



Studies on hydrometallurgical processes using nuclear techniques to be applied in copper industry.

II. Application of radiotracers in copper leaching from flotation tailings*

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Abstract. The use of radiotracers in the present study is intended to replace traditional steps of metal quantitative analysis (solution sampling and instrumental chemical analysis) and to allow real-time measurements of metal concentrations during the leaching process. In this study, ^{64}Cu , an isotope of copper, was selected as a radiotracer. Samples of copper flotation tailings were irradiated in the Maria research reactor (Świerk, Poland) and mixed with an inactive portion of the milled flotation waste. The leaching process was carried out in a glass reactor, and the radiation spectrum was measured using a gamma spectrometer. The material was then treated using various acids (sulphuric acid, nitric acid, acetic acid, citric acid, and ascorbic acid) in a wide range of their concentrations. Experiments with the radiotracer were conducted in sulphuric and nitric acids. The amount of the leached metal (copper) was calculated on the basis of the peak area ratio in the gamma-ray spectrum of the activated tailings and standard samples. Inductively coupled plasma mass spectrometry (ICP-MS) was also used to analyse the metal content. Maximum recovery of 56% Cu was achieved using 9 M HNO_3 , whereas the recovery was lowest for ascorbic acid (<1%). Both analytical methods were compared, and the results presented in this paper are in good agreement with radiometric measurements obtained using ICP-MS analysis.

Keywords: flotation waste • hydrometallurgy • leaching • radiotracer

Introduction

Copper mining and its ore processing is one of the most stable and profitable branches of economy in Poland and one of the most intensively developed industry sectors. However, commonly used technologies cause high losses of valuable and so-called deficit metals in streams of their solid wastes. Development and implementation of hydrometallurgical technologies is a solution, which is feasible for a higher efficiency of the element recovery and for decreasing hazardous environmental impact of the wastes dumped at the vicinity of a mine. A large amount of flotation wastes has been land-filled from the time since the ore exploitation started. The wastes contain almost similar metal content to presently exploited world primary deposits. In this study, we are dealing with a similar situation in a Polish copper sector. Due to the relatively high content of copper and other metals in the wastes, their storage areas (Żelazny Most or Gilów reservoirs) can be regarded as a secondary accumulation of a poor placer deposit [1, 2]. The copper ore mining activities generate annually about 28 million tons of

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mineral wastes. The largest amount of the wastes, about 90%, comes from the ore concentration plants. The waste generated in the process of the ore flotation is transferred in the form of aqueous slurry to a pond. The surface area of the Żelazny Most reservoir is 1580 ha, and its capacity is over 590 million m³ [3]. Gilów sedimentary pond covers an area of 600 ha. It reached the maximum damming level in 1980 and was then closed down, thus becoming the largest inactive facility of this type in Poland. Since that time, it has been functioning as an emergency retentive facility for the Żelazny Most reservoir. The total amount of wastes deposited in the Gilów flotation tailings reservoir is 68 million m³ [4]. The overview of the management of flotation wastes was discussed in the study by Łuszczkiewicz [5].

Hydrometallurgical processes are currently extensively scrutinized to recover valuable metals from ores and various industrial wastes. Many investigations have been carried out using the hydrometallurgical route to effectively leach copper raw materials. Many solutions with or without special treatment can be used as leaching agents. Sulphuric(VI) acid is the most commonly used agent due to its low price and availability. Other exemplary copper leachants are as follows: H₂SO₄+H₂O₂, H₂SO₄+HNO₃, NH₃+H₂O, HCl, CH₃COOH, FeCl₃, H₂SO₅, NaOH, NaCN, glycine NH₂CH₂COOH, and methanesulfonic acid CH₃SO₃H [6–13]. A brief overview of copper recovery, in the similar conditions to those with sulphuric acid presented in this paper, is shown in Table 1. Organic acids, such as citric acid [14, 15] or ascorbic acid [16], can work as leachants to recover other metals. Generally, there are no universal methods to recover copper and other metals from copper-bearing minerals as their chemical and phase compositions depend on the type of mined ore, type of pyrometallurgical process, temperature, fraction size, and so on.

One of the most commonly used methods to analyse metals in geologic materials is neutron activation analysis (NAA). Other techniques include an inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectroscopy (OES), X-ray fluorescence (XRF), and atomic absorption

spectroscopy (AAS). NAA is a non-destructive, accurate, highly selective, sensitive, and precise method, which does not require any sample pre-treatment. Moreover, some chemical interferences, such as matrix effect, are avoided. Nevertheless, it is a relatively slow technique and not all chemical elements can be measured simultaneously. In the majority of the cases of hydrometallurgical and similar processes described in the literature, NAA is used for elemental analysis of raw materials (for example, ashes, ores, and organic matter) only before the leaching process is carried out. Sometimes, it is also used to analyse solid residues after the leaching process. Column studies on leaching (by water and simulated acid rain: H₂SO₄, pH = 2.5) of trace elements from neutron-irradiated fly-ash samples were described by Dybczynski *et al.* [17]. Disintegration process of realgar ore was examined by the neutron activation method to determine the amount of arsenic sulphide dissolved from As₂S₃ [18]. NAA was also used to detect lanthanides and other elements in pure elemental gallium, which was recovered from the Bayer process alkaline leach solution [19]. In another work on the Bayer process, a combination of analytical techniques (inductively coupled plasma mass spectrometry and optical emission spectroscopy as well as instrumental neutron activation analysis) was used. The aim of the work was to establish distribution patterns of selected bauxite trace elements (Ga, V, As, Cr, REE, and Sc) in the Bayer process and their by-products by formulating mass balance models of the above-mentioned elements based on a case study [20]. Bacterial leaching of rare and valuable metals from low-grade ores, complex composition ores, rocks, and industrial wastes was carried out in the study by Tsertsvadze *et al.* [21]. Elemental composition of the primary and processed samples was investigated by epithermal neutron activation analysis.

The ⁶⁴Cu isotope was treated as a tracer in the investigations described below. Tracer research is a useful tool to measure fluid flow dynamics in industrial installations and laboratory systems. Radiometric methods rely on the use of some ra-

Table 1. Selected conditions for copper leaching with H₂SO₄ from metallurgical wastes. L/S means liquid/solid ratio

Materials	Conditions	%Cu	Ref.
Brass slag	30% acid, L/S 5:1 (w/w), T = 35°C ^(a)	90	[6]
1) Copper smelter slag	3.0 M acid, L/S 30:1 (v/w), T = 25°C ^(b)	1) 26.0	[7]
2) Copper smelter slag flotation tailings		2) 13.5	
Intermediate of base metal production	1.95 M acid, L/S 40:1 (v/w), T = 25°C ^(c)	81	[8]
Flotation tailings	9 M acid, L/S 5:1 (v/w), T = 20°C ^(d)	72	[9]
Copper smelter slag	1.2 M acid, L/S 10:1, T = 20°C ^(e)	78	[11]
Copper converter slag flotation tailings	pH 1.5, [Fe ³⁺] = 15.7 g/dm ³ , L/S 3:1, T = 28°C ^(f)	45	[12]
Copper flotation tailings	0.428 M acid, L/S 3:1, T = 23°C ^(g)	45	[13]

Other conditions were also investigated:

^(a) [H₂SO₄] = 5–50%, T = 10–70°C, L/S 3–8:1.

^(b) [H₂SO₄] = 0.5–3.0 M, [Fe₂(SO₄)₃] = 5–40 g/dm³ in 1.0 M acid, [H₂O₂] = 0.5–3.0 M in 1.0 M acid, T = 30–50°C.

^(c) [HCl] = 0.5–5 M, [H₂SO₄] = 0.5–3 M, [HNO₃] = 1 M, CuCl₂, NaOH.

^(d) [H₂SO₄] = 0.001–9 M, tap water, distilled water, [Fe₂(SO₄)₃] = 0.5–10 g/dm³ in 0.1 M acid, L/S 2–5:1, T = 20–60°C.

^(e) [H₂SO₄] = 0.2–1.2 M.

^(f) T = 28–85°C, [Fe₂(SO₄)₃] = 0–15.7 g/dm³, L/S 3–10:1 (v/w).

^(g) [H₂SO₄] = 0.230–0.494 M, T = 23–88°C, L/S 1–5:1.

radioactive isotopes of the elements contained in a material introduced into the examined system. The introduction of a small amount of the radiotracer, which is characterized by some identical or similar properties to the medium transported in the tested system, allows tracing its motion *in vivo*. The improved methods for the detection of the radiation emitted by the radiotracer ensure high measurement accuracy of defined parameters. The full picture of the system dynamics can be obtained by combining the results of the radiotracer studies with the results of the measurements of physicochemical properties of the given medium [22].

This paper presents the selected results of the leaching process of flotation tailings. The changes in copper concentrations were monitored radio-metrically during the process.

Experimental section

Reagents and apparatus

The following reagents were used for leaching experiments: sulphuric(VI) acid (98% pure p.a., Chempur), nitric(V) acid (65% pure p.a., POCH), citric acid monohydrate (pure p.a., Chempur), L(+)-ascorbic acid (pure p.a., POCH), and acetic acid (99% pure p.a., POCH). Analytical grade reagents, nitric(V) acid, hydrofluoric acid, and boric acid were used for the digestion of the solid materials for quantitative analyses. Distilled water was used in all experiments.

The concentration of elements was analysed by the ICP-MS technique (ELAN DRC II PerkinElmer™) with a cross-flow nebulizer and a Scott double-pass spray chamber. Nickel cones were used in the measurements. Standard solutions (1 mg·mL⁻¹) used for ICP-MS analyses were supplied by the manufacturer. The concentration of copper was examined and calculated using an instrumental neutron activation analysis (INAA) method and confirmed by ICP-MS. The activity measurements were performed by the Gamma Spectroscopy System (Canberra Industries) with an HPGe (high-purity germanium) detector.

Flotation tailing characterization

Flotation waste material was provided by Polish Geological Institute – National Research Institute. The material was powdered in a ball mill (Retsch) and then dried at 120°C for 2 hours. The coning and quartering method was used to prepare the samples for digestion. This procedure was carried out in a Microwave Reaction System Multiwave 3000 (Anton Paar) with the addition of 65% HNO₃ with 40% HF during the first stage and then 4% H₃BO₃ during the second stage. The concentration of copper and other elements in the as-obtained solutions was determined by ICP-MS. Table 2 shows the results as an arithmetic mean of 10 measurements. The results obtained for rare earth elements (REE) are presented as a sum of light- and heavy-REE (LREE and HREE). Fine Fly Ash (CTA-FFA-1) was used as a certified reference material (CRM) for multi-element trace analysis. The high variability of the elements content in the tailing samples was noticeable. Variation coefficient ranged from 10 to 43%. Trace elements can thus be set in the following content sequence: Cu > Fe > Pb > Mn > Zn > V > Co. A very similar outcome was obtained in the study by Baran *et al.* [4]. The rest of the analysed metals occurred at a concentration below 100 ppm.

Radiotracer preparation

Natural copper consists of two different stable isotopes as follows: ⁶⁵Cu (30.9%) and ⁶³Cu (69.1%). Flotation tailing samples and a standard (high purity copper) were irradiated and activated in the Maria research reactor (Świerk, Poland). Parameters of neutron activation and activity of nuclides as well as computing methods of their concentration are presented in Part I of this paper [23] according to Bujdoso *et al.* [24].

Copper was selected for INAA analysis not only due to its presence in relatively large amount in wastes but also due to short half-life (12.8 h) of its isotope. Such a choice was meant to avoid produc-

Table 2. Total content of selected elements in flotation tailings

Element(s)	Mean [ppm]	Standard deviation [ppm]
Ag	61.1	13.2
Cd	2.8	0.6
Co	123.8	28.8
Cu	10 686.7	1 774.7
Fe	8 879.5	1 442.3
HREE: Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu	8.5	0.8
LREE: La, Ce, Pr, Nd, Sm, and Eu	55.8	6.1
Mn	1 239.4	275.7
Mo	34.6	10.7
Ni	70.3	28.2
Pb	3 087.7	1 312.4
Sb	4.2	1.7
Th	4.2	1.3
U	6.3	0.8
V	137.1	53.4
Zn	524.3	115.9

tion and accumulation of radioactive wastes. Radioisotope ^{64}Cu was produced in the $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$ reaction by thermal neutrons during sample irradiation in a nuclear reactor [25].

Leaching process procedure

Flotation tailings were crushed, milled, and sieved to obtain 0.2–0.5 mm powder fraction. The activated sample was then mixed with 20 g of an inactive portion of the milled flotation waste. All the experiments in the leaching process were carried out at 25°C in a periodic glass reactor equipped with a mechanical stirrer, pump, filter system, and gamma spectrometer. The material was added to 300 mL of acidic lixiviant. Various acids (sulphuric(VI), nitric(V), acetic, citric, and ascorbic acids) were used in a wide range of their concentrations. Sulphuric acid was chosen for the procedure because it is the commonly known and used leachant in leaching processes, whereas nitric acid is a stronger oxidant than sulphuric acid. Organic acids are relatively inexpensive, environmentally harmless, and biodegradable. Furthermore, the acids have the ability to chelate metal ions.

In the experiments with the radiotracer, a comparative method was used for determining the amount of leached copper, which was calculated on the basis of the ratio of areas under photopeaks in a gamma ray spectrum (see Eq. (3) in Part I of this article [23]).

Results and discussion

Leaching with sulphuric(VI) acid

The influence of sulphuric acid concentration (0.1–18 M) on metal dissolution was investigated. The process was conducted for 24 hours. In the case of metals in the given sequence, $\text{Cu} > \text{Fe} > \text{Pb} > \text{Mn} > \text{Zn} > \text{V} > \text{Co}$, there was a certain limit of the acid concentration above which the degree of leaching decreases. Except for Pb and Zn, the acid concentration was 8–10 M. For these two elements, an increase in the acid concentration results in improved leaching efficiency. It was observed by Ahmed *et al.* [6] that sometimes a similar effect appears, that is, extraction of a metal decreased with an increased sulphuric acid concentration. It can be explained by the formation of calcium sulphate and/or other insoluble sulphates on the surface of a particle at higher acid concentration, which hinders mass transfer across particles. Another explanation is that high acidity leads to an increase in the viscosity of the solution, which in turn inhibits the leaching process. The viscosity of sulphuric acid is rapidly increasing above its 60% concentration. Further research was performed using 2 M and 8 M acid solutions in which the highest degree of copper leaching was obtained. Copper concentration was calculated using the radiometric method and confirmed by ICP-MS analysis. Figures 1 and 2 present

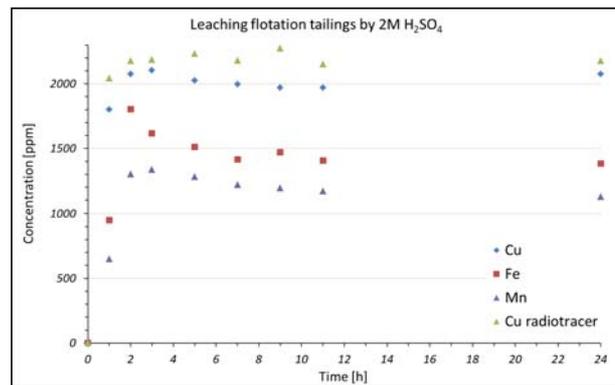


Fig. 1. The results of leaching metals from flotation tailings by 2 M H_2SO_4 .

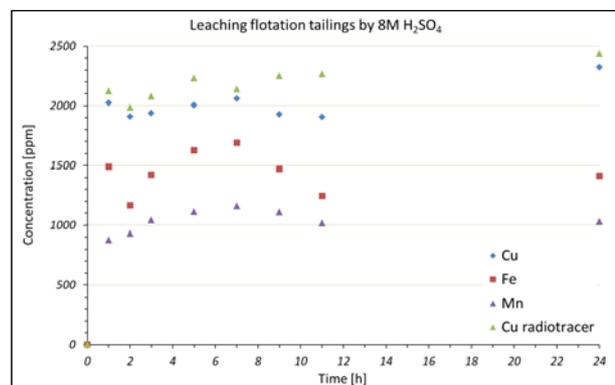


Fig. 2. The results of leaching metals from flotation tailings by 8 M H_2SO_4 .

the results of the tests. Only Cu, Fe, and Mn are included in the graphs above, as the quantities of the remaining metals leached were below 50 ppm. It can be noticed that the optimal time to achieve the highest leaching level was 3 and 1–2 hours for 2 M and 8 M acid solutions, respectively. The recovery of copper, and other metals occurring in the largest amount in tailings, is quite low and it is ca. 15–22% (Fig. 3). The higher acid concentration does not improve leachability of many metals, except REE, which were much more modestly extracted by the stronger acid. It should be perceived that these results are given only for two acid concentrations. No linear relationship was observed for other concentrations.

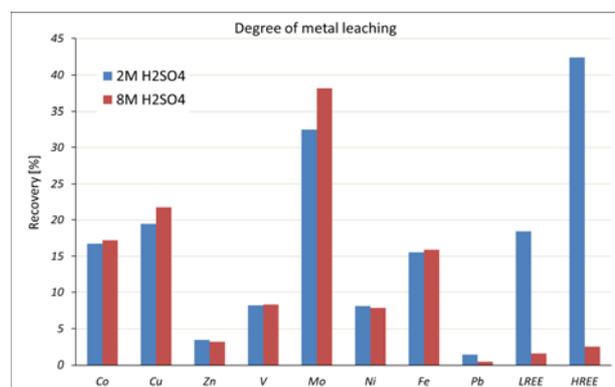


Fig. 3. The leaching degree of selected elements after 24 hours using sulphuric acid.

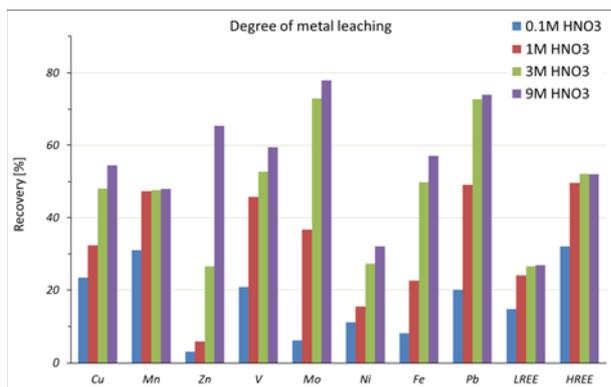


Fig. 4. The leaching degree of selected elements after 24 hours using various concentrations of nitric(V) acid.

Leaching with nitric(V) acid

Acid concentrations (0.01–14 M) and time of leaching (24 or 48 hours) were used as variables of the process. The highest leaching level of copper was obtained by using 10.5 M acid after 24 and 48 hours. Extended leaching time causes a higher level of leaching – 71% vs. 56%. However, in the case of the acid concentration higher than 9 M, the changes are quite small, about 2–3% for each time duration of the process. Some of the results after 24-hour-lasting process are shown in Fig. 4. The extraction of metals was found to increase with an increase in acid concentration. Nitric acid was more effective in leaching metals compared to sulphuric acid.

The sample of flotation tailings with a ⁶⁴Cu radiotracer was leached using 3 M HNO₃. The results are presented as the amount of copper and selected metals in the function of process time in Fig. 5. The results obtained for copper are consistent with the data from ICP-MS analysis.

Leaching with other acids

Other acids such as acetic acid (0.1, 2, 5, and 10 M), citric acid (0.1 and 1 M), and ascorbic acid (0.1, 1, 1.4 M), were also tested during the studies. Ligands from organic acids can form stable metal complexes

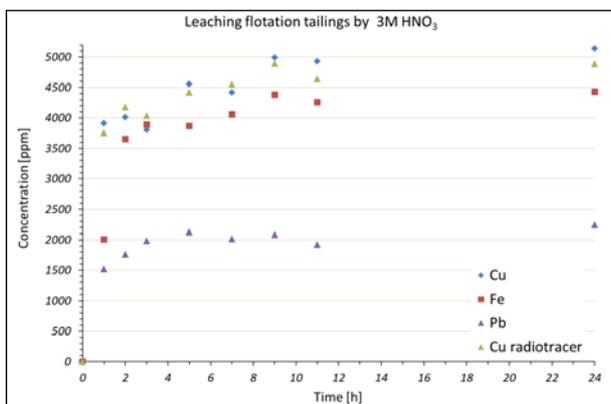


Fig. 5. The results of leaching of flotation tailings by 3 M HNO₃.

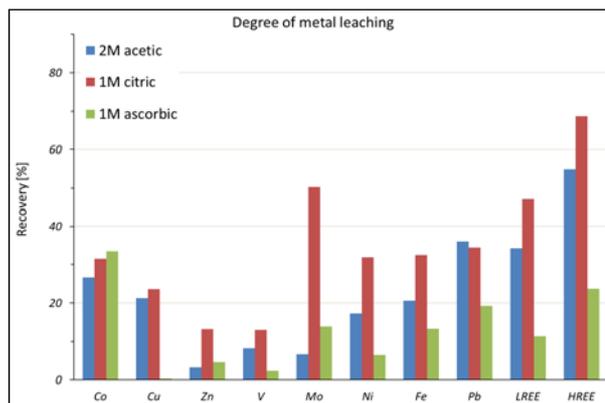


Fig. 6. The leaching degree of selected elements after 24 hours using various acids.

that can increase metal solubility. The results for some metals are shown in Fig. 6. Overall copper recovery was quite low, and for ascorbic acid it was below 1%. Satisfactory results were obtained for rare earth elements using citric acid, in which about 70% HREE and 45% LREE were recovered.

Accuracy of analytical methods

The accuracy of the ICP-MS and INAA methods was determined based on the analysis of the CRM (Fine Fly Ash, CTA-FFA-1). For both analytical methods used, degree of accuracy of the quantitative analysis is slightly different based on the element under consideration. The certified value with confidence intervals for copper is $158 \pm 9 \mu\text{g/g}$ (ppm). The degree of accuracy (relative error) was calculated as a modulus of the difference between the arithmetic mean value of the results and the certified value, and then divided by the certified value. It was shown that the ICP-MS method was characterized by the accuracy of 2.9%, whereas the INAA method by 9.2%. The measurement uncertainty of the copper in the experiments was also estimated to be 12% for ICP-MS and 10% for INAA. Therefore, both methods have similar accuracy.

Summary

The leaching experiments with and without ⁶⁴Cu as a radiotracer were carried out to examine the recovery of copper and some other metals derived from flotation tailings. The use of the radiotracer allows us to get real-time measurements of the metal concentrations in reaction medium and to stop the leaching at the optimal point. Various acids were used as leaching agents. In general, the highest dissolution of metals was obtained in nitric acid. About 50% of copper was recovered in 3–9 M nitric acid, 20% in 2–8 M sulphuric acid, and 20% in organic acids except ascorbic acid. However, in Polish circumstances, an important criterion for the selection of leaching environment for copper-producing company KGHM is an easy access to sulphuric acid, which is produced in the KGHM-owned smelters (~650 tons per year) [26]. Analytical methods used

in this study gave comparable results. Such radio-tracer experiments were not much troublesome to be performed on the laboratory scale. Besides the specific equipment, an access to the research nuclear reactor or the neutron generator is necessary. This concept of radiometric quantitative measurements of elements still needs an improvement and some testing on other isotopes as well. After developing an appropriate measurement methodology, this kind of research could be feasibly used on the industrial scale if radiological safety would be ensured. The copper isotope was already used in the industry, for example, in a flotation process. Efficiency of flotation and mean residence time of granulometric fractions were received for activated ore samples [27].

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