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INFLUENCE OF METALLIFEROUS MINERALS ON BIOTIC COMPONENTS OF TOPSOIL IN ZINC-LEAD FLOTATION TAILINGS PONDS

WPŁYW MINERAŁÓW METALONOŚNYCH NA BIOTYCZNE SKŁADNIKI WIERZCHNICH WARSTW SKŁADOWISK ODPADÓW Z FLOTACJI RUD CYNKU I OŁOWIU

Abstract: The mineral components of topsoil in the zinc and lead flotation tailings ponds were analyzed. To examine such mineral components the authors used methods such as scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and atomic absorption spectroscopy (AAS). The goal of this study was to pay particular attention to the secondary metalliferous mineral phases formed in rhizosphere zones mainly on plant roots and the influence of autochthonous sulphur bacteria and ferric bacteria on the chemical mechanism of waste components. This study aims both to recognize the (bio)chemical change of flotation tailings which is of great significance for the vegetation of plants, fungi and microorganisms and to properly plan the treatment connected with reclamation and phytoremediation of the area affected by waste disposal.

Keywords: Zn-Pb flotation tailings, secondary mineral transformations, autochthonous bacteria.

Mining activity and exploitation of sulphidic metal ores can produce large amounts of waste particularly during the Zn–Pb processing. One of the areas where the exploitation of Zn-Pb ores occurs on a large scale is the Olkusz region. Over 1.3 million Mg of flotation tailings are deposited in the pond per year. Nowadays this settling pond covers more than 130 hectares and it is 37 m above surface level. The waste produced includes considerable quantities of fine-grained metalliferous minerals (Zn, Pb, Fe, Cd, Cu, As, Sb and Tl) with a fraction of up to 0.04 mm (55–81 % of wastes) and a contribution of grains over 0.2 mm amounting to 3.9 % [1]. Because of easy transport by the wind the fine-grained structure allows the waste to become a source of heavy metal pollution for the soil, water and atmosphere within several kilometres of the tailings ponds [2].

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The vegetation in waste disposal sites becomes sparse and it is particularly difficult to cultivate with respect to a deficiency of water as well as the loss of nutrients (K, N and P). However, the negative impact of sulphidic mine waste and tailings on the environment can be significantly reduced in the cases where appropriate reclamation and phytoremediation is applied. Solutions infiltrating through the topsoils of tailings are enriched with chemically active ions such as SO_4^{2-}, Zn^{2+}, Pb^{2+}, Fe^{2+}, Cd^{2+}, Tl^{+} and Cu^{2+} which affect plant roots, symbiotic fungi and microorganisms. In conditions of high stress on metals the plants [3] and symbiotic mycorrhizal colonization [4] initiate their biological immune defences which can reduce the transfer of toxic heavy metals into the root system of plants. The reaction between biotic excretion of roots and fungi and a solution rich with metal ions results in the crystallization of the secondary metalliferous phases [5, 6]. Up to now these phases have been slightly recognized because of difficulties in their identification. As it turns out the best possibilities for their study appear on flotation tailings sites settled by plants and other living organisms. Scanning methods such as BSE and EDS can be used for an examination of the secondary phases formed on a root's rhizoderm [7] to identify the metalliferous phases.

The authors' achievements to date show that bacterial strains of species such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* isolated from tailings sites can have an influence on the ionic concentration level of heavy metals (Fe, Zn, Pb and Cd) in eluate solutions [8, 9]. Simultaneously these bacteria show a considerably low resistance both to metal ions considered to be toxic, Cu^{2+}, Cd^{2+} and Ag^{+} [10] and to residues of flotation reagents on tailings sites [11]. That is why their metabolic activity is reduced.

The chemical change, mainly Acid Waste Drainage (AWD) [5, 6], limits the plant vegetation and the development of biotic components. Submicroscopic mineral phases can be formed as a result of the interaction of metalliferous solutions with excretion of roots and fungi or bacteria metabolism products. Products of the chemical change of unstable metalliferous mineral components taken from tailings can be recognized in the BSE images [7].Their identification can prove that the organic ligands participate actively in the migration of metal ions. The primary aim of this study was to analyse the impact of metalliferous minerals occurring on Zn-Pb ore waste sites on the biotic components of rhizosphere zones and on microorganisms settled on the surface of flotation tailings ponds.

Material and methods

Samples used for study were taken from the scarp and top soils of flotation tailings ponds of ZGH Boleslaw SA located 2 km to the west of Olkusz in May, 2006. The mineralogical composition of tailings was determined using the X-ray diffraction method (XRD) with a 3710 PW Philips X-ray-diffractometer with gas monochromator. Scanning research (SEM) was done using a 30 XL Philips microscope with EDAX analyser and also an S-3400N Hitachi microscope. Accelerating voltage of 15 or 25 kV and the low vacuous mode were applied. XRD and SEM analyses were done in the laboratory at the Faculty of Earth Sciences (University of Silesia) and in the laboratory at Faculty of Materials Engineering and Metallurgy (Silesian University of Technology).

Chemical analyses of heavy metal contents were determined using the atomic absorption spektrometry (AAS) with an M6 SOLAAR spectrometer in the BOL-THERM SA laboratory in Bukowno.

Results and discussion

Mineralogical and chemical composition of flotation tailings

The mineral composition of tailings formed in zinc-lead ore processing is similar to primary ores. X-ray identification (XRD) of the mineral components in the investigated tailings reveals the presence of minerals such as dolomite $CaMg(CO_3)_2$, ankerite $Ca(Fe,Mg,Mn)(CO_3)_2$, calcite $CaCO_3$, quartz SiO_2, illite and montmorillonite $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$, sphalerite α(Zn,Fe)S, galena PbS, marcasite FeS_2, pyrite FeS_2, smithsonite $ZnCO_3$, cerussite $PbCO_3$, monheimite $(Zn,Fe)CO_3$, gypsum $CaSO_4 \cdot 2H_2O$, goethite αFeO(OH), barite $BaSO_4$ and Fe sulphates eg, $FeSO_4 \cdot nH_2O$.

Table 1 shows the chemical analyses. It can be seen that the topsoils of tailings which can be found in the parts of the pond with the earliest deposits are characterised by high contents of Fe, Zn, Pb in comparison with those where deposition occurred later which showed considerably lower contents of the metals mentioned above. The predominant parts of Fe and Zn are bound in unstable sulphide phases, whereas Pb occurs in the secondary carbonate phases, which is proved by the great participation of Pb_{PbO} (Table 1) – all this confirms the results of previous studies [2, 7]. The large concentration of alkaline components in the investigated tailings results in the stabilisation of metals in slightly insoluble carbonate phases. A high content of sulphur bound mainly in marcasite and pyrite can have a significant impact on the chemical mechanism of flotation tailings. The contents of sulphate compounds in tailings occurring in the oldest part of the waste dump is significantly higher and this can result in the chemical or biochemical weathering of minerals. Within an early period of waste disposal the flotation reagents, supporting selective flotation, have a certain influence on the chemical mechanism of tailings.

Table 1

Chemical composition [%] of waste samples taken from topsoils of tailings ponds

Symbol of sample	Zn	Zn_{ZnO}	Pb	Pb_{PbO}	Fe	Fe_{FeO}	FeS_2	S
A-1*	2.98	0.83	1.32	0.94	16.10	2.35	29.60	14.70
A-2**	1.63	0.40	0.64	0.35	13.10	1.48	25.10	13.50
A-11***	0.95	0.20	0.48	0.26	8.35	1.26	15.20	7.39
	S_s	S_{SO_4}	As	Tl	Sb	Cu	CaO	MgO
A-1*	14.40	0.30	0.098	0.0083	0.0063	0.0040	18.20	8.80
A-2**	13.30	0.23	0.085	0.0059	0.0052	0.0044	21.20	9.94
A-11***	7.21	0.18	0.062	0.0021	0.0047	0.0021	24.50	12.30

* – the part of the tailings pond with the earliest waste deposits; ** – the part of the tailings pond with the latest waste deposits; *** – the part of the tailings pond with the mixed waste deposits.

Transformation of mineral composition in rhizosphere zones

Fine-grained mineral components of tailings characterised by the great participation of metalliferous minerals occur in the rhizosphere of root plants (Fig. 1a–f). The biological activity of roots favours the formation of polymineral aggregates on their surface. The aggregates consist of carbonates, clay minerals, Fe oxides, sulphides, Zn, Pb and Fe carbonates and sulphates (Fig. 1a). Zn and Pb, Fe sulphides undergo a secondary chemical change in subsurface layers, and as a result of oxidation SO_4^{2-} ions are released and then they are stabilised in calcium sulphate. Gypsum $CaSO_4 \cdot 2H_2O$ and bassanite $CaSO_4 \cdot 0.5\ H_2O$ crystallize in masses on polymineral aggregations (Fig. 1b) and Fe sulphides. Fe, Pb and Mg sulphates can also be identified. The oxidation and dissolution processes have an influence on the morphology of metalliferous mineral grains which show traces of erosion, leaching and recrystallization (Fig. 1b, d, f). These features imply that they become the source of heavy metal ions and sulphate ions. In the waste sites where tailings are enriched with Fe sulphides AWD can be developed. As a result of this, the secondary sulphates, seldom Fe oxides and hydroxides, crystallize on plant roots, the hyphae of fungi and other organic elements. The development of these processes on a mass scale reduces the ability of plant vegetation to occur.

Effect of metalliferous sulphide minerals on microorganisms

Metalliferous sulphide minerals become the natural habitat for chemolithoautotrophic bacteria which are characterised by the ability to oxidize iron (II) compounds such as *Acidithiobacillus ferrooxidans* and other genera eg, *Leptospirillum* or *Sulfolobus* and also oxidized sulphur compounds eg, *Acidithiobacillus thiooxidans* or *Acidithiobacillus caldus* [12]. That is why the presence of Fe, Zn, Pb and Cd sulphides occurring in flotation tailings can stimulate their metabolic activity through oxidation and solubilization of sulphides in the oxygen-rich top layer of the tailings pond. Bioleaching processes take place where there is a contact between microorganisms adhesion and the surface of the mineral in the exopolimer layer. In Figure 1c the bacterial active cells of B1 = WB1 strain belonging to the *Acidithiobacillus thiooxidans* species are presented. These cells adhere to the sulphur-rich grain. The bacteria were isolated from flotation tailings (A1).

Minerals including iron and sulphur compounds are mainly subjected to bacterial solubilization whose final products can be solutions of Fe(III) compounds and sulphuric acid as well as sulphur compounds such as jarosite as well as elementary sulphur. The oxygen-rich environment favours these processes. Figure 1 d, e, f present BSE images of Fe sulphides (marcasite and pyrite) taken from different layers of flotation tailings ponds (A1) characterised by the intermittant access to oxygen. In the top layer the most intensive chemical and biological weathering of pyrite took place (Fig. 1d). In the study area in a subsurface layer (0.3 m and 3.0 m) of the tailings pond, the biological and chemical leaching of pyrite is reduced (Fig. 1e, f).

Conclusions

Scanning methods used for research into the mineral components of waste deposited in ponds can prove that they undergo essential chemical changes when subjected to oxidation, dissolution and interaction with aggressive solutions which are generated by the biotic components of the flotation tailings.

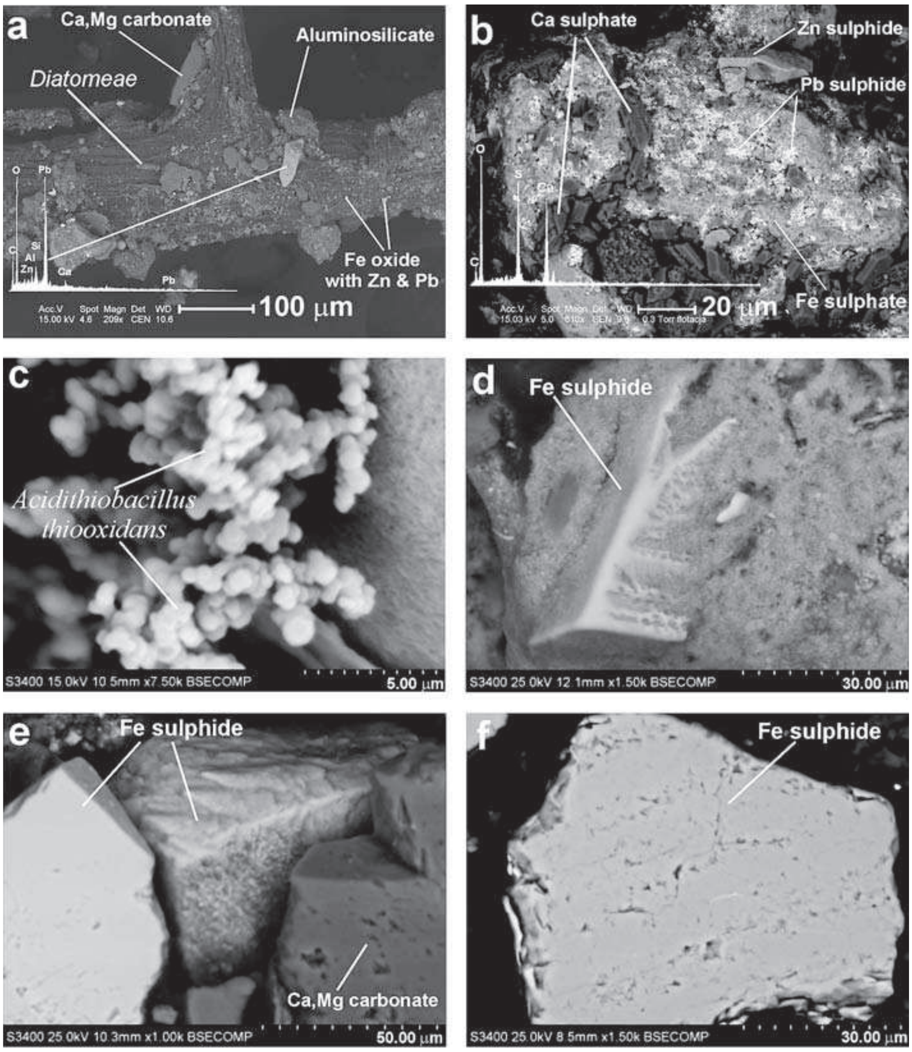

Fig. 1 BSE images of Zn-Pb flotation waste. a – Roots vegetated in the top layer of tailings ponds, b – sulphide aggregates from the top layers of tailings ponds, c – bacterial cells, B1 = WB1 strain *Acidithiobacillus thiooxidans* isolated from flotation tailings – A1 surface layer, d – corroded Fe sulphide crystal, – the place of isolated active sulphide and ferric bacteria, top layers of tailings ponds A1, e – Fe sulphide crystal from 0–0.3 m layers A1, f – surface of Fe sulphide subjected to bacterial medium stimulating metabolic activity of *Acidithiobacillus ferrooxidans* bacteria.

The morphological features of marcasite, pyrite, sphalerite and galena show that in topsoils of a tailings pond the development of the leaching process enriching the solutions with active ions of metals and sulphates occurs.

The development of the secondary mineralization that occurred on plant roots has an influence on the conditions of plant vegetation, microorganisms and fungi. Moreover, it reduces the spontaneous succession of plants and can hinder phytoremediation in sulphide-rich tailings ponds.

The ability to develop autochthonous sulphur bacteria and ferric bacteria diminishes as the quantity of oxide in flotation tailings ponds decreases. The intensive biological weathering processes of sulphide minerals take place mainly in the topsoils of tailings ponds.

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Abstrakt: Autorzy za pomocą metod elektronowej mikroskopii skaningowej (SEM), mikroanaliz (EDS) oraz analiz chemicznych (AAS) badali składniki mineralne wierzchnich warstw odpadów zdeponowanych na składowiskach poflotacyjnych rud Zn-Pb. Szczególną uwagę zwrócono na wtórne, metalonośne fazy mineralne powstałe w strefach ryzosferowych, na powierzchni korzeni roślin oraz na wpływ autochtonicznych bakterii siarkowych i żelazowych na chemizm odpadów. Przeprowadzone badania są przydatne dla poznania (bio)chemicznych przemian odpadów poflotacyjnych, które mają duże znaczenie dla wegetacji roślin, grzybów i mikroorganizmów. Są one ważne dla prawidłowego projektowania zabiegów rekultywacyjnych i fitostabilizacji składowisk.

Słowa kluczowe: Odpady z flotacji rud Zn-Pb, składowiska odpadów, wtórne przemiany składu mineralnego, autochtoniczne bakterie