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# Bioleaching of copper from samples of old flotation tailings (Copper Mine Bor, Serbia)

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*Abstract*: Bioleaching of samples taken from depths of 10, 15, and 20 m from old flotation tailings of the Copper Mine Bor was conducted in shaken flasks using the extremely acidic water of Lake Robule as lixiviant. The yields of copper after five weeks of the bioleaching experiments were  $68.34\pm1.21$  % for the 15-m sample,  $72.57\pm0.57$  % for the 20-m sample and  $97.78\pm5.50$  % for the 10-m sample. The obtained results were compared to the results of acid leaching of the same samples and it was concluded that bioleaching was generally more efficient for the treatment of samples taken from depths of 10 and 20 m. The content of pyrite in the 20-m sample, which contained the highest amount of this mineral, was reduced after bioleaching. The benefits of this approach are recovery of substantial amounts of copper, reducing the environmental impact of flotation tailings and the application of abundant and free water from the acidic Robule Lake as lixiviant. The obtained results showed that bioleaching for copper extraction from flotation tailings with higher sulfide contents.

Keywords: bioleaching; flotation tailings; Lake Robule; Bor.

# INTRODUCTION

The Bor Mining and Smelting Company, one of the largest industrial facilities in the Republic of Serbia, is the only producer of copper, gold and silver in the country. The Copper Mine Bor has been operating since 1903 and since then, approximately 650 million tons of waste, including both overburden and flotation tailings, were generated.

In the early years of exploitation, the ore from the Copper Mine Bor was generally richer in copper.<sup>1</sup> The abundance of copper in combination with the

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relatively inefficient technology used for flotation resulted in the production of flotation tailings containing significant amounts of copper. It is estimated that the old flotation tailings of the Copper Mine Bor, used from 1933 to 1987, contains about  $27 \times 10^6$  tons of tailings with an average copper content in the range 0.2–0.3 wt. %, a gold content of 0.3–0.6 g t<sup>-1</sup> and a silver content of 2.5–3 g t<sup>-1.2–6</sup> Hence, the best estimate of the total copper content in the old flotation tailings of the Copper Mine Bor ranges between 54000 and 81000 t.

Previous detailed analyses of the mineral and chemical composition of samples of the old flotation tailings<sup>5,6</sup> showed that the copper content in the dump could reach 0.5 %. The analysis also revealed that the old flotation tailings consists mainly of quartz, silicates, carbonates (77 %), pyrite (21.57 %) and other metal sulfides (1.43 %). The most abundant copper sulfides are covellite (0.21 %), chalcopyrite (0.16 %), enargite (0.14 %) and chalcocite (0.04 %). The flotation tailings is finely ground, with 55.3 % of the particles being smaller than 0.074 mm.<sup>6</sup> The average liberation of pyrite is around 91 % that, in the presence of water and atmospheric oxygen, represents an important reactive potential for the mobilization of heavy metal ions and the generation of acid mine drainage for many years to come.<sup>5</sup>

Currently, the Bor Mining and Smelting Company is processing low-grade ores, since the average content of copper in the ores from the open pit mines is around 0.3 %.<sup>7</sup> Therefore, the old flotation tailings in Bor are, potentially, a valuable source of copper for the Company.

As copper sulfides are acid soluble, copper from flotation tailings can be leached by sulfuric acid solutions.<sup>4–6</sup> Another approach for the recovery of copper from tailings would include the use of acidophilic iron oxidizing microorganisms. This process is referred to as "bioleaching".<sup>8</sup> It is generally known that many acidophilic microorganisms provide metabolic energy by oxidizing ferrous iron, generating ferric iron:

$$2FeSO_4(aq) + H_2SO_4(aq) + 0.5O_2(g) \rightarrow Fe_2(SO_4)_3(aq) + H_2O(l)$$
(1)

Ferric iron is a powerful oxidizing agent that is able to oxidize metal sulfides, such as pyrite and copper sulfides.<sup>4</sup>

$$2\text{FeS}_2(s) + 7\text{Fe}_2(\text{SO}_4)_3(\text{aq}) + 8\text{H}_2\text{O}(1) \rightarrow 15\text{FeSO}_4(\text{aq}) + 8\text{H}_2\text{SO}_4(\text{aq})$$
(2)

Acidophilic microorganisms very efficiently oxidize the ferrous iron released from pyrite and regenerate ferric iron, accelerating the process of metal sulfide oxidation.<sup>9</sup> Oxidation of the most important copper sulfides (covellite, enargite, chalcocite and chalcopyrite, respectively) is presented in Eqs. (3)–(6):<sup>4</sup>

$$CuS(s) + Fe_2(SO_4)_3(aq) \rightarrow CuSO_4(aq) + S(s) + 2FeSO_4(aq)$$
(3)  

$$2Cu_3AsS_4(s) + 11Fe_2(SO_4)_3(aq) + 8H_2O(l) \rightarrow$$
  

$$\rightarrow 6CuSO_4(aq) + 2H_2AsO_4(aq) + 5H_2SO_4(aq) + 8S(s) + 22FeSO_4(aq)$$
(4)

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$$Cu_2S(s) + Fe_2(SO_4)_3(aq) \rightarrow 2CuSO_4(aq) + S(s) + 4FeSO_4(aq)$$
(5)

$$CuFeS_{2}(s) + Fe_{2}(SO_{4})_{3}(aq) \rightarrow CuSO_{4}(aq) + 2S(s) + 5FeSO_{4}(aq)$$
(6)

Some species of acidophilic microorganisms are able to oxidize sulfur, producing sulfuric acid and lowering the pH of the environment. Oxidation of copper sulfides produces soluble copper that can be recovered from the solution by application of solvent extraction/electrowinning technology.<sup>8</sup>

Open pit acidic lakes are widespread in mining areas and they present the potential source of acidophilic microorganisms that could be used for bioleaching of copper. The Robule Lake is an extremely acidic water body that is located near the town of Bor, at the foot of the overburden of the open pit. The input of acid mine drainage from the overburden had caused the lake water to become highly acidic and deep red in color due to the high concentrations of ferric iron. The redox potential of the lake water measured in July 2012 was +850 mV.<sup>11</sup> Korać and Kamberović<sup>9</sup> reported that the concentration of suspended solids in a water sample collected in February 2005 was 199.6 mg L<sup>-1</sup>. Previous studies confirmed the presence of acidophilic bacteria in the Lake water.<sup>10,11</sup> The latter study<sup>11</sup> showed that the most abundant bacteria identified in a sample of the Lake water were the heterotrophic bacteria *Acidiphilium cryptum* and the autotrophic iron-oxidizers *Leptospirillum ferrooxidans*, with a relatively small number of autotrophic iron- and sulfur-oxidizers *Acidithiobacillus ferrooxidans*.

Besides Lake Robule, there are also other sources of acidic wastewaters in the Bor Mine area, which could be used for leaching copper from waste material. For instance, the wastewater streams originating from the open pit Bor, copper refinery and smelting plants are also characterized by low pH values and high concentrations of iron.<sup>9</sup>

The aim of this work was to investigate the possible applications of the acidic water of Lake Robule in the process of bioleaching of copper from the flotation tailings.

#### EXPERIMENTAL

### Samples

The flotation tailings samples were collected from 20 m-deep drill holes drilled in 2007. Chemical and mineral compositions of the selected samples were previously determined.<sup>5,6</sup> The samples used in this work were taken from depths of 10, 15 and 20 m, and contained 5100 mg kg<sup>-1</sup>, 3300 mg kg<sup>-1</sup> and 4300 mg kg<sup>-1</sup> of copper, respectively.

The sample of the water from the Lake Robule was collected on June 12<sup>th</sup>, 2013. The water temperature and pH of the sample were measured on site using a Hanna Instruments HI 98312 device.

### Copper analysis

The total copper concentration in the water sample was measured using a modified method described by Anwar *et al.*<sup>12</sup> Copper (II) was reduced to Cu(I) by the addition of 200  $\mu$ L of 10 % hydroxylamine solution to 100  $\mu$ L of water sample. The solution was mixed well

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and incubated for 5 min at room temperature. Tartrate buffer (1 mL of 0.5 M HCl added to 100 mL of 0.5 M sodium tartrate and pH adjusted to 5.5) was added to the sample and the solution was mixed. Then, 500  $\mu$ L of phosphate buffer (87.7 mL of 0.2 M NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O) with 13.3 mL of 0.2 M Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O) and 100  $\mu$ L of 0.1 % bicinchoninic acid (Sigma Chemicals, USA) diluted in tartrate buffer were added and the sample well mixed. Finally, 0.8 mL of distilled water was added, mixed and after 10 min at room temperature, the absorbance at 562 nm was measured.

### Iron analysis

Amounts of soluble ferrous and ferric iron were determined spectrophotometrically by the phenanthroline assay<sup>13</sup> and thiocyanate assay,<sup>14</sup> respectively. Briefly, the supernatants were collected after centrifuging 1 mL of bioleaching cultures for 10 min at 13000 rpm. For the determination of Fe(II) ions, the samples were prepared by mixing 50  $\mu$ L of supernatant with 20  $\mu$ L 1 M Na-acetate and 150  $\mu$ L 5 mM 1,10-phenantroline-monohydrate and, finally, filled to 1 mL with deionized water. After 15 min incubation at room temperature, the absorbance was read at 510 nm. The Fe(II) concentration was determined based on the standard curve prepared using FeSO<sub>4</sub>·7H<sub>2</sub>O. For the Fe(III) determination, 500  $\mu$ L of appropriate dilution of supernatant was mixed with 500  $\mu$ L of 1 M NaSCN and incubated for 15 min at room temperature. The concentration of ferric ions was determined by comparing the absorbance readings at 490 nm to standard curve prepared with FeCl<sub>3</sub>·6H<sub>2</sub>O.

#### **Bioleaching experiments**

Water from the Lake Robule (100 mL was poured into each of three 250-mL conical flasks and 5 g of different samples of flotation tailings were added to each flask. The flasks were labeled S-10, S-15 and S-20, referring to the depth from which the samples were collected. Abiotic controls were prepared in a similar manner, except the samples of flotation tailings were incubated with 100 mL of sulfuric acid solution. Sulfuric acid was dissolved in distilled water, final pH of the solution was 2.5 in order to match the pH value of the Lake water. The control samples were labeled as CS-10, CS-15 and CS-20.

An additional control contained solely 100 mL of water from the Lake and was labeled LW. All samples and controls were incubated for five weeks at 30 °C under constant rotation of 150 rpm. One mL of sample from each flask was taken once a week for determination of the concentrations of copper, ferric and ferrous ions and pH, as described. Distilled water was added in order to compensate the evaporated water. All measurements were performed in triplicate.

### X-Ray powder diffraction analysis

The samples were analyzed in the Laboratory for Crystallography at the Faculty of Mining and Geology, University of Belgrade, on a Philips PW 1710 X-ray powder diffractometer. Experimental conditions were as follows: U = 40 kV, I = 30 mA, CuK<sub>a</sub> = 1.54178 Å,  $2\theta$  range of examination 4–90°, step 0.02° and time constant 1 s (per step). The source of X-rays was a copper anticathode with a graphite monochromator. The minerals were identified by comparing the obtained relative intensities  $I/I_{max}$  and d values with data from the JCPDS database. Semi-quantitative analysis of the diffraction data was preformed using computer software Powder Cell (Federal Institute for Materials Research and Testing, BAM, Berlin, Germany).

### Statistical analysis

Values of copper concentrations released over time from the same flotation tailings sample by acid leaching and bioleaching were compared using the *t*-test. The effects of the solutions used for bioleaching on copper recovery were determined by one-factor ANOVA at a threshold level of P = 0.05 and by the Bonferonni test. All statistics analyses were performed using SPSS 20 (SPSS Inc., Chicago, IL) software.

# RESULTS

### Physical and chemical properties of the water from Lake Robule

The color of the lake water is deep red due to the presence of a high concentration of ferric iron in the water. The temperature and pH of the water measured on site were 21 °C and 2.53, respectively. The concentrations of copper and iron were determined in the laboratory the day after sampling. The concentration of iron in the water sample was  $250\pm1.54$  mg L<sup>-1</sup> and that of copper was  $47.24\pm \pm 0.610$  mg L<sup>-1</sup>.

### **Bioleaching experiment**

Changes in the concentrations of copper, and ferrous and ferric irons during the bioleaching experiment are presented in Fig. 1. Since the lake water itself contained copper, the concentration of extracted copper was calculated by sub-tracting the copper concentration measured in flask with the lake water only (flask LW) from the total copper concentration measured in the leaching solution (flasks S-10, S-15 and S-20). The yields of copper after five weeks of bioleaching are presented in Table I.

Parameter	Sample				
1 arameter	S-10	S-15 3300	S-20	Mean	
Cu content, mg kg <sup>-1</sup>	5100	3300	4300	4233	
Cu bioleached, mg L <sup>-1</sup>	249±14	113±2.1	156±1.2	173±14	
Yield of Cu, %	98±5.5	68±1.2	73±0.6	82±8.2	

TABLE I. Copper contents and the yield of copper after five weeks of bioleaching

According to one-way ANOVA (leaching solution) and the Bonferonni test (P < 0.001), the extraction of copper from flotation tailing samples collected at depths of 10 and 20 m was significantly more efficient during bioleaching in comparison to acid leaching (Fig. 1). The differences in concentrations of copper recovered from the 15-m samples by bioleaching and acid leaching were not statistically significant ( $P \ge 0.05$ , Fig. 1). Notably, there was no significant increase of the released copper concentration during acid leaching over the period from the second to fifth week ( $P \ge 0.05$ , *t*-test). On the other hand, statistical analysis (Bonferroni test) showed that the concentrations of copper obtained after five weeks of bioleaching of the 10-m and 20-m samples were significantly higher than the concentrations measured in the previous four weeks.





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The changes in pH values during bioleaching with lake water, and leaching with sulfuric acid solution pH 2.5 are presented in Table II.

Sample	Week				
	1	2	3	4	5
S-10	2.54	2.58	2.43	2.24	2.22
S-15	2.53	2.50	2.33	2.26	2.20
S-20	2.55	2.88	2.36	2.33	2.31
CS-10	2.50	3.44	3.27	3.02	3.34
CS-15	2.50	2.80	2.65	2.67	2.68
CS-20	2.50	2.88	2.63	2.70	2.77

TABLE II. Changes in pH during the bioleaching experiment

## X-Ray powder diffraction analysis

Results of the X-ray powder diffraction analysis of the flotation tailing samples before and after treatment are shown in Figs. 2 and 3, respectively. The results of the quantitative analysis of the diffraction data are presented in Table III. The most abundant mineral in all samples was quartz  $(SiO_2)$ . Pyrite  $(FeS_2)$  and secondary copper-containing mineral langite  $(Cu_4[(SO_4)(OH)_6] \cdot 2H_2O))$  were also detected in all samples.

# DISCUSSION

The aim of the study was to test the potential of acid water from Lake Robule for bioleaching of copper from the old flotation tailings of the Copper Mine Bor. In order to evaluate this, changes in concentrations of copper, and ferrous and ferric iron were monitored for five weeks in the bio- and acid- leaching experiments.

The obtained results showed that changes in the concentrations followed a similar pattern regardless of which sample of flotation tailings was used (Fig. 1). Within the first two weeks of bioleaching, the copper concentration in all three samples rose rapidly, and continued to rise during the third week but more slowly. Although decreases in the copper concentrations were observed during the fourth week, in the last week of the bioleaching experiment, the concentration of copper increased and reached the maximal level (Fig. 1A). The increase in concentrations of ferrous iron during bioleaching (Fig. 1B), which coincided with the initial rise in the copper concentrations, indicates that leaching of copper during the first three weeks was, at least partly, mediated by the presence of ferric iron that originated from the lake water. On the other hand, the increase in concentrations of ferric iron were slower until the fourth week, when a steep increase in its concentrations (Fig. 1C) and a decrease in ferrous iron concentrations (Fig. 1B) were detected. Although changes in the concentrations of copper, ferrous and ferric iron in the acid leaching experiments showed a certain similarity with those during bioleaching, differences were clearly visible in the fourth week, especially in the ferric iron concentrations (Fig. 1C). These results suggest





Fig. 2. X-Ray powder diffraction analysis of the tailings samples before treatment with lake water. Changes in peak heights that appear to be significant are marked with arrows. The samples of flotation tailings taken from depths of: a) 10, b) 15 and c) 20 m.

that bacterial influence on the oxidation of sulfide minerals in the first three weeks was lower than in the last two weeks, when the bacteria exhibited their maximal activity.

During the process of bioleaching, acidophilic iron oxidizers, such as *Acidi*thiobacillus ferrooxidans or Leptospirillum ferrooxidans, attach to the mineral surface and produce a biofilm of exopolysaccharides, which facilitates the oxidation of pyrite and other sulfide minerals. After attachment, the bacteria in the biofilm multiply rapidly<sup>15–18</sup>. Zeng *et al.* tracked a number of attached and planktonic moderately thermophilic acidophiles during bioleaching of chalcopyrite.<sup>18</sup>

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Fig. 3. X-Ray powder diffraction analysis of the tailings samples after treatment with lake water. Changes in peak heights that appear to be significant are marked with arrows. The samples of flotation tailings taken from depths of: a) 10, b) 15 and c) 20 m.

TABLE III. Results of the semi-quantitative analysis of the X-ray powder diffraction data of the samples of flotation tailings before and after bioleaching. Content of the mineral in the sample, %. Abbreviations: BT – before treatment, AT – after treatment

Sample	Component			
	Quartz	Pyrite	Langite	
S-10 BT	76	3	22	
S-10 AT	86	2	12	
S-15 BT	74	10	16	
S-15 AT	76	11	13	
S-20 BT	72	20	8	
S-20 AT	80	11	9	

The authors reported that during bioleaching, the number of attached cells reached its maximum on the 20<sup>th</sup> day and remained stable until the 36<sup>th</sup> day, when it began to decline. On the other hand, the number of free cells was lower in comparison to attached cells during the first three weeks of the experiment. Subsequently, the number of free cells began to increase rapidly and significantly outnumbered the attached cells. The attached cells oxidized chalcopyrite causing the release of ferrous iron that was rapidly oxidized to ferric iron by the free bacterial cells, stimulating the growth of planktonic iron oxidizing bacteria and causing an increase in the concentration of ferric iron in the solution. After approximately 30 days of the experiment, the number of free cells started to decrease. Similarly, Zao et al. reported that the number of free cells during bioleaching of chalcopyrite with a pure culture of Acidithiobacillus ferrooxidans was the highest on the 50<sup>th</sup> day of experiment, as well as concentration of ferric iron and positive redox potential.<sup>17</sup> The concentration of ferrous iron increased until the 50<sup>th</sup> day, when a drop in its concentration was detected. After 50 days of bioleaching, the number of free cells in the solution began to decline, causing, on one hand, a decline in the concentrations of ferric iron and the redox potential, and, on the other hand, an increase in the concentrations of ferrous iron.<sup>18</sup>

These studies and the present results indicate that after three weeks of the bioleaching experiment presented in this paper, the number of attached cells probably reached its maximum, causing a rapid dissolution of pyrite and other sulfide minerals. Simultaneously, the ferrous iron that was released into solution was quickly oxidized to ferric iron by the fast growing free bacterial cells, stimulating further oxidation of pyrite and other metal sulfides. The number of free cells probably reached its maximum during the fourth week of the experiment, and after this period, their number started to decline.

The efficiency of bioleaching depends strongly upon the minerals that make up the treated material. Bioleaching of copper oxide minerals, such as tenorite (CuO), cuprite (Cu<sub>2</sub>O), malachite (Cu<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>) and chrysocolla (CuSiO<sub>3</sub>· 2H<sub>2</sub>O) are the most efficient.<sup>8</sup> Generally, bioleaching of copper sulfides is more difficult and requires more time than the bioleaching of copper oxides.<sup>8</sup> Copper sulfides, such as covellite (CuS), bornite (Cu<sub>5</sub>FeS<sub>4</sub>) and chalcocite (Cu<sub>2</sub>S), can be successfully oxidized during bioleaching and the yield of copper is usually substantial.<sup>20</sup> On the other hand, the formation of a passivation layer of jarosites during the bioleaching of chalcopyrite(CuFeS<sub>2</sub>) prevents its oxidation in the early stage of the bioleaching process and hence, the yield of copper after bioleaching of chalcopyrite at ambient temperature is significantly lower in comparison to the bioleaching of covellite, chalcocite and bornite.<sup>17,20</sup> Dew *et al.* studied the bioleaching of various types of sulfide minerals and reported leaching rates of minerals from high to low: chalcocite, bornite, cubanite, covellite, enargite, carrolitte and chalcopyrite.<sup>21</sup> The most abundant copper sulfide mineral in the old flotation tail-

ings of the Copper Mine Bor is covellite, followed by chalcopyrite, enargite and chalcocite. $^{4-6}$ 

The yield of copper after five weeks of bioleaching was 68.34±1.21 % for the S-15 sample, 73±0.6 % for the S-20 sample and 98±5.5 % for the S-10 sample (Table I). The unusually high content of copper in the S-10 sample (5100 mg kg<sup>-1</sup>) is the consequence of precipitation of copper sulfate in the upper layers of the flotation tailings, which have been in contact with air and water for decades. Stevanović reported that the surface layers of the flotation tailings dump at depths of 0 and 1 m contain only 260 and 320 mg kg<sup>-1</sup> of copper, respectively.<sup>5</sup> Content of copper in the dump is the highest at depths of 10 m and 20 m.<sup>4–6</sup> The exposure of the surface layers of the dump to air and water for years have initiated chemical and biological processes that led to almost complete oxidation of pyrite and other sulfide minerals (Table III, Fig. 2). X-Ray powder diffraction analysis revealed the presence of the secondary copper-containing mineral langite  $Cu_4[(SO_4)-$ (OH)<sub>6</sub>]·2H<sub>2</sub>O in all samples (Fig. 2). Langite usually occurs in mine dumps in which copper sulfate forms because of oxidation of the copper sulfides.<sup>22</sup> The content of this mineral was highest in the S-10 sample, and was significantly reduced after bioleaching (Table I, Fig. 1). Dissolution of the copper sulfate and langite in acidic solution was, presumably, the reason for a very high yield of copper, which was detected during both bioleaching and acid leaching of the S-10 sample (Fig. 1; Table I). Certain amounts of copper were also released from copper oxides that were formed during the oxidation of copper sulfides.<sup>4–6</sup> The content of copper in the 15-m sample was lower in comparison to the 20-m sample (3300 and 4100 mg kg<sup>-1</sup>, respectively). This finding was expected assuming that the content of copper in the mined ore had been gradually decreasing over the years, and that the flotation technology improved and become more efficient with time. According to the data presented in this paper and data published by other authors,<sup>4–6</sup> the old flotation tailings can be divided into three zones: oxidized zone with the lowest content of copper (0-5 m) where sulfide minerals are almost completely oxidized, zone of precipitation (5-15 m) where precipitation of copper sulfate occurred, and unoxidized zone (15-30 m) where the oxidation rate of sulfide minerals was the lowest (Fig. 4).

The amount of pyrite in the 15-m sample was higher in comparison to that in the 10-m sample, and the content of langite was lower (Table III), which implies a lower oxidation rate of sulfide minerals in this layer. The content of pyrite and langite in the 15-m sample remained unchanged after bioleaching (Fig. 3, Table III). The highest amount of pyrite and lowest amount of langite were detected in the 20-m sample. Deeper sections of the old flotation tailings were in contact with air and water for a shorter period than the tailings in the upper sections of the dump. Due to a lower oxidation rate of sulfide minerals, the content of pyrite in the deeper sections is higher than its content in the upper sections of the

tailings and, consequently, the content of langite in the 20-m sample was much lower in comparison to that in the 10-m sample (Table III). After the bioleaching experiment, the content of pyrite in the 20-m sample was reduced (Fig. 3, Table III), as the process of bioleaching generates ferric iron that is able to oxidize pyrite, and thus reduce the amount of this mineral in the tailings.



Fig. 4. Stratification of the old flotation tailings dump based on the content of copper. Shades of grey indicate copper concentrations in different zones.

Stevanović *et al.* performed an acid leaching experiment on the old flotation tailings samples in columns with or without the addition of oxidizing agents, with a 1:1 sample to acid solution ratio.<sup>5</sup> The highest yield of copper during this acid leaching experiment was demonstrated for the 10-m sample and it was 89.87 %. Maximal yields of copper detected after acid leaching with the addition of oxidizing agents were 73.97 and 48.12 % for the 15-m and the 20-m samples, respectively.<sup>5</sup> The degree of copper leaching from the 20-m sample was lower than those from the 10-m and 15-m samples,<sup>5</sup> which was not surprising, since the results of X-ray powder diffraction (Fig. 2) showed that the content of sulfide minerals was the highest in the 20-m sample.

The yield of copper detected after bioleaching of the 20-m sample reported in this paper was  $73\pm0.6$  % (Table I). By comparing the results obtained after acid leaching of the flotation tailings<sup>4–6</sup> and the results obtained by bioleaching of these samples presented in this paper, it could be concluded that bioleaching was more efficient than acid leaching for the treatment of the flotation tailings with higher sulfide mineral contents, which is located in the deep layers of the dump. In order to confirm further this conclusion, the next stage of the research will focus on the bioleaching of flotation tailings samples in columns. These column bioleaching tests will also provide an estimation of amounts of copper that could be recovered from the flotation tailings during large-scale heap bioleaching.

Lake Robule is marked as an environmental "hot spot" in the Bor mining area. In order to stop further pollution, treatment of the acidic water that constantly flows from the Lake is urgently required. The most efficient approach for such treatment of highly polluted acidic waters is the application of technology based on  $H_2S$  produced by sulfur-reducing bacteria in sulfidogenic bioreactors.

Hydrogen sulfide reacts with metal cations in wastewater thereby forming metal sulfides. Due to their low solubility, the metal sulfides precipitate and their selective precipitation is accomplished by controlling the pH of the solution.<sup>23,25</sup> The precipitated metal sulfides could be used for the production of pure metals, such as copper and zinc. This technology successfully removes As, Sb, Cu, Fe, Ni, Zn, Co, Cd, Mn and Pb from acidic waste waters.<sup>23</sup> After neutralization of the acidity, the treated water is pure enough to be released into the environment.<sup>23</sup> Heap bioleaching using acidic lake water as lixiviant, coupled with the above described technology, could turn the expensive process of wastewater purification into a profitable operation. The main disadvantage of this technology is the substantial initial capital investment.<sup>23</sup>

### CONCLUSIONS

Basic bioleaching experiments in shaken flasks showed that significant amounts of copper could be recovered from samples taken from the old flotation tailings of the Copper Mine Bor (around 80 % on average), by application of water from the extremely acidic metal-rich water body of Lake Robule as lixiviant. It was also shown that after bioleaching of the 20-m sample, the content of pyrite in the sample was reduced. This last finding is especially important if one considers the fact that reducing the amount of pyrite could decrease the negative environmental impact of the tailings. It is an obvious advantage of bioleaching over acid leaching, since protons alone are not able to break the chemical bonds in the pyrite molecule; hence, this mineral is unaffected by acid leaching.

In general, there are at least three benefits of the presented approach: the recovery of substantial amounts of copper, a reduction of the environmental impact of the Lake of the tailings, and the use of abundant and free water from an extremely acidic lake.

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### ИЗВОД

# БИОЛУЖЕЊЕ УЗОРАКА ФЛОТАЦИОНЕ ЈАЛОВИНЕ ИЗ СТАРОГ ФЛОТАЦИОНОГ ЈАЛОВИШТА РУДНИКА БАКРА БОР

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У раду је описан експеримент биолужења узорака флотационе јаловине узетих са дубина од 10, 15 и 20 m из старог флотационог јаловишта Рудника бакра Бор. Као лужни

раствор је употребљена вода из екстремно киселог језера Робуле (Бор). Принос бакра након пет недеља лужења је био:  $68\pm1,2$  %, након третмана узорка са дубине од 15 m,  $73\pm0,6$  %, за узорак са дубине од 20 m и  $98\pm5,5$  %, за узорак са дубине од 10 m. Најмањи садржај сулфидних минерала је детектован у узорку са дубине од 10 m, а највећи у узорку узетом са дубине од 20 m. Резултати биолужења су упоређени са резултатима лужења истих узорака раствором сумпорне киселине. Применом методе биолужења добијен је значајно већи принос бакра из узорака са дубине од 10 и 20 m у односу на лужење истих узорака раствором сумпорне киселине. Такође, садржај пирита у узорку са дубине од 20 m је смањен након биолужења. Предности примене технологије биолужења за добијање бакра из флотационе јаловине су: екстракција значајне количине бакра из третираних узорака, смањење утицаја третиране јаловине на животну средину и употреба воде из екстремно киселог језера Робуле, које има у изобиљу. Резултати указују на то да би биолужење могло бити ефикасније у односу на киселинско лужење за екстракцију бакра из дубљих слојева старог флотационог јаловишта, које карактерише висок садржај сулфидних минерала.

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