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INFLUENCE OF AUTOCHTHONOUS SULPHUR BACTERIA ON METALS LEACHING FROM ZINC AND LEAD FLOTATION TAILINGS

WPŁYW AUTOCHTONICZNYCH BAKTERII SIARKOWYCH NA ŁUGOWANIE METALI Z ODPADÓW POFLOTACYJNYCH RUD CYNKOWO-OŁOWIOWYCH

Summary: Zinc- and lead-ore processing in the Bolesław Mine and Metallurgical Plant S.A. results in annual formation up to 1.6 million Mg of flotation tailings which are deposited in sedimentary ponds. Apart from dolomite, the wastes contain variety of chemical compounds, including heavy metal sulphides: pyrite and marcasite (FeS_2), sphalerite (ZnS), galena (PbS) and other minerals. The results of research on the influence of autochthonous sulphur bacteria on metals release from flotation tailings have been presented. It has been demonstrated that these bacteria growing under favorable conditions can intensify the metals bioleaching. This process leads to increase in efficiency of heavy metals extraction, for example Zn and Cd are many times higher as compared with systems without stimulation of sulphur bacteria growth and activity.

Keywords: Zn-Pb flotation tailings, leaching, autochthonous sulphur bacteria

Since the 19th century zinc ores have been extracted by underground methods in the Silesian-Cracow region. The Boleslaw Mine and Metallurgical Plant and the Trzebionka Mine Plant produce and process sphalerite and galena concentrates. The metals are extracted from sulphide ores containing approx. 3.3 % Zn and approx. 1.2 % Pb. Annually 2.6–2.7 mln Mg of ore is processed by flotation methods. About 52.0 mln Mg of flotation tailings are deposited in the aboveground storage facilities located in the area between Olkusz and Boleslaw (Fig. 1). The mineral composition of the tailings is dominated by carbonates (72 %) represented by dolomites $Ca(Mg,Fe)[CO_3]_2$, ankerites $Ca(Mg,Fe)[CO_3]_2$ and calcite $CaCO_3$, whereas the fraction of silty minerals (8 %) (illite,

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montmorillonite, kaolinite) is considerably lower. The flotation tailings are characterized by very high contents of heavy metals: Fe, Zn, Pb, Cd, Tl, Cu, Sb, As, Ag and others [1÷5]. Their source are ore minerals, the weight fraction of which reaches 20 %. The quantity of pyrite and marcasite is the most substantial (14–18 %). Iron is chemically bonded not only to sulphides FeS_2 (about 7 mln Mg) but also to sulphates (0.8 mln Mg), oxides, hydroxides FeOOH (about 0.8 mln Mg). Zinc is found in sulphides and carbonates (0.465 and 0.487 mln mg). Extremely toxic Cd and Tl are chemically bond in Zn and Fe sulphide minerals. Small quantities of active chemical substances *eg.*, xanthates, pine oils, sulphates of Cu, oxides of Ca and other compounds used in flotation are sent to the flotation ponds [5]. The development of secondary chemical changes of tailings stimulates the release of a considerable quantity of metal ions (Zn, Pb, Cd, and Fe) and SO_4^{2-}. They are dissolved in rain and over-sedimentary waters which infiltrate to the level of underground waters. The fine-grained character of the tailings and their chemical composition make the phytostabilization of the facility surfaces difficult and metalliferous minerals are redeposited in the soils of the Olkusz area by wind [1, 2]. Oxidization of sulphide minerals [1, 6] influences the changes in chemism of tailings enormously. The rate of the development of these processes depends on abiotic and biotic factors [7]: oxygenation conditions, mineral composition, water balance and microorganisms occupying the facilities.

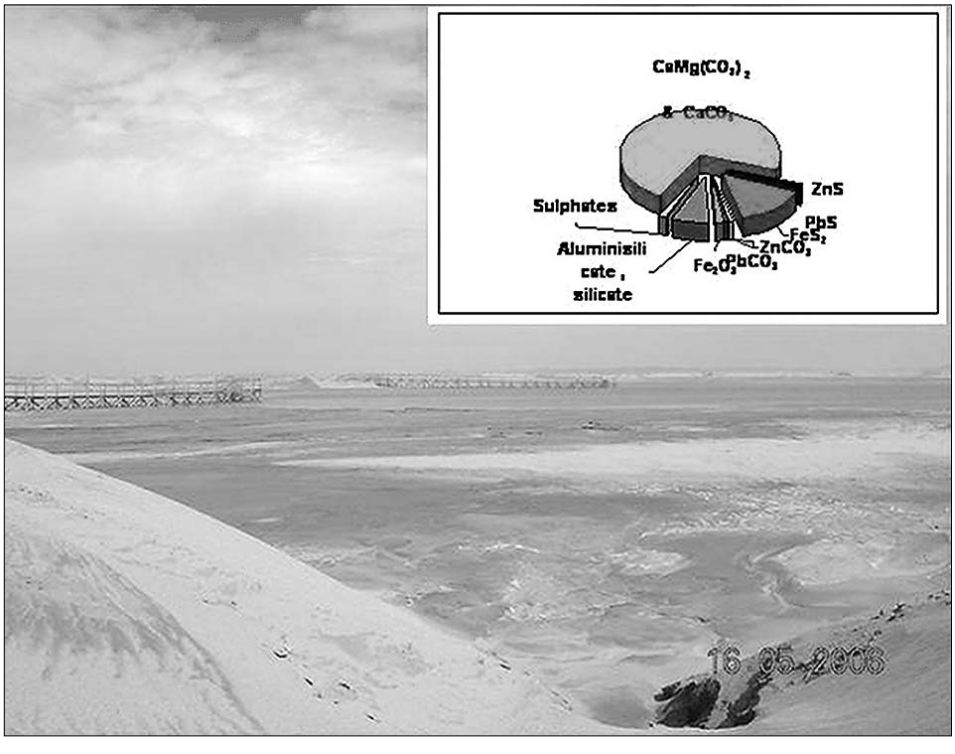

Fig. 1 Speciation of minerals in flotation tailing storage facility – a sedimentation pond at the Boleslaw Mine and Metallurgical Plant

The objective of this research was to determine the influence of autochthonous microflora, possessing the ability to oxidize mineral sulphur compounds, on the process of metals release from flotation tailings. The consequence of metabolic activity of this type of bacteria should be environmental acidification and increase in heavy metals concentration of wastewaters. This increase is connected with the development of acid drainage of flotation tailings [6].

Methods

The flotation tailings in the process of leaching (during 168 h) are characterized by considerable concentration changeability of metals and sulphide compounds, which depends on the level of sampling. For the superficial layers the concentration of basic metals amounts to [in %]: Fe – 16.1; Zn – 2.98; Pb – 1.32; Cd – 0.0143; Ss(sulphide) – 14.3, CaO – 18.20, MgO – 8.80. And for the deeper layers, in particular at the depth of 3 m, it amounts to: Fe – 8.06; Zn – 1.4; Pb – 0.67; Cd – 0.0092; Ss(sulphide) – 7.52, CaO – 23.20, MgO – 10.20. The liquid nutrient mediums used in the process of leaching consist of in [g/dm^3]:

a) Waksman and Joffe medium (W/J) on the basis of thiosulphates: $Na_2S_2O_3 \cdot 5H_2O$ – 5.0; KH_2PO_4 – 3.0; $MgCl_2 \cdot 6H_2O$ – 0.1; $CaCl_2 \cdot 6H_2O$ – 0.25; NH_4Cl – 0.1; $FeSO_4 \cdot 7H_2O$–trace; initial pH 4.0.

b) Silverman and Lundgren medium (S/L) – iron-free: $(NH_4)_2SO_4$ – 3.0; KCl – 0.1; $MgSO_4 \cdot 7H_2O$ – 0.5; $Ca(NO_3)_2$ – 0.01; K_2HPO_4 – 0.5; initial acidification up to pH 2.5 with H_2SO_4; in order to intensify biological utilization of pyrite compounds from wastes as an energy substrate for bacteria.

The tailings were treated with a leaching solution in a ratio solid phase/liquid phase = 5 g/100 cm^3 and the whole was placed in Erlenmeyer flasks closed with bacteriological plugs. The solutions were aerated with a laboratory shaker at 130 r.p.m. and vibration amplitude 5 and at a temperature of 20–22 °C. The changes of chemical constitution of the solutions were analysed by absorption spectroscopy AAS on Solar M6 Unicam with the use of an air-acetylene flame. The experiment was repeated three times.

Results and discussion

An analysis of changes in metal concentrations of Cd, Fe, Mg, Pb, and Zn in the solutions after the leaching of floatation tailings during 168 h, showed an immense diversity depending on the kind of a nutrient medium. In the case of W/J mediums containing reduced sulphur compounds – thiosulphates, the efficiency of leaching of Cd – 6.07 % and Zn – 3.16 % was considerably higher in comparison with S/L mediums (Cd – 0.81 %, Zn – 0.75 %) where the concentration of released metals into the solution was several times lower. It was found that with time the concentration of Cd and Zn in W/J mediums went up to 0.434 mg/dm^3 of Cd and 47.12 mg/dm^3 of Zn whereas in S/L mediums up to 0.058 mg/dm^3 of Cd and 11.22 mg/dm^3 of Zn – Table 1, during the leaching process of flotation tailings from the superficial layer.

Table 1

Change in metal concentrations during the leaching process (168 h) of flotation tailings from the superficial layer. Nutrient mediums stimulating sulphur bacteria activity – W/J and in the configurations without stimulation – S/L mediums

Nutrient medium	**Zn [mg/dm³]**	Pb [mg/dm³]	Fe [mg/dm³]	**Cd [mg/dm³]**	Mg [mg/dm³]
W/J	**47.12 ± 7.36**	0.991 ± 0.375	3.529 ± 2.115	**0.434 ± 0.075**	81.22
S/L	**11.22 ± 2.44**	2.518 ± 1.833	3.634 ± 3.179	**0.058 ± 0.026**	96.93

This regularity concerned leaching of tailings both from the surface and deeper levels of the facility – Table 2. It was found, that change in efficiency of leaching of flotation tailings from 3 m depth under the surface was 3.72 % Cd and 6.83 % Zn in W/J nutrient mediums and 2.06 % Cd and 0.99 % Zn in S/L mediums. This tendency was found also during the further leaching process (1512 h) of flotation tailings [8].

Table 2

Change in metal concentrations during the leaching process (168 h) of flotation tailings from 3 m depth under the surface of a tailing storage facility. Nutrient mediums stimulating sulphur bacteria activity – W/J and in the configurations without stimulation – S/L mediums

Nutrient medium	**Zn [mg/dm³]**	Pb [mg/dm³]	Fe [mg/dm³]	**Cd [mg/dm³]**	Mg [mg/dm³]
W/J	**47.81 ± 2.20**	3.360 ± 2.202	4.009 ± 0.114	**0.171 ± 0.052**	165.14
S/L	**6.98 ± 0.77**	2.764 ± 1.522	2.910 ± 1.619	**0.095 ± 0.019**	116.52

An analysis of Fe and Pb concentrations, revealed a decrease in metals content in the solutions with time, which is probably connected with normalizing acid-base balance in the solutions and stability of a particular phase in the investigated configuration [8]. Its caused by digestion of alkaline tailings components – ferruginous dolomite of an alkaline character, fast neutralisation took place in the S/L solutions and pH increased dramatically to about 7.64–7.67. In the case of W/J solutions pH reached 4.47, which was more beneficial for digestion and stability of Cd and Zn compounds in the solutions. This fact also favoured and stimulated the activity of bacterial microflora possessing an acidophilic character and oxidation ability of reduced sulphur compounds. This ability was found in simultaneously conducted research [9].

Taking into consideration the fact that a flotation tailing storage facility contains some easily accessible sulphuric compounds (pyrite, sphalerite, galena) from which local microareas of lowered pH may be created under the influence of some bacterial activity, it may be supposed that digestion of tailings components and metals release from them follow as a consequence [8–10]. However, high contents of alkaline components in flotation tailings prevent generating acid drain water from the tailing storage facility. That fact is proven by an analysis of drain waters from the facility. These waters have a weak alkaline reaction pH about 7.20. The only fact that indicates the opportunities of developing acid drainage of flotation tailings is high electrical conductivity bound up with a high level of mineralization and presence of well-soluble components, among which Mg^{2+} and SO_4^{2-} ions play a dominant role.

Conclusions

1. The results of flotation tailings leaching from the Boleslaw Mine and Metallurgical Plant by means of a bacterial nutrient medium, supporting the growth of the bacteria with an ability to oxidize sulphur compounds, showed that the level of metals release, in particular of Cd, Zn, from tailings exceeds the concentration of these metals several times in comparison with the configurations without stimulation of sulphur bacteria activity.

2. Except of bacteria activity it was found, that heavy metal concentrations of Cd, Fe, Mg, Pb, and Zn is under the influence of the following abiotic parameters: normalization of acid-base balance, presence of alkaline gangue and changeability of a chemical composition depending on the depth of a tailing storage facility.

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References

[1] Cabała J.: *Occurrence of sulphides minerals in soils in the immediate vicinity of Zn-Pb post flotation tailings*. Zesz. Nauk. Pol. Śl. 1592, Górnictwo, 2003, **256**, 43–50, (in Polish with English summary).

[2] Krzaklewski W. and Pietrzykowski M.: *Selected physico-chemical properties of zinc and lead ore tailings and their biological stabilisation*. Water, Air, Soil Pollut., 2002, **141**, 125–142.

[3] Jarosiński A. and Natanek W.: *Niektóre właściwości fizykochemiczne odpadów poflotacyjnych w aspekcie ich utylizacji*. [In:] Materiały Konferencyjne Waste Recycling, Politechnika Krakowska, Kraków 2005.

[4] Pajor G.: *Gospodarka odpadami poflotacyjnymi w ZGH Bolesław S.A. w Bukownie*, Międz. Konferencja Zrównoważone Zarządzanie Obszarami Przemysłowymi, Wyd. Sigma PAN, Kraków 2005, 5–19.

[5] Cabala J., Teper E. and Teper L.: Mine-waste impact on soils in the Olkusz Zn-Pb ore district (Poland). [In:] Mine Planning and Equipment Selection. Taylor & Francis Group, London 2004, 755–760.

[6] Cabała J.: *Acid drainage of postflotation wastes from Zn-Pb ores: changes of mineral composition in rhizosphere zones developed on tailings pond*, Zesz. Nauk. Pol. Śl., 1690, Górnictwo, 2005, **267**, 63–70, (in Polish with English summary).

[7] Pacholewska M., Frąckowiak A. and Willner J.: *Rola czynników fizykochemicznych i biologicznych w przerobie odpadów flotacyjnych*, Prace Instytutu Metalurgii Żelaza, 2006, **58**(4), (Płyta CD)

[8] Pacholewska M., Cabała J., Cwalina B. and Sozańska M.: *Środowiskowe uwarunkowania procesów (bio)ługowania metali z odpadów poflotacyjnych rud cynkowo-ołowiowych*, Rudy i Metale Nieżelazne, 2007, **52**(6), 337–342, (in Polish with English summary).

[9] Cwalina B. and Jaworska-Kik M.: *Sulfur-oxidizing activity of bacteria isolated from Zn-Pb flotation tailings*, Ecol. Chem. Eng., 2008, **15**(1/2).

[10] Malki M., Gozalez-Toril E. and Sanz J. L.: *Importance of the iron cycle in biohydrometallurgy*, Hydrometallurgy, 2006, **83**, 223–228.

WPŁYW AUTOCHTONICZNYCH BAKTERII SIARKOWYCH NA ŁUGOWANIE METALI Z ODPADÓW POFLOTACYJNYCH RUD CYNKOWO-OŁOWIOWYCH

S t r e s z c z e n i e

Procesom produkcji cynku i ołowiu metoda hydrometalurgiczną w Zakładach Górniczo-Hutniczych Bolesław S.A. towarzyszy wytwarzanie odpadów poflotacyjnych, pochodzących ze wzbogacania rud Zn-Pb, w ilości około 1,6 mln Mg rocznie, składowanych w osadnikach – stawach osadczych. Podstawowym składnikiem

odpadów jest skała płonna – dolomit oraz minerały siarczkowe metali ciężkich: piryt i markasyt (FeS_2), sfaleryt (ZnS), galena (PbS) i inne. W pracy przedstawiono wyniki badań nad wpływem autochtonicznych bakterii mających zdolność utleniania zredukowanych związków siarki na efektywność uwalniania metali z opadów. Stwierdzono, że efektywność ługowania Cd, Zn z odpadów z warstw powierzchniowych oraz z warstw głębszych, (3.0 m) poniżej poziomu składowiska, przewyższa wielokrotnie koncentrację tych metali w porównaniu z układami bez stymulacji aktywności bakterii siarkowych.

Słowa kluczowe: Zn-Pb odpady poflotacyjne, ługowanie, autochtoniczne bakterie siarkowe