoloških uslova pod kojima će se luženje izvoditi i same mikroflore koja će se upotrebiti. Preporučuje se korišćenje autohtone bakterioflore, kako bi se usmerili i intenzivirali već postojeći prirodni procesi [2].

Mikrobiološki postupci dobijanja metala značajni su iz sledećih razloga:

- Kao sirovina se upotrebljava otpadni materijal, a dobija se potrebni metal koji bi se nepovratno gubio;
- Postupci mikrobiološkog luženja su nekoliko puta jeftiniji od konvencionalnih, koji su u većini i neprimenljivi za siromašne sirovine;
- Zagađenje životne sredine je svedeno na najmanju moguću meru [1].

Cilj ovog rada je bio da se ispita mogućnost mikrobiološkog luženje bakra iz jalovine (raskrivke starog kopa u Boru) u laboratorijskim uslovima, korišćenjem kulture *Acidithiobacillus ferrooxidans*. Laboratorijskim istraživanjima su definisani sledeći parametri: fizičko-hemijske karakteristike jalovine, odnos tečne i čvrste faze, broj bakterija, vreme luženja, pad pH vrednosti tokom procesa, procenat utrošenog piritnog sumpora, kao i procenat izluženja bakra.

Mikrobiološki postupci luženja siromašnih ruda i jalovina, imaju značajnu ulogu kako za dobijanje "dopunskih" količina metala, tako i u konceptu zaštite okoline, jer se jednostavnom tehnologijom, stavljaju pod kontrolu i usmeravaju, a time i sprečavaju nekontrolisani odlivi metala u vodotokove i zemljište (koji u ovoj sredini predstavljaju polutante).

MATERIJAL I METODE

Hemijske analize

Hemijska karakterizacija jalovišta urađena je konvencionalnom metodom, alkalnim stapanjem sa $NaKCO_3$i rastvaranjem u HCl [3]. Iz filtrata su određivanji Fe, Al, Ti, Ca, Mg, a talog je dalje tretiran sa HF, u cilju dobijanja isparljivog SiF_4, tj. određivanja SiO_2 Ostatak taloga je ponovo tretiran kao silikatni materijal.

Za određivanje alkalnih metala i elemenata u tragovima uzorak je razlagan smesom $HClO_4$ i HF, a za određivanje fosfora uzorak je razlagan smesom carske vode i $HClO_4$.

Alkalni metali su određivani metodom atomske emisione plamene spektrofotometrije, Fe, Al, Ti, Ca, Mg i metali u tragu, metodom atomske apsorpcione plamene spektrofotometrije, a fosfor je određivam spektrofotometrijski u obliku žutog fosfomolibdatnog kompleksa.

Sulfidni sumpor iz jalovišta je određivan gravimetrijski, posle oksidacije sa $KClO_3$ i HNO_3 i taloženja u obliku $BaSO_4$. Korekcija na sulfatni sumpor iz jalovišta rađena je iz «sodnog ekstrakta» (ključali rastvor Na_2CO_3), u obliku $BaSO_4$ [3].

Rendgenska difrakciona analiza

Rendgenska difrakciona analiza (RDA) urađena je na difraktometru Philips PW -1710, sa bakarnom antikatodom, pri opterećenju cevi 40 kV i 20 mA.

Uzorci su snimani u području 2θ 5-60^0. Podaci su prikupljeni tako što je meren svaki 0,02^0 u trajanju od po 0,5 s. Prorezi ('slitovi') su bili fiksni 1,0 -0,10 mm [4].

Identifikacija minerala je urađena korišćenjem programa MPDS i baze podataka JCPDS.

Mikrobiologija

Čista kultura *Acidithiobacillus ferrooxidans* za eksperimente je pripremana trostrukim presejavanjem u erlenmajerima od 500 ml sa 100 ml sveže podloge 9K [5], pH vrednost podloge je podešena sumpornom kiselinom na 2.5. Treće presejavanje je izvedeno u erlenmajeru od 5 dm^3 sa 1 dm^3 9K podloge. Svi erlenmajeri su mućkani na horizontalnom šejkeru pri frekvenci od 200 tresaka u minuti na 28^{0}C. Nakon pet dana, bakterijska kultura je proceđena kroz membran filter (veličina pore 0.45 μm), oprana podlogom 9K bez gvožđa (0 K). Po završenom ceđenju, bimasa dobijena iz 1 dm^3 podloge, sa membrane je isprana sa 20 cm^3 podloge 0K.

Broj mikroorganizama je određivan metodom najverovatnijeg broja [6].

Opis eksperimenta luženja

Eksperiment je izveden sa bakterijskom kulturom *Acidithiobacillus ferrooxidans* i trajao je 21 dan, sa 100 ml rastvora za luženje 9K [5], sledećeg sastava (g/dm^3): $Fe_3(SO_4)_2$ (44.8) $(NH_4)_2SO_4$-3, K_2HPO_4-0.5, $MgSO_4 \cdot 7H_2O$-0.5, KCl-0.1, $Ca(NO_3)_2$-0.01, u erlenmajerima zapremine 500 ml pri početnoj vrednosti pH od 2,5 i gustini pulpe 5% (m/V) (5gr jalovišta u 100 ml rastvora). Kontrolna suspenzija je istog hemijskog sastava, istog pH kao i suspenzija sa *Acidithiobacillus ferrooxidans,* samo je u njoj sterilizacijom inaktivisana kultura *Acidithiobacillus ferrooxidans*.

Eksperiment je izveden na horizontalnoj tresilici firme New Brunswick Scientific. Temperatura inkubacije je bila 28^{0}C, a frekvenca rada tresilice 100 tresaka u minuti. Svakih sedam dana je analiziran pH, broj mikroorganizama i koncentracija bakra.

Sam postupak luženja se zasniva na oksidaciji Fe^{2+} u Fe^{3+}, koji zatim napada pirit, pri čemu je tiosulfat glavni intermedijer, a sulfat krajnji produkt. Oksidacija pirita se opisuje sledećim jednačinama:

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow S_2O_3^{2-} + 7Fe^{2+} + 6H^+ \quad (1)$$

$$S_2O_3^{2} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \quad (2)$$

Fe^{2+} (nastao u reakcijama 1 i 2) može biti reoksidovan do Fe^{3+}, zahvaljujući gvožđe - oksidujućem mikroorganizmu *Acidithiobacillus ferrooxidans*.

$$2Fe^{2+} + 0{,}5O_2 + 2\ H^+ \xrightarrow{\text{MIKROBI}} 2Fe^{3+} + H_2O$$

Ključna uloga *Acidithiobacillus ferrooxidans* je u regeneraciji Fe^{3+}, kao jakog oksidacionog sredstva i sumporne kiseline [7, 8], što sve zajedno dovodi do smanjenja pH vrednosti i prevođenja bakra iz čvrstog stanja u rastvor.

REZULTATI ISTRAŽIVANJA

Lužena je jalovina, tačkasto uzeta na 12 mesta sa raskrivke starog borskog kopa. Hemijski sastav jalovine prikazan je u Tabeli 1.

Tabela 1. Hemijski sastav jalovine

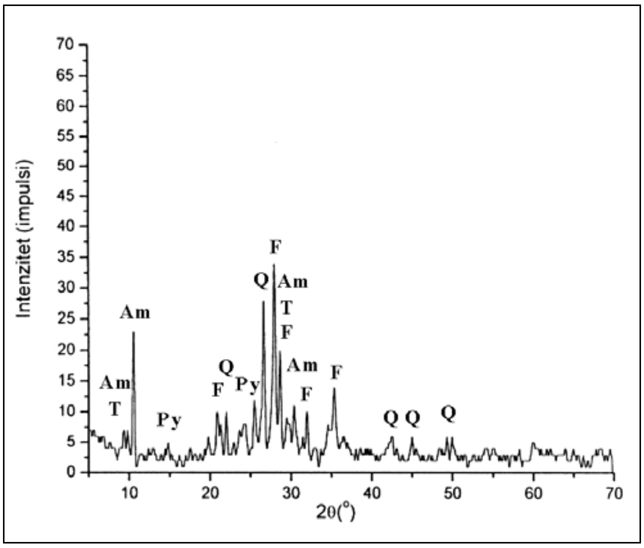
Komponenta	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	S	P_2O_5
%	58.92	15.12	2.98	0.91	0.90	1.12	2.96	0.071
Komponenta	Fe_{uk}	Fe^{2+}	Cu	Cu_{ox}	Zn	Pb	MnO	g.ž.
%	8.60	4.70	0.205	0.015	0.060	0.15	0.028	6.99

U Tabeli 2. je data distribucija jedinjenja sumpora. Sulfidni supstrati, dominantno pirit, prisutni su i u površinskom delu jalovišta borskog rudnika.

Tabela 2. Raspodela jedinjenja (i elementarnog) sumpora u uzorcima

Uzorak	Elementarni S [%]	Sulfidni S [%]	Sulfatni S [%]	Ukupni S [%]
B_3	0,23	1,19	1,54	2,96

Rendgensko-difrakciona analiza je pokazala da se jalovina sastoji od kvarca (Q), feldspata (F), amfibola (Am), pirita (Py) i talka (T). Difraktogram praha uzorka jalovine je prikazan na Slici 1.



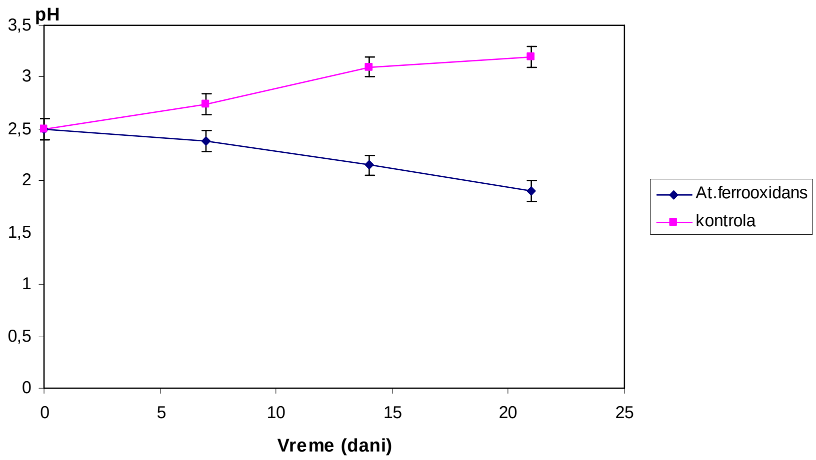
Sl. 1. *Difraktogram praha uzorka jalovine*

Eksperiment luženja bakra iz jalovišta izveden je sa bakterijskom kulturom *Acidithiobacillus. ferrooxidans*, koja kao izvor elektrona za svoj metabolizam koristi $FeSO_4$ iz podloge, pri čemu nastaje $Fe_2(SO_4)_3$, koji dalje oksiduje pirit. Hemijska oksidacija pirita kao rezultat daje redukovani oblik jona gvožđa, koji opet *Acidithiobacillus ferrooxidans* oksiduje do Fe(III) – jona. To znači da je proces cikličan i u prirodi poznat kao "fero-feri" ciklus.

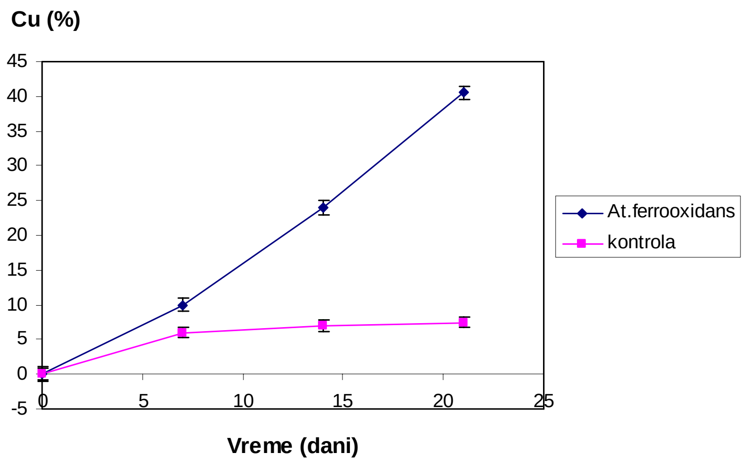
Početni broj *Acidithiobacillus ferrooxidans* je bio 2 x 10^5/ml. Vremenom se broj mikroorganizama povećavao tako da je sedmog dana eksperimenta iznosio 2,8 x 10^5/ml, četrnaestog 5,3 x 10^6/ml, a na kraju eksperimenta 7,5 x 10^6/ml.

Što se tiče sulfidnog sumpora, tokom procesa luženja, njegova količina je opala sa početnih 1,19 % na 0,4 %, u suspenziji sa *Acidithiobacillus ferrooxidans*, dok je u kontrolnoj suspenziji, pad iznosio sa 1,19 % na 1,05 %. Dobijeni rezultati potvrđuju ulogu mikroorganizma u oksidaciji pirita, a samim tim i u procesu izluženja bakra iz jalovišta.

Promena pH vrednosti i procenat izluženja bakra u suspenziji sa bakterijama kao i u kontrolnoj suspenziji, određivana su na početku i nakon 7., 14. i 21. dana eksperimenta. Dobijene vrednosti su prikazane na Slikama 2. i 3.



Sl. 2. *Promena pH vrednosti u kontrolnoj i u suspenziji sa Acidithiobacillus ferrooxidans tokom inkubacije na tresilici*



Sl. 3. *Izluženje bakra tokom inkubacije na tresilici*

Dobijeni rezultati pokazuju da je rastvaranje bakra povezano sa smanjenjem pH vrednosti, tj. povećanjem koncentracije bakterijski generisanog $Fe_2(SO_4)_3$ i sumporne kiseline u rastvoru za luženje.

Procenat izluženja bakra koji se može pripisati dejstvu *Acidithiobacillus ferrooxidans* (tj. efektivno izluženje) se dobija oduzimanjem procenta izluženja bakra iz kontrolne suspenzije od procenta izluženja metala iz suspenzije sa *Acidithiobacillus ferrooxidans* i iznosi 34%.

ZAKLJUČAK

Rezultati pokazuju da je mikrobiološki tretman jalovine bio efikasan, ali je ipak potrebno optimizovati proces u cilju dobijanja većeg stepena izluženja bakra, što se verovatno može postići povećanjem broja mikroorganizama u suspenziji, povećanjem gustine suspenzije, kao produžavanjem vremena luženja.

Mikrobiološko luženje predstavlja jeftin metod za tretman siromašnih i sekundarnih sulfidnih ruda bakra. Predviđa se da će razvoj ovog postupka ići u pravcu tretmana primarnih ruda bakra (halkopirit) i ruda drugih metala kao što je sfalerit.

Što se tiče naše zemlje, neophodno je da se naučni i tehnički napori usmere u pravcu izdvajanja korisnih komponenti iz siromašnih ruda i jalovišta mikrobiološkim luženjem. Pored toga, što se ovim putem dobijaju korisne komponente, sprečava se odliv štetnih elemenata u prirodnu sredinu, pri čemu se izbegava potencijalna opasnost od toksičnog delovanja nekog od metala na živi svet.

LITERATURA

[1] Vrvić M., Dejstvo tionskih bakterija na sulfidne supstrate – fundamentalni i primenjeni aspekti, Doktorska disertacija, Hemijsi fakultet, Beograd, (1991).

[2] Gregory K. Druschel, Brett J. Baker, Thomas M. Gihring, Jullian F. Banfield: Acid mine drainage biogeochemistry at Iron Mountain, Geochemical Transactions, California, 5 (2004), 13.

[3] Savić J., Savić M., Osnovi analitičke hemije: klasične metode, Sarajevo, (1990), str. 278.

[4] Đurić S., Metode istraživanja u kristalografiji, Tehnički fakultet u Čačku i Institut tehničkih nauka SANU, Čačak i Beograd, 2002.

[5] Silverman M.P., Lundgren D.G., J. Bacteriol. 77, (1959), str. 642.

[6] Collins C., Lyne P., Grange J., Falkinham J., Microbiological Methods, Arnold, London, (2004), str. 144.

[7] Rawlings E. Duoglas, Microbial Cell Factories, 4 (2005), 13.

[8] Crundwell F., Hydrometallurgy 71, (2003) 75.

MINING AND METALLURGY INSTITUTE BOR | YU ISSN: 1451-0162
COMMITTEE OF UNDERGROUND EXPLOITATION OF THE MINERAL DEPOSITS | UDK: 622

UDK: 579.6:628.4.038:546.56(045)=20 doi:10.5937/rudrad1204079A

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INVESTIGATION THE POSSIBILITY OF APPLICATION THE MICROORGANISMS IN COPPER RECOVERY FROM WASTE MINERAL MATERIALS**

Abstract

Microbiological leaching is a widely accepted method for the extraction of useful components from low-grade ores and secondary mineral row materials.

The main advantages of this process are low investment, simple operation and its environmentally friendly property.

The object of this paper was to examine the possibility of microbiological leaching of copper from ore dump by Acidithiobacillus ferrooxidans.

Leaching experiments were performed by the shake flask testing technique at 28^0C, during three-week period. The percentage of the copper leached at the end of this experiment was 34 %.

The obtained results should serve as a basis for reuse this widely accepted technology for exploitation of mineral row materials in order to obtain useful components from poor ores, as well as for the remediation of contaminated soils.

Keywords: *copper, leaching, Acidithiobacillus ferrooxidans*

INTRODUCTION

In last decades, intensive population growth and industrial and technological development caused serious water, air and soil contamination and raised concern for the environmental protection. Microorganisms play an important role in preserving the environment by decomposing the waste materials. Their heterogenic metabolic activity provides decomposition of the organic molecules, recycling the biogenic elements and transformation of large numbers of inorganic compounds.

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** *This paper is the result of the study on the Project TR 33007 „Implementation of New Technical, Technological and Environmental Solutions in the Mining and Metallurgical Operations RBB and RBM" financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.*

Transformations, cyclic reactions, migrations and concentration of chemical elements in the atmosphere, hydrosphere, lithosphere and entire biosphere can be simultaneously preformed both, by abiogenic and biogenic way. One of the microorganisms that are especially involved in many transforming and cyclic reactions are the lithotrophs. These microorganisms have a main role in recovering metals, by leaching low soluble compounds (mainly sulphides). Naturally, spontaneous occurring processes are directed and enhanced in such a way to recover metals from the low-grade ores and waste materials [1].

Today, microbial leaching of raw minerals is a world-widely accepted, indicating that this method is theoretically and practically well-developed and is possible to obtain significant amounts of metals. However, it should be noted that those parameters are different in each case, and that they are dependant on the characteristics of region and type of mineral raw material. Each specific case of bacteria application in leaching system requires detailed study of mineral raw material that is to be treated, environmental conditions for leaching and the microflora that will be used. It is recommended to use native bacterioflora in order to intensify the already existing natural processes [2].

Microbial methods for recovering metals are important for following reasons:

- Waste materials is being used as a raw material giving the metal as that final product, that would be irretrievably lost;
- Microbial leaching methods are several times cheaper compared to the conventional one that are inapplicable for the low grade ores;
- Minimum threats to the environment [1].

In order to extract copper from the tailings, microbial leaching has been conducted in laboratory using the culture of *Acidithiobacillus ferrooxidans*. Parameters, like physical and chemical characteristics of tailings, solid-liquid ratio, number of bacteria, leaching time, pH decreasing, percentage of pyrite sulphur consumption as well as the percentage of the leached copper, were determined.

Microbial methods of leaching low-grade raw materials and tailings plays very important role for obtaining the additional amounts of metals and in the concept of environmental protection, because it allows use of relatively simple technology to control and redirect uncontrolled loss of metals into the soil and waterstreams.

MATERIALS AND METHODS

Chemical analysis of the ore dumps

Silicate analysis of the ore dumps was conducted using the conventional method, by alkaline fusion with $NaKCO_3$ and dissolution in HCl [3]. From the filtrate Fe, Al, Ti, Ca and Mg, were determined while the residue was further treated with HF in order to obtain volatile SiF_4, from which the SiO_2 content was determined. The remaining precipitate was treated again as silicate material.

For the determination of alkaline metals and trace elements, the sample was decomposed with a mixture of $HClO_4$ and HF, while for the determination of phosphorus, the sample was decomposed with a mixture of aqua regia and $HClO_4$.

The alkaline metals were determined by atomic emission flame spectrophotometry; Fe, Al, Ti, Ca, Mg and trace metals by atomic absorption flame spectrophotometry, while phosphorus was determined by spectrophotometry, as yellow phosphomolybdate complex.

Sulphide sulphur from the ore dumps was determined gravimetrically after oxidation with $KClO_3$ and HNO_3 followed by precipitation as $BaSO_4$. Correction on sulphate sulphur from the ore dumps was determined in the "soda-extract" (boiling solution of Na_2CO_3), as $BaSO_4$ [3].

X-ray diffraction (XRD) analysis

The XRD patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 20 mA. The diffraction data were collected in the 2θ Bragg angle range from 5 to 60°, counting for 0.5 s at every 0.02° step. The divergence and receiving slits were fixed at 1 and 0.1 units, respectively [4]. The minerals were determined using MPDS software and JCPDS diffraction library.

Microbiology

Pure culture of *Acidithiobacillus ferrooxidans* was prepared for the experiments with three successive reseedings in 500 ml Erlenmeyer flasks containing 100 ml of 9K medium [5] adjusted to pH 2.5 with sulphuric acid. The third reseedings were carried out in 5 dm^3 flasks that contained 1 dm^3 of 9K medium. All flasks were shaken using a horizontal shaker with rotation and temperature set at 200 rpm and 28 ± 1°C, respectively. After five days, the bacterial culture was filtered through 0.45 μm membrane filters, washed with 9K iron-free medium (0K) and subsequently resuspended in 20 cm^3 of 0K medium.

The number of microogranisms was determined by the Most Probable Number Method [6].

Leaching experiments design

The leaching experiments were carried out with bacterium *Acidithiobacillus ferrooxidans*. Experimental conditions were: leaching period of 21 d, leaching solution (g/dm3): $Fe(SO_4)_2$ (44.8), $(NH_4)_2SO_4$ (3), K_2HPO_4 (0.5), $MgSO_4 \cdot 7H_2O$ (0.5), KCl (0.1), Ca(NO3)2 (0.01), (9K) at a pH of 2.5 in 500 mL Erlenmeyer flasks at a pulp density of 5% (m/V) (5 g leaching substrate in 100 ml solution). The control suspension had the same chemical content and pH value as the suspension with *Acidithiobacillus ferrooxidans,* but the *Acidithiobacillus ferrooxidans* culture had been inactivated by sterilization. Experiment was performed on a horizontal shaker New Brunswick Scientific. The incubation temperature was 28°C and the rotation speed 100 rpm. Number of microorganisms, concentration of copper and pH were analysed each seven days.

The process of leaching is based on Fe^{2+} oxidation to Fe^{3+}, which after that attacks pyrite, with thyosulphat as major intermedier, and sulphat as terminal product. Oxidation of pyrite can be described with following equations:

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow S_2O_3^{2-} + 7Fe^{2+} + 6H^+ \quad (1)$$

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \quad (2)$$

Fe^{2+} (produced in reactions 1 and 2) can be reoxydized to Fe^{3+} by acting of iron-oxydizing microorganism *Acidithiobacillus ferrooxidans.*

$$2Fe^{2+} + 0{,}5O_2 + 2\,H^+ \xrightarrow{\text{MICROBES}} 2Fe^{3+} + H_2O$$

Key role of *Acidithiobacillus ferrooxidans* is to regenerate sulphur acid and Fe^{3+}, which is strong oxidizing agent [7, 8]. All these things lead to lower pH and leaching of copper from solid phase.

RESULTS AND DISCUSSION

Samples were taken from twelve different locations on Bor ore dumps. Chemical analyses of ore dumps are presented in Table 1.

Table 1. *Chemical analyses of waste*

Component	SiO_2 %	Al_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	S %	P_2O_5 %
%	58.92	15.12	2.98	0.91	0.90	1.12	2.96	0.071
Component	Fe_{total} %	Fe^{2+} %	Cu %	Cu_{ox} %	Zn %	Pb %	MnO %	LOI %
%	8.60	4.70	0.205	0.015	0.060	0.15	0.028	6.99

Table 2. explains a distribution of sulphur compounds. Sulphide substrates, and dominantly pyrite, are also present in surface parts of Bor mine ore dump.

Table 2. *Distribution of compounds (end elemental) sulphur in samples*

Sample	Pure element S[%]	Sulhide S [%]	Suljate S [%]	Total S [%]
B_3	0.23	1.19	1.54	2.96

The X-ray powder diffraction analyses show that ore dump contens quartz *(Q),* feldspars *(F),* amphibole *(Am),* pyrite *(Py),* talc *(T).*

X-ray diffractogram of ore dumps is shown on Figure 1.

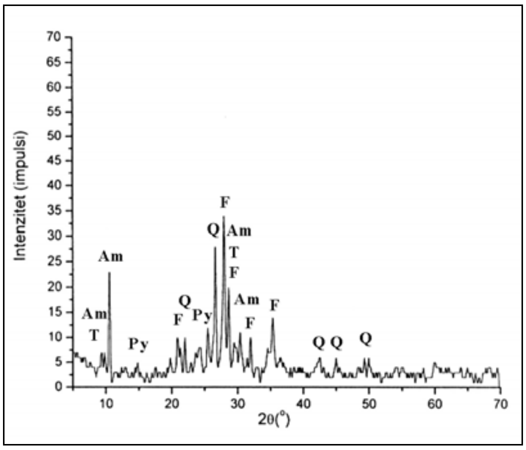

Fig. 1. *XRD diffractogram of ore dumps*

The experiment of copper leaching from ore dump was conducted with bacterial culture *Acidithiobacillus ferrooxidans*, which uses $FeSO_4$ from medium as a source for its own metabolism producing $Fe_2(SO_4)_3$, which later oxydises pyrite. Fe^{3+} ion is use as an oxidizing agent in pyrite leaching, leading to increase in Fe^{2+} levels, which is going to be again bacterially oxidized to Fe^{3+}.

Bioleaching of pyrite is continued, due to regeneration Fe^{3+} ion as oxidizing agent. This process is cyclic and well-known as “fero-feri” cycle.

The initial number of micrograms was 2x10^5 per ml. This number increased during experiment , and after seven days it was 2,8 x10^5/ml, after fourteen it was 5,3 x10^6/ml, and on the end of the experiment it was 7,5 x10^6/ml.

During the leaching process, sulphide sulphur content in suspension with *Acidithiobacillus ferrooxidans* decreased from 1.19% to 0.4%, while in the control suspension its content decreased from 1.19% to 1.05%. Obtained results confirm the role of microorganism in pyrite oxidation, as well as in process of copper leaching from ore dump.

Change of pH and percentage of copper leached in suspension with bacteria, as well as in control suspension, were determined on start and after 7, 14, and 21 days of experiment. The results obtained are presented on Figure 2. and Figure 3.

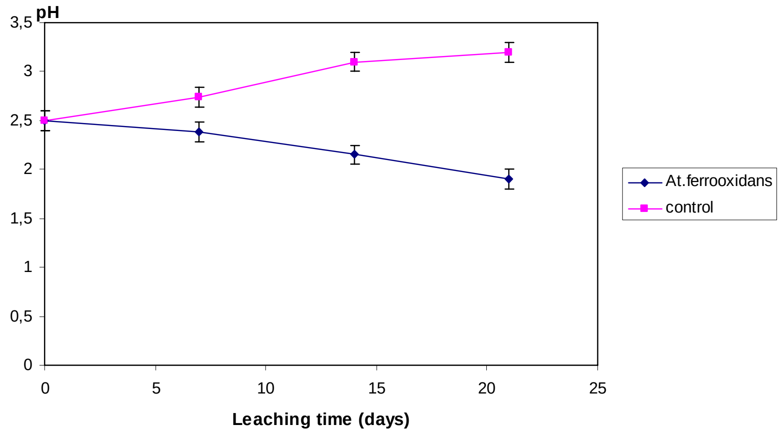

Fig. 2. *pH profiles during bioleaching of ore dumps in suspension with Acidithiobacillus ferrooxidans and control suspension, during the incubation process on shaker*

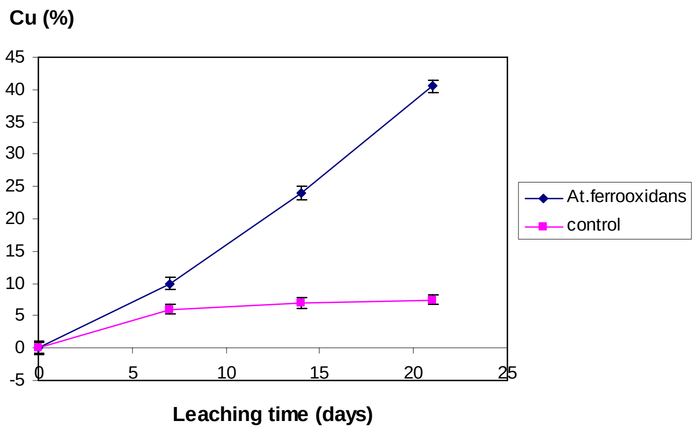

Fig. 3. *Amount of Cu leached during the incubation process on shaker*

Obtained results indicate that there is relationship between copper leaching and decrease of pH value, which is directly correlated with concentration of bacterially produced sulfuric acid and $Fe_2(SO_4)_3$ in leaching medium.

The percentage of leached copper, resulting from the activity of *Acidithiobacillus ferrooxidans, (i.e.*the effective metal leaching), was calculated by subtraction of percentage metal leaching in the control suspension from that in the *Acidithiobacillus. ferrooxidans* suspension, and it equals 34 %.

CONCLUSION

These results undoubtly proved that microbiological treatment of ore dump had been efficient, and the future task is to optimize this process in order to get larger amount of copper leached. It could be probably achieved by increasing the number of microorganisms in suspension, increasing the density of suspension, or increasing the time of leaching.

Microbial leaching is an inexpensive method for treatment of low-grade and secondary copper sulfide ores. Therefore, it would be significant and beneficial, for country like Serbia, to focus scientific and technical efforts toward separation of useful components from raw materials by this method. Furthermore, microbial leaching of low-grade ores and ore dumps also plays very important role in the concept of environmental protection, because it allows use of relatively simple technology to control and redirect uncontrolled loss of metals into the soil and water-streams.

REFERENCES

[1] Vrvić M., Dejstvo tionskih bakterija na sulfidne supstrate – fundamentalni i primenjeni aspekti, Doktorska disertacija, Hemijsi fakultet, Beograd, (1991)

[2] Gregory K. Druschel, Brett J. Baker, Thomas M. Gihring, Jullian F. Banfield: Acid mine drainage biogeochemistry at Iron Mountain, Geochemical Transactions, California , 5 (2004), 13.

[3] Savić J., Savić M., Osnovi analitičke hemije: klasične metode, Sarajevo, (1990), p. 278.

[4] Đurić S., Metode istraživanja u kristalografiji, Tehnički fakultet u Čačku i Institut tehničkih nauka SANU, Čačak i Beograd, 2002.

[5] Silverman M.P., Lundgren D.G., J. Bacteriol. 77, (1959), p. 642.

[6] Collins C., Lyne P., Grange J., Falkinham J., Microbiological Methods, Arnold, London, (2004), p. 144.

[7] Rawlings E. Duoglas, Microbial Cell Factories, 4 (2005), 13.

[8] Crundwell F., Hydrometallurgy 71, (2003) 75.