



FROM WASTE TO RESOURCE: LEACHING METALS FROM FLOTATION TAILINGS AT THE “RUDNIK” MINE FOR SUSTAINABLE DEVELOPMENT

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Abstract: *Modern industries engaged in the design and development of high-technology products are highly dependent on the availability of critical materials. Due to the increasingly rapid depletion of primary raw materials, there is growing interest in processing secondary raw materials, such as mining waste and flotation tailings. In this study, leaching experiments were conducted on a sample of flotation tailings from the Rudnik mine (Serbia) containing copper (0.081%), lead (0.132%), zinc (0.510%) and iron (6.88%). The influence of hydrogen peroxide concentration in sulfuric acid solution on metal leaching was examined. It was established that in the system of sulfuric acid (1 mol/dm³ H₂SO₄) and hydrogen peroxide (H₂O₂, 1–3 mol/dm³), the highest leaching of metals was achieved at the lowest concentration of hydrogen peroxide over 120 minutes, amounting to 81.97% Cu, 48.84% Fe, and 45.58% Pb. Increasing the concentration of hydrogen peroxide (1–3 mol/dm³) leads to a decrease in the degree of leaching of the tested metals, except for Zn. The highest zinc extraction was 97.72% (2.0 mol/dm³ H₂O₂). The obtained leaching values are higher compared to leaching flotation tailings with sulfuric acid solution.*

Keywords: Flotation Tailings, Leaching, Sulfuric Acid, Hydrogen Peroxide.

1. INTRODUCTION

With the rapid development of industrial society, the demand for valuable metals is constantly increasing. Today, traditional energy sources such as fossil fuels (coal, oil, natural gas) are increasingly being replaced by sustainable and renewable energy sources, including solar, wind, hydropower, geothermal and biomass [1]. Modern industry and economic transition are heavily dependent on metals, given the growing demand for energy storage solutions such as batteries and power-to-X technologies [2-4]. However, intensive mining activity in recent decades has led to the accumulation of large amounts of mining and flotation tailings, especially those containing sulphide minerals [2,4]. Due to the rapid depletion of primary sources, the processing of secondary raw materials, such as mining waste (mine and flotation tailings), is becoming increasingly important. The valorisation of useful elements from mining waste offers both economic and ecological advantages, as it enables a sustainable supply of critical materials and contributes to environmental preservation [5]. Mining waste can contain significant amounts of elements from the list of critical raw materials (e.g. Co, Bi, V, Sb, Ta), as well as other elements of secondary or strategic importance (Cu, Zn, Ni, Ag). Closed and abandoned mining waste dumps often contain toxic elements (As, Cr, Pb, Cd) whose mobility can threaten soil, water, ecosystems, and human health. Some of these toxic elements are also on the list of critical raw materials (CRM) [2,3,6]. The use of mining waste aligns with the principles of the circular economy, reduces risks to the environment and health, and can help offset the costs of remediating abandoned sites. Although reserves from mining waste will not fully meet demand, they can reduce heavy dependence on imports.

Research into the valorisation of useful elements from mining waste is not new, but it has recently been gaining increasing attention, as it can represent an alternative source of critical and strategic raw materials. Recycling mining waste can be carried out using current mineral processing methods [4]. Since tailings have already been excavated and crushed, processing secondary raw materials from mining waste is significantly cheaper than extracting them from primary deposits. The most frequently tested method for leaching sulphide residues is acid leaching in a sulphate environment with sulfuric acid using oxidants (O_2 , Fe^{3+} , H_2O_2) [3,7,8].

The "Rudnik" Mine (Municipality of Gornji Milanovac) has been operating since 1953, and over 11 million tonnes of flotation tailings have been deposited on its tailings area of more than 30 hectares [9]. Flotation tailings are fine-grained waste residues from the flotation process of sulphide minerals, such as galena (PbS), chalcopyrite ($CuFeS_2$), and sphalerite (ZnS).

The investigations presented in this paper are part of the technological research programme within the project "Characterization and technological processes for recycling and reuse of flotation tailings from the "Rudnik" Mine - REASONING" (2024–2026), from the Prizma programme, approved by the Science Fund of the Republic of Serbia. The project aims to develop strategies for the valorisation of precious metals, non-ferrous metals, and critical elements, with the additional utilisation of the remaining aluminosilicate residue for the production of construction materials, ultimately seeking to achieve the zero-waste principle. This paper presents the results of the leaching of Pb, Cu, Zn, and Fe from the flotation tailings of the "Rudnik" Mine during leaching in acidic sulphate solutions in the presence of hydrogen peroxide as an environmentally friendly reagent for the oxidation of metallic sulphide minerals.

2. EXPERIMENTAL

2.1 Materials and methods

The composite sample were collected from four boreholes in the tailings pond at the "Rudnik" Mine. The chemical composition was determined using Inductively Coupled Plasma (ICP) spectroscopy and is shown in Table 1.

Table 1. Chemical composition of the initial tailings samples of "Rudnik" Mine

Source: original author's

Components	Al	Ca	Mg	Cu	Fe	Zn	Pb	K	Ag _{ppm}	Au _{ppm}	As
Content (%)	1.07	4.52	0.78	0.08	6.88	0.50	0.13	0.08	9.7	0.0061	0.097

The qualitative mineralogical composition of the analyzed tailings sample from boreholes includes: quartz, calcite, K-feldspars, plagioclase, kaolinite, pyrite, pyrrhotite, arsenopyrite, sphalerite, chalcopyrite, galena, smectite/chlorite minerals, irregularly interstratified clays, and magnetite. Calcite and quartz are the most abundant minerals. Feldspars (K-feldspars and plagioclase) are present in smaller amounts. Among the ore minerals, pyrrhotite, arsenopyrite, and pyrite are the most abundant. Among the valuable minerals, sphalerite is the most common, followed by chalcopyrite in lower quantities, while galena is the least abundant [9].

The influence of acid concentration ($1.0 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$) with and without the oxidant, solid/liquid ratio (1:60), stirring speed (400 rpm), and hydrogen peroxide concentration ($1\text{--}3 \text{ mol/dm}^3$) were examined.

A 600 cm^3 glass reactor equipped with a magnetic stirrer was used. After the experimental conditions were set, 5 g of tailings sample was added into 300 cm^3 of the leaching solution of a defined concentration. The stirring speed was maintained at 400 rpm. At predetermined time interval (120 minutes), 2 cm^3 of leach liquor sample was taken, filtered, the filtrate was transferred and filled with distilled water to the 50 cm^3 volumetric flask. The concentration of copper, iron, lead and zinc were analyzed using optical emission spectrometer with inductively coupled plasma (ICP-OES Optima 8300; Perkin Elmer) and multiparameter photometer Hanna (HI 83200).

3. RESULTS AND DISCUSSION

3.1 Effect of hydrogen peroxide concentration

The influence of hydrogen peroxide concentration on metal leaching from flotation tailings was investigated at initial concentrations of 1, 2, and 3 mol/dm³ in a 1.0 mol/dm³ H₂SO₄ solution at room temperature. The preliminary results obtained are shown in Figure 1.

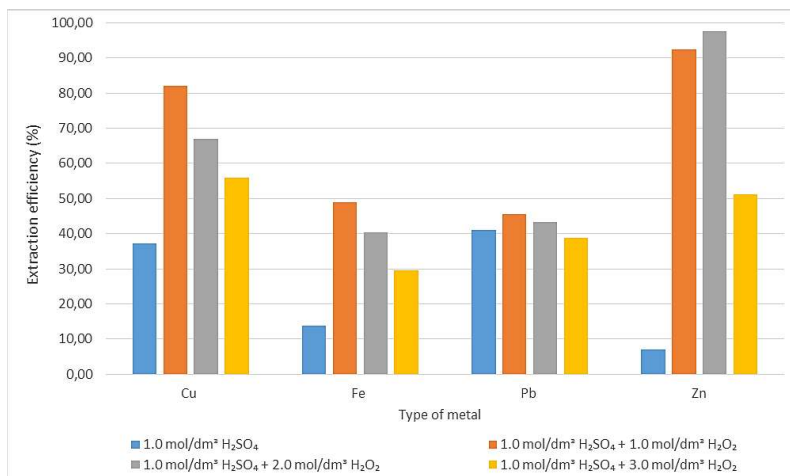


Figure 1. Effect of hydrogen peroxide concentration on copper, iron, lead and zinc recovery (1 mol/dm³ H₂SO₄; S:L=1:60 g/cm³; stirring speed 400 rpm; ambient temperature)

Source: original author's

Figure 1 shows that, after 120 minutes of leaching, copper leaching ranges from 37.26% (1.0 mol/dm³ H₂SO₄ without oxidant) to 81.97% (1.0 mol/dm³ H₂O₂); iron ranges from 13.74% (without oxidant) to 48.84% (1.0 mol/dm³ H₂O₂); lead ranges from 38.74% (3.0 mol/dm³ H₂O₂) to 45.58% (1.0 mol/dm³ H₂O₂); and zinc ranges from 7.06% (without oxidant) to 97.72% (2.0 mol/dm³ H₂O₂). The leaching values of all tested metals are highest with the addition of the lowest oxidant concentration (1 mol/dm³ H₂O₂) and are higher than the leaching values with only sulfuric acid.

With an increase in the concentration of hydrogen peroxide (2.0–3.0 mol/dm³), the degree of leaching of Cu, Fe and Pb decreases, while zinc leaching is highest at 2.0 mol/dm³ H₂O₂, reaching 97.72%. With a further increase in hydrogen peroxide concentration, zinc leaching decreases. These data indicate that the concentration of hydrogen peroxide affects the oxidative leaching of metals from flotation tailings [10]. As the concentration of oxidants increases, the leaching degree of lead from galena decreases, suggesting that oxidants have a minor effect on its dissolution [11]. The increase in the dissolution rate of chalcopyrite and other sulphide minerals in the presence of hydrogen peroxide is attributed to the high redox potential in the solution, which leads to the partial conversion of sulphide sulfur to elemental sulfur and then to sulphate [12]. In his research, Karppinen et al. [13] monitored the leaching of Cu and Zn from sulphide tailings using sulfuric acid and O₂, as well as O₂ combined with H₂O₂ as oxidants. The results showed that introducing hydrogen peroxide as an additional oxidant improved the leaching of copper and zinc. After adding hydrogen peroxide, the degree of Zn extraction after 2 hours was about 92%. These results are significantly better compared to those obtained when only O₂ was used, where zinc leaching was about 56%. In contrast, copper extraction increased from 23.1% to around 30%, with continuous growth after 6 hours.

4. CONCLUSION

Based on experimental data, the following could be concluded:

- A sample of flotation tailings from the "Rudnik" Mine is a low-grade raw material containing 0.08% Cu, 0.50% Zn, 0.13% Pb, and 6.88% Fe.

- Mineralogical analysis showed that sphalerite is the most abundant non-ferrous metal mineral. The most abundant minerals in the tailings are quartz and aluminosilicates.
- During the leaching of flotation tailings with a 1.0 mol/dm³ H₂SO₄ solution for 120 minutes, 37.26% Cu, 41.02% Pb, 7.06% Zn, and 13.74% Fe were leached.
- The concentration of hydrogen peroxide in 1.0 mol/dm³ H₂SO₄ affects the dissolution of metals from flotation tailings.
- The maximum final metal extraction values of 81.97% Cu, 45.58% Pb, and 48.84% Fe were obtained under the following conditions: 1.0 mol/dm³ H₂SO₄ and 1.0 mol/dm³ H₂O₂, a solid/liquid ratio of 1:60, a leaching time of 120 minutes, and a stirring speed of 400 rpm. Under the same conditions, the maximum final zinc extraction value of 97.72 % was obtained in 1.0 mol/dm³ H₂SO₄ and 2.0 mol/dm³ H₂O₂.

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