FORMS OF HEAVY METALS (Zn, Pb, Cd) OCCURING IN RHIZOSPHERES FROM THE AREAS OF FORMER AND CONTEMPORARY Zn-Pb ORE MINING

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Abstract: The research areas were selected in the regions heavily polluted by wastes from the former washing plant, flotation waste dump and by non-sulphide Zn-Pb ores from open pit mining in the Olkusz region. The submicroscopic phases occurring in the surface of plant roots and in the rhizospheres were investigated by XRD and SEM/EDS methods. Morphology of submicroscopic metalliferous phases and their manner of occurrence were the subject of study. The analysis of EDS spectra enabled to identify phases and mineral aggregates including Zn, Pb, Fe, Mn, Cd in their structure. The soils from the washing plant and areas of open pit exploitation are contaminated by diverse complexes of minerals. The occurrence of unstable Fe, Pb, Ca sulphates indicate that these wastes are still intensively geochemically active.

Keywords: heavy metals, rhizosphere, Zn-Pb secondary minerals, Olkusz Zn-Pb mining region, historical mining

1. INTRODUCTION

In the areas where ore deposits occur shallowly or in the surface, the soils are particularly strongly exposed to heavy metals (HM) contamination. Some natural factors like geological setting, climate, hydrogeological system, weathering and related to them chemical alterations of metalliferous minerals affect the increase of bioavailable metals in the environment. The anthropogenic factors like the development of metals mining, processing and smelting are also significant. In Europe, regions of shallowly-

lying coloured and noble metals ore, such as Pb-Ag, Zn-Pb, Cu, Sn, Hg, Au have been the centres of development of metals mining and processing since antiquity. The exploitation and smelting of valuable metals like Au, Ag, Cu, Sn, Pb, Hg substantially affected water and soil contamination. The penetration of toxic metals into the trophic chains has been the subject of wider studies in the second half of the XXth century. The identification of mechanisms of e.g. Cd, Hg, Pb transfer into plants (Banfield et al., 1999; Dahmani-Muller et al., 2000) or animals organisms (Appleton et al., 2000) and HM influence on human health (Gulson et al., 2004) have been the most popular research subjects.

The metalliferous wastes deposited in England in the Roman Period still contaminate water by Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} ions (Merrington and Alloway, 1994; Maskall et al., 1996). The former post-mining wastes in Belgium and the Netherlands show geochemical activity for over 200 years (Degryse and Smolders, 2006). The metals activated in various periods of Zn-Pb ore exploitation in Spain (Marques et al., 2001), Ireland (Moles et al., 2004) and other countries also affect the environment.

In Poland, a particularly high degree of soil contamination by metals (Zn, Pb, Fe, Cd, Tl) and metalloids (Sb, As) is listed on the areas adjacent to Zn-Pb ore mines, smelters and waste dumps in the Olkusz, Bytom and Tarnowskie Góry areas and Cu ore mines and waste dumps in the region of Legnica and Głogów. The naturally developed and industrial soils in the vicinity of the Pb-Ag ore exploitation have been contaminating since the early Middle Ages by zinc, lead, cadmium, thallium, arsenic building minerals derived from primary ore and post-mining tailings (Cabała, 2009). The similar mineral complexes and metals pollute the soil in the area of former Zn-Pb ores exploitation and processing in Belgium (Lock et al., 2003), Ireland (Good, 1999) and France (Dahmani-Muller et al., 2000).

The development of lead and silver, iron, and then zinc and lead mining was connected to transfer of large loads of lead, zinc, iron, cadmium, arsenic and thallium to the surface layers. The mines, metal smelters and ores washing plants around which the processing tailings were deposited, had been the source of HM. In addition, the pollution of environment in the areas of shallowly-lying Zn-Pb-Ag and Fe ores (Fig. 1) is connected with the natural geochemical aureole of metal dispersion arising in the weathering processes. Metals in the environment can come from different kinds of sources, which are very difficult to identify. The authors have attempted to identify metal-bearing phases present in the soil, especially in the immediate vicinity of the root zone (rhizosphere). The topsoil layers rich in organic matter are a specific medium, in which metals can be activated from the mineral phases owing to the sorptive properties of organic matter, the presence of micro-organisms, biotic root exudates and/or they can be stabilized in the new secondary minerals or organometallic phases. The areas of lasting many years of metals exploitation, such as the Olkusz region, are a good research ground for some detailed surveys (e.g. Rożek and Cabała, 2013). The recognition of forms and regularity of metal concentrations is particularly interesting.
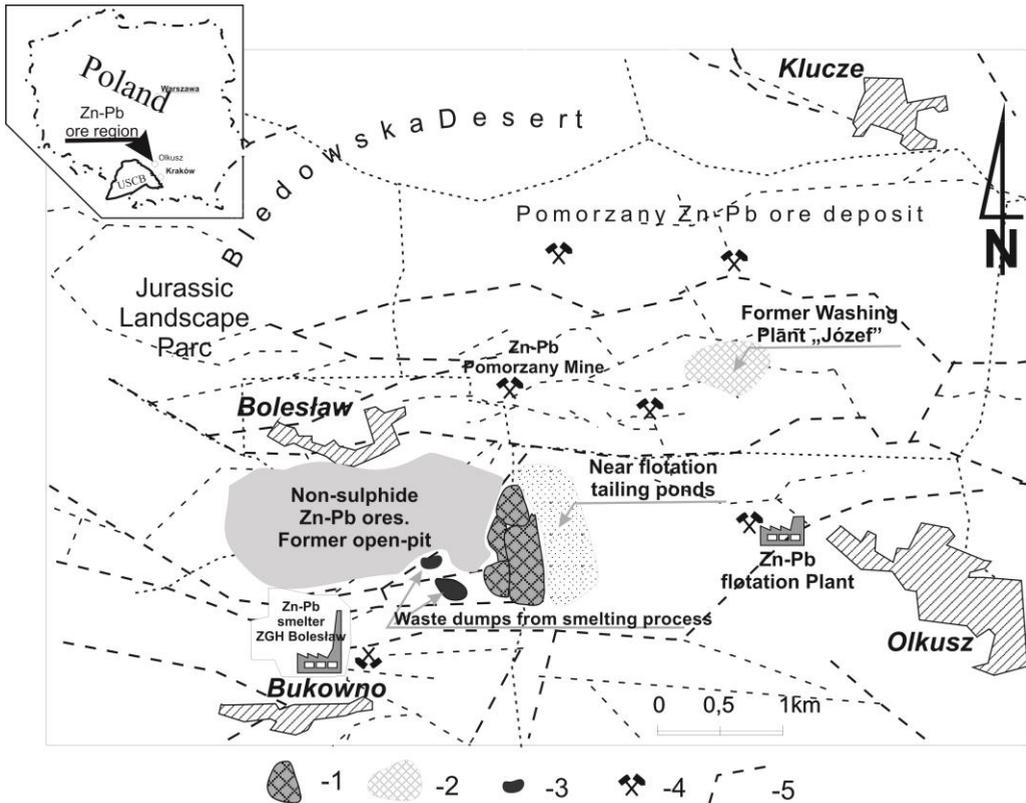
Fig. 1. Location of research areas. 1 – flotation waste ponds, 2 – area of historical washing plant "Józef", 3 – post-smelting waste dumps (1950-1980), 4 – pit shafts, 5 – main tectonic faults, USCB – Upper Silesia Coal Basin

2. GEOLOGY, MINERALOGY AND PEDOLOGY

2.1. GEOLOGICAL SETTING

In deep-seated basement Devonian and Carboniferous carbonic and argillic deposits occur. Conglomeratic and argillic Lower Permian deposits lie on their erosional surface. Shallow layers and surface area are formed of limestones, dolomites, Lower and Middle Triassic marls, Upper Triassic argillic deposits and Jurassic limestones forming erosional remnants. Horizon of irregular, epigenetic metalliferous dolomites, which Zn-Pb-Fe mineralization is involved with, occur in paleosome of Triassic carbonic deposits. Silesian-Cracovian Zn-Pb ore deposits included in Mississippi Valley type (MVT) deposits were formed in Early Creataceous (135±4 million years) (Heijlen et al., 2003). Mesozoic layers lying horizontal were tectonically reconstruct-

ed in alpine period. As a result of their upthrusting in Olkusz region Jurassic and Triassic deposits were partially sheared by erosion. The highest degree of ore horizons exposure is marked on tectonic fault ridges (e.g. Olkusz-Bolesław Horst), on which area deposits lie on the surface or they perform shallowly (Cabala, 2001). Paleogenic and Holocene fluvioglacial and eolic deposits, represented by quartz sands and silts fill morphological depressions of Mesozoic paleosurface.

2.2. Zn-Pb ORE - MINERALOGY AND GEOCHEMISTRY

Primary mineralization is represented by a complex of simple sulphides such as: sphalerite (ZnS), galena (PbS), pyrite and marcasite (FeS_2) and greenockite (CdS), containing traces of Ag, As, Tl, Sb, Ba (Heijlen et al., 2003). Ores in carbonate deposits usually include also minerals like: dolomite, kalcite, quartz, barite, illite, kaolinite, more rarely As and Pb sulfosalts (Jerzykowska et al., 2014).

During the Miocene and Pleistocene, weathering processes led to geochemical transformation of the primary ore and the formation of supergene, nonsulphide Zn-Pb-Fe deposits. In the surface zones secondary, geochemical aureoles of Zn, Pb, Fe, Cd, As dissemination originated (Cabala, 2001). Hydrated Fe sulphates formed first as a product of Fe sulphides oxidation. The unstable hydrated Fe sulphates transform further into hydrated Fe oxide-hydroxides forming limonites. Primary Zn sulphides were oxidized to unstable sulphates, which in turn changed to stable Zn carbonates, mainly smithsonite ($ZnCO_3$) and rarely monheimite $(Zn,Fe)CO_3$. Advanced chemical weathering lead to formation of Zn silicates, like hemimorphite $Zn_4Si_2O_7(OH)2 \cdot H_2O$. More rarely secondary, non-durable minerals occur, such as: melanterite, jarosite, epsomite, gypsum, hydrozincite, anglesite, psilomelane and pyrolusite (Cabała, 2009).

2.3. SOIL CHARACTERISTICS

Soils occurring on areas within direct impact of ore mining are highly degraded and locally original soil covers were completely removed (Trafas et al., 1990). This soils are represented by acid or weakly acid sandy initial soils, podzols, arenosols and pedalfer type brown soils. Brown rendzinas and other types of pedocal soils with incomplete profiles dominate in the areas of supergene type of Zn-Pb ores and regions of shallow occurrence of Jurassic and Triassic deposits. Technosols occur in regions of open pit exploitation and in reclaimed areas. Lasting many years shallow exploitation of Pb-Ag and Zn-Pb ores essentially influenced soil covers degradation and HM contamination (Cabała and Sutkowska, 2006).

3. MATERIALS AND METHODS

The study was performed in the area of shallowly-lying Zn-Pb deposits in the Southern Poland between Boleslaw, Bukowno and Olkusz. This area is a part of the Silesian-Cracow region of exploitation of Pb-Ag ores (from the XIIth century) and Zn-Pb ores (from the XIXth century). Samples were collected: (1) in the area of the former Zn-Pb washing plant "Józef" in Olkusz, (2) in the vicinity of the flotation tailings dumps, (3) on the territory of the historical exploitation of supergene type Zn-Pb ore in Boleslaw (4) in the vicinity of the waste dumps from ZGH Bolesław zinc smelter. The research material came from topsoil layers where the plants root were present. SEM studies were performed on the roots of plants and on soils from their immediate vicinity (rhizospheres). Rhizospheres are these zones where the influence of root exudates, root symbiotic bacteria and fungi is directly or indirectly observed (Courchesne and Gobran, 1997).

3.1. SEM INVESTIGATION

On plant roots and in soil the grains morphology was investigated using an Environmental Scanning Electron Microscope (ESEM) Philips XL30 with EDAX analyzer. Soil used in this studies was earlier sieved into the fraction below 0.045 mm. Researches were performed in low-pressure mode (0.3 Torr). Back Scattered Electron (BSE) images were reached using the Centaurus attachment with a detector resolution of 0.3Z. EDS spectra analyses were processed using Philips software. Studied samples were fixed to carbon tapes stuck on aluminium stubs. The accelerating voltage was 15 kV and current was 20 nA.

3.2. XRD STUDIES

Soil samples were examined using X-ray Diffraction (XRD) method. Investigated material was taken from the topsoil layer (0-30 cm). Mineral composition was determined using X'Pert PANalytical PRO PW 3040/60 Diffractometer (range of researches: from 2.50 to 64.98 ˚2θ, step size 0.008 ˚2θ and scan step size equalled 300 s). Current parameters were 30 mA and 40 kV and radiation Co K_α. XRD analyses were performed using X'Pert software.

All analyses (XRD, SEM/EDS) were carried out in the laboratories of the Faculty of Earth Sciences at the University of Silesia in Sosnowiec.

4. TYPE AND FORM OF METALLIFEROUS MINERALS IN RHIZOSPHERES

In significant degree, type and share of individual mineral phases in studied soils depend on the distance from contamination source, which former and contemporary

coal waste dumps or after processing dumps are. On the ground of XRD studies minerals in crystalline phases were identified (Tab. 1).

Soils near flotation dumps are polluted by fine-grained fractions, which come from their wastes. Pyrite and marcasite phases have a significant share and easily undergo chemical changes. As their result in soil solutions regulated in carbonate waste environment SO_4^{2-} ions are present in a form of gypsum. There are observed Pb and also Zn sulphides and Zn-Pb carbonate minerals (Tab. 1).

Soils in old open pit exploitation areas of non-sulphide Zn-Pb ores are characterized by absence of non-durable, sulphate minerals (Fig. 2a, b). Metals (Zn, Pb, Fe, Cd) occur in durable, slightly soluble phases, such as smithsonite, cerussite, goethite, otavite. Hemimorphite is rarely observed and it indicates on strong oxidizing processes development, when zinc fixation in silicate minerals structure can occur. Presence of sulphides and cadmium carbonates originated as a consequence of geochemical separation zinc from cadmium, which is a result of oxidizing cadmium bearing zinc sulphides is characteristic.

Soils weakly colonized by plants occurring adjacent to Zn-Pb washing plant "Józef" working in years 1896-1930, have especially complicated and differential mineral composition. An absence of iron sulphides, little quantity of dolomite, high percentage share of gypsum and other sulphates e.g. anglesite, melanterite and jarosite (Tab. 1, Fig. 2a) indicate on an intensive development of acid waste drainage processes. Metals (Pb, Zn, Fe) occur in unstable, strongly soluble sulphate phases. Only some part of lead performs in final oxidizing product, which cerussite is. Zinc stabilized in smithsonite and iron practically on the whole is bound in goethite type slightly soluble oxides.

Soils located near historical smelting waste dumps (formed 1950-1980) are contaminated with synthetic phases containing lead and zinc.

Table 1. Mineral composition of soil from areas of contemporary and historical Zn-Pb ores mining activity. Identification was made with XRD methods

Localisation of soil profiles	Primary minerals	Primary ore minerals	Secondary minerals
Near present postflotation wastes dump	dolomite $CaMg(CO_3)_2$, quartz SiO_2, kalcite $CaCO_3$, kaolinite $Al_2Si_2O_5(OH)_4$, illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, feldspar $(Ca,Na)Al_2Si_2O_8$	piryte & marcasite FeS_2, galena PbS, sphalerite ZnS, barite $BaSO_4$	goethite $Fe^{3+}O(OH)$, smithsonite $Zn(CO_3)$, cerussite $PbCO_3$ gypsum $Ca(SO_4)\cdot2H_2O$
Historical open pit of non-sulphide Zn-Pb ore	dolomite, kalcite, quartz, illite	galena, sphalerite, grenockite CdS, barite	goethite, smithsonite, cerussite, hemimorphite $Zn_4Si_2O_7(OH)_2\cdot(H_2O)$, otavite $CdCO_3$
Historical (XIX-XX century) washing plant "Józef"	quartz, dolomite, ankerite $Ca(Fe^{2+},Mg)(CO_3)_2$, kaolinite, illite	galena, sphalerite, barite	gypsum, goethite, anglesite $Pb(SO_4)$, smithsonite, cerussite, minrecordite $CaZn(CO_3)_2$, plumbojarosite $PbFe^{3+}_6(SO_4)_4(OH)_{12}$, jarosite $KFe^{3+}_3(SO_4)_2(OH)_6$, hydronium jarosite $(H_3O)Fe_3(SO_4)_2(OH)_6$, melanterite $FeSO_4\cdot7H_2O$
Near waste dump from smelting process	kalcite, quartz, ankerite, illite	galena, sphalerite	goethite, mullite, maghemite, hemimorfite, magnetite, magnesioferryte, hematite, gypsum, melilite, Ti-Al klinopiroksenite, monticellite, pirotyne, Zn,V,Mg spinels, mackinawite, srebrodolskite, Pb metalic, hydrotalkite group minerals

XRD methods allow to identify crystalline phases occurring in significant amount (>0,5%). In rhizosphere processes of secondary minerals forming proceed in submicroscopic scale, thus these phases can be investigated by SEM/EDS methods. In studied rhizospheres were identified:

1. metalliferous crystalline phases represented mainly by Zn, Pb, Fe sulphides, Ca, Pb, Fe sulphates, Zn and Pb carbonates, barite, rarely Zn silicates. Zircons, magnetites and apatites with REE come from fluvioglacial sands,
2. finely crystalline or cryptocrystalline and amorphous aluminosilicates, Ca-Mg carbonates, Ca-Mg-Fe carbonates, quartz,

3. finely crystalline and cryptocrystalline aggregates composed of Fe and Mn oxides or hydroxides, sometimes containing other metals (Zn, Pb),
4. spherical aluminosilicate forms and metalliferous phases with Fe, Zn, Pb, Mn, As,
5. aggregates built of organic matter, which metals (Zn, Fe, Pb, Mn) were identified in.

Main minerals which build studied soils are aluminosilicates and among them clay minerals and feldspars dominate. Silica occurs as a quartz, rarely as amorphous forms.
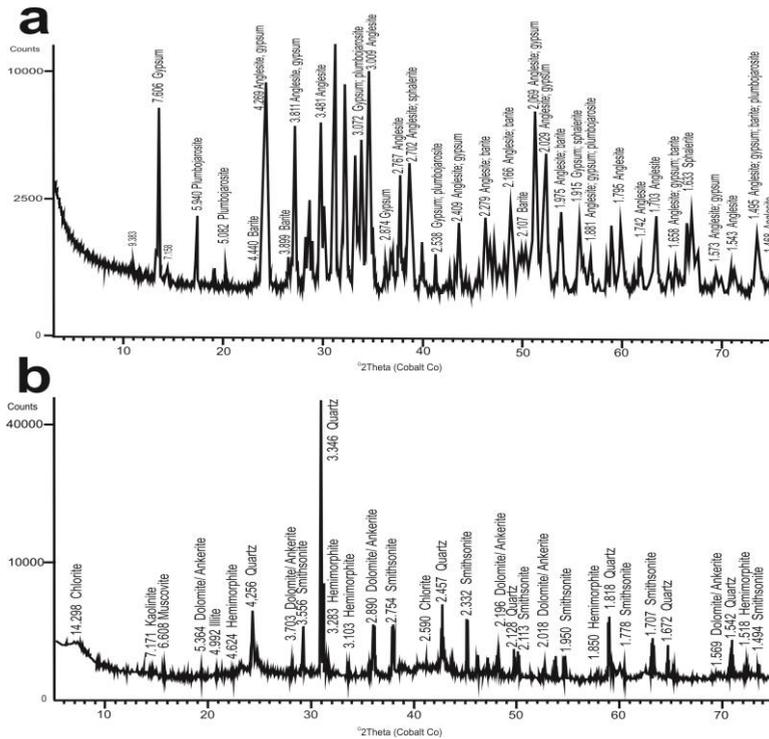

Fig. 2. XRD spectra. a – soil from washing plant "Józef" area, b – soil from non-sulphide Zn-Pb ore historical open pit area

In soils in direct vicinity of roots Fe, Mn, V oxides, barite, Fe-Zn sulphates, gypsum, Mn and Ti oxides, Cd carbonates, Zn silicates, arsenic-lead sulfosalts, zircon and apatite with REE were recognized. These minerals are generally in form of irregular grains, more rarely they have crystalline forms. They build coats, varnishes, botryoidal or skeletal forms.

Fe oxides and hydroxides are present almost in all studied soils and in their composition Zn and Pb are often identified (Fig. 3a, f; Fig. 4a, b).

Zn, Pb and Cd carbonates (Fig. 3c, e) occur in rhizospheres from areas of open pit exploitation. They have forms of submicroscopic, crystalline grains (0.5-20 μm) performing on epidermis or its direct vicinity. Rarely small, submicroscopic Zn sulphides grains (Fig. 3c) were observed, thus further changes of non-durable Zn sulphides can be possible and they can be a source of Zn^{2+} ions.

Others with regard to mineral composition are soils occurring in washing plant "Józef" region. In these soils among metalliferous minerals Pb, Fe sulphates and gypsum have a high share. There are a lot of Zn sulphides (Fig. 3b) and crystalline Pb sulphides (Fig. 3d). Zn sulphides grains surface has traces of dissolution (Fig. 3b), probably as a consequence of oxidizing development.

Globular and spheroidal aggregates with aluminosilicate composition are characteristic components, silica is represented often by mullite (Fig. 3c, f). Spherules surfaces show weathering traces involved with eolic transport or chemical dissolution. Their size reach to 50 μm, they can form botryoidal forms too. Some part of globular aggregates is built of metalliferous minerals, such as: Fe oxides and Pb carbonates (Fig. 3c, 4c). There were identified polymineral aluminosilicate forms also, where Fe, Mn, Zn, Pb, Cd and As were recognized in. Identification of submicroscopic phases in aluminosilicate aggregates is very difficult. Presence of silica globular forms and characteristic micropores in spherules indicate that they were formed in high temperature conditions.

In studied rhizospheres there were mycorrhizal fungi hyphae identified. On their surface carbonic cadmium bearing phases occur (Fig. 3e, 4d).
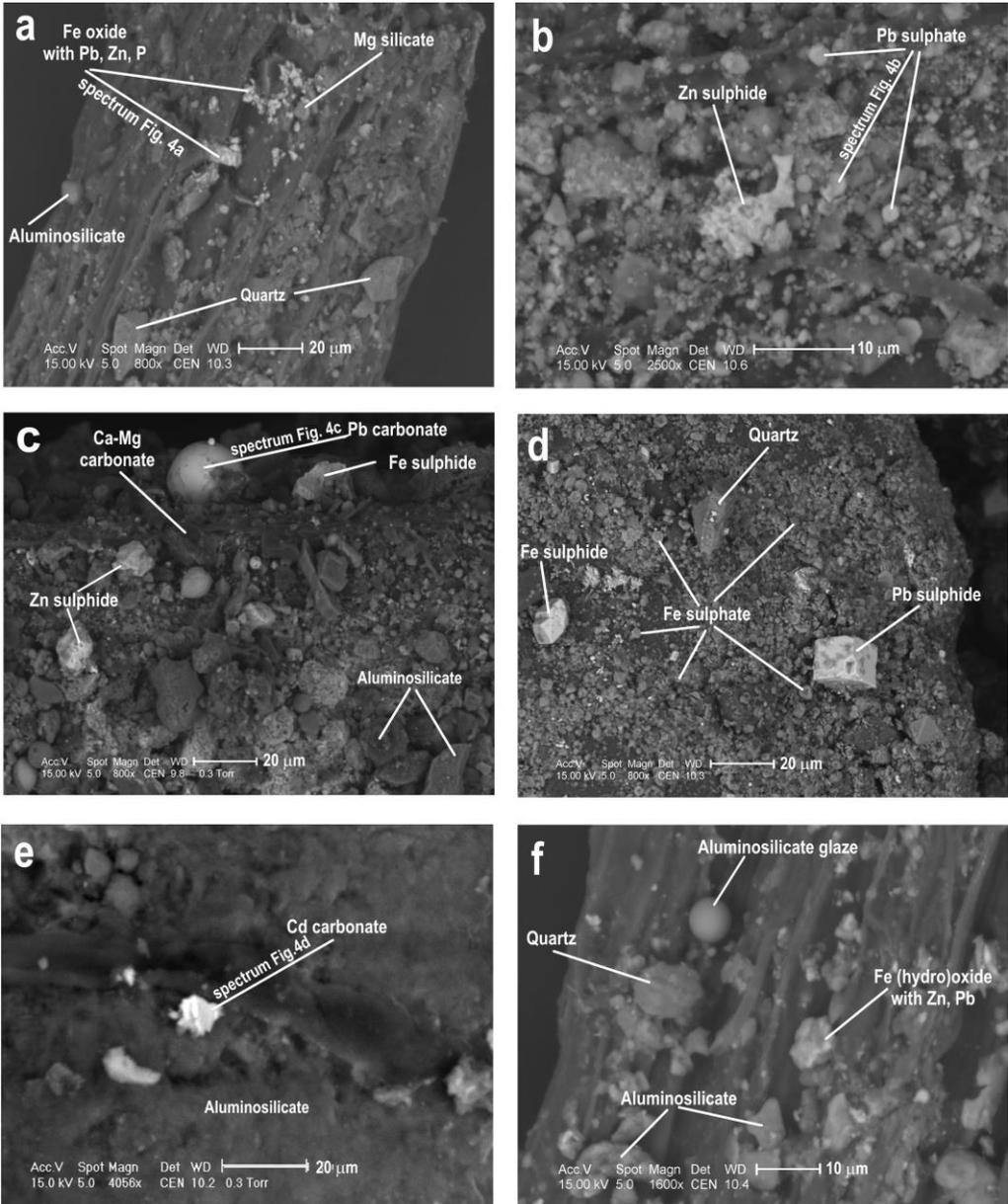
Fig. 3. BSE images: a – Festuca ovina rhizosphere, soil after reclamation, area of non-sulphide Zn-Pb ore historical open pit, b – Festuca ovina rhizosphere, initial soil, washing plant "Józef" area, c – soil from area of non-sulphide Zn-Pb ore historical open pit, d – initial soil, washing plant "Józef" area, mycorrhized rhizosphere, e – soil from area of non-sulphide Zn-Pb ore historical open pit, f – Festuca ovina rhizosphere, soil after reclamation, area of non-sulphide Zn-Pb ore historical open pit
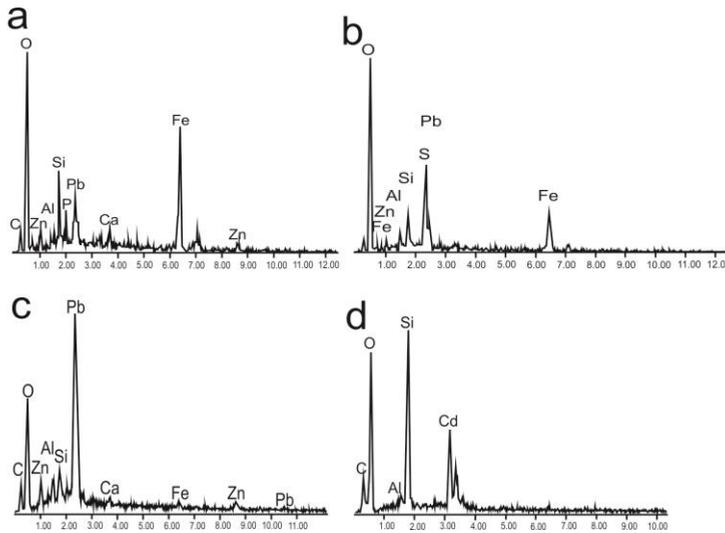
Fig. 4. EDS spectra a – Fe oxide with Pb, Zn, P; b – Pb sulphate on aluminosilicate and Fe oxide aggregate with Zn; c – Pb carbonate; d – Cd carbonate on silicate matrix

5. DISCUSSION

The metalliferous minerals frequently occurring in the investigated soils have a direct impact on the high levels of Zn, Pb, Fe, Cd, Tl identified in the area of the former washing plant and in calamine areas (Lis & Pasieczna, 1999). The concentration of Zn reaches 68 800 mg kg^{-1}, Pb – 85 060 mg kg^{-1}, Fe – 170 000 mg kg^{-1}, Cd – 369 mg kg^{-1} and Tl – 355 mg kg^{-1} (Cabała, 2009).

In the investigated soils from areas of shallow, former non-sulphide ore mining and washing plant "Józef" the most diverse complex of secondary mineral phases was observed. They were formed as a result of chemical changes of ore minerals in the shallow parts of the deposit or in the rhizosphere. In rhizospheres from areas of open pit exploitation the substantial part of HM (Zn, Pb, Cd) is attached to the crystal lattice of secondary carbonate minerals, zinc silicates were rarely identified (Tab. 1). The aggregates of iron oxides (Fig. 3a, f) in the crystal lattice of which zinc and lead were identified (Fig. 4a) are much more common. Considerable quantitative amount of Fe oxides enriched in Zn and Pb lead to the conclusion that in their structure a part of zinc and lead is stored. The low solubility factors of the Fe oxides, Zn and Pb carbonates and Zn silicates indicate that these metals can be delivered to the environment in a very low degree.

Occurrence forms and manner of some Fe oxides with Zn and Pb (Fig. 3a) may indicate that they could arise as a result of chemical transformations on the surface of

epidermis. However, only further research can clearly indicate whether the formation of metalliferous Fe oxides or other minerals is biochemically stimulated by root exudates.

The presence of diverse mineral phases crystallizing on epidermis is often the result of the development of secondary chemical transformations occurring in the soil environment. This process is best illustrated by the very frequent presence of crystalline gypsums in the cavities of epidermis (Cabała and Teper, 2007).

The presence of mycorrhizal fungi in the rhizospheres colonizing heavily contaminated soil in the area of washing plant "Józef" (Fig. 3b) and areas of open pit exploitation (Fig. 3e) indicates that the symbiotic fungi play an important role in the plant vegetation in the areas heavily contaminated with metals (Cabała et al., 2009). In the vicinity of mycorrhizal fungi hyphae the Cd-bearing carbonate phases were identified. Cadmium carbonates in the oxidation zones are the result of geochemical zinc separation from lead. There is no information whether $CdCO_3$ crystallization processes can be stimulated by biotic secretions of roots, fungi or microorganisms. J. Cabała (2009) drew attention on the fact of metal remobilisation (including Cd) in the immediate vicinity of the mycorrhisal roots. The research of (bio)chemical transformation is extremely important to clarify the processes of biotic metals remobilisation (Banfield et al., 1999). Submicroscopic size of these phases ($<3\mu m$) impede research.

6. SUMMARY AND CONCLUSIONS

The researches of metalliferous mineral phases in the environment of plant vegetation, fungi, algae and micro fauna are important for understanding the (bio)geochemical processes of HM (Zn^{2+}, Pb^{2+}, Cd^{2+}, Mn^{4+}, Tl^+) and metalloids (As, Sb, Se) remobilisation.

1. After 100 years, minerals from the historical wastes deriving from the Zn-Pb ore washing plant still undergo the geochemical transformations which evidence is the presence of unstable Fe and Pb sulfate.

2. In the soils contaminated with historical and contemporary wastes which are rich in Fe sulphides, the processes of acidic waste drainage develop and the presence of gypsum is one of their products.

3. The presence of synthetic spherical phases containing metals (Fe, Pb, Zn) or metalloids (As and Sb) in their compositions shows, that they come from the smelting emissions probably from the period when smelter processes of non-sulphide Zn-Pb ores were active (1950-1980).

4. The exudates of roots, fungi and bacteria may affect the chemistry and phase formation of secondary minerals in the zone of the rhizosphere, so further research of rhizospheres contaminated by HM may provide new data.

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