Treatment of the acidic effluent from a copper smelter by flotation tailings

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Abstract
Since commissioning in 1961, the copper mine Majdanpek, a part of the Mining and Smelting Complex Bor (RTB Bor), produced approximately 378 million tons of flotation tailings. Semi-quantitative mineralogical analysis of the flotation tailings revealed significant content of carbonate minerals (approximately 20-25 %), indicating high acid neutralization capacity. Also, approximately 70 % of copper is in the form of the oxide mineral cuprite (Cu2O). Copper can be easily leached from cuprite by using sulphuric acid. The RTB Bor copper smelter generates 8.7 m³h⁻¹ of extremely acidic waste effluent (142.4 kgm⁻³ of sulphuric acid, pH = 0.464) with relatively high concentrations of dissolved metals and metalloids (Cu, Fe, Zn, Pb and As). The effluent is currently treated with hydrated lime. The present study focused on application of flotation tailings as a neutralizing agent for acidic effluents. Laboratory experiments followed by computer simulation of the industrial process showed that 99% of the acid can be neutralized with flotation tailings in a series of six reactors resulting in the final copper concentration of 1.55 gL⁻¹. Benefits of the proposed process are: lower environmental impact of the process and reduced costs of neutralization of the acidic effluent from the copper smelter.

Keywords: flotation tailings; acidic effluent neutralization; copper leaching

1. INTRODUCTION

Production of mineral concentrates by froth flotation generates huge amounts of waste – flotation tailings. Approximately 99 % of the ore processed in flotation plants becomes flotation tailings [1,2]. Flotation tailings consist mainly of gangue minerals, mostly quartz, pyrite and silicates with low contents of copper and other valuable metals that were not extracted from the ore by froth flotation. Production of copper in the Mining and Smelting Complex Bor (RTB Bor), Serbia, began in 1903. Since then, approximately one billion tons of overburden and flotation tailings were deposited in the proximity of copper mines [3]. There is a growing interest in valorisation of copper from the mining waste of the RTB Bor. Antonijević et al. [4] tested leaching of copper from flotation tailings of the copper mine Bor in a glass reactor with addition of ferric chloride in 0.1 M sulphuric acid as an oxidant with the solid - liquid ratio of 1:5. After 30 h of leaching, extraction yield of copper was 88 %. Stevanović et al. [5] performed an acid leaching experiment of old flotation tailings from the same copper mine in columns by using 0.01 M sulphuric acid, with or without addition of oxidizing agents at solid - liquid ratio of 1:1. The highest yield of copper of 89.87 % achieved during acid leaching in columns was demonstrated for a sample taken from the depth of 10 m without addition of oxidizing agents. Stanković et al. [6] used water rich in acidophilic bacteria and ferric iron obtained from the extremely acidic lake Robule, Serbia,
to leach copper from flotation tailings of the RTB BOR in a shaken flask experiment. The average copper leaching degree was approximately 80%. Sokić et al. [7] performed acid leaching of copper from a copper oxide-sulphide ore excavated from the copper mine Cerovo, a part of the RTB Bor. These authors reported the leaching degree of copper of 73.8% after 3 h in 0.3 M sulphuric acid solution. Stevanović et al. [8] tested acid leaching of copper from overburden of the Cerovo mine, which contains mostly copper oxide minerals, followed by copper extraction by the process of solvent extraction and electrowinning (SX/EW). Recently, Stanković et al. [9] tested leaching of copper from Bor flotation tailings in 0.2 M sulphuric acid followed by concentration of the residual copper sulphide minerals by froth flotation. Although the mining waste of the copper mine Bor was extensively studied, such research on wastes from the copper mine Majdanpek is lacking. The copper mine Majdanpek is a part of the RTB Bor. Since commissioning of the mine in 1961, approximately 378 million tons of flotation tailings were generated during the process of froth flotation. According to data provided by the management of this copper mine, the average metal contents in the flotation tailing dump are 770 g t⁻¹ copper, 0.155 g t⁻¹ gold and 1.066 g t⁻¹ silver. Based on these data, it can be calculated that the flotation tailing dump contains approximately 292,000 t of copper, 59 t of gold and 403 t of silver.

The mineral concentrate produced in flotation facilities of the RTB Bor is transferred to the copper smelter. Pure copper is produced by autogenous smelting in a flash smelting furnace and by the matte converting process in a Pierce-Smith converter. Smelting and converting processes generate huge amounts of the waste gas SO₂. The waste SO₂ is treated in a wet scrubber and a cooling tower for wet gas cleaning. The result of this treatment is generation of wastewater characterized by high contents of free sulphuric acid and toxic metals and metalloids. Radovanović et al. [10] published an estimated composition of the wastewater from the smelter. Namely, the smelter generates 8.7 m³ h⁻¹ of the waste effluent at the temperature of 55 °C with the concentration of sulphuric acid of 142.4 g L⁻¹ and concentrations of Cu, Fe²⁺, Zn, Pb and As of 0.53, 0.38, 0.54, 0.45 and 1.37 g L⁻¹, respectively. The acidic wastewater from the primary copper production is treated by hydrated lime (Ca(OH)₂). Due to low price of the lime and its high efficiency, it is widely used for neutralization of acidic effluents. The main disadvantage of this process is generation of huge amounts of sludge, which is considered to be a hazardous waste since it contains toxic elements [11-13].

In this work, usage of the waste material (flotation tailings) was proposed for acid neutralization instead of lime. Benefits of this approach would be lowered costs of the waste effluent neutralization and a lower environmental impact. Flotation tailings are a free and abundant material. Treatment of flotation tailings with acidic effluents results in leaching of residual copper from copper oxide minerals, leading to increased concentration of copper in the leach solution. Dissolved copper can be extracted by solvent extraction and electrowinning (SX/EW) or some other hydrometallurgical process. Production of pure copper from waste materials could generate additional income and contribute to the overall economy of the process. Two acid leaching experiments were conducted at the laboratory scale. The aim of the leaching experiments with the use of sulphuric acid, and sulphuric acid in combination with hydrogen peroxide, was to estimate the total amount of copper available for leaching from oxide and sulphide mineral phases, and to get an insight into kinetics of the leaching process. After initial experiments, the next leaching experiment was performed with the use of acidic solution that corresponds to the effluent from the smelter. Experimental conditions were set according to literature data [4,14-16]. Data obtained during that experiment were used as input parameters for computer simulation of the acid neutralization and copper leaching process at the industrial scale.

2. MATERIALS AND METHODS

Approximately 20 kg of flotation tailings were collected at several locations in the flotation tailings dump of the copper mine Majdanpek (RTB Bor, Serbia). Particle size of the flotation tailings was determined as ~37 μm by sieving. Leaching experiments were performed by application of sulphuric acid (MOSS & HEMOSS, Serbia) and sulphuric acid with hydrogen peroxide (MOSS & HEMOSS, Serbia). All chemical were of p.a. grade.
2.1. Determination of the copper concentration in the leach solution and chemical and mineralogical characterization of the flotation tailings

Concentration of copper in the leach solution was determined by atomic absorption spectrophotometry (AAS) by using a Perkin Elmer Aanalyst 300 device (Norwalk, USA). Prior to the AAS chemical analysis, solid samples of the flotation tailings were dissolved in aqua regia. Mineralogical characterization of the tailings was performed by optical microscopy and XRD (X-Ray Diffraction) methods. A polarizing microscope Carl-Zeiss, model “JENAPOL-U” (Germany) equipped with 10×, 20×, 50×, 100× (oil immersion) objectives and a system for photomicrography (“Axiocam105 colour” camera and “Carl Zeiss AxioVision SE64 Rel. 4.9.1.” software package with “Multiphase” module, Carl Zeiss, Germany) was used for morphological investigations in reflected light. X-ray diffraction (XRD) patterns were obtained by using a Philips PW-1710 automated diffractometer (Philips, Netherlands) equipped with a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter. Diffraction data were collected in the 2θ/Bragg angle range of 4–65°, counting for 1 s. Semi-quantitative analysis of the data obtained by XRD was performed by “Powder Cell” computer software (Federal Institute for Materials Research and Testing, Germany) [17].

2.2. Leaching experiments

Leaching experiments were performed in a 2 L glass reactor equipped with a stirrer, thermometer and funnel for addition of the sample. Temperature control of the reactor was provided by a heating mantle (Electrothermal, UK). Total volume of the leaching solution was 1.2 L. In the first leaching experiment, the concentration of sulphuric acid was 1 M, temperature 80 °C, stirring speed 300 rpm, duration of the experiment 240 min and the quantity of the flotation tailings sample was 20 g (yielding the solid to liquid mass ratio S:L = 1:60). The second leaching experiment was performed with addition of H₂O₂ as the oxidant. Experimental conditions were: total volume of the leaching solution 1.2 L, the concentration of sulphuric acid 1 M, temperature 40 °C, stirring speed 115 rpm, duration of the experiment 240 min, and the quantity of the flotation tailings sample 20 g (yielding the solid to liquid mass ratio S:L = 1:60). Total amount of the 30 wt.% hydrogen peroxide solution was 122 mL. Half of the solution was added after 30 min and the other half after 120 min of the experiment. The third experiment simulated copper leaching by the acidic effluent from a smelter: the volume of leaching solution was 1.2 L, the concentration of sulphuric acid was 1.45 M, temperature was 55 °C, stirring speed 300 rpm, and the experiment duration was 240 min. The solid to liquid mass ratio was 1:5 (240 g of tailings was added to 1.2 L of the acidic solution).

2.3. Computer simulation of the smelter effluent neutralisation by flotation tailings

Simulation of the copper smelter effluent neutralisation process by using flotation tailings was conducted by “SuperPro Designer” software version 6.0 (Intelligen Inc, US). The aim of the simulation was to evaluate the feasibility of the treatment process. Input data for the simulation were: projected amount and composition of the effluent [10,18], calculated amount of flotation tailings to obtain the mass solid to liquid ratio of 1:5 in reactors and the chemical composition of the tailings. The expected simulation outputs were amounts and compositions of the liquid phase – treated wastewater, and the solid phase – components of the tailings, which were not leached by sulphuric acid. Possible reactions during the treatment process and thermodynamic data were determined by the HSC Chemistry software version 6.12 (Outotec Research Oy, Finland) [19]. The necessary number of reactors for acid neutralization was determined from the requirement to obtain a solution with a pH value of 2, suitable for further copper valorisation, with the defined solid to liquid ratio.

3. RESULTS AND DISCUSSION

3.1. Results of the chemical and mineralogical characterization of flotation tailings

Results of the chemical characterization of the flotation tailings used in this work (the copper mine Majdanpek) are presented in Table 1.
Table 1. Chemical composition of the copper mine Majdanpek flotation tailings

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
<th>S</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>0.072 %</td>
<td>0.086 %</td>
<td>10.70 %</td>
<td>7.01 %</td>
<td>1.667 ppm</td>
<td>0.405 ppm</td>
</tr>
</tbody>
</table>

The X-ray diffractogram of the flotation tailings is presented in Figure 1.

![X-ray diffractogram of the flotation tailing sample](image)

Figure 1. X-ray diffractogram of the flotation tailing sample

The most abundant minerals in the tailings sample identified by the X-ray diffraction analysis were quartz, pyrite and carbonates (calcite and dolomite), followed by feldspar, clay minerals, mica and illite, which were present in far lower amounts. The most abundant copper minerals identified by optical microscopy were cuprite (Cu$_2$O) at 70 wt.%, chalcopyrite (CuFeS$_2$) at 20 % and tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) ≤ 10 %. Microphotographs of the flotation tailings sample, in which the presence of cuprite, chalcopyrite, and pyrite was determined, are presented in Figures 2 and 3. Results of the semi-quantitative analysis of the data obtained by XRD were: quartz 50-55 wt. %, total carbonates 20-25 wt. %, pyrite = 5 wt. %, illite = 5 wt. %, and kaolinite 5-10 wt. %.

![Optical photomicrograph of a flotation tailing sample in which cuprite (Cp) is visible marked by arrows](image)

Figure 2. Optical photomicrograph of a flotation tailing sample in which cuprite (Cp) is visible marked by arrows. (scale bar: 50 µm)

![Optical photomicrograph of a flotation tailing sample in which inclusions of chalcopyrite (Ccp) in pyrite (Py) are visible](image)

Figure 3. Optical photomicrograph of a flotation tailing sample in which inclusions of chalcopyrite (Ccp) in pyrite (Py) are visible. (scale bar: 50 µm)
3. 2. Acid leaching experiments

Results of the leaching experiments are presented in Figures 4-6. Based on the measured copper concentrations in tailings by AAS, the leaching degree was calculated by the equation:

\[
\text{Leaching degree} = \frac{C_{\text{Cu(l)}} V}{m_{(s)} m_{f_{\text{Cu(l)}}}} \times 100
\]  

where \(C_{\text{Cu(l)}}\) is the mass concentration of copper in the leach solution, \(V\) is the volume of the leach solution, \(m_{(s)}\) is the mass of the solid sample, and \(m_{f_{\text{Cu(l)}}}\) is the copper mass fraction in the solid sample.

Course of the leaching experiment with 1M sulphuric acid is presented in Figure 4, that with 1 M sulphuric acid and 1 M hydrogen peroxide in Figure 5 and that with the acidic solution containing 1.45 M sulphuric acid and corresponding to the effluent from a smelter is shown in Figure 6.

![Figure 4. Extraction of copper during leaching with 1 M sulphuric acid, S:L = 1:60](image)

![Figure 5. Extraction of copper during leaching with 1 M sulphuric acid and 1 M hydrogen peroxide, S:L = 1:60](image)

![Figure 6. Extraction of copper during leaching with 1.45 M sulphuric acid, S:L = 1:5 simulating the smelter effluent](image)

Effects of the composition of the leaching acidic solution as well as the solid to liquid mass ratio are clearly visible so that the highest copper extraction yield of ~66 % is obtained in the solution of sulphuric acid with addition of hydrogen peroxide at the S:L ratio of 1:60 (Fig. 5).

3. 3. Microscopic analysis of the leaching residue after leaching with addition of hydrogen-peroxide

Solid residue after the second leaching experiment with addition of hydrogen peroxide was examined by optical microscopy. Minerals identified in the residue were: pyrite, magnetite, rutile, chalcopyrite, elemental sulphur and...
gangue minerals. Chalcopyrite was present as inclusions in pyrite and quartz (Figs. 7 and 8). Figure 9 shows partially dissolved pyrite after leaching with addition of $\text{H}_2\text{O}_2$. Copper oxide minerals were not detected in the sample.

![Image of chalcopyrite in quartz](image1.png)

Figure 7. Inclusions of chalcopyrite (Ccp) in quartz

![Image of chalcopyrite in pyrite](image2.png)

Figure 8. Inclusions of chalcopyrite (Ccp) in pyrite (Py)

![Image of partially dissolved pyrite](image3.png)

Figure 9. Partially dissolved pyrite (Py) after leaching with addition of $\text{H}_2\text{O}_2$

3. 4. Computer simulation of neutralisation of the acidic effluent by using flotation tailings

The scheme presented in Figure 10 presents the computer simulation model of the acidic effluent neutralization process by using flotation tailings.

![Diagram of process acidic effluent neutralization](image4.png)

Figure 10. Scheme of the process acidic effluent neutralization by flotation tailings used for computer simulation: the process consists of 6 serially connected reactors each followed by a phase separator; the process contains 19 streams in total
Inputs in the simulation were compositions of wastewater from the copper smelter (acidic effluent) and Majdanpek flotation tailings (Table 2). The chemical composition of the acidic effluent was determined previously by Radovanović et al. [10].

Table 2. Compositions of the acidic effluent and flotation tailings as inputs in the simulation (data reprinted from [10] with permission of The Organizing Committee of the 47th International October Conference on Mining and Metallurgy, 4th – 6th October 2015)

<table>
<thead>
<tr>
<th>Acid effluent</th>
<th>Component</th>
<th>Content, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂AsO₄⁻</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>CuS</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>CuSO₄⁺</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>FeSO₄⁺</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>PbO</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>PbSO₄⁺</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>PbS</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>H₂SO₄</td>
<td>13.41</td>
</tr>
<tr>
<td></td>
<td>ZnSO₄</td>
<td>0.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flotation tailings</th>
<th>Component</th>
<th>Content, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂SiO₅⁻</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>CaCO₃⁻</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td>Cu₂O</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>CuFeS₂⁻</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>K₂SiO₅⁻</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>MgCO₃⁻</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td>FeS₂⁻</td>
<td>19.00</td>
</tr>
<tr>
<td></td>
<td>SiO₂⁻</td>
<td>54.78</td>
</tr>
<tr>
<td></td>
<td>ZnS</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>85.06</td>
</tr>
</tbody>
</table>

The acidic effluent is formed by mixing wastewater streams generated in wet scrubbers treating gases originating from smelting and converting processes in the copper smelter. It is characterized by a high acid content accompanied with dissolved metals, present as sulphates, as well as dispersed insoluble particles, being metallic or sulphides (Table 2). Flotation tailings, besides the gangue material, also contain carbonates (calcite and dolomite) that could be used for acid neutralization, and copper oxide mineral (cuprite), which can be dissolved by sulphuric acid. Possible reactions that occur during the treatment, and thermodynamic data for enthalpy changes (ΔH), entropy changes (ΔS) and changes in the Gibbs free energy (ΔG) were determined by the HSC Chemistry software and presented in Table 3.

Table 3. Thermodynamic data for possible reactions during the acidic effluent treatment at 25 °C; changes in enthalpy (ΔH), entropy (ΔS) and the Gibbs free energy (ΔG)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reactions</th>
<th>ΔH / kJ</th>
<th>ΔS / J K⁻¹</th>
<th>ΔG / kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CaCO₃(s) + 2H⁺ + SO₄²⁻ = CaSO₄(s) + H₂O(l) + CO₂(g)</td>
<td>-9.65</td>
<td>278.62</td>
<td>-84.035</td>
</tr>
<tr>
<td>2.</td>
<td>MgCO₃(s) + 2H⁺ + SO₄²⁻ = MgSO₄(s) + H₂O(l) + CO₂(g)</td>
<td>64.257</td>
<td>290.145</td>
<td>-22.250</td>
</tr>
<tr>
<td>3.</td>
<td>Cu₂O(s) + 2H⁺ + SO₄²⁻ = 2Cu²⁺ + SO₄²⁻ + H₂O(l)</td>
<td>-68.290</td>
<td>-22.580</td>
<td>-62.123</td>
</tr>
</tbody>
</table>

Table 3 shows that all three reactions are possible due to negative values of ΔG, and that reactions of acid neutralization (reaction 1) and copper leaching (reaction 3) are exothermic (negative values of ΔH) resulting in the temperature increase. Descriptions of process streams, presented in Figure 10, are given in Table 4.

Table 4. Description and flowrates of process streams in the simulation

<table>
<thead>
<tr>
<th>Stream</th>
<th>Characteristic</th>
<th>Place in simulation</th>
<th>Flowrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flotation tailings</td>
<td>Input</td>
<td>1073 kg h⁻¹</td>
</tr>
<tr>
<td>2</td>
<td>Acid effluent</td>
<td>Input</td>
<td>8700 L h⁻¹</td>
</tr>
<tr>
<td>3</td>
<td>Solution</td>
<td>Transfer</td>
<td>8647 L h⁻¹</td>
</tr>
<tr>
<td>4</td>
<td>Solid residue</td>
<td>Output</td>
<td>1329 kg h⁻¹</td>
</tr>
<tr>
<td>5</td>
<td>Flotation tailings</td>
<td>Input</td>
<td>1073 kg h⁻¹</td>
</tr>
<tr>
<td>6</td>
<td>Solution</td>
<td>Transfer</td>
<td>8564 L h⁻¹</td>
</tr>
<tr>
<td>7</td>
<td>Solid residue</td>
<td>Output</td>
<td>1261 kg h⁻¹</td>
</tr>
<tr>
<td>8</td>
<td>Flotation tailings</td>
<td>Input</td>
<td>1073 kg h⁻¹</td>
</tr>
<tr>
<td>9</td>
<td>Solution</td>
<td>Transfer</td>
<td>8481 L h⁻¹</td>
</tr>
<tr>
<td>10</td>
<td>Solid residue</td>
<td>Output</td>
<td>1261 kg h⁻¹</td>
</tr>
</tbody>
</table>

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The acidic effluent enters the process as the stream 2 at the flowrate of 8700 L h⁻¹, and is neutralized by addition of 1073.31 kg h⁻¹ of flotation tailings into each of the five reactors (Streams 1, 5, 8, 11 and 14) and 442.00 kg h⁻¹ into the sixth reactor (Stream 17) to achieve the pH value of 2 in the output solution (Stream 18). Solid and liquid phases are separated in phase separator after each reactor and solid residues exit the process as output Streams 4, 7, 10, 13, 16 and 19. After the phase separation, the obtained solutions are transferred to the next reactor. The main output from the simulation is Stream 18 with the final copper concentration of 1.55 g L⁻¹ and the sulphuric acid concentration that corresponds to the pH value of 2.

3. 5. Discussion

Results of the first leaching experiment with 1 M sulphuric acid revealed that most of the copper that was extracted in total in this experiment (84 %) was dissolved during the first five minutes of leaching; the total copper extraction degree after 240 min was 51.6 %. Other authors also reported fast dissolution of copper (85 % of totally extracted) from copper oxide minerals during first five minutes of leaching with sulphuric acid [15]. Copper from copper sulphide minerals can be extracted by addition of oxidizing agents [16,20]. Copper extraction increased to 66% after addition of 1 M hydrogen peroxide (Fig. 5). Microscopic analysis of the leaching residue (Figs. 7, 8, 9) showed that most of chalcopyrite minerals were not dissolved after this leaching process. Chalcopyrite was mostly present as inclusions in quartz and pyrite, and, as a consequence, unavailable for leaching, as well as concentration by froth flotation. At the industrial level, hydrogen peroxide would increase costs of the process, and the obtained increase in the copper extraction degree would probably not justify the additional costs. Therefore, it was decided to continue leaching experiments with sulphuric acid only, which is available free as a waste effluent from the smelter.

The aim of the next experiment was to simulate acid neutralization and copper leaching on the industrial scale by using a solution with the sulphuric acid concentration and temperature corresponding to smelter acidic effluents with the solid to liquid mass ratio of 1:5. Again approximately 85 % of the totally extracted copper in this process was leached after five minutes of the experiment. The copper leaching degree was lower in this experiment as it reached 33.5 % after 240 min, due to S:L. Copper oxide minerals, which account for 70 % of the total copper minerals in flotation tailings samples, are readily soluble in acidic solutions. This fact explains the observed rapid increase in the copper concentration at the beginning of the experiment. Accordingly, copper oxide minerals were not detected by the microscopic examination of the solid residue after leaching.

Results of the chemical and mineralogical analysis of the tailings and data obtained by the leaching experiment with 1 M sulphuric acid were used as input parameters for computer simulation of the process at the industrial scale. According to data obtained by simulation, 5808 kg h⁻¹ of flotation tailings is required to neutralize 8.7 m³ h⁻¹ of the acidic effluent from the smelter to the pH value of 2 in the series of six agitation tanks. The final concentration of copper at the output from the sixth reactor is 1.55 g L⁻¹, indicating that the resulting solution is suitable for extraction of copper by the SX/EW technology. The final concentration of copper is achieved by combining copper contained in the acidic effluent (0.53 g L⁻¹) and copper extracted from flotation tailings (1.02 g L⁻¹).

The conventional method for neutralization of the acidic effluent is application of hydrated lime. Radovanović et al. [10] performed computer simulation of neutralization of the acidic effluent from the RTB Bor copper smelter by this component. Neutralization of 8.7 m³ h⁻¹ of the acidic effluent was predicted to generate over 10 t h⁻¹ of the hazardous sludge and consume approximately 7 m³ h⁻¹ of the hydrated lime solution. On the contrary, neutralization by using flotation tailings is predicted to produce nearly 7 t h⁻¹ of the solid residue, which can be deposited in flotation tailings dumps. It should be noted that safe deposition of the voluminous sludge predicted in the first process is a serious environmental issue [11-13]. Obviously, the usage of flotation tailings instead of lime decreases the overall amount of the waste in the process and reduces water consumption, resulting in a decreased environmental impact of the proposed process as compared to the acid neutralization by lime.

According to data obtained by computer simulation, instead of losing copper [21], approximately 100 t of copper could be produced annually by the proposed process. In the software simulation, the leaching duration in each reactor was set to 1 h. Laboratory experiments showed that 85 % of the extractable copper was obtained during the first five
minutes. By decreasing the leaching time in each reactor, improved process efficiency can be achieved as even more copper can be produced during the same time interval.

4. CONCLUSION

Flotation tailings of the copper mine Majdanpek exhibited a good acid neutralization capacity due to the relatively high content of carbonate minerals. Results presented in this paper show that these flotation tailings can be used instead of hydrate lime for neutralization of acidic effluents from the copper smelter of RTB Bor. The environmental impact of the proposed process is lower in comparison to the acid neutralization by using lime. The computer simulation showed that copper present as copper oxide minerals and leached by sulphuric acid could be concentrated up to 1.55 g L\(^{-1}\) in a series of six reactors. The predicted copper concentration in the pregnant leach solution is suitable for copper extraction by the SX/EW technology. The proposed process for neutralization of acidic effluent from copper smelters by using flotation tailings can lead to cheaper and cleaner production of copper in the RTB Bor and contribute to a circular economy by copper valorisation instead of its loss in flotation tailings and the acidic effluent.

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SAŽETAK

Tetman kiselih otpadnih voda iz topionice bakra flotacijskom jalovinom

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Od otvaranja 1961. g. rudnik bakra Majdanpek (deo RTB Bor) je proizveo približno 378 miliona tona flotacijske jalovine. Iako su koncentracije vrednih metala (bakra, cinka, zlata i srebra) u jalovini veoma male, ukupna količina metala deponovanih u jalovini je značajna. Zbog malih koncentracija, valorizacija metala iz ove flotacijske jalovine nije bila ekonomski opravdana. Semi-quantitativnom mineraloškom analizom uzoraka flotacijske jalovine utvrđeno je da jalovina sadrži znatne količine karbonatnih minerala (približno 20-25%), što ukazuje na to da ova jalovina ima značajan kapacitet za neutralizaciju kiseline. Oko 70 % bakra prisutnog u jalovini je u obliku oksidnog minerala kuprita (Cu2O). Bakar se lako može izlužiti iz kuprita pomoću sumporne kiseline. Topionica bakra RTB Bor proizvodi 8,7 m3h-1 izuzetno kisele otpadne vode (142,4 kgm-3 sumporne kiseline, pH = -0,464) sa relativno velikim koncentracijama rastvorenih metala i metaloida (Cu, Fe, Zn, Pb i As). Otpadna voda se tretira hidratisanim krećom. U ovom radu je ispitana mogućnost primene flotacijske jalovine u cilju neutralizacije kiselosti otpadne vode uz istovremeno luženje bakra prisutnog u jalovini. Laboratorijski eksperimeneti i softverska simulacija su pokazali da je primenom flotacijske jalovine moguće neutralizati 99 % sumporne kiseline u seriji od šest reaktora sa mešanjem. Rezultati dobijeni softverskom simulacijom pokazuju da bi konačna koncentracija bakra u rastvoru nakon postupka neutralizacije bila 1,55 gL-1, što bi omogućilo izdvajanje čistog bakra tehnologijom solventne i elektrolitičke ekstrakcije. Prednosti ovog postupka su: manji uticaj na životnu sredinu i niži troškovi postupka neutralizacije kisele otpadne vode iz topionice bakra.

Ključne reči: flotacijska jalovina, neutralizacija kiselih otpadnih voda, luženje bakra