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BIOHYDROMETALLURGICAL TREATMENT
OF THE Fe NANODISPERSION
FROM THE METALLURGICAL WASTES

BIOHYDROMETALURGICZNA OBRÓBKA
NANODYSERSJI Fe Z ODPADÓW METALURGICZNYCH

Abstract

Mineral biotechnologies, the domain of which is primary raw material processing, are increasingly diversifying into some metallurgical areas. The presented results of research carried out with metallurgical wastes from aluminium production, lead waste remaking and desulphurization zinc-ferrite-based sorbents regeneration prove the possibility of use of biochemical methods. The results obtained and the proposed technologies employing biochemical processes enable complex processing and the use of waste sludge from aluminium production as well as the use of wastes from matte-based copper production for the production of hematite pigments.

Keywords: bioleaching, lead matte, red pigment, high magnetic red pigment

Streszczenie

Biotechnologia minerałów – dziedzina, której obszarem jest wstępna obróbka surowców, jest coraz częściej stosowana w niektórych gałęziach metalurgii. Przedstawione wyniki badań potwierdziły możliwość zastosowania metod biochemicznych do obróbki odpadów z produkcji aluminium i ołowiu oraz do regeneracji sorbentów cynkowo-żelazowych z procesów odsiarczania. Opracowane na podstawie uzyskanych wyników technologie umożliwiają wytwarzania pigmentów żelazowych z zastosowaniem procesów biochemicznych na drodze kompleksowej przeróbki odpadów z produkcji aluminium, jak również szlamów odpadowych z produkcji miedzi z kamienia miedzianego.

Słowa kluczowe: lugowanie biologiczne, kamień ołowiowy, czerwony pigment, silnie magnetyczny czerwony pigment

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1. Introduction

Biotechnologies are considered as one of the basic pillars of the 21st century development and they are not developing and will not be developing only in the traditional areas like medicine, food-processing and pharmaceutical industries. In the recent past the diversification of biotechnologies into heavy industry seemed absurd, but the study of exogenous natural processes brought a range of information, which initiated the establishment of a specific branch “mineral biotechnologies” which embrace oxidation and reduction processes of inorganic substrates with the help of autochthonous and modified chemolithotrophic microorganisms or their metabolites. As the composition of many metallurgical wastes is very close to that of primary raw materials, we considered useful to study the possibility of the use of these bio-chemical processes in this area. The research was focused on the existing ecological load of metallurgical industry, which is produced during:

- bauxite processing in ZSNP a.s. in Žiar nad Hronom,
- lead waste remaking in Kovohuť Příbram.

The performed research confirmed the possibility of application of bio-chemical processes and in some cases resulted in the presentation of proposals of industrially applicable procedures.

2. Biological and chemical treatment of waste sludge from aluminium production

Except for some single cases, waste sludge from aluminium production is not currently used and represents a serious environmental danger. Depending on the geographical location of individual production plants, waste sludge is either dumped directly in the sea or stored on the man-made waste disposal sites occupying vast soil areas. Individual sludge boxes occupy on average 900–1,300 hectares. In Slovakia there are about 10,000,000 tonnes of waste dumped next to production plants. The first attempts at a complex use of sludge from aluminium production date back to the period before the World War II. Up till now there have been a number of research projects focused on the possibility of re-use of utility elements (Fe, Al, Ti, Ga) and on the massive direct use of this material in the production of various kinds of construction materials, ceramic materials, pigments and fillers. Several different technically interesting technologies have been developed but in most cases they were not viable due to economic reasons. A lot of procedures showed to be partially viable, e.g. in the production of cement, ceramic floor tile materials, bricks, fillers and iron production charge additives providing the receiving plants are situated close to the source of produced waste. From the relative area of the use of bio-chemical processing of this type of sludge it is possible to use results available from the research of chemolithotrophic bacteria *Thiobacillus ferrooxidans*, carried out by Hungarian researchers in the form of pilot operation experiments, which were aimed at obtaining Na₂O and Al₂O₃ and achieving relatively good yield parameters, but this procedure has not dealt with the issue of detoxication, processing and use of large quantities of acid sludge with Fe, Ti and V concentrations [1–3].

The set of technological knowledge on the possibility of a complex use of sludge from aluminium production has been extended with the results of study carried out in our

institution focused on the usability of combined bio-chemical procedures based on the application of selected species of chemolithotrophic microorganisms [4], which resulted in the technological procedure design protected by the patent of the Slovak Republic.

The most significant changes have been observed during the application of leaching agent based on metabolic products of microorganisms, which are considered to be involved in the proposed procedure. The full decomposition of original waste sludge components was achieved by sludge processing applying an optimised procedure, while it consequently and partly parallelly came to a gradual precipitation of autogenous compounds. The designed technology of bio-chemical processing of sludge from aluminium production (Fig. 1), tested by the laboratory model, enables to transform the phase composition of sludge and to incorporate the majority of elements into forms of compounds industrially usable in the building industry and production of plastic materials. The designed procedure represents a waste free technology with a high degree of recycling of technological extraction media. The presented technology is protected by the Bureau of Industrial Property of the Slovak Republic. It allows to process sludge in the form of two to four final products. The simplest two-product variant allows to process sludge into hemihydrate and high magnetic red pigment (magnetic susceptibility $96\ 698 \times 10^{-6}$ [JSi]).

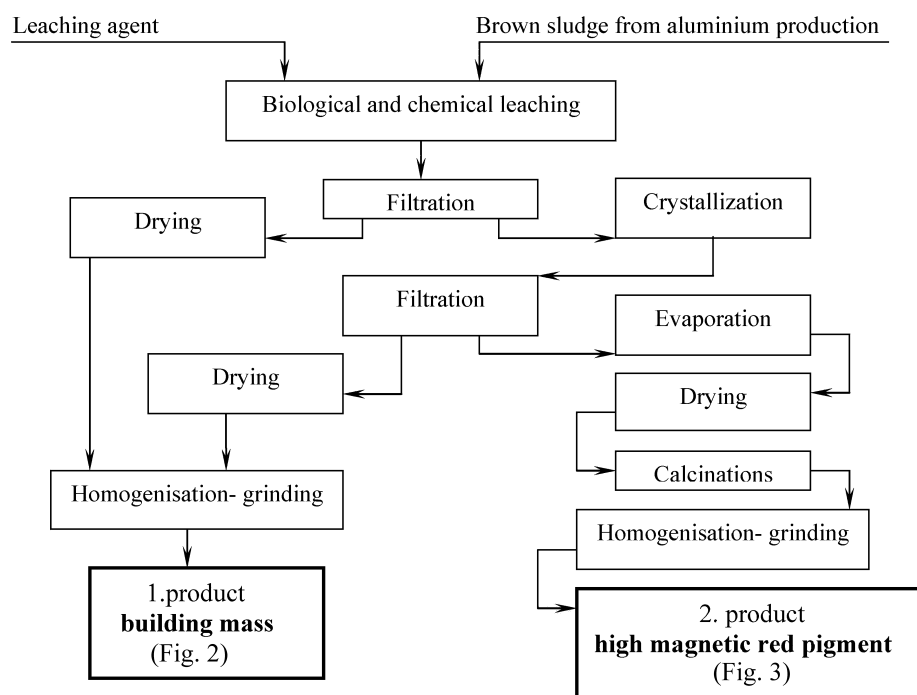
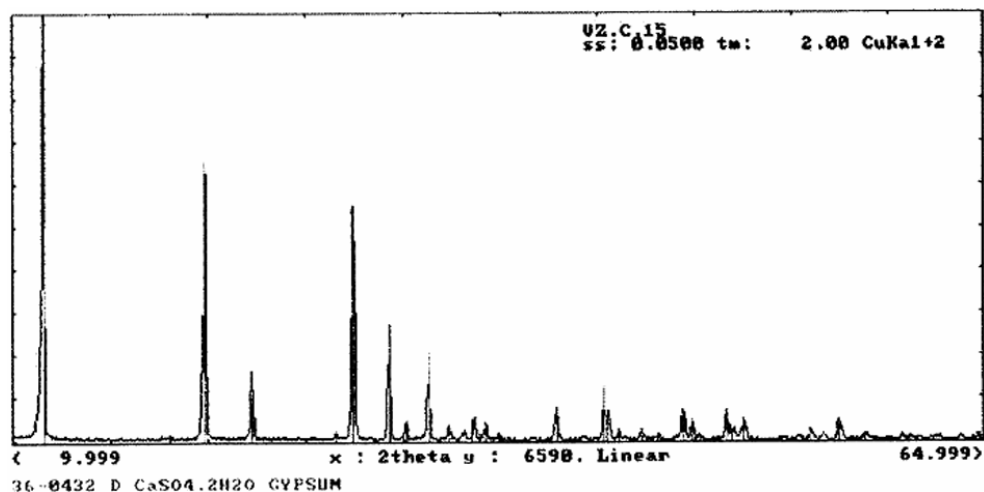
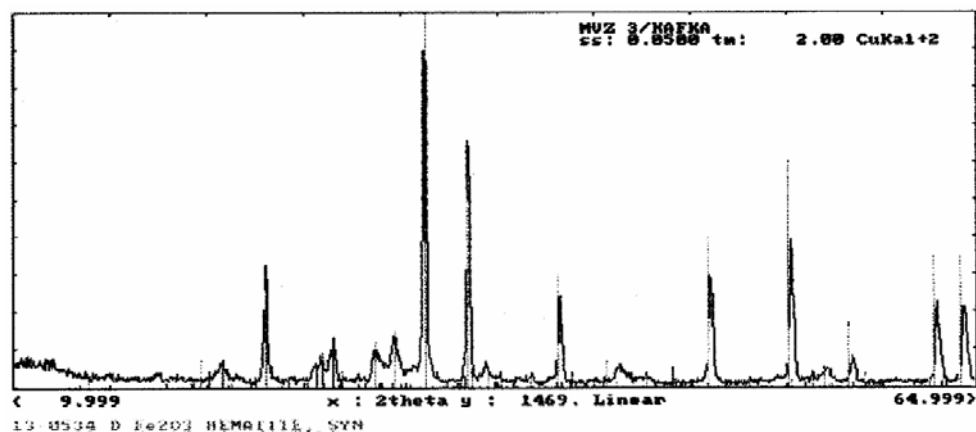


Fig. 1. Technology of complex treatment of waste sludge from the aluminium production

Rys. 1. Kompleksowa technologia przeróbki szlamów odpadowych z produkcji aluminium

Fig. 2. X-ray diffraction of 1st product – CaSO₄·2H₂ORys. 2. Dyfraktogram produktu 1 – CaSO₄·2H₂OFig. 3. X-ray diffraction of 2nd product – Fe nanodispersion (pigment/sorbent)

Rys. 3. Dyfraktogram produktu 2 – nanodispersja Fe (pigment/sorbent)

After the corrective treatment of radioactive properties, hemihydrate can be used in the complex gypsum plasterboard program (in Slovakia this program is currently fully covered by import and its introduction in Slovakia in co-operation with the corrective anhydrite material producers could contribute to the creation of jobs). On the basis of preliminary tests, red pigments can be used in plastic material processing. The world demand for quality red pigments is not sufficiently satisfied by the industrial production and it is expected that they will represent a profitable product on the commodity market [5].

3. Bio-chemical preparation of hematite pigment from lead matte

The major element of lead matte is Fe, which is bound mainly in sulphidic form of pyrrhotine (FeS). Matte contains admixtures like Zn and Pb, which are also bound in sulphidic form.

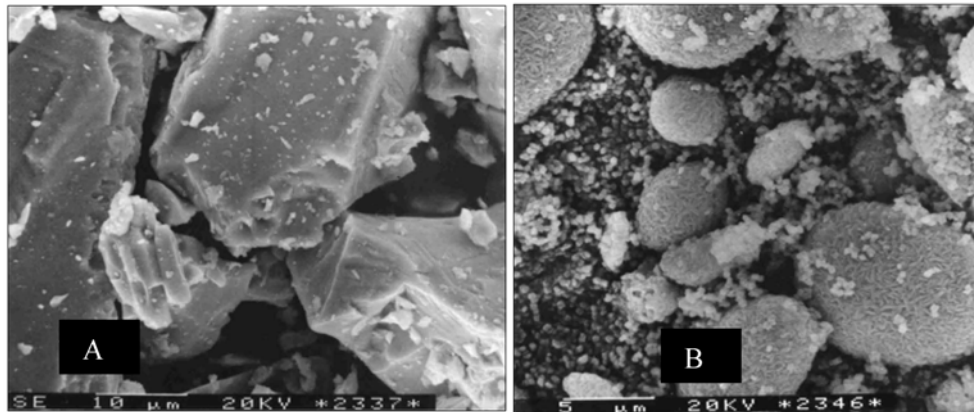


Fig. 4. Morphology of the lead matte particle: A – before and B – after biological and chemical leaching

Rys. 4. Morfologia ziaren kamienia ołowianego: A – przed; B – po lugowaniu biologicznym i chemicznym

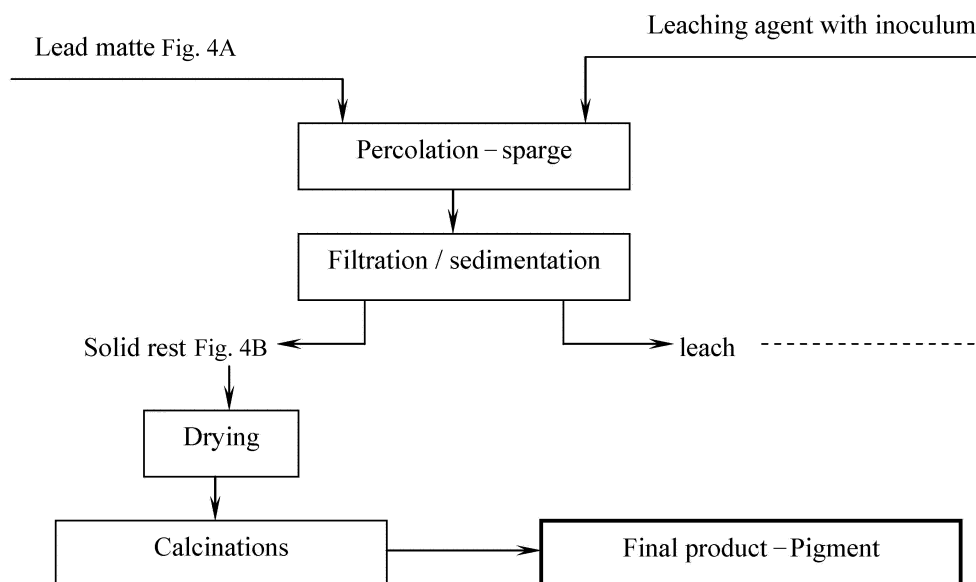


Fig. 5. Technology of treatment of lead matte

Rys. 5. Technologia obróbki kamienia ołowianego

The bio-chemical oxidation processes are industrially applied in the primary sulphidic ore processing and that is why there was a realistic assumption that it would be possible to apply these methods in the lead matte processing. The research confirmed that the application of a mixed culture of thionic bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* [4] is optimal for matte processing.

The product of the matte biological-chemical leaching (Fig. 5) is a fine ochre coloured material whose chemical composition and grain size composition correspond to the produced brown pigment.

The calcinations of the obtained bacterial leached materials enable to prepare a red commercially utilizable pigment from waste matte whose demand in the world markets exceeds the present production.

The bio-chemical leaching processes with uncontrolled kinetics and a minimal degree of optimisation of sprinkling can also proceed *in situ* with very low economic costs.

4. Conclusion

The presented results confirm the possibility of utilization of the biological-chemical method as:

- 1) the main operation of the processing and complex use of waste brown sludge from aluminium production,
- 2) the basic process of hematite pigment production from metallurgical lead-matte-based waste.

However, in the metallurgy there is a wide range of other options for the use of bio-chemical processes, e.g. ferric-sulphate-based leaching agent regeneration (and pickling baths) and it is possible to assume that much bigger part of the options has not been researched yet.

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