

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

## I. Application of $^{64}\text{Cu}$ radiotracer for investigation of copper ore leaching\*

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**Abstract.** Scientific objective of this work was elaboration of radiometric method for the development of hydrometallurgical process for recovery of Cu from the copper ore. A neutron activation analysis (NAA) was identified as a very convenient tool for the process investigation. The samples of copper ore were activated in a nuclear reactor. The parameters of the neutron activation were calculated. Radioisotope  $^{64}\text{Cu}$  was selected as an optimal tracer, and it was used for the investigation of the leaching process. During the experiments, various processes applying leaching media such as sulphuric acid, nitric acid, and organic acids were investigated. The recovery of the metals using sulphuric acid was insufficient, around 10%. Investigated organic media also did not meet expectations. The best results were obtained in experiments with nitric acid. Up to 90% of Cu and other metals were extracted from the copper ore. Copper concentration calculations obtained by NAA were confirmed by inductively coupled plasma mass spectrometry (ICP-MS) technique. Both techniques gave comparable results, but the advantage of the NAA is a possibility for easy online measurements without shutting down or disturbing the system.

**Keywords:** copper ore • hydrometallurgy • leaching • NAA

### Introduction

The copper industry is one of the most profitable branches of the Polish economy and the fastest growing industry. Currently KGHM Company (Polish multinational corporation) has become one of the leaders of global electrolytic copper and silver markets [1]. The company's position is the result of good management, investment, and development of an integrated processing technology, in which the product from one stage of production constitutes as the substrate for the next. The technology commonly used in KGHM is based on pyrometallurgy [2]. Wastes after copper processing still contain significant quantities of metals (Me) such as copper, iron, lead, vanadium, silver, and other valuable metals [3]. High costs of present ore processing and possibility for recovery of other metals induce the research for new technological solutions. Hydrometallurgy may meet requirements for more quantitative resources exploitation. Techniques of extractive metallurgy involve aqueous chemistry for the recovery of metals from the various raw materials such as ores, residual materials, and wastes. The main advantages of hydrometallurgical technology are high efficiency,

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possibility of recovering extremely low concentration of metals, less energy demand in comparison to pyrometallurgical processes, and so on [4]. The hydrometallurgy processes are constantly improved and adjusted for various technologies and became more and more popular in copper industry [5–7]. The process has been studied as an alternative route to ores and concentrates treatment. A several chemical and biological processes for copper recovery have been developed [8–17].

The challenge of process development is generally to leach raw material quickly and completely. The composition of the leach solution is chosen depending on the type of raw material subjected to leaching. These can be acids:  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ; hydroxide:  $\text{NaOH}$ ; chlorides:  $\text{NH}_4\text{Cl}$ ,  $\text{FeCl}_3$ ; carbonates:  $\text{Na}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ , and biological consortia as well [13, 18–23].

Since 1980s, a hydrometallurgy technology has been under development at the Institute of Nuclear Chemistry and Technology (INCT) [24]. At present, in cooperation with the International Atomic Energy Agency (IAEA) in frame of Coordination Research Project (CRP) a new project is carried out. The development of a technology needs efficient and less time-consuming analytical methods. Radiometric methods are the suitable tool for process investigation [24]. Most of the metals may be activated and radionuclides can be easily detected. Several process characteristics such as separation efficiency, process kinetics, and flow dynamics parameters or concentration of metals can, therefore, be qualitatively and quantitatively evaluated [24–27]. At this step of research, the raw material characterization and the leaching process were carried out. Several leaching media such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and organic acids were investigated, and the concentration of the leached Cu was determined using activated  $^{64}\text{Cu}$ . The measurement method is based on the neutron activation analysis (NAA). Despite the rapid development of other techniques, such as X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), NAA still holds an important place in the metal trace analysis. It has a lot of advantages such as it is one of the most sensitive analytical techniques used for multielement analysis; it allows providing quantitative and qualitative results for several individual elements with high sensitivities impossible by any other analytical technique; it does not need the so-called blind test; no sample extraction, digestion, volume loss, or dilution is required; and no potential for contamination because of handling or laboratory chemicals. One simple procedure can analyse several elements simultaneously. The biggest advantage of the method is easy online measurements without shutting down or disturbing the plant or system. The measurements are possible through walls of pipes or apparatus (no sampling).

Copper isotope was already used in industry, for example, in flotation process to research the efficiency of flotation and mean residence time of granulometric

fractions, where ore samples were activated [28]. The NAA technique is mainly used for elemental analysis of the raw material (e.g., ores, organic matter, and ashes waste) before or after process. The NAA was also used to detect lanthanides and other elements in pure elemental gallium that was prior recovered from the Bayer process alkaline leach solution [29]. Complex analyses and processes using activation analyses are investigated by CSIRO [26, 30].

The idea of this work was to find and optimize sufficient analytical technique for continuous measurements during the process and select the optimal leaching medium for future experiments.

## Experimental section

### Reagents and apparatus

For leaching experiments, following reagents were used: Chempure sulphuric acid solution 98% pure p.a., POCH nitric acid 65% pure p.a., Chempure citric acid monohydrate pure p.a., POCH L(+)-ascorbic acid (ASC) pure p.a., POCH acetic acid 99% pure p.a. For preparation of the solid materials for quantitative analyses, analytical grade reagents were used: nitric acid, hydrofluoric acid, and boric acid. Distilled water was used in all experiments.

The concentration of Me was chemically analysed using ICP-MS instrument (ELAN DRC II PerkinElmer™) with a cross-flow nebulizer and a Scott double-pass spray chamber. Ni cones were used in the measurements. Standard solutions ( $1 \text{ mg}\cdot\text{mL}^{-1}$ ) used for ICP-MS analyses were supplied by producer. The concentration of Cu was analysed and calculated using NAA and confirmed using ICP-MS analyses. The activity measurements were performed by Canberra gamma spectrometer with Ge detector.

### Cu ore characterization

The ore samples from the Legnica-Głogów Copper Mining District used in experiments were obtained from the Polish Geological Institute – National Research Institute. The most important mineral components of the ore are chalcocite ( $\text{Cu}_2\text{S}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), chalcopyrite ( $\text{CuFeS}_2$ ), and covellite ( $\text{CuS}$ , whose content is significantly lower) [30, 31].

Samples were grounded to powder and then dried at  $120^\circ\text{C}$  for 2 h. Quartered samples were mineralized in a microwave furnace with the addition of acids and then analysed using ICP-MS. The uncertainty of elemental determination by this technique was evaluated at 5–10% depending on the element. The results are presented in Table 1. The highest Me concentration in the raw materials was determined for Cu, Pb, Fe, Mn, and V. The concentration of other metals such as Co, Zn, Ni, Mo, Ag, light rare earth elements (LREE), and heavy rare earth elements (HREE) was significantly lower. Recovery of these metals seems to be economically justified only as a co-product in the copper extraction process.

**Table 1.** Metal concentration in Cu ore sample

Element	Concentration [mg/g]
Cu	39 720 ± 3 986
Pb	27 210 ± 1 904
Fe	23 912 ± 1 896
Mn	1 422 ± 114
V	1 416 ± 113
Co	403.3 ± 21.1
Zn	393.2 ± 36.1
Ni	382.3 ± 9.3
Mo	341.4 ± 7.2
Ag	219.8 ± 18.6
LREE: La, Ce, Pr, Nd, Sm, Eu	104.1 ± 9.7
HREE: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	14.2 ± 0.7

LREE – light rare earth elements. HREE – heavy rare earth elements.

**Radiotracer preparation**

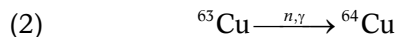
The radiotracer was obtained by activating 1-g samples of the ore. The process was carried out in a reactor Maria at the Nuclear Centre for Nuclear Research in Poland. The conditions of activation were activation time of 50 min and neutron flux of  $10^{14}$  [n/(cm<sup>2</sup>·s)]. The samples were cooled down for 3 days. The main activation parameters are presented in Table 2.

The activity of particular radionuclide was calculated using Eq. (1) [32].

$$(1) \quad A = \frac{6.023 \cdot 10^{23} \cdot \Phi \cdot m \cdot G \cdot \sigma_{at} \cdot 10^{-24}}{100M} \cdot \left(1 - e^{-\frac{0.693\tau}{T_{1/2}}}\right) \cdot e^{-\frac{0.693t}{T_{1/2}}}$$

where *A* is the activity,  $\Phi$  is the neutron flux, *m* is the mass of element, *G* is the abundance,  $\sigma_{at}$  is the cross section, *M* is the molar mass,  $\tau$  is the irradiation time,  $T_{1/2}$  is the half-life, and *t* is the time of activity decay.

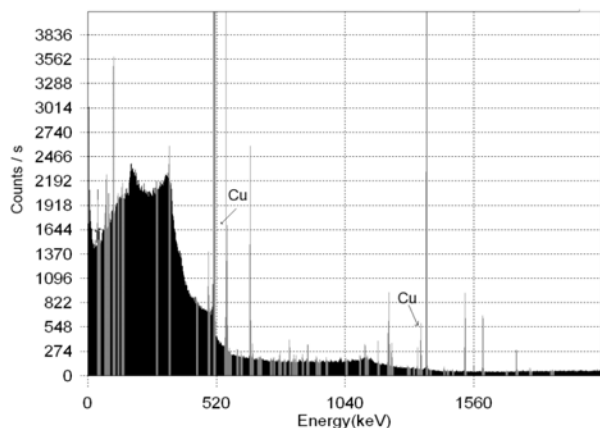
As a tracer for the process, radioisotope <sup>64</sup>Cu was selected, which was obtained according to the following reaction:



There are two main characteristic peaks of <sup>64</sup>Cu for gamma spectrum (see Fig. 1). The first peak is at 511 keV but is useless because of interference with signals emitted by other radionuclides. Therefore, for analytical method, peak at 1345.78 keV is meaningful, which is ‘clean’ from other interferences. Cu standard material for calibration of Cu concentrations was activated as well.

**Cu ore leaching procedure**

Samples were prepared using the following procedure. The material was grounded and sieved on the sieves to separate different fractions. The 0.25- to 0.5-mm sized fractions were selected for the experiments. At next step, 20 g of the powdered ore was added to 300 mL of various solution reactants at various concentrations and stirred (100 rpm) into chemical glass reactor for 24–48 h. Experiment was conducted at 25°C. The solution was filtered on a Büchner funnel. The concentration of leached copper was determined using radionuclide <sup>64</sup>Cu. The concentration of Cu was calculated according to Eq. (3). The concentration of copper calculated from gamma spectrum corresponds with ICP-MS results. The difference is below 10%.



**Fig. 1.** <sup>64</sup>Cu into gamma spectrum.

**Table 2.** Activation parameters calculated for 1-g copper ore sample

	Copper ore / Sample mass: 1 g					
	Neutron flux $\Phi$ : $1 \cdot 10^{14}$ cm <sup>-2</sup> ·s <sup>-1</sup>					
Chemical element	Cu	V	Mn	Zn	Co	Ag
Nuclide to be activated	<sup>65</sup> Cu	<sup>51</sup> V	<sup>55</sup> Mn	<sup>64</sup> Zn	<sup>59</sup> Co	<sup>109</sup> Ag
Abundance, <i>G</i> [%]	69.17	99.75	100	48.89	100	48.65
Mass of element, <i>m</i> [g]	$3.59 \cdot 10^{-2}$	$1.20 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$	$4.20 \cdot 10^{-4}$	$4.80 \cdot 10^{-4}$	$2.40 \cdot 10^{-4}$
Cross section, $\sigma_{at}$ [barns]	4.5	4.8	13.3	0.82	17	4.2
Activated nuclide	<sup>64</sup> Cu	<sup>52</sup> V	<sup>56</sup> Mn	<sup>65</sup> Zn	<sup>60</sup> Co	<sup>110m</sup> Ag
Irradiation time, $\tau$ [h]	0.83	0.83	0.83	0.83	0.83	0.83
Half-life, $T_{1/2}$ [h]	12.69	0.06	2.58	5 880	46 103.88	6 120
Atomic mass, <i>M</i> [g·mol <sup>-1</sup> ]	63.54	50.94	54.94	65.37	58.93	107.87
Time of activity decay, <i>t</i> [h]	75	75	75	75	75	75
Activity, <i>A</i> [Bq]	80 159 975	0	6	15 042	103 926	25 516

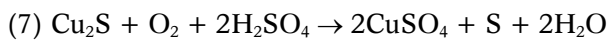
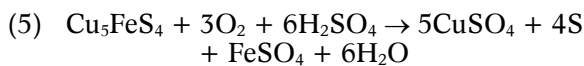
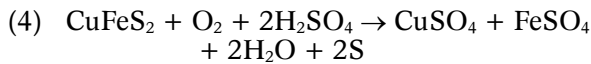
$$(3) \quad X = \frac{\frac{P}{D \cdot C \cdot m}}{\frac{P_0}{D \cdot C \cdot m_0}}$$

where  $X$  is the concentration of element [ppm],  $P$  is the counts number of radionuclide [1/min],  $P_0$  is the counts number of radionuclide for standard sample [1/min],  $D$  is the half-life correction for radionuclide,  $C$  is the correction factor related to the decay of the radionuclide at the time of measurement,  $m$  is the mass of the sample [g],  $m_0$  is the mass of the standard sample [ $\mu\text{g}$ ].

## Results and discussion

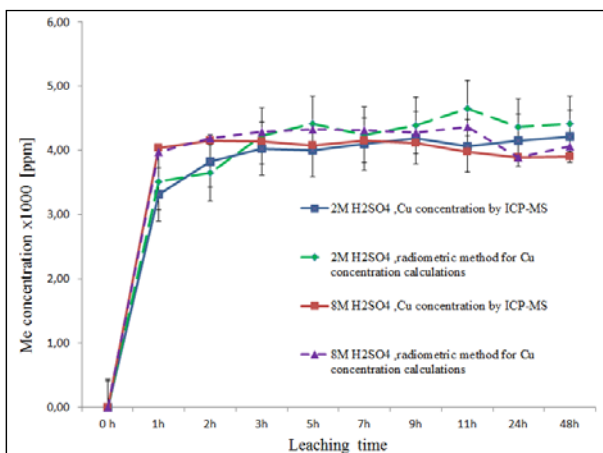
### Cu ore leaching by $\text{H}_2\text{SO}_4$

Primary copper leaching processes using chemical oxidation [16] is presented below:

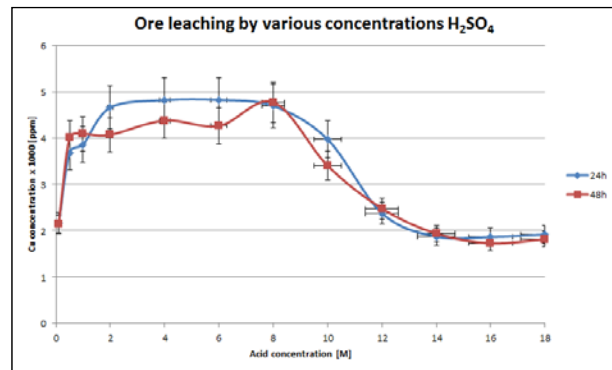


The minerals react also with  $\text{FeSO}_4$  in next reactions. Sulphide can be oxidized in acidic media with the formation of elemental sulphur, sulphides, thiosulphates, and so on.

At first experiment, the material was treated with sulphuric acid. The effect of acid concentration was investigated at various concentrations: 0.1, 0.5, 1, 2, 4, 6, 8, 10, 14, 16, and 18 M. The concentration of copper was calculated using radiometric method and controlled by ICP-MS analyses (see Fig. 2). The method allowed online controlling and optimization of the process. Because of relatively short half-life of  $^{64}\text{Cu}$  ( $T_{1/2} = 12.7$  h), it would be impossible for using



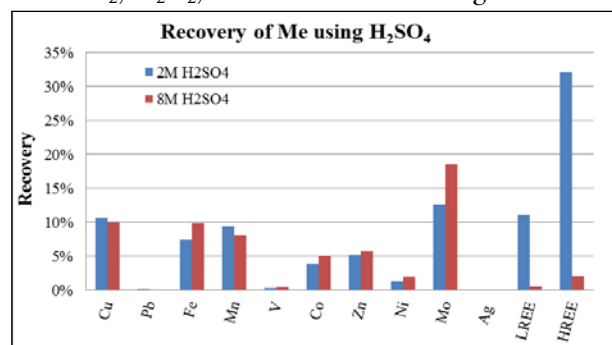
**Fig. 2.** Comparison of copper concentration measurements with using radiometric method and ICP-MS analyses.



**Fig. 3.** Results of copper ore leaching by various concentrations of  $\text{H}_2\text{SO}_4$  using radiometric method.

it after 76 h ( $6 \cdot T_{1/2}$ ) of the process [33]. An optimal time to reach the highest leaching efficiency was 3 h for 2 M  $\text{H}_2\text{SO}_4$  and 1 h for 8 M  $\text{H}_2\text{SO}_4$  (Fig. 2), but experiments were performed for 48 h. The extraction of Cu was found to increase with an increase in acid concentration between 0.1 M and 8 M (Fig. 3) and then decreased with a further increase in sulphuric acid concentration what leading to an increase in the viscosity of the solution that consequently inhibits the leaching process. This phenomenon was previously observed in  $\text{H}_2\text{SO}_4$  medium [34–36]. The other problems of the process are passive films on the grain's surface and the potential blocking and wetting of minerals grains by liquid elemental sulphur [36]. The highest efficiency of leaching obtained at concentrations of acid between 2 M and 8 M (see Fig. 3).

These concentrations of sulphuric acid are not commonly reported for studying copper sulphide ores. Typically used concentrations of acid are lower, about 0.1–3 M  $\text{H}_2\text{SO}_4$  [10, 17–19, 37, 38], with the recovery of Cu of up to 99%. In this work, the recovery of the Cu was very low, around 10%, and other metals were eluted at this level as well. Only HREE in 2 M acid solution was around 35%, but it is insufficient (see Fig. 4). A low concentration of Me after leaching process by  $\text{H}_2\text{SO}_4$  is the result of the absence of oxidizing agents in leaching solution. The leaching operation to dissolve Cu, Zn, Co, Ni, Re, V, and Mo needs sulphuric acid solutions containing iron(III) sulphate as necessary oxidant and gaseous oxygen for regeneration of Fe(II) to Fe(III) during leaching [30, 39, 40]. Other oxidants such as  $\text{MnO}_2$ ,  $\text{H}_2\text{O}_2$ , or ozone were investigated in the

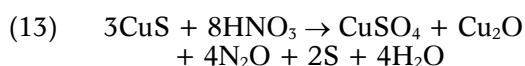
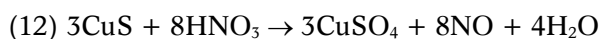
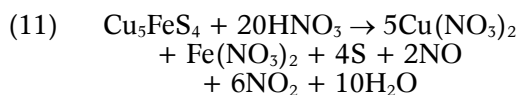
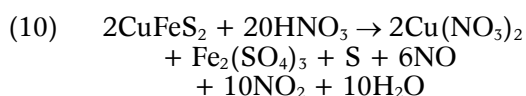
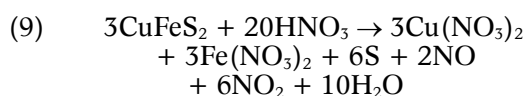
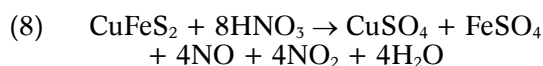


**Fig. 4.** Selected results of Me recovery from copper ore treated by  $\text{H}_2\text{SO}_4$ .

literature as well [19, 41, 42]. The experiments with oxidizing agents are performed and will be published in the near future.

### Cu ore leaching by HNO<sub>3</sub>

The main components of copper sulphide minerals can form water, soluble, solid, and gaseous products when interacting with nitric acid. Example of reactions is given as follows [43]:



If the leaching is performed with an air supply, we can expect the oxidation of NO to NO<sub>2</sub>. Sulphur oxidizes to sulphate in the presence of strong oxidizing agents.

The procedure of leaching process with the use of nitric acid was similar, and similar material was treated with nitric acid at various concentrations: 0.1, 0.5, 1, 2, 3, 5, 8, 8.5, 9, 9.5, 10, 10.5, and 11 M. The highest leaching yield (ca. 90%) was obtained at acid concentration 11 M (see Fig. 5) after 24 h of the process. The extraction of Cu and other metals was

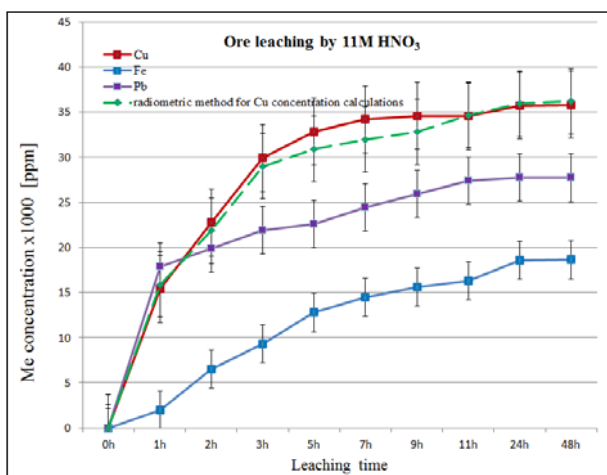
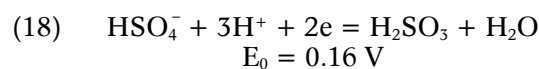
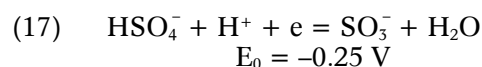
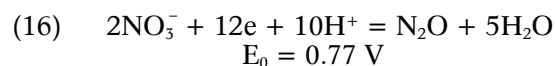
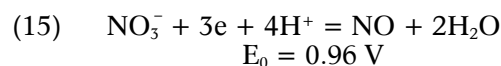


Fig. 5. Results of copper ore leaching by 11 M HNO<sub>3</sub> with controlling Cu concentration using radiometric method.

increasing with an increase in acid concentration. Leaching time extension up to 48 h affects slightly on the Me concentration. Radiometric procedure was applied in this experiment as well. The results of the leaching in these conditions were better probably because of oxidizing nature of HNO<sub>3</sub>. Considering the oxidation of sulphides as electrochemical process, its implementation is determined by the oxidizing potential of the solvent. From this point, nitric acid is highly efficient, because the determining reactions of the nitrate ion in the acidic medium are characterized by high potentials [41–43]:



NO<sub>3</sub><sup>-</sup> oxidizing potential is 0.96 V, which is much higher than that of SO<sub>4</sub><sup>2-</sup> [44]; therefore, as we expected, the recovery of the metals was much higher in this case, approximately 90% Cu, 99% Pb, 76% Fe, and so on. Detailed recovery results are shown in Fig. 6. The metals behave similar to copper. The recovery of them is higher when nitric acid is used. Because of relatively low concentration (14–400 ppm) of these metals into raw material, the extraction from mineral grain might be more difficult. Moreover, it can be disturbed by passive films on the grain's surface or may be trapped into insoluble grains (at this process conditions). Although the concentration of other valuable metals was very low, the recovery of some of them such as Co, Zn, Ni, Mo, and rare earth elements (REE) still can be considered as added value improves the economy of the process. Moreover, some of them can be activated and used as a radiotracer as well (Table 2). The experiments will be carried out in the future.

During the experiments, organic media such as ascorbic acid (ASC), acetic acid (CH<sub>3</sub>COOH), and citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>8</sub>) in various concentrations were investigated as well. In Fig. 7, the results are

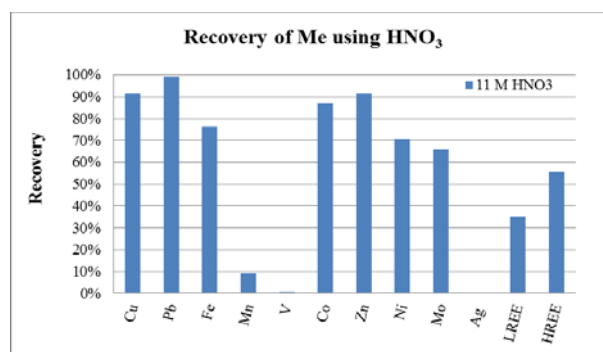
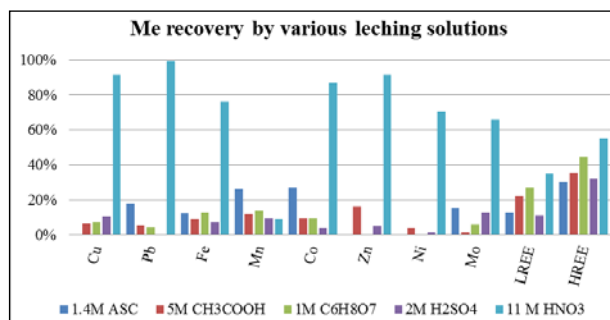


Fig. 6. Selected results of Me recovery from copper ore treated by nitric.



**Fig. 7.** Comparison of the results of Me recovery from copper ore treated by various acids.

compared. As you can see, in almost every case, nitric acid is the most effective probably because of oxidizing potential. Organic acids might be used only for the recovery of LREE and HREE, but still nitric acid is more effective.

The leaching process can be improved. Increasing the temperature, extending the time of the process, or adding oxidants could improve the recovery of Cu up to almost 100%, what was reported in many literature sources [39–42].

## Summary

In this work, experiments using radiotracer were carried out to investigate the recovery of Cu, and other present elements from copper ore using sulphuric acid, nitric acid, and other leaching reagents. The highest recovery of Cu (ca. 90%) and other metals was obtained with the use of the nitric acid. Regardless of the results of leaching yield, the effective radiotracer method based on NAA technique for online controlling and optimizing of the process was developed, what was the main objective of the research. Cu concentration obtained by NAA technique was confirmed using ICP-MS analyses. Both analytical methods used in this study gave similar results. The measurement uncertainty of each technique was 10% for NAA and 12% for ICP-MS, what makes NAA a convenient alternative to classic analytical techniques. The biggest advantage of the NAA is easy online measurements without shutting down or disturbing the system. No sampling is required as opposed to ICP-MS analyses. The measurements are possible through walls of pipes or apparatus. This method can be used for research on an industrial scale, although it may be difficult to apply because of the necessity of having a neutron source. On the other hand, the radiotracer method can be used only to optimize the operation of the installation or for periodic controls.

This work will be continued with other leaching solutions especially with strong oxidation agents such as ozone or hydrogen peroxide.

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## References

1. KGHM Polska Miedź S.A. (2016). *Integrated report for 2015*. Retrieved August 30, 2017, from <http://kgmh.com/pl/node/4990>.
2. KGHM Polska Miedź S.A. (2016). *KGHM Polska Miedź S. A. Strategy for 2017–2021 with an outlook to 2040*. Retrieved November 10, 2017, from [kgmh.com/sites/kgmh2014/files/kgmh\\_strategy\\_2017-2021\\_1.pdf](http://kgmh.com/sites/kgmh2014/files/kgmh_strategy_2017-2021_1.pdf).
3. Baran, A., Śliwka, M., & Lis, M. (2013). Selected properties of flotation tailings wastes deposited in the Gilów and Żelazny Most waste reservoirs regarding their potential environmental management. *Arch. Min. Sci.*, 58(3), 969–978. DOI: 10.2478/amsc-2013-0068.
4. Gupta, C. K., & Mukherjee, T. K. (1990). *Hydrometallurgy in extraction processes* (Vol. 1). Boca Raton: CRC Press.
5. Fleming, C. A. (1992). Hydrometallurgy of precious metals recovery. *Hydrometallurgy*, 30(1/3), 127–162.
6. Tuncuk, A., Stazi, V., Akcil, A., Yazici, E. Y., & Devenci, H. (2012). Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling. *Miner. Eng.*, 25(1), 28–37.
7. Yang, R., Wang, S., Duan, H., Yan, X., Huang, Z., Guo, H., & Yang, X. (2016). Efficient separation of copper and nickel from ammonium chloride solutions through the antagonistic effect of TRPO on Acorga M5640. *Hydrometallurgy*, 163, 18–23.
8. Dreisinger, D. B., Richmond, G., Hess, F., & Lancaster, T. (2002). The competitive position of the Mt. Gordon copper process in the copper industry. In Proceedings of the ALTA 2002 Copper Hydrometallurgy Forum, Perth, Australia. ALTA Metallurgical Services.
9. Antonijevic, M. M., Diminrijevic, M., & Jankovic, Z. (1997). Leaching of pyrite with hydrogen peroxide in sulphuric acid. *Hydrometallurgy*, 46, 71–83.
10. Marsden, J., Brewer, B., & Hazen, N. (2003). Copper concentrate leaching developments by Phelps Dodge Corporation. In C. Young, C. Anderson, D. Dreisinger, A. Alfantazi, A. James, & B. Harris (Eds.), *Hydrometallurgy 2002. Proceedings of the 5th International Symposium honouring Professor Ian M. Ritchie* (Vol. 2, pp. 1429–1446). Warrendale, PA: The Minerals, Metals and Materials Society.
11. Dreisinger, D. (2004). New developments in hydrometallurgical treatment of copper concentrates. *Eng. Min. J.*, 205, 32–35.
12. Ngulube, R. (2016). Application of biohydrometallurgy to copper mining in Zambia: Prospects and opportunities. *Int. J. Mineral Processing and Extractive Metallurgy*, 1(4), 19–25.
13. Baxter, K., Dreisinger, D. B., & Pratt, G. (2013). The Sepon Copper Project: Development of a flowsheet. In C. Young, A. Alfantazi, C. Anderson, A. James, D. Dreisinger, & B. Harris (Eds.), *Electrometallurgy and environmental hydrometallurgy* (Vol. 2, pp. 1487–1502). Warrendale, PA: The Minerals, Metals and Materials Society.

14. Watling, H. R. (2006). The bioleaching of sulphide minerals with emphasis on copper sulphides – A review. *Hydrometallurgy*, 84, 81–108.
15. Hyvärinen, O., Hämäläinen, M., & Leimala, R. (2002). Outokumpuhydrocopper™ process: A novel concept in copper production. *Metall-Fachzeitschrift für Metallurgie*, 56(11), 712–713.
16. Dreisinger, D. (2006). Copper leaching from primary sulphides: Options for biological and chemical extraction of copper. *Hydrometallurgy*, 83(1/4), 10–20.
17. Stiksmma, J., Collins, M. J., Holloway, P., Masters, I. M., & Desroches, G. J. (2000). Process development studies by Dynatec for the pressure leaching of HBMS copper sulphide concentrates. *CIM Bull.*, 93, 118–123.
18. Wawszczak, D., Deptula, A., Lada, W., Smolinski, T., Olczak, T., Brykala, M., Wojtowicz, P., Rogowski, M., Milkowska, M., & Chmielewski, A. G. (2014). Studies of leaching of copper ores and flotation wastes. *J. Radioanal. Nucl. Chem.*, 300, 243–247.
19. Senanayake, G. (2009). A review of chloride assisted copper sulphide leaching by oxygenated sulphuric acid and mechanistic considerations. *Hydrometallurgy*, 98, 21–32.
20. Guettaf, H., Becis, A., Ferhat, K., Hanou, K., Bouchiha, D., & Ferrad, Y. F. (2009). Concentration-purification of uranium from an acid leaching solution. *Physics Procedia*, 2, 765–771.
21. Edwards, C. R., & Oliver, A. J. (2000). Uranium processing: A review of current methods and technology. *JOM*, 52(9), 12–20.
22. Roshani, M., & Kazemi, M. (2009). Studies on the leaching of an arsenic-uranium ore. *Hydrometallurgy*, 98, 304–307.
23. Leung, S., Heymann, L., & King, D. (2010). The recovery of uranium from acid leached ore using resin-in-pulp technology. In Proceedings of the 3rd International Conference on Uranium 40th Annual Hydrometallurgy Meeting, August 15–18, 2010 (Vol. 2, pp. 15–26). Saskatoon, Saskatchewan, Canada.
24. Chmielewski, A. G., Urbański, T. S., & Migdał, W. (1997). Separation technologies for metals recovery from industrial wastes. *Hydrometallurgy*, 45, 333–344.
25. Dybczyński, R. (1985). Zastosowania analizy aktywacyjnej. *Chem. Anal.*, 30, 749–760.
26. Cutmore, N. (2014). Nuclear technologies in mining and mineral processing. In P. Brisset, & S. Miskovic (Eds.), *Development of radiometric methods for exploration and process optimization in mining and mineral industries. Report of the Consultant meeting Vienna, IAEA, 1–5 September 2014* ([1] p., section 4.1). Vienna: International Atomic Energy Agency.
27. Palige, J., Chmielewski, A. G., Dziewoński, Z. R., Rahimi, H., Naimpour, A., Amini, A., Abedinzadeh, A., & Khalilipour, E. (1995). Radiotracer glass furnaces investigations. *Nukleonika*, 40(1), 67–80.
28. Petryka, L., & Przewlocki, K. (1983). Radiotracer investigations of beneficiation copper ore in the industrial flotation process. *Isotopenpraxis Isot. Environ. Health Stud.*, 19(10), 339–341.
29. Figueiredo, A. M. G., Avristcher, W., Masini, E. A., Diniz, S. C., & Abrão, A. (2002). Determination of lanthanides (La, Ce, Nd, Sm) and other elements in metallic gallium by instrumental neutron activation analysis. *J. Alloy. Compd.*, 344(1/2), 36–39. DOI: 10.1016/S0925-8388(02)00301-8.
30. CSIRO. (2018). Retrieved August 30, 2018, from www.csiro.au/en/Research/Mining-manufacturing.
31. Chmielewski, T. (2007). Atmospheric leaching of shale by-product from Lubin concentrator. *Physico-chem. Probl. Minerals Pro.*, 41, 337–348.
32. Chmielewski, T. (2009). Ługowanie atmosferyczne frakcji łupkowej jako alternatywa zmian technologicznych w ZWR Lubin. In Materiały XII Seminarium “Metody hydrometalurgiczne a rozwój produkcji w KGHM Polska Miedź S.A.”, 17 February 2009 (pp. 37–53). Wrocław: KGHM Cuprum.
33. Bujdoso, E., Feher, I., & Kardos, G. (1973). *Activation and decay tables of radioisotopes*. Amsterdam, New York: Elsevier.
34. Abdel-Aal, E. A. (2000). Kinetics of sulphuric acid leaching of low grade zinc silicate ore. *Hydrometallurgy*, 55(3), 247–254.
35. Espiari, S., Rashchi, F., & Sadrnezhaad, S. K. (2006). Hydrometallurgical treatment of tailings with high zinc content. *Hydrometallurgy*, 82(1/2), 54–62.
36. Ahmed, I. M., Nayl, A. A., & Daoud, J. A. (2016). Leaching and recovery of zinc and copper from brass slag by sulphuric acid. *J. Saudi Chem. Soc.*, 20, S280–S285. DOI: 10.1016/j.jscs.2012.11.003.
37. Bodas, M. G. (1996). Hydrometallurgical treatment of zinc silicate ore from Thailand. *Hydrometallurgy*, 40(1/2), 37–49.
38. Akcil, A. (2002). A preliminary research on acid pressure leaching of pyritic copper ore in Kure Copper Mine, Turkey. *Miner. Eng.*, 15(2), 695–699.
39. Antonijevic, M. M., & Bogdanovic, G. D. (2004). Investigation of the leaching of chalcopyritic ore in acidic solutions. *Hydrometallurgy*, 73, 245–256.
40. Chmielewski, T. (2015). Development of a hydrometallurgical technology for production of metals from KGHM Polska Miedz S.A. concentrates. *Physico-chem. Probl. Mineral Pro.*, 51(1), 335–350.
41. Kumar, M., Lee, J. C., Kim, M. S., Jeong, J., & Yoo, K. (2014). Leaching of metals from waste printed circuit boards (WPCBs) using sulphuric and nitric acids. *Environ. Eng. Manag. J.*, 13(10), 2601–2607.
42. Havlik, T., Dvorscikova, J., Ivanova, Z., & Kammel, R. (1999). Sulphuric acid chalcopyrite leaching using ozone as oxidant. *Metall-Fachzeitschrift für Metallurgie*, 53(1), 57–60.
43. Tsogtkhankhai, D., Mamyachenkov, S. V., Anisimova, O. S., & Naboichenko, S. S. (2011). Thermodynamics of reactions during nitric acid leaching of minerals of a copper concentrate. *Russ. J. Non-Ferrous Metals*, 52(2), 135–139.
44. Vanýsek, P. (2002). Electrochemical series. In D. R. Lide (Ed.), *CRC Handbook of chemistry and physics* (83rd ed.) (pp. 823–833). Boca Raton: CRC Press.