Ewa Kisielowska*, Rafał Wojtasik*, Ewelina Kasińska-Pilut**, Anna Hołda*

THE BIOLEACHING OF SILVER FROM THE "ŻELAZNY MOST" DISPOSAL AFTER-FLOTATION WASTES IN LUBIN WITH APPLICATION OF MICROFUNGI FROM GENUS ASPERGILLUS NIGER

1. Introduction

Silver is a precious metal used to make jewellery, in electrical contacts and conductors, in mirrors, in catalysis of chemical reactions and also its compounds are used in photographic film. Dilute silver nitrate solutions and other silver compounds are used as disinfectants and microbiocides.

Silver is found in native form, as an alloy with gold and in ores containing sulfur, arsenic, antimony or chlorine. The sources of silver are the ores of copper, copper-nickel, lead, and lead-zinc obtained from Peru, Bolivia, Mexico, China, Australia, Chile, Poland (Rudna) and Serbia. Silver is primarily produced through electrolytic copper refining, gold, nickel and zinc refining, and by application of the Parkes process on lead metal obtained from lead ores that contain small amounts of silver.

The interest in the possibility of the application of the microorganisms metabolic activity in mining and mineral processing is connected, among others, with the exhaustion of the rich metal ores deposits and necessity of the utilization of the larger and larger amount of metal-containing wastes.

The polish copper mining, from the beginning of its existence, accumulate the wastes, being produced during flotation process, in local disposals. Although, from the very beginning the possibility of their management is being searched, the effects are rather slight and still remain not used.

^{*} AGH University of Science and Technology, Krakow

^{*} KGHM Polska Miedź SA, Lubin

The exploitation of the "Żelazny Most" disposal is still conducted. The copper and other metals contents, located in the disposal are not precisely estimated.

Because of the copper and silver contents, the disposal may be treated as anthropological accumulation of the modest crumb deposit type. However, these beds do not qualify to application and processing by traditional methods because of the lack of efficient metal recovery technologies. This explains why there is so large interest of the alternative methods of metal collection, among which one is bioleaching.

The alkaline character of the after-flotation wastes from "Żelazny Most" disposal cause that the very well known bioleaching with application of thionic bacteria from the genus Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans is not possible because it requires a huge amount of the sulfuric acid, negatively reacting with environment.

The experiments, conducted earlier in Department of Mineral Processing and Environmental Protection AGH (now Department of Environmental Engineering and Mineral Processing), over the copper bioleaching from the wastes disposed in "Gilów" disposal by application of mildew fungi *Aspergillus niger* gave very good results (yield of over 80% of leached copper), what allowed thinking that this fungi, being also autochthonic organisms of disposal, may be applied in bioleaching processes of other metals.

In this paper a research of the bioleaching process of the after-flotation waste was conducted using microfungi of the *Aspergillus niger* species, which dominate in the autochthonous environment. The previous researches describe the applications of this fungi to accumulation of silver from solution containing high cyanide concentrations (cyanide is commonly used in the extraction of gold from ores) [7, 11].

2. Purpose and methodology of investigation

The purpose of the conducted researches, presented in this paper, was checking of the efficiency of silver bioleaching process from after-flotation wastes from "Żelazny Most" disposal, by application of the mildew fungi from the genus *Aspergillus niger*.

The microfungis applied to the silver bioleaching process are the autochthonic organisms, dominating in this environment, what was proved by the conducted microbiological analysis, performed in laboratory of Department of Mineral Processing and Environmental Protection AGH in time of 24 hours from the moment of collecting samples.

The feed to bioleaching process were the samples of after-flotation wastes, taken from "Żelazny Most" disposal, distributed by KGHM Polska Miedź SA.

They originated from three excavations, performed 40 m from the barrier and from the depth of about 20–40 cm.

In cone bulbs, 10 g of the previously sterile after-flotation wastes was placed in each one. Every sample was contained with 100 ml of liquid nourishment, prepared according to the Czapek-Dox recipe, containing the components necessary to growth of mildew fungi

culture. Finally, the suspension was grafted with the *Aspergillus niger* biomass, which was given earlier.

The bioleaching process was conducted during 30 days, in temperature 28°C. In purpose of better oxygenation of the material, the suspension was shaken.

After the required time was up, three products of bioleaching were collected: fungi, suspension and mineral wastes. They were then analyzed for the silver contents chemically in Center of the Quality Research in Lubin.

Before sending to chemical analysis, the products given by bioleaching process were weighted on the analytical balance (Tab. 1) and the given results were the basis to calculate the qualitative and quantitative factors of bioleaching process.

TABLE 1
The juxtaposition of the obtained masses and silver contents in bioleaching process products

Number	Sample mark	Sediment mass, [g]	Incinerated fungi mass, [g]	Ag contents in waste, [g/Mg]	Ag contents in fungi, [g/Mg]
1	I/O	8.3169	_	7.4	_
2	I/1	7.5954	0.3143	5.7	7.2
3	I/2	7.9548	0.4318	6.8	7.2
4	I/Fe	9.8369	0.6744	6.2	5.1
5	II/0	9.1892	-	17	_
6	II/1	8.5965	0.7359	14	10
7	II/2	8.7668	0.2021	15.5	7.9
8	II/Fe	10.2801	0.9292	11.7	6.4
9	III/0	9.2976	-	16.9	-
10	III/1	9.1828	0.3588	16.2	6.5
11	III/2	8.8761	0.4324	14.3	9.2
12	III/Fe	10.98	0.5914	11	6.1

3. Investigation results

The mean silver contents in researched material, which was the feed to the bioleaching process, was the basis to calculate the initial silver amount, potentially possible to leach.

The contents for the individual samples were as following:

- I 7 g/Mg,
- II 17.4 g/Mg,
- III 16.9 g/Mg.

The sum of the metal contents in after-extractive suspension and fungi biomass is the total effect of the metal leaching (Tab. 2, column 5), because compounds passed to the suspension may be recovered by the next hydrometallurgical methods (like cementation) and the silver absorbed in microorganisms may be recovered by connecting fungi with the flotation concentrates and passing them to the processing in metallurgical plants.

The samples marked with symbols I/0, III/0 were done as the zero samples, without presence of the fungus *Aspergillus niger*, in purpose of comparing the bioleaching process course. And, from the following samples I, II, III, two repetitions were performed and they were marked with the appropriate cipher, respectively.

The juxtaposition of the results concerning the silver yields in individual products after the bioleaching process with application of *Aspergillus niger* and products of zero samples is presented in Table 2.

TABLE 2
The juxtaposition of the results concerning the silver yields in individual products after the bioleaching process

Number	Sample mark	Ag yield in incinerated fungi, [%]	Ag yield in suspension, [%]	Total Ag yield, [%]	Ag loss in waste, [%]
1	I/O	_	16.831	16.831	83.169
2	I/1	3.058	38.437	41.495	58.505
3	I/2	4.201	22.701	26.902	73.098
4	I/Fe	4.648	12.935	17.583	82.417
5	II/0	_	8.108	8.108	91.892
6	II/1	4.329	24.876	29.205	70.795
7	II/2	0.939	19.128	20.067	79.933
8	II/Fe	3.498	25.751	29.249	70.751
9	III/0	-	7.024	7.024	92.976
10	III/1	1.380	10.596	11.976	88.024
11	III/2	2.354	22.541	24.895	75.105
12	III/Fe	2.135	26.398	28.533	71.467

On the basis of measurement results the Figures 1–3 were prepared.

It occurred from the conducted researches that the silver leaching with application of the fungi from the genus *Aspergillus niger* is characterized with low efficiency and amounts from 7.024% to 41.495% (look Tab. 2).

The cause of such low yields is, probably, the change of silver in ratio to the both — bacteria and fungi, organisms.

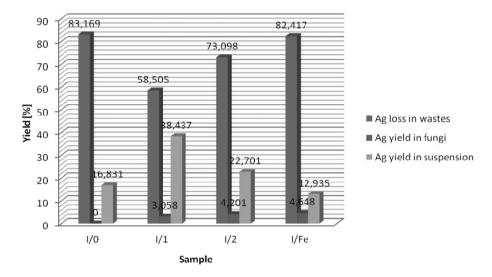


Fig. 1. Graphical presentation of the given results from sample I

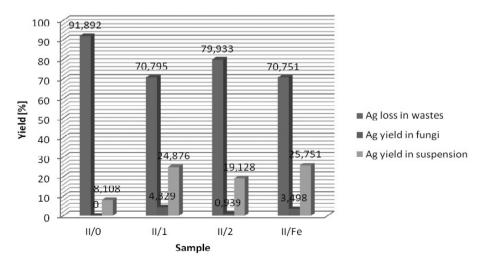


Fig. 2. Graphical presentation of the given results from sample II

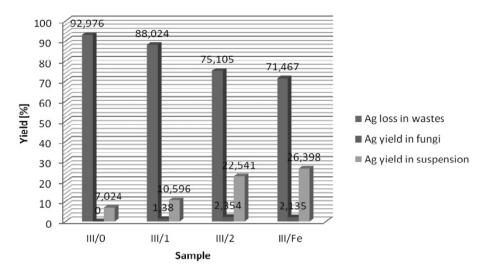


Fig. 3. Graphical presentation of the given results from sample III

The concept of these researches was based on the thought that for the applied "ubiquitous" mildew fungi from the genus *Aspergillus niger*, of the known resistance to the harmful environmental influence, such type of toxicity would not influence on its bio-mechanism during silver bioleaching. It is possible that the works connected with adaptation of the selected *Aspergillus niger* strain to bigger silver concentrations in environment, would allow obtaining better effects in this element bioleaching processes.

4. Final conclusions

- The microbiological analysis of the after-flotation wastes from "Żelazny Most" disposal proved the modest microflora. The microorganisms, being presented there, are, inter alia, psychrophil and mesophil bacteria and mildew fungi with the dominant genus *Aspergillus* niger.
- 2) The objective after-flotation wastes, apart from copper and other elements, contain 7–17.4 g/Mg of silver.
- 3) The researches over the possibility of application of mildew fungi from the genus *Aspergillus niger* as one of the autochthonous organisms of disposal to silver bioleaching were initiated.
- 4) The laboratory experiments, grafting the wastes into the environment of liquid nourishmentby the fungi *Aspergillus niger* were conducted in optimal conditions for this microorganism (temperature 28°C, pH 6.5). After 30 days of performing experiment, the given products were chemically analyzed.

- 5) The given results show that the silver bioleaching process from the after-flotation wastes with application of the fungus from the genus *Aspergillus niger* is, unfortunately, relatively low efficient. The total silver yield is within the range from 7.024% to 41.495% Ag.
- 6) The relatively low yields of silver in conducted bioleaching process may be caused by the silver toxic influence on the applied fungi microorganism. Probably, the adaptive processes, basing on the progressive increase of the silver contents in this fungus growth environment would allow the receiving better effects of bioleaching process.

REFERENCES

- [1] Charewicz W., Apostoluk W.: Hydrometalurgia miedzi i metali towarzyszących. Seminarium Naukowe "Współczesne problemy przeróbki rud miedzi w Polsce, Wydawnictwo Popularnonaukowe "Linea", Lubin 2000.
- [2] Charewicz W.: Biotechnologia metali nieżelaznych. Podstawy i zastosowanie. CBPM "Cuprum" Sp. z o.o, Wrocław 2002.
- [3] Chmiel A.: Biotechnologia. Podstawy mikrobiologiczne I biotechnologiczne. Wydawnictwo PWN, Warszawa 1991.
- [4] Chmielewski T.: Hydrometalurgia w procesach odzyskiwania metali. Biometalurgia metali nieżelaznych podstawy i zastosowanie. CBPM "Cuprum" Sp. z o.o, Wrocław 2002.
- [5] CPM Group: CPM Silver Yearbook. NY: Euromoney Books, New York 2011.
- [6] Goląb Z.: Biotechnologia w otrzymywaniu metali. Rudy metali nieżelaznych, 1994, 3.
- [7] Gomes N.C.M., Camargos E.R.S., Dias J.C.T. and Linardi V.R.: Gold and silver accumulation by Aspergillus niger from cyanide-containing solution obtained from the gold mining industry. World Journal of Microbiology & Biotechnology, 14, 149.
- [8] Hammond C.R.: Handbook of Chemistry and Physics 81st edition. The Elementary, CRC press. 2000.
- [9] Kisielowska E., Kasińska-Pilut E.: Copper bioleaching from after-flotation waste rusing microfungi. Acta Montanistica Slovaca, 2005, 1/R10.
- [10] Klimiuk E., Łebkowska M.: Biotechnologia w ochronie środowiska. Wydawnictwo PWN, Warszawa 2003.
- [11] Newton C.M. Gomes, Marianne M. Figueira, Elizabeth R.S. Camargos, Leda C.S.Mendonça-Hagler1, João C.T. Dias, Valter R. Linardi: Cyano-metal complexes uptake by Aspergillus niger. Biotechnology Letters 1999, 21, 487–490.
- [12] Ostrowska A., Skłodowska A.: Małe bakterie wielka miedź. Wydawnictwo SCI&ART, Warszawa 1996.
- [13] Pacholewska M., Bator J.: Metody biotechnologii w metalurgii. Rudy i metale nieżelazne, 1998.
- [14] Piontek M.: Grzyby pleśniowe. Wydawnictwo Politechniki Zielonogórskiej, Zielona Góra 1999.
- [15] Skłodowska A.: Biologiczne metody ługowania metali ciężkich. Postępy mikrobiologii, 2000, 2.
- [16] Slaba M., Długoński J.: Mikrobiologiczne usuwanie i ługowanie metali ciężkich. Postępy mikrobiologii, 2002, 3.
- [17] Walkowiak W., Charewicz W., Chmielewski T.: Przemysłowe procesy hydrometalurgiczne stan i perspektywy. VII Seminarium Problemy współczesnej hydrometalurgii, Lubin 2002.
- [18] Żak Z.: Z przeszłości do współczesnej biotechnologii. Mikrobiologia Medyczna, 1997.
- [19] Żymalski G., Ziomek M., Kowalska A.: Zakłady Wzbogacania w nowej strukturze organizacyjnej KGHM "Polska Miedź S.A.". Seminarium Naukowe Współczesne problemy przeróbki rud miedzi w Polsce, Wydawnictwo Popularnonaukowe Linea, Lubin 2002.