Jadwiga FARBISZEWSKA-KICZMA[1]
and Joanna MAKUCHOWSKA-FRYC[1*]

UTILIZATION OF STEELWORK WASTE HEAPS – RECOVERY OF METALS BY ACIDIC BIOLEACHING

UTYLIZACJA HAŁD ODPADÓW POHUTNICZYCH – ODZYSK METALI METODĄ BIOŁUGOWANIA KWAŚNEGO

Abstract: The paper presents the results of preliminary research conducted by the acid bioleaching method, with the use of autochthonous *Acidithiobacillus ferrooxidans* bacteria and museum strains of *Acidithiobacillus thiooxidans*, on recovery of metals contained in selected metallurgical waste. The material contained mainly oxidative minerals Fe_2O_3, SiO_2, and Al_2O_3 as well as lead, zinc, copper and nickel sulphides. Concentrations of the key metals were respectively: zinc 3.46 %, lead 13.8 %, copper 0.4 %, nickel 0.06 %. The works were carried out on a small laboratory scale. The results confirmed that the method is effective. The most effective process of bacterial leaching in the heap was for zinc – a 28 % yield in 96 days.

Keywords: bioleaching, polymetallic waste

Introduction

Modern biohydrometallurgy dates back to 1947, when Colmer and Hinckle in their studies confirmed the biological nature of iron(II) oxidation to iron(III) in the waters of a closed pyrite mine, and then isolated from these waters a previously unknown bacterial species, which they called *Thiobacillus ferrooxidans*. Although the methodology of bioleaching was well known, the first technology on an industrial scale (Biox) was introduced in the late 1990s at Fairview plants in South Africa. However, this area is developing very slowly, despite the fact that technical progress nowadays allows to increase the efficiency and effectiveness of bacterial leaching processes, and these processes can be used not only for enrichment of minerals (Taalvivaara mine in Finland), but also for disposal of electronic waste or disposal of toxic post-mining and metallurgical waste dumps with the recovery of metals at the same time [1–11].

[1] Institute of Technical Sciences, University of Opole, R. Dmowskiego 7–9, 45-365 Opole, Poland.

* Corresponding author: amak@uni.opole.pl

The aim of our research was to examine the possibility of using the acidic bioleaching method to remove heavy metals present in metallurgical waste. In order to carry out this project, we decided to conduct an initial bioleaching test on a so-called small laboratory scale, and then, after obtaining a positive result, to proceed with the process in the waste heap. The considerable amount of waste in the heap under study makes the application of other bioleaching methods, e.g. in bioreactors, difficult and uneconomic to implement [10–12].

The process of bioleaching depends on a number of physicochemical factors. The most important are, of course, the mineralogical and chemical composition of the raw materials (minerals, waste, deposits), the presence of certain metals (e.g. arsenic, silver, molybdenum), which may further inhibit the growth of bacteria, the pH of the environment. Climatic conditions, especially the total rainfall and temperature, are of great importance to the bioleaching process in the heap [9, 11, 13]. The process of bioleaching in heaps (heap or dump leaching) is mainly used to enrich poor ores or to remove metal residues from the waste of ore processing plants. The simplicity of the method and the relatively low investment and technological costs make it increasingly used today. Additional advantages are: ease of process control and low probability of ecological contamination provided that the technological regime is maintained [9].

Material and methods

The research material was metallurgical waste. According to the chemical analysis obtained from the steelworks' laboratory, the material contained mainly: oxidative minerals Fe_2O_3, SiO_2, and Al_2O_3 as well as lead, zinc, copper and nickel sulphides. Concentrations of the key metals were respectively: zinc 3.46 %, lead 13.8 %, copper 0.4 %, nickel 0.06 %. These results indicate the possibility of the presence of autochthonous ferric bacteria of the *At. ferrooxidans genus*. Therefore, in order to recover metals present in the tested waste in the form of sulphides, we decided to use the method of acid bioleaching with the use of autochthonous *Acidithiobacillus ferrooxidans* bacteria and museum strains of *Acidithiobacillus thiooxidans*.

In order to obtain autochthonous bacteria of the genus Acidithiobacillus ferrooxidans the method of isolation based on the dilution method was chosen. Periodic culture was applied, carried out alternately on liquid and solid medium, which was Silverman's medium and Lundgren 9 K [14]. Next, biochemical identification of the isolated bacteria was carried out by checking the presence of tethionate ions and the ability to oxidize Fe(II) in culture. For this purpose, the medium was centrifuged and the tionates contained in it were chromatographically separated. The obtained chromatogram did not contain stains indicating the presence of tethionate ions. The result did not clearly indicate that we were dealing with *At. ferrooxidans*, because the same effect would have been achieved if they had been bacteria such as *Thiobacillus thioparus* or *Thiobacillus denitrificans*, but in turn these bacteria do not oxidize Fe(II) ions. The ability of the isolated bacteria to oxidize iron was checked therefore by growing them on the medium containing iron(II) sulfate. During culture the concentration of Fe(II) and (III) ions in the medium was determined. An increase in the concentration of Fe(III) ions with a simultaneous decrease in the concentration of Fe(II) ions clearly indicated that the bacteria were *At. ferrooxidans* [15, 16].

The next stage of the study was to conduct a preliminary verification of the susceptibility of the test material to the process of acid bioleaching. From the heap, 10 samples were taken from places selected in such a way that the material was representative for the whole heap. After mixing and averaging, the samples were reduced. The sample to be tested was then crushed and ground in a Krupp laboratory jaw crusher. At the beginning the influence of the test material on the pH of the lye was determined. For this purpose, lye was added to 500 mg of the material; the ratio 1: 3. The initial pH was 5.7, after the addition of 5 cm^3 of 10N H_2SO_4, the pH dropped to 2.42. Over the next days this value changed slightly, the pH remained within the limits appropriate for a good acidic bioleaching process, the test material was not alkaline, so that no chemical pre-treatment was required [12]. The bioleaching process was carried out simultaneously with the control process without bacteria, in which only chemical leaching took place. A 5 K desiccant was applied, with the composition consistent with Silverman's and Lundgren's 9 K medium, in which the content of Fe(II) ions was reduced to 5 g/dm^3 [14]. The initial pH of the lye was 2.5.

Results and discussion

During the process pH of the lye, concentration of Fe(II) and (III) ions and concentration of metal ions: zinc, copper, nickel and lead were determined in both research systems (in the bacterial system and in the control system). The results obtained are shown in the following charts.

Zinc bioleaching in the bacterial system started from the first day of the process and was evenly distributed throughout the measurement period, reaching 3000 mg/dm^3 on the last day, which constituted 34.7 % of zinc contained in the test material. In the control system the leaching process began after the third day of the process, and on the last day it reached the concentration of 100 mg/dm^3, which constituted 1.2 % of zinc removed from the research material.

Copper leaching started on the 3rd day of the process and in the control system chemical leaching started on the 5th day. After thirteen days in both cases the process stopped. Due to the participation of bacteria, 10 % of Cu contained in waste and 3 % in the bacterial-free system was leached.

Nickel leached chemically only, in both systems after 19 days of the process the concentration of nickel ions in fluids the lye was 16 %. Lead did not leach biologically, nor chemically.

The obtained results indicate that in the case of zinc and copper, effective recovery of metals occurs only due to the presence of bacteria.

The next stage of the research was to carry out the process of bioleaching in the heap. It was carried out in a laboratory stand.

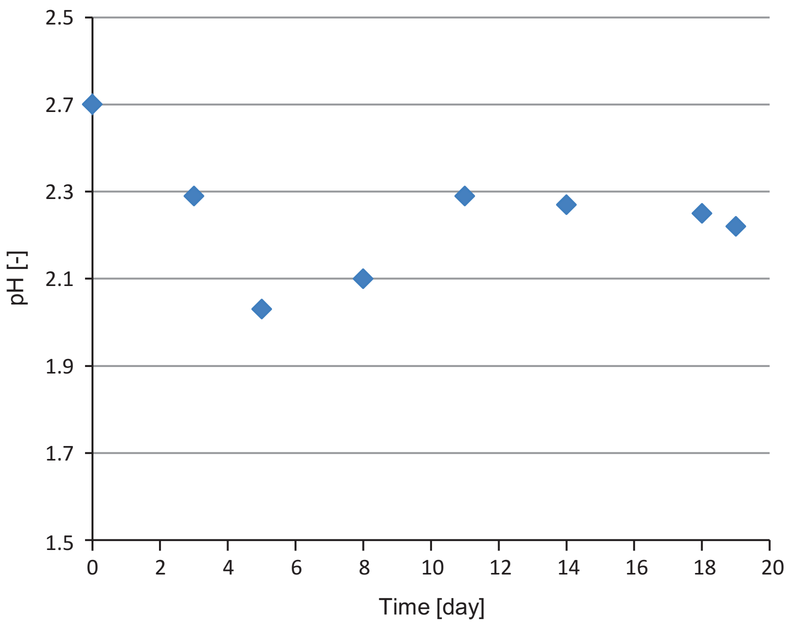

Fig. 1. Changes in pH of the lye in the bacterial test

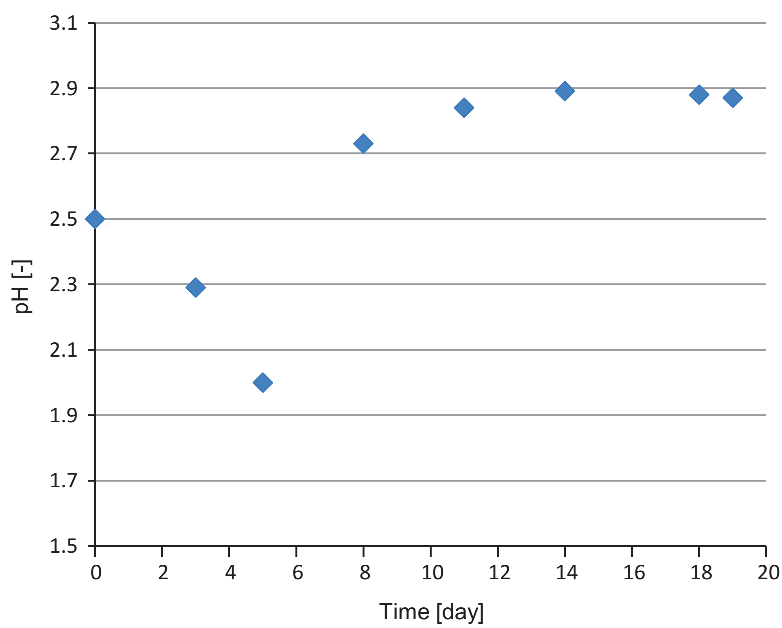

Fig. 2. Changes in pH of the lye in the control test

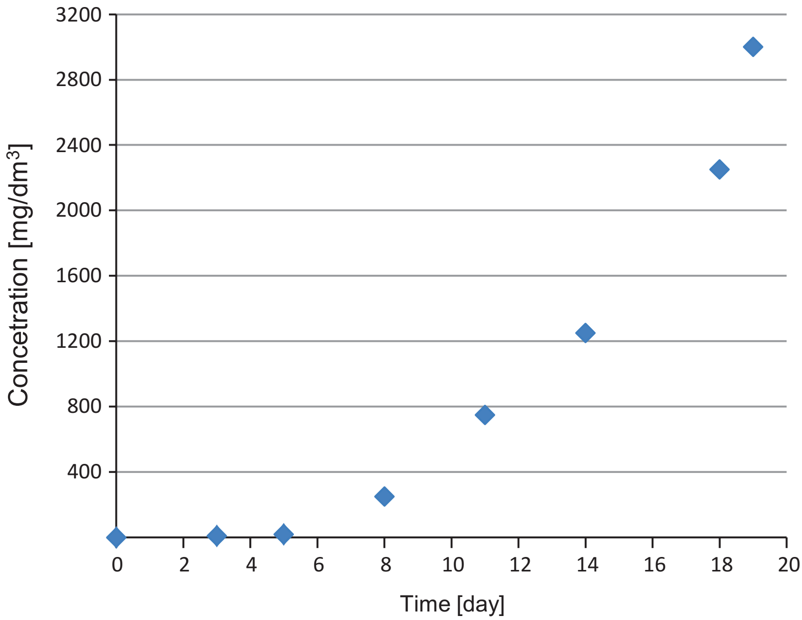

Fig. 3. Change in the concentration of zinc ions in the bacterial system

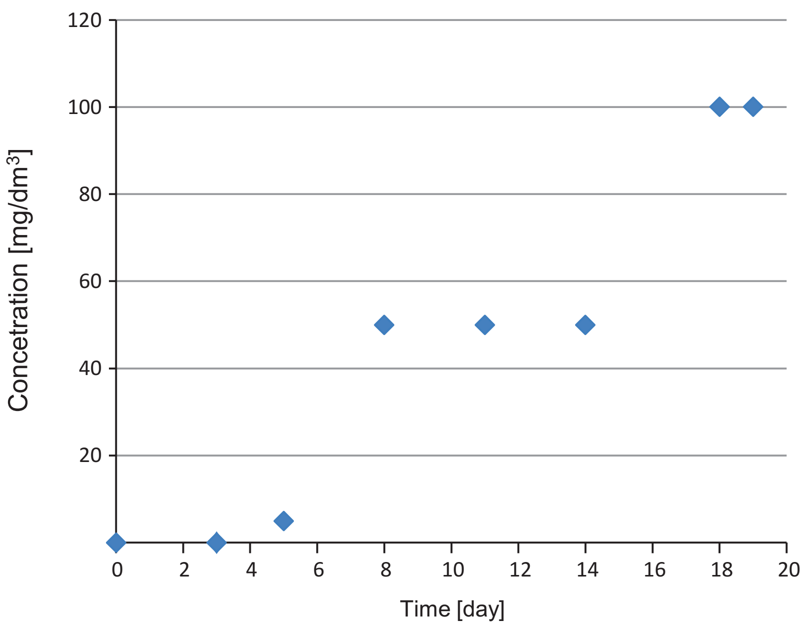

Fig. 4. Change in the concentration of zinc ions in the control system

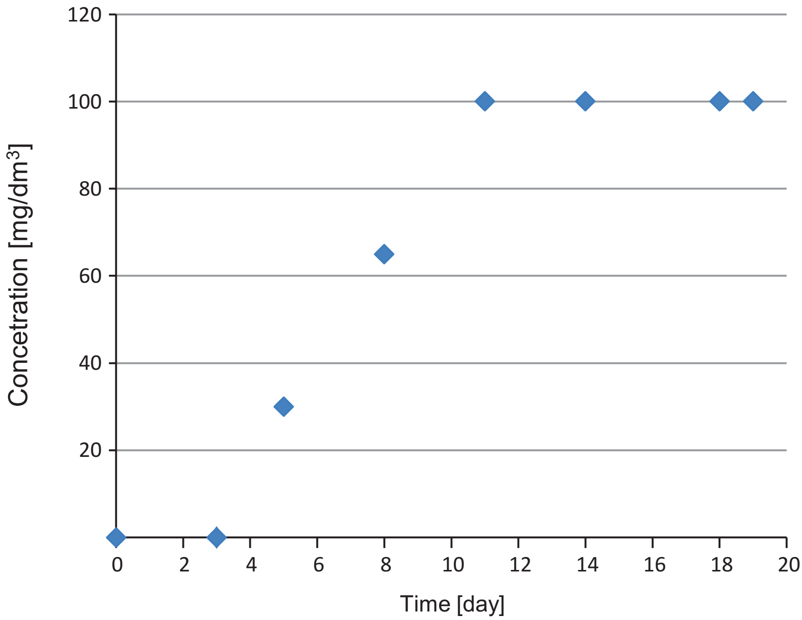

Fig. 5. Change in the concentration of copper ions in the bacterial system

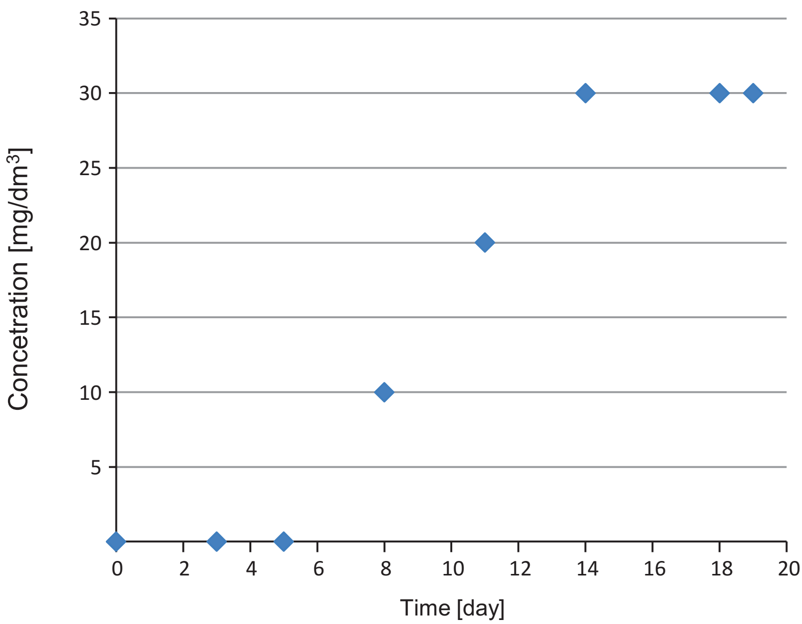

Fig. 6. Change in the concentration of copper ions in the control system

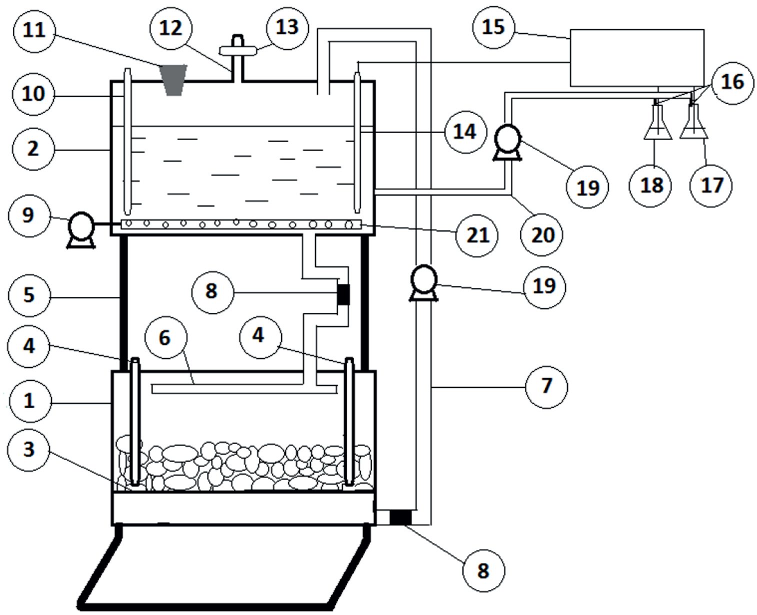

Fig. 7. Bioleaching station for bioleaching in heaps: 1 – container of materials; 2 – lye tank; 3 – filter barrier; 4 – thermometer; 5 – tripod; 6 – sprinkler; 7 – return pipe for tank no. 1; 8 – valve; 9 – membrane aerator; 10 – thermometer; 11 – intake inlet; 12 – air vent; 13 – biological filter; 14 – pH electrode; 15 – pH-meter and control system; 16 – solenoid valves; 17 – NaOH tank; 18 – H_2SO_4 tank; 19 – peristaltic pump; 20 – line; 21 – aerator

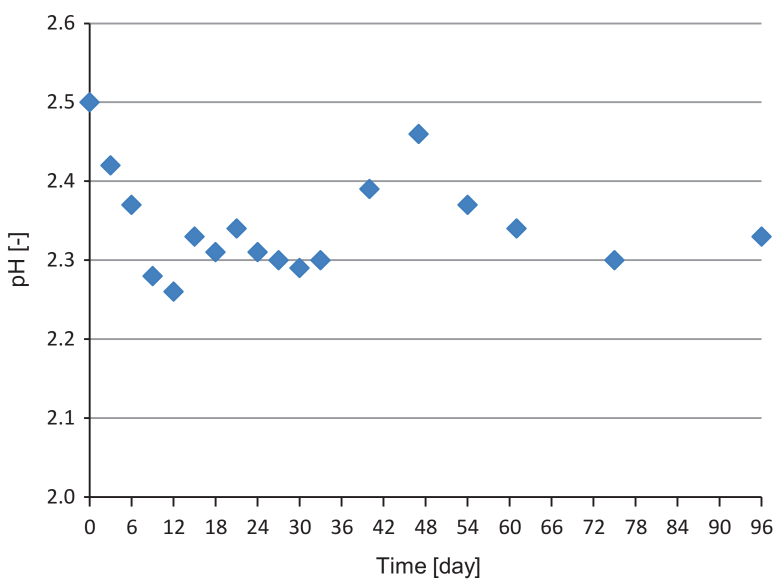

Fig. 8. PH changes in the lye during the bioleaching process in the heap

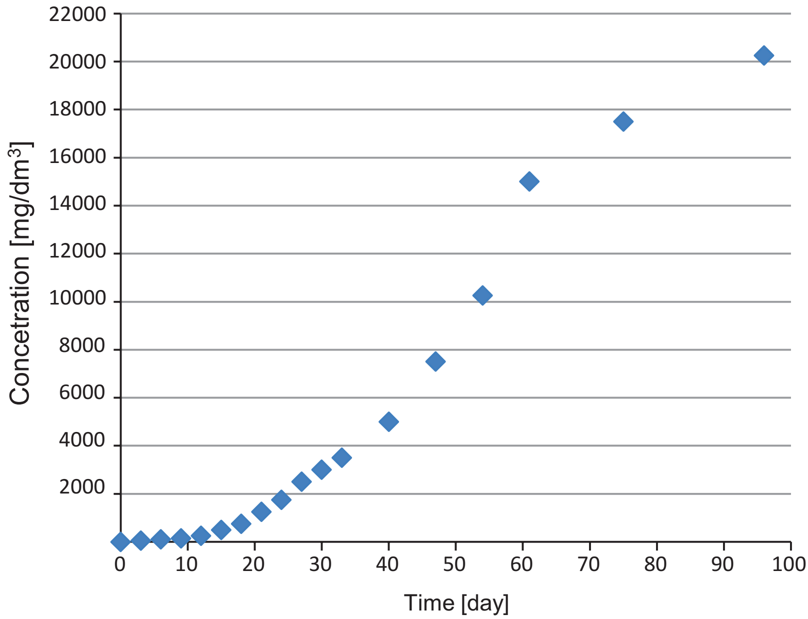

Fig. 9. Change in the concentration of zinc ions during the process of heap bioleaching

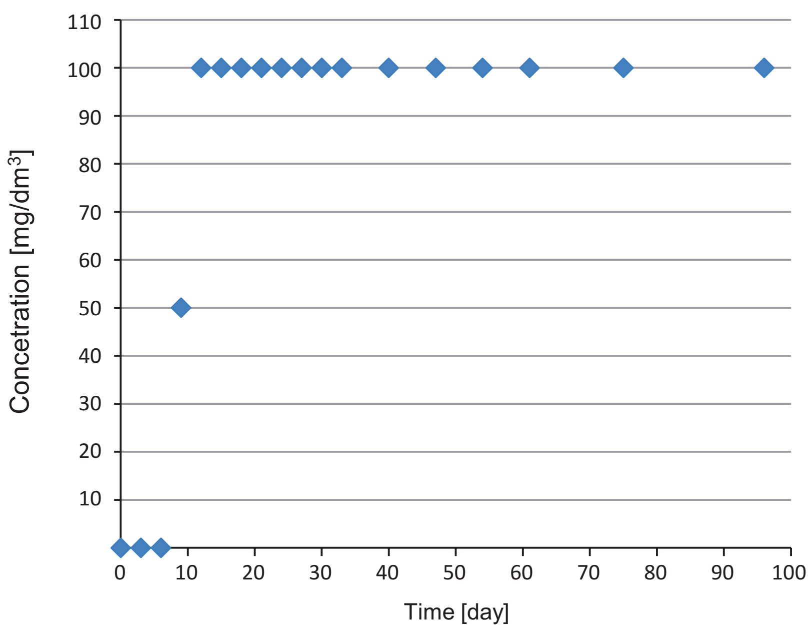

Fig. 10. Change in the concentration of copper ions during bioleaching in the heap

Physicochemical parameters were the same as in the first experiment. The duration of the process was 90 days. There was no control system. The results obtained are shown in the following charts.

Zinc bioleaching in the bacterial system started from the first day of the process and was quite intensive throughout the measurement period, reaching 20250 mg/dm^3 on the last day, which constituted 28 % of zinc contained in the test material. Copper bioleaching began in the fifth day of the trial, and came to an end after day 12, and nothing changed to the end of the process. As a result, only 6 % of the copper contained in the waste transferred into the solution. The leaching of nickel was similar to copper and by the end of the process 16 % was recovered.

Conclusions

In the studies presented, the possibility and rationale for conducting the process of bioleaching of metallurgical waste was confirmed. The waste was subjected to both biological and chemical leaching.

Zinc recovery by bioleaching in the heap with the use of autochthonous *At. ferrooxidans* and museum strains of *At. thiooxidans* was satisfactory and amounted to 28 % (heap), with as much as 34.7 % obtained on a small laboratory scale and 1.2 % for the control sample. 6 % of copper was recovered by bioleaching in a heap, 10 % on a small laboratory scale, compared to the control sample of 3 %. 16 % of nickel was leached in the heap. Lead would not leach.

Steelworks waste can be considered a "secondary" polymetallic ore deposit and can be successfully enriched by acidic bioleaching with the use of *Acidithiobacillus* type bacteria. The results obtained indicate that this process should be examined further, in order to increase yields.

References

[1] Barmettler F, Castelberg C, Fabbri C, Brandl H. Microbial mobilization of rare earth elements (REE) from mineral solids – A mini review. Microbiology. 2016;2(2):190-204. DOI: 10.3934/microbial.2016.2.190

[2] Diaz JA, Serrano J, Leiva E. Bioleaching of Arsenic-Bearing Copper Ores, Minerals. 2018;8:215. DOI:10.3390/min8050215

[3] Ghosh S, Mohanty S, Akcil A, Sukla L.B, Das A.P. A Greener approach for resource recycling: Manganese bioleaching, Chemosphere. 2016;154:628-639. https://doi.org/10.1016/j.chemosphere.2016.04.028

[4] Johnson DB. The Evolution, Current Status, and Future Prospects of Using Biotechnologies in the Mineral Extraction and Metal Recovery Sectors. Minerals. 2018;8:343. DOI:10.3390/min8080343

[5] Panda S, Akcil A, Pradhan N, Deveci H. Current scenario of chalcopyrite bioleaching: A review on the recent advances to its heap-leach technology. Bioresource Technol. 2015;196:694-706. https://doi.org/10.1016/j.biortech.2015.08.064

[6] Pathak A, Morrison L, Healy MG. Catalytic potential of selected metal ions for bioleaching, and potential techno-economic and environmental issues: A critical review, Bioresource Technol. 2017;229:211-221. DOI: 10.1016/j.biortech.2017.01.001

[7] Swain B. Recovery and recycling of lithium: A review. Sep Purif Technol. 2017;1(172):388-403. https://doi.org/10.1016/j.seppur.2016.08.031

[8] Wajda Ł, Kamiński P, Herezy Ł. Przegląd nowych kierunków badań nad technologiami wykorzystującymi procesy bioługowania. (The review of new research directions on technologies using bioleaching processes). Rudy i Metale Nieżelazne. Recykling. 2015;60(2):79-85. DOI: 10.15199/67.2015.2.5
[9] Charewicz W. Biometalurgia metali nieżelaznych- podstawy i zastosowania. (Biometalurgy of non-ferrous metals – basics and applications). Wrocław; CBPM [Centrum Badawczo-Projektowe Miedzi] „Cuprum". Uniwersytet Wrocławski, Instytut Nauk Geologicznych: 2002. ISBN 8390688565
[10] Gericke M., Govender Y. Bioleaching strategies for the treatment of nickel-copper sulphide concentrates. Minerals Eng. 2011;24(11):1106-1112. DOI: 10.1016/j.mineng.2011.02.006
[11] Kaksonen AH, Lavonen L, Kuusenaho M, Kolli A, Narhi H, Vestola E, et al. Bioleaching and recovery of metals from final slag waste of the copper smelting industry. Minerals Eng. 2011;24(11):1113-1121. DOI: 10.1016/j.mineng.2011.02.011
[12] Grobelski T, Farbiszewska-Kiczma J, Farbiszewska T. Bioleaching of Polish Black Shale. Physicochemical Problems Mineral Processing. 2007;41:259-264. http://www.minproc.pwr.wroc.pl/journal/pdf/2007/259-264.pdf
[13] Sadowski Z. Biogeochemia – wybrane zagadnienia. [Biogeochemistry – selected issues], Wrocław: Ofic Wyd Politechniki Wrocławskiej; 2005. ISBN 837085896
[14] Silverman MP, Lundgren DG. Studies on the chemoautotrophic iron bacterium Ferrobacillus ferrooxidans. I. An improved medium and a harvesting procedure for securing high cell yields, J Bacteriol. 1959;77:642-647. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC290434
[15] Whitman WB. Bergey's Manual of Systematic Bacteriology. New York: Springer; 2010. ISBN 0387950435
[16] Grobelski T, Farbiszewska-Kiczma J, Farbiszewska T. Effect of Heterotrophic Bioleaching on Effeciency of Autotrophic Bioleaching of Metals from Toxic Waste Heaps in Zloty Stok Region. Ecol Chem Eng A. 2009;16(11):1467-1472. https://drive.google.com/drive/folders/1EYNz9V1-8apDLBJ-vQiv6dj95AA6ry4Z

UTYLIZACJA HAŁD ODPADÓW POHUTNICZYCH – ODZYSK METALI METODĄ BIOŁUGOWANIA KWAŚNEGO

Instytut Nauk Technicznych, Uniwersytet Opolski, Opole

Abstrakt: W pracy przedstawiono wyniki badań wstępnych, prowadzonych metodą bioługowania kwaśnego, z wykorzystaniem autochtonicznych bakterii rodzaju *Acidithiobacillus ferrooxidans* i muzealnych szczepów bakterii rodzaju *Acidithiobacillus thiooxidans*, nad odzyskiem metali zawartych w wybranych odpadach pohutniczych. Materiał zawierał głównie minerały tlenkowe Fe_2O_3, SiO_2 i Al_2O_3 oraz siarczki ołowiu, cynku, miedzi i niklu. Stężenia najważniejszych metali wynosiły odpowiednio: 3,46 % cynku, 13,8 % ołowiu, 0,4 % miedzi, 0,06 % niklu. Prace prowadzono w małej skali laboratoryjnej. Uzyskane rezultaty potwierdziły, że zastosowana metoda jest skuteczna. Najefektywniej proces ługowania bakteryjnego w hałdzie przebiegał dla cynku – uzysk 28 % w czasie 96 dni.

Słowa kluczowe: bioługowanie, odpady polimetaliczne