

Bioleaching of polymetallic sulphide concentrate using thermophilic bacteria

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Abstract

An extreme thermophilic, iron-sulphur oxidising bacterial culture was isolated and adapted to tolerate high metal and solids concentrations at 70 °C. Following isolation and adaptation, the culture was used in a batch bioleach test employing a 5-l glass standard magnetic agitated and aerated reactor, for the bioleaching of a copper-lead-zinc collective concentrate. The culture exhibited stable leach performance over the period of leach operation and overall copper and zinc extractions higher than 97%. Lead sulphide is transformed into lead sulphate remaining in the bioleach residue due to the low solubility in sulphate media. Brine leaching of bioleach residue yields 95% lead extraction.

Keywords: bioleaching, bacteria, chalcopyrite, sphalerite, galena, thermophiles.

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Biohydrometallurgy, biotechnology or bioprocessing, is a new approach used for extraction of metals; it offers the opportunity to reduce environmental pollution. Namely, biological processes are conducted under mild conditions, usually without the addition of toxic substances. Also, the products of these processes end up in an aqueous solution which is more amenable to containment and treatment than gaseous waste. Biotechnological approach consists of four distinct techniques: bioremediation, biosorption, bioaccumulation and bioleaching.

The bioleaching technology involves the extraction of useful elements from ores by bacteria and solution. The whole process consists of six steps: outer diffusion, inner diffusion, leaching reaction, process of precipitation and hydrolysis of the element, transportation of microorganisms, heating and cooling of the bed [1]. Bioleaching is used extensively to recover copper and uranium from low grade ores [2–5].

The bacteria most frequently used in bioleaching are of two types: *Chemolithotrophic* and *Heterotrophic*. *Acidithiobacillus ferrooxidans* is a chemolithotrophic bacterium capable of utilizing ferrous iron as the only source of energy for its growth. This bacterium oxidizes Fe(II) and elemental sulphur to Fe(III) and H₂SO₄, respectively, at low acidic conditions as well as high metal ion concentrations. Due to its capacity to oxidize metal sulphides, low concentrations of metals in ores are not a problem for these bacteria because they simply neg-

lect the waste which surrounds the metals, attaining extraction yields of over 90% in some cases [6]. In short, acidolysis is the principle mechanism of the bioleaching process. Various acids produced by microorganism such as citric, oxalic and sulphuric help in the metal dissolution process from ores. Bacterial microorganisms, in fact, gain energy by breaking down ores into their constituent elements.

The bioleaching process is commercially used to process minerals of copper, nickel, cobalt, zinc, lead and uranium. The applicability of this process is not limited to heap or dump leaching, but has been extended to reactor bioleaching [7,8]. Most secondary copper sulphides can be bioleached successfully at 35–45 °C, using mesophilic *Thiobacillus-Leptospirillum* bacterial cultures. However, the bioleaching of chalcopyrite, the major copper-bearing sulphide mineral of commercial interest, is still a major challenge. This is due to relatively slow kinetics and poor extractions, which have mainly been attributed to passivation [9].

The interest in extreme thermophilic bacteria lies in the potential for improving the leach rates of sulphides such as chalcopyrite, pyrite and arsenopyrite. The potential to achieve this is clear from the extensive published data that has been obtained using shake flask and other laboratory-scale methods, but employing low solids concentrations and relatively mild agitation conditions. However, it has been claimed that the potential for using extreme thermophiles, such as *Sulfolobus*, at temperatures in the range 60–84 °C, may not be realized commercially unless their sensitivity to agitation at high solids concentrations can be overcome [10]. Solutions suggested by these authors include the selection or isolation of more robust bacteria or the development of improved reactor designs.

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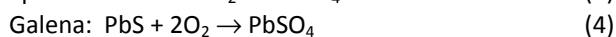
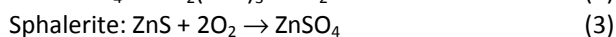
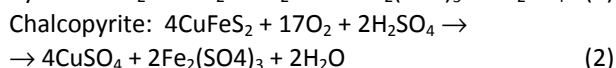
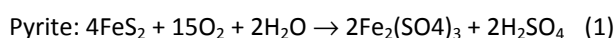
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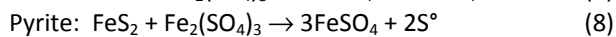
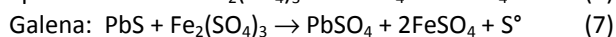
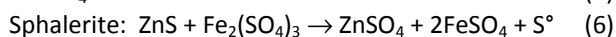
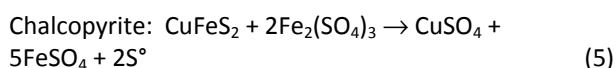
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Numerous studies indicate that chalcopyrite leaching depends on redox potential, and occurs between 510 to 610 mV at 70 °C. Metal sulphides, such as chalcocite, covellite, sphalerite and galena generally leach far more easily. However, even with these metal sulphides, extended residence times are often required to achieve high metal extractions, using mesophilic *Thiobacillus-Leptospirillum* bacteria operating at temperatures in the range of 35–45 °C.

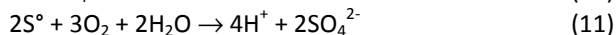
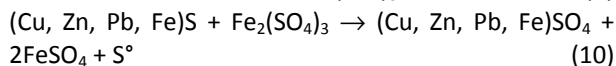
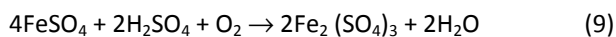
The following equations describe the direct and indirect mechanism for the bio-oxidation of Cu–Zn–Pb–Fe sulphides. In the direct mechanism, metal sulphides can be directly oxidised by extreme thermophiles or *thiobacillus* strains to soluble metals sulphates according to Eqs. (1)–(4):



The direct mechanism means that bacteria attach onto the mineral particle surfaces, where they facilitate mineral dissolution through direct bacterial metabolism. In the indirect mechanism, however, the oxidation of sulphide minerals is represented by the oxidation of sulphide minerals by ferric ions, with bacteria oxidising ferrous ions to ferric ions, and elemental sulphur to sulphate ions, according to the reactions (5–8):



Therefore, the metal dissolution occurs by a cyclic process between reactions (9) and (10), and the formation of H^+ during the sulphur biooxidation (11) enhances the overall efficiency:



Besides these two bioleaching mechanisms, a third mechanism has been proposed, the indirect contact, under which bacterial microorganisms attach onto the mineral particle surfaces, where they increase the ferric ion and acid concentrations in the immediate vicinity of the mineral particles. At present, it is believed that the leaching of all sulphides of the form $\text{M}^{2+}\text{S}^{2-}$ proceeds according to an indirect mechanisms.

Since the bioleaching reactions imply intensive mass transfer requirements for oxygen and carbon dioxide, there is a need to clearly define the process require-

ments to maximise the reaction kinetics [11]. This may be more critical in terms of significantly reduced solubilities of these gases at the operating temperatures required for the extreme thermophiles. Compared to mesophilic and moderately thermophilic bioleaching bacteria, the extreme thermophiles appear to exhibit greater sensitivity to the solids concentration employed; however, this is also influenced by the particle size of the feed solids. Therefore, the aim of this study is to examine the opportunities for further increasing rates of oxidation using extreme thermophiles for treatment of the pollymetallic concentrates originating from the Bor mining area (Eastern Serbia), used in intensively agitated laboratory reactors.

EXPERIMENTAL

Microorganisms present in RTB Bor resources

Natural population of bacteria on Bor site

Specific organisms that exist in the RTB Bor resources (copper ores, concentrates, tailings and mine waters) have been identified using molecular tools based on Quantitative Polymerase Chain Reaction (Q-PCR analysis) and quantified in different bioleaching processes [12]. Natural population of microorganisms in RTB Bor resources is presented in Table 1.

The results were then combined with process conditions, in order to search and find relations between the appearance of specific organisms and environmental conditions/process conditions. The relative proportions of the cultures present in the analysed mine samples did not vary much, except in the Bor tailings where fairly high amount of bacteria ($4,3 \times 10^6$ per g) and archaea exist. It was shown that the dominant organism was *Acidianus* sp., with *Metallosphaera* sp. and *Sulfolobus* sp. present in lower numbers.

Quantification of microbial population

The characterization of the microbial communities present in RTB Bor mine sulphide minerals has been performed in line with bench-scale bioleach amenability testing and integrated piloting in Mintek laboratory. The microbial populations present in the bioleach reactors were identified and quantified by Mintek, Bioclear and the University of Bangor, using Q-PCR and T-RFLP techniques, respectively [14].

Two sets of samples were analysed; the first was collected after reaching steady-state conditions during open-circuit operation, whereas the second set was taken while the system operated as a fully integrated plant. Similar results were obtained on the two sets of samples and total recorded cell numbers varied between 4×10^8 and 3×10^9 cells/ml. Quantification of microbial population is shown in Table 2. *Acidianus brieryleyi* dominated the population in all four bioleach

Table 1. Natural population of bacteria on Bor/Majdanpek sites

Program PCR-analyse	Target-PCR	Bacteria/g
Bor-tailing		
P059P427	Universal; Bacteria	4.3×10^6
P418P419	Universal; Archaea	3.0×10^5
Ores, concentrates, mine waters		
M039M040	<i>Acidianus</i> sp.	$< 4.6 \times 10^4$
M026P258	<i>Acidimicrobium</i> sp.	1.1×10^5
P242P243	<i>Acidiphilium</i> sp.	$< 4.6 \times 10^4$
M038P352	<i>Acidothiobacillus caldus</i>	$< 2.3 \times 10^4$
P363P364	<i>Acidothiobacillus</i> sp.	$< 2.3 \times 10^4$
P353P354	<i>Acidothiobacillus thiooxidans</i>	$< 2.3 \times 10^4$
P361P362	<i>Alicyclobacillus</i> sp.	$< 8.5 \times 10^3$
P365P366	<i>Ferroplasma</i> sp.	$< 4.6 \times 10^4$
P071M041	<i>Leptospirillum ferrooxidans</i>	$< 2.3 \times 10^4$
P251P252	<i>Metallosphaera</i> sp.	$< 4.6 \times 10^4$
P368P369	<i>Sulfobacillus</i> sp.	$< 4.7 \times 10^5$
P372P377	<i>Sulfolobus</i> sp.	$< 4.6 \times 10^4$

reactors, while *Metallosphaera sedula* was present at much lower levels [6,7].

Relative abundance of microbial populations is presented in Table 3. Although little is known about the physiology of *Acidianus brierleyi* thermoacidophiles, current research indicates that the relatively poor iron-oxidation capacity of *A. brierleyi* compared to other thermoacidophilic archaea may make it a more suitable microorganism for the oxidative dissolution of secondary copper sulphides and chalcopyrite [13,14].

Bacterial culture and nutrients

Isolation

An extremely thermophilic, iron–sulphur oxidising bacterial culture *Acidianus brierleyi*/*Metallosphaera sedula*, isolated from a moderate hot mine water of RTB Bor complex was used in the study. The culture was grown in a mineral salts solution (substrate) with the following composition: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (15 g/l),

$(\text{NH}_4)_2\text{SO}_4$ (3.0 g/l), KCl (0.1 g/l), K_2HPO_4 (0.5 g/l), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 g/l) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.01 g/l).

Adaptation of culture

The mixed culture, prepared from isolates obtained in enrichment culture was adapted to oxidise polymetallic copper-lead-zinc sulphide concentrate in a 5 l glass magnetic stirred reactor (220 rpm) at 70 °C. The culture was exposed to increasing concentrations of the concentrate and grew well in the presence of 50 g/l of the concentrate and 2.4 g/l of zinc and 12 g/l of copper in solution over a 40-day period.

Mineral characteristics

The test was performed on a copper–lead–zinc sulphide concentrate, fine-milled in a standard laboratory ring mill unit to particle sizes of $d_{90} = 10 \mu\text{m}$. Modal analysis of the sample presented in Table 4, showed that the major sulphides present were chalcopyrite 69%, galena 10%, sphalerite 7% and pyrite 6%.

Table 2. Quantification of microbial populations using Q-PCR

Sample	<i>Acidianus brierleyi</i> cells/ml	<i>Metallosphaera sedula</i> cells/ml
Open circuit		
Reactor 1	2.6×10^9	1.1×10^7
Reactor 2	3.6×10^8	7.5×10^5
Reactor 3	4.5×10^9	1.4×10^7
Reactor 4	8.3×10^8	1.7×10^6
Integrated circuit		
Reactor 1	7.6×10^8	2.0×10^5
Reactor 2	2.4×10^9	8.1×10^5
Reactor 3	8.1×10^8	7.3×10^4
Reactor 4	2.9×10^9	3.6×10^5

The chemical composition of the Cu/Zn/Pb concentrate is shown in Table 5.

Table 3. Relative abundance of microbial populations in the bioleach reactors; ND = not detected; NA = not analysed

Sample	<i>Acidianus brierleyi</i> , %		<i>Metallosphaera sedula</i> , %	
	Q-PCR	T-RFLP	Q-PCR	T-RFLP
Open circuit				
Reactor 1	99.6	99.8	0.4	2.0
Reactor 2	99.8	ND	0.2	ND
Reactor 3	99.7	99.0	0.3	1.0
Reactor 4	99.8	ND	0.2	ND
Integrated circuit				
Reactor 1	99.9	NA	0.02	NA
Reactor 2	99.9	NA	0.03	NA
Reactor 3	99.9	NA	0.01	NA

Table 4. Mineralogical analyses of the pollymetallic concentrate

Element	Content, mass%
CuFeS ₂	69
PbS	10
ZnS	7
FeS ₂	6
Gangue	8
Total	100

Particle size analyses

The concentrate was milled to a particle size of $d_{90} = 10 \mu\text{m}$. The particle-size distribution of the received and milled concentrate is illustrated in Fig. 1. The fine-milled concentrate was used as feed material in the test work programme.

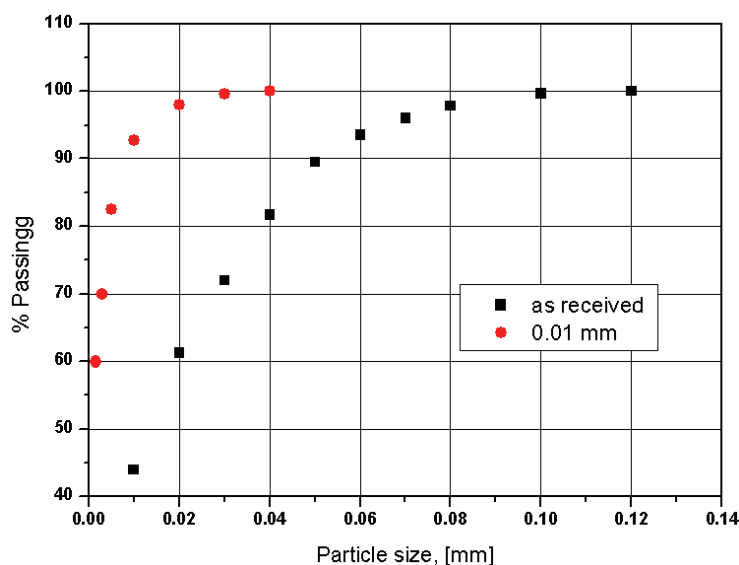


Figure 1. Particle-size distribution.

Table 5. Chemical analyses of the pollymetallic concentrate

Element	Content, mass%
Cu	24.2
Pb	8.7
Zn	4.9
Fe	25.6
Ag (g/t)	600
S ^{tot}	29
Gangue	7.7
Total	100

The Veliki Krivelj concentrate was first wet-milled in a stirred ball mill in order to achieve a target particle size with a d_{90} of 10 to 12 μm . The pulp from the mill was filtered to remove excess water, and then the filter cake was dried on a hot drying table. The dried solids were screened through a 600 μm to break up the lumps, formed during the drying process. Finally, the milled dry products were packed and stored.

The particle size distribution in this study corresponds to the chosen bioleaching operation mode. While dump and heap leaching utilizes run-of-mine lumps of several inches in size and particles of controlled size in the range of half inch, respectively, bioleaching in stirred test reactor requires particle sizes up to 100 μm or less in order to keep them suspended by mechanical means or by air/lift agitation.

Batch test

A batch bioleach test was performed on the concentrate with a particle size of $d_{90} = 10 \mu\text{m}$, at 5% (w/V) pulp density. The test was performed in a 5 l magnetic stirred reactor (220 rpm) at 70 °C, as used for culture adaptation. Air enriched with CO₂ (0.15%) was intro-

duced into the reactor *via* an air sparger. The test gave an initial cell concentration of about 10^8 cells/ml. Distilled water was added on a daily basis to compensate for evaporation. The initial pH was set at 2 with sulphuric acid. The progress of the leachates was followed by daily measurement of pH levels and ORP. The amount of Cu and Zn released during the test were determined by periodic liquor analysis.

RESULTS AND DISCUSSION

Batch test

Batch bioleach adaptation

The batch test started with the adaptation of the culture. Chalcopyrite leaching occurs between 510 to 610 mV. Metal sulphides, such as sphalerite and galena, generally leach far more easily. Pyrite oxidation

would only have been significant once the ORP was higher than 450 mV [15]. The pH of the bioleach test solution was adjusted on the first day to the value of 2 with sulphuric acid. During the bioleach adaptation, pH value was controlled by adding sulphuric acid to maintain pH 1.3, as illustrated in Fig. 2.

Despite the fact that microorganisms involved in copper bioleaching are also acidophilic, (they are active in the pH range from 1.5 to 3.0), operating pH over 2.0 is not allowed mostly because some chemical reactions can occur such as, for instance, the precipitation of jarosites – various types of ferric hydroxides. Also, pH cannot drop down to 1.0–1.5 since the viability of cell could be severely affected.

The operating redox potential (ORP) showed an increase from 486 to 610 mV (referred to the Ag/AgCl electrode, 0.207 V vs. SHE at 25 °C), as illustrated in Fig. 3. Batch chemical ferric leach tests carried out on the

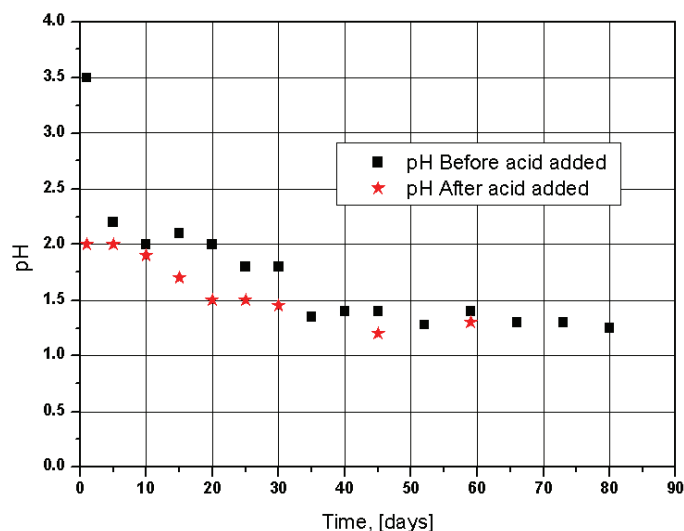


Figure 2. pH levels measured during the bioleach test.

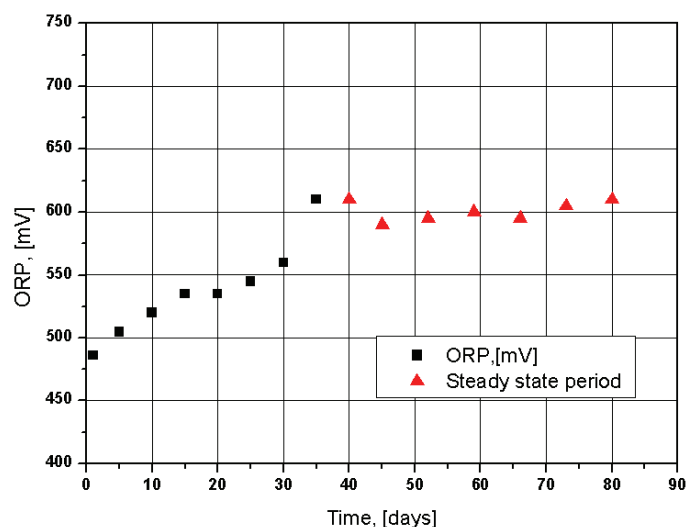


Figure 3. ORP levels measured during the bioleach test.

concentrates under conditions of controlled operating redox potential (ORP), showed that the Cu leach rate is significantly increased at an ORP level of 550 mV compared to an ORP of 430 mV. This indicates that significantly reduced residence times may be possible in bioleach processes, using the extreme thermophiles, if higher ORP levels can be maintained.

Therefore, this increase of ORP may clearly indicate a change in the concentration of Cu, Zn and Fe in solution, as illustrated in Fig. 4. Over the 40-day period of adaptation the final measured Cu concentration was 12 g/l and zinc 2.4 g/l (after first five days of test), while a final Fe concentration was of 3.8 g/l.

Steady state batch bioleach

To maintain steady state conditions, a batch bioleach test started on day 40. The test comprised a

several steady state tests carried out under the same conditions in a 5 l magnetic stirred reactor. The magnetic speed in reactor was set at 250 rpm. The feed pulp density was maintained at 5%. The investigated feed was ground to achieve a target particle size with a $d_{90} = 10 \mu\text{m}$ and the overall unit residence time lasted seven days. The steady state data across the reactor for Cu and Zn extractions at the constant pH 1.3 and ORP 610 mV are shown in Fig. 5. During the bioleach process, jarosite-type compounds form when sulphides undergo strong oxidation under highly acidic conditions [16].

The jarosite compounds has the theoretical formula $M\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, where „M“ is a monovalent cation from the group H_3O^+ , Na^+ , K^+ , Ag^+ , NH_4^+ or $\frac{1}{2}\text{Pb}^{2+}$. The results indicated that jarosite compounds were

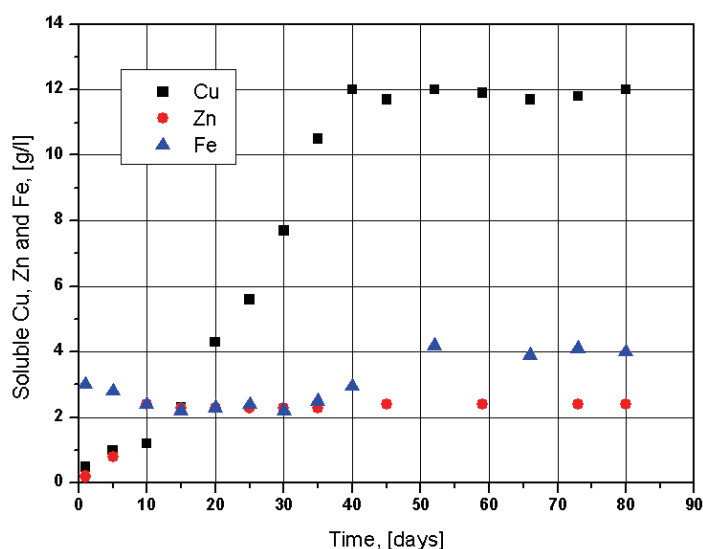


Figure 4. Cu, Zn and Fe extractions obtained during the bioleach test at 70 °C.

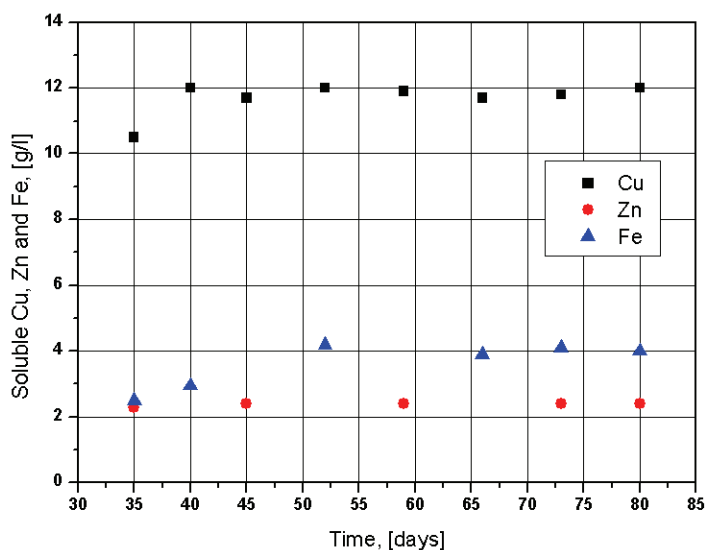


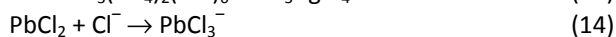
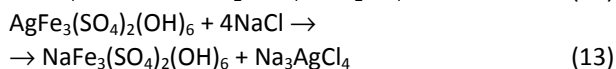
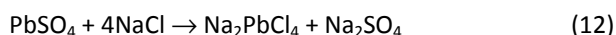
Figure 5. Cu, Zn and Fe extractions obtained in steady state bioleach test at 70 °C.

precipitated effectively from sulphuric acid solution acid at 70 °C while maintaining pH of about 1.3. After the bioleaching, the amount of Pb decreases from 8.7% contained in concentrate to 7% in the primary bioleach residue due to jarosite precipitation and minor increasing of residue weight of 25%, compared to the sulphide concentrate processed.

Batch brineleach test

Bioleach residue could be treated by means of different techniques to get efficient extraction of valuable metals, namely precious metals and lead. The PLINT process was selected to carry out lead recovery [17]. It was shown that NaCl concentration and solid/liquid ratio (pulp density) are very effective parameters for lead recovery at room temperature, while hydrochloric acid addition in brine leachant causes minor effects on lead recovery [18].

Main chemical reaction involved in the brine leaching of lead is according to Eq. (12). Silver follows a similar pathway according to reaction (13). Several researchers emphasized that the solutions having reactions (14 and 15) due to their solubilities being higher than PbCl_2 , resulted in an increase in the concentration of Pb^{2+} in solution [19]:



For lead recovery, brine leaching tests were done on the secondary leach residue obtained after acid leaching of primary bioleach residue, using 150 g/l H_2SO_4 at 95 °C in 2 h with pulp density of 200 g/l to

transform all backward lead sulphide and precipitated lead jarosite in lead sulphide.

In this study, six different aqueous NaCl solutions for lead recovery from 50 to 350 g/l were tested at the following constant conditions: solid/liquid ratio 1/8 kg/dm^3 ; reaction duration 20 min; reaction temperature 25 °C. The experimental results are shown in Fig. 6. On the basis of these results, one can accept that the brine concentration is an effective parameter for lead recovery. In short, the higher the NaCl concentration, the higher the Pb extraction degree.

However, it is suggested not to use greater than 350 g/l NaCl concentration in brine leaching because when greater values are used NaCl solution becomes saturated. NaCl solubility in 0.1 l cold water is given as 35.7 g [20,21]. This means that maximum NaCl concentration can be chosen as 357 g/l. Over the 20 min period of extraction, the measured lead concentration was 7.3 g/l. Finally, the lead could be precipitated with an alkali to produce pure lead oxide or carbonate concentrate able to be commercialised.

A summary of base metal extractions based on the analysis of the final residues is given in Table 6. Final extractions of 97% Cu, 97% Zn and 95% Pb were achieved. Ninety-nine percent of the sulphides were oxidised, indicating that most of chalcopyrite, sphalerite and pyrite were leached, while galenite was transformed into insoluble lead sulphate. According to the residue analysis, no elemental sulphur was formed, which is consistent with results previously obtained using the extreme thermophilic culture on other Cu-sulphide concentrates [11,13].

Much more attention, therefore, has to be paid to the bioleaching of galena. Namely, in a sulphate system galena is oxidized to insoluble lead sulphate and the

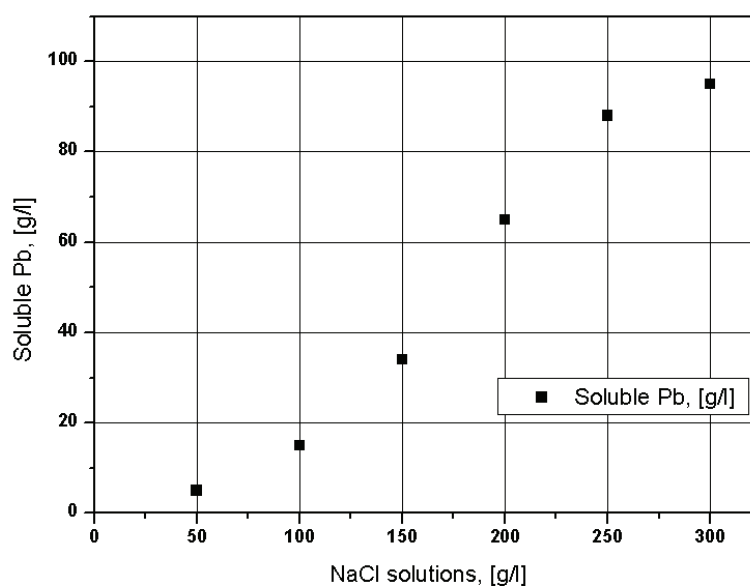


Figure 6. Pb extractions data obtained during the brine bioleach test at 25 °C.

creation of this compound does not allow the recovery of lead from bacteria and ferric sulphate leaching via integrated solvent extraction/electrowinning process. It also creates an environmental risk due to the increased solubility of lead sulphate over galena.

Table 6. Summary of the metal extractions

Element	Extraction, %
Cu	97
Zn	97
Pb	95

An attempt done by da Silva, for instance, revealed that the galena bio-oxidation required considerable acid consumption, because of the occlusion of the produced elemental sulphur by precipitated lead sulphate [22]. This means that galena oxidation may hinder the bioleaching of other sulphide minerals.

CONCLUSION

An extremely thermophilic, iron–sulphur oxidising bacterial culture, isolated from a moderate hot mine water of Mining and Smelting Company Bor was used in the study. However, for the subsequent use of the culture in bioleach applications, it was necessary to carry out an adaptation step. This included maintenance of bacterial oxidative activity at sufficient sulphide solids concentrations, tolerance to high metal ions concentrations such as copper, zinc and lead, and tolerance to flotation reagents associated with sulphide concentrates.

The bacterial culture was employed in a batch test continuously operated 5 l magnetic stirred reactor over a period of 80 days including the period of isolation and adaptation of the bacterial culture, treating a pollymetallic chalcopyrite–zinc–lead sulphide concentrate. Once established in the reactor, employing standard bioleach conditions, the extreme thermophile bacterial culture exhibited stable leaching performance over the period of batch bioleach operation.

The batch bioleach test confirmed that 97% Cu, 97% Zn and in a brine leaching 95% Pb extractions could be obtained on the chalcopyrite–sphalerite–galena concentrate at a solids concentration of 5% in an agitated stirred reactor.

A combined bioleach and hydrometallurgical process has the advantage over the RTB Bor smelting process, because of lower capital costs, flexibility to treat lower grade copper concentrates, pollymetallic concentrates, gold bearing concentrates, smelter slags, flotation tailings, mine waters and, it is environmentally more acceptable because it does not produce hazardous sulphur-containing gaseous waste products and reduces the requirement for imported concentrates.

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IZVOD

BIOLUŽENJE POLIMETALIČNOG SULFIDNOG KONCENTRATA TERMOFILNIM BAKTERIJAMA

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Biotehnologija kao noviji pristup za ekstrakciju metala nudi mogućnosti za smanjenje zagađenja životne sredine. U ovom radu se od četiri biotehnološka postupka – bioremedijacija, biosorpcija, bioakumulacija i bioluženje – sagledavaju različiti aspekti (uključujući i ekološke) bioluženja polimetalnih sulfidnih koncentrata koji potiču iz borske rudarske oblasti. Ispitana je mogućnost povećanja brzine oksidacije sulfida bakra u laboratorijskim uslovima u prisustvu termofilnih bakterija. Ekstremno termofilna i oksidaciona bakterijska kultura, razvijena u prisustvu sumpora i gvožđa, izolovana je i adaptirana na visoku koncentraciju jona metala i čestica materijala u rastvoru na temperaturi od 70 °C. Nakon izolacije i adaptacije mikroorganizama, kultura je korišćena u staklenom reaktoru zapremine pet litara za bioluženje (potpomognuto magnetnom agitacijom i aeracijom) polimetalnih sulfidnih koncentrata koji je od metala sadržavao bakar, cink i olovo. Eksperimenti sprovedeni u ovoj specifičnoj bakteriološkoj sredini pokazali su da je moguće, posle postizanja ravnotežnih uslova, postići visoke stepene ekstrakcije bakra i cinka (do 97%) u dužim vremenskim intervalima – do 80 dana. Olovo-sulfid je tokom ovog procesa oksidacijom prešao u olovo-sulfat, te ostao u biolužnom ostatku zbog neznatne rastvorljivosti u sulfatnom rastvoru. U ovom radu je bioluženje bioostatka sprovedeno po PLINT tehnologiji koja omogućava rastvaranje jedinjenja olova u prisustvu natrijum-hlorida. Rezultati ovih eksperimenata su potvrdili rezultate sličnih istraživanja po kojima je moguće dobiti visoke stepene ekstrakcije olova iz biolužnog ostatka polimetalnih koncentrata – i do 95%.

Ključne reči: bioluženje • Bakterije • Halkopirit • Svalerit • Galenit • Termofili