

Mineral composition and weathering processes in soils on oxidized zinc ore mine waste

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Introduction

Polish zinc and lead ores occur in the Triassic carbonate rock of the geological unit of the Silesian-Cracow Monocline. In the regions of Bolesław, Bukowno and Olkusz, where there are shallow and rich deposits of these ores, two types of ores were extracted: sulphide ores of zinc, lead, and silver, and the so-called calamine zinc ores (Cabała 2009, Cabała and Badera 2015). These two types of ores occur in Triassic ore-bearing dolomites. The mineral composition of sulphide ores is relatively simple. The prevailing sulphides are sphalerite, marcasite, pyrite, and galena, while other minerals are less frequent (Harańczyk 1962, Sass-Gustkiewicz and Kucha 2005). Part of the sulphide deposits, which occur in the tectonically uplifted areas, were exposed to weathering over the last several million years. As a result, the oxidation zone of sulphide ores, including oxidized zinc ores (calamine), was

formed (Cabała 2009). The main components of calamine ores are zinc carbonates, such as smithsonite, as well as goethite and cerussite (Żabiński 1960). Less common are hemimorphite and clay minerals (zinc-bearing sheet aluminosilicate) (Coppola et al. 2009), hydrozincite, sulphates of zinc and lead, and other minerals (Żabiński 1960, Cabała 2009).

Flotation tailings remaining after the enrichment of sulphide ore, extracted in a contemporary underground mine, is the main deposit in the post-mining area of the Olkusz region. Additionally, there is mine waste from opencast calamine ore mining in the 19th and 20th centuries (Liszka and Świć 2013). Millions of tonnes of waste have accumulated in heaps of different sizes. The active, vast flotation waste heap with a height of about 50 m above ground level towers the landscape. However, due to the processes of weathering and erosion, and consecutive reclamation work, heaps of mine waste are no longer prominent features of the area. Diverse vegetation has developed on these heaps as a consequence of

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either natural succession or deliberate introduction during reclamation work (Holeksa et al. 2015). The spontaneous colonization of mine waste by plants resulted in the development of unique calaminarian grassland communities with the buckler mustard (*Biscutella laevigata* L.) (Szarek-Łukaszewska et al. 2015, Jędrzejczyk-Korycińska and Szarek-Łukaszewska – Chapter 10 of this volume) and shallow skeletal soils. The characterization of these soils, in this chapter, is mainly based on studies by Jerzykowska (2013) and Jerzykowska et al. (2014). The methods used in the studies are summarized at the end of the chapter.

General characteristics

In the post-mining area around Olkusz, Bolesław and Bukowno, soils were formed mostly on dolomites, limestones, sands, conglomerates, claystones, and on post-industrial waste heaps. Soils formed on mine waste, in the area where calamine ores were extracted, are mostly initial rendzinas with poorly developed soil profiles, classified as Technosols (IUSS Working Group WRB 2007). According to the Polish classification (Kabała et al. 2019), they may be considered anthropogenic soils the type of 11.2. technogenic soils (AI). The detailed description of soils in these areas is given in Gruszczyński et al. (1990).

The profiles of soils on mine waste show similar characteristics to brown pararendzinas or poorly developed brown soils (Leptosols or Cambisols according to IUSS Working Group WRB, 2007) (Jerzykowska 2013, Jerzykowska et al. 2014). They are characterized by neutral or alkaline pH (from 6.8 to 7.9) and high content of skeletal components. According to the particle size distribution classification of the Polish Society of Soil Sciences 2008 (Anonymous, 2009), most of these soils can be classified as sandy loam (bordering on light loam and clay).

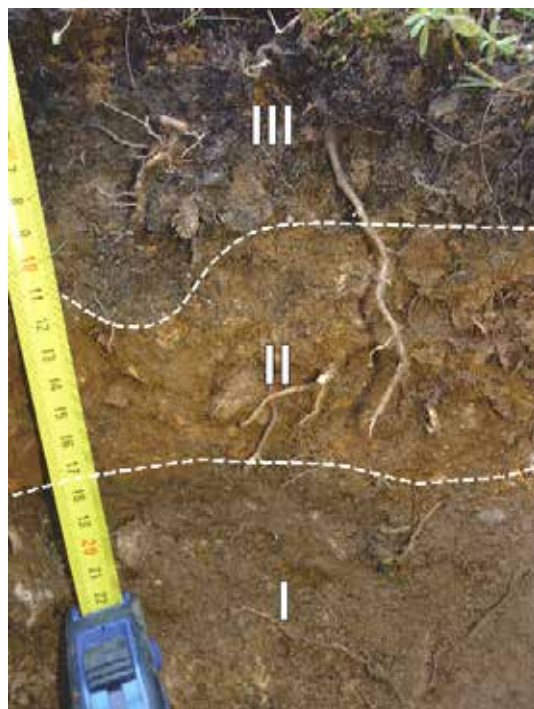


Fig. 1. Typical soil profile on mine waste heaps. I – heap material (wastes), II – mineral horizon, III – organic horizon (from Jerzykowska 2013)

Ryc. 1. Typowy profil glebowy gleby na hałdach odpadów górniczych. I – materiał odpadów, II – poziom mineralny, III – poziom organiczny (za Jerzykowska 2013)

During field observations, one can usually distinguish two horizons in the soil profile formed on the gravel substrate of the heap (Fig. 1). In the lower beige-yellow mineral soil horizon, which shows signs of browning, mineral components prevail over organic ones. The upper grey-brown humic horizon is characterized by a high content of humus, numerous skeletal components, single organic-mineral aggregates, and loose organic material.

Mineral composition

Material deposited in heaps (i.e. mine waste) is composed mainly of gravel fraction, and dolomite prevails in its mineral

composition. There are also small amounts of iron oxides, smithsonite, calcite, quartz, clay minerals, hemimorphite (Fig. 2) and manganese oxides (0.1–0.2% parts by weight). The mineral composition of soils is similar to that of mine waste, but the proportions of minerals are different; there is less dolomite and more iron oxides and clay minerals. The uppermost horizons contain a notable amount of quartz of aeolian origin, fragments of organic matter, and atmospheric dusts (Fig. 2).

Figures 3 and 4 show the photomicrographs of soils from mine waste heaps, obtained using scanning electron microscope (SEM) imaging. They show minerals occurring in these soils, which are described in detail below: dolomite, smithsonite, hemimorphite, zinc-containing sheet aluminosilicates, manganese, and iron oxides.

Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is a major mineral in the substrate of soils on mine waste. It is the principal mineral component of ore-bearing dolomites, in which the primary mineralisation of zinc-lead-iron sulphides occurs. Dolomite usually occurs in the form of rock fragments (Fig. 3A) and, less commonly, single crystals. Occasional corrosion cracks and pits are evidence of dolomite dissolution in the soils. Cavities in dolomite are often filled with other minerals, e.g. smithsonite, or iron oxides.

Smithsonite (ZnCO_3) is the most common zinc-bearing mineral in mine waste heaps and their soils. It occurs in the form of massive (up to several cm), irregular aggregates, which fill voids and cracks in dolomite (Fig. 3A). Alternatively, smithsonite occurs in the form of idiomorphic, colomorphous aggregations of minute acicular or tabular crystals (Fig. 3B), and less commonly, as isometric (dodecagonal) pseudomorphic sphalerite crystal remains (Fig. 3C). The surface of some smithsonite grains and aggregates is etched (Fig. 3D), mostly those occurring in the mineral and humic horizons

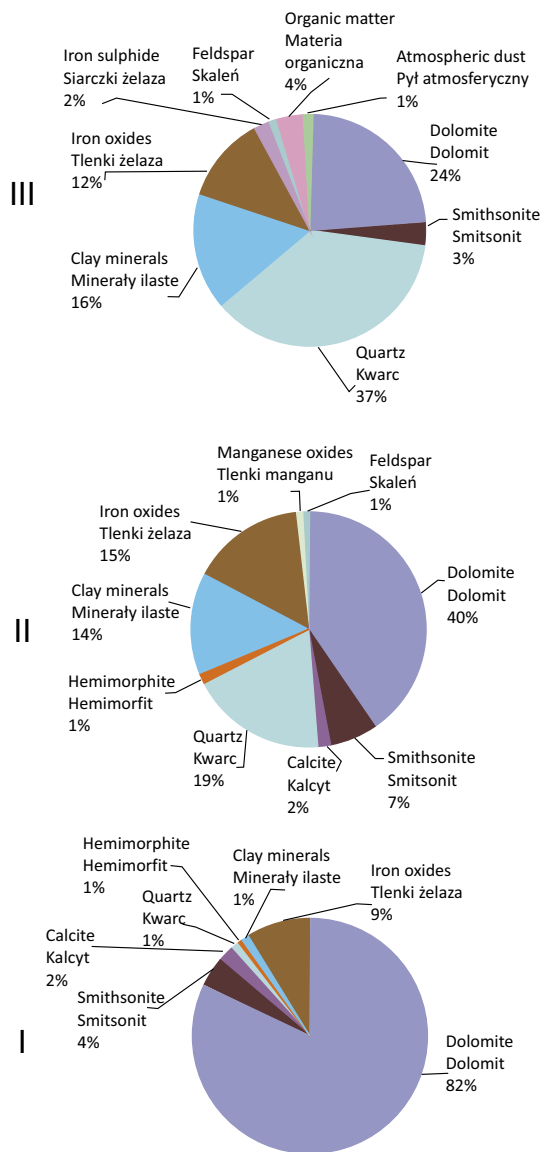


Fig. 2. Mineral composition of soil horizons (I, II, III) in soil profile of mine waste heaps (according to microscopy and XRD analyses). I – dump material (wastes), II – mineral horizon, III – organic horizon (from Jerzykowska 2013)

Ryc. 2. Skład mineralny poziomów (I, II, III) wyodrębnionych w profilu glebowym gleb na hałdach odpadów górniczych (według obserwacji mikroskopowych i wyników dyfrakcji rentgenowskiej). I – materiał odpadów, II – poziom mineralny, III – poziom organiczny (za Jerzykowska 2013)

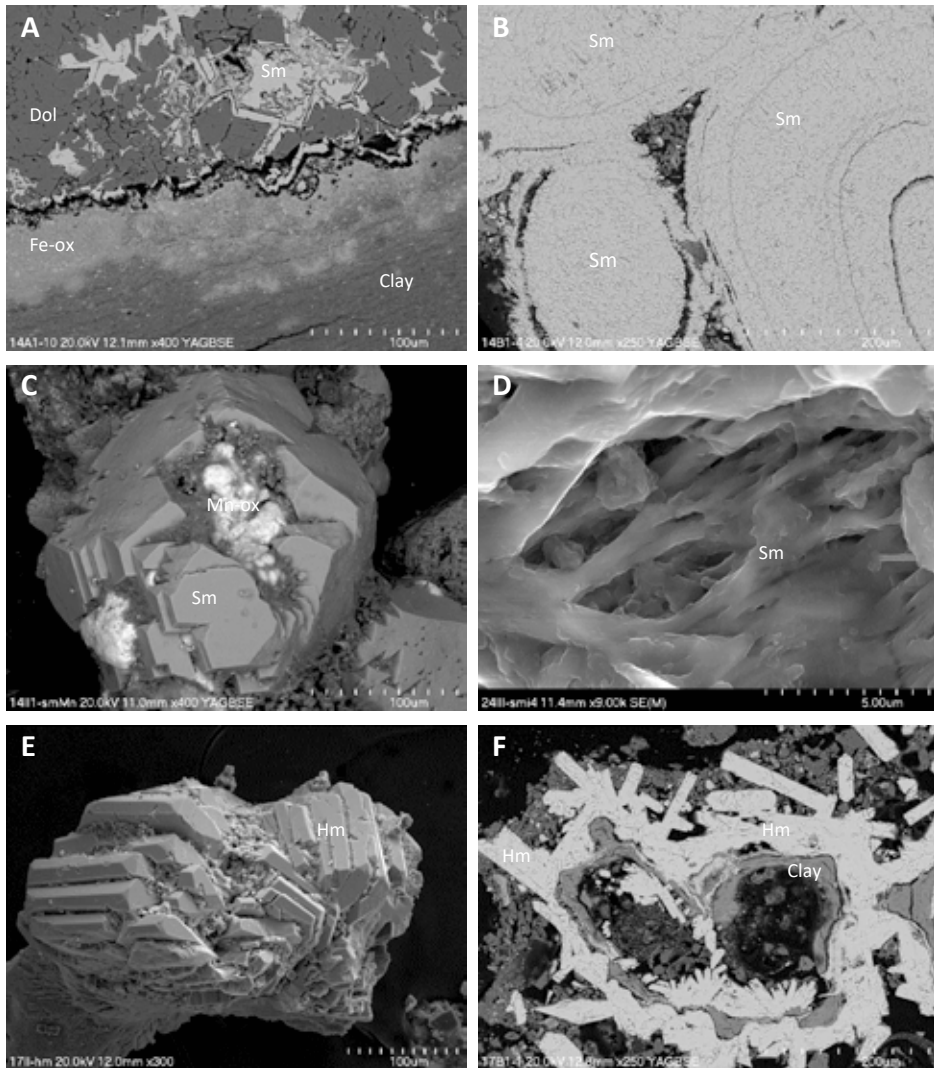


Fig. 3. Scanning electron microphotographs (SEM) of soil (for details of the method see Jerzykowska et al. 2014) samples of mine waste heaps: A – pores in dolomite filled with smithsonite, iron-oxide and clay envelope, B – colomorphic smithsonite aggregate, C – smithsonite pseudomorph after sphalerite and the accumulation of manganese oxides, which are rich in lead, D – etch pits in smithsonite, E – an aggregate of platy hemimorphite crystals, F – zinc containing sheet silicates as filling of cavities in an aggregate of hemimorphite crystals, clays filled pores. Back scattered electron images (BSE): A, B, F; secondary electron images (SE): C, D, E (from Jerzykowska 2013). Dol – dolomite, Sm – smithsonite, Fe-ox – iron oxides, Mn-ox – manganese oxides with lead impurities, Hm – hemimorphite, Clay – mineral aggregates

Ryc. 3. Mikrofotografie preparatów z gleb hałd odpadów górniczych wykonane przy pomocy skaningowego mikroskopu elektronowego (SEM): A – pory w dolomicie wypełnione smithsonitem, otoczka ilasto-żelazista, B – kolomorficzne skupienie smitsonitu, C – pseudomorfoza smithsonitu po sfalerycie i skupienie tlenków manganu bogatych w ołów, D – rozpuszczony smithsonit, E – skupienie płytkowych kryształów hemimorfitu, F – płytkowe skupienie hemimorfitu, ilaste wypełnienie porów. Obraz elektronów wstecznie rozproszonych (BSE): A, B, F; obraz elektronów wtórnych (SE): C, D, E (za Jerzykowska 2013). Dol – dolomit, Sm – smithsonit, Fe-ox – tlenki żelaza, Mn-ox – tlenki manganu z domieszką ołowiu, Hm – hemimorfit, Clay – agregaty ilaste

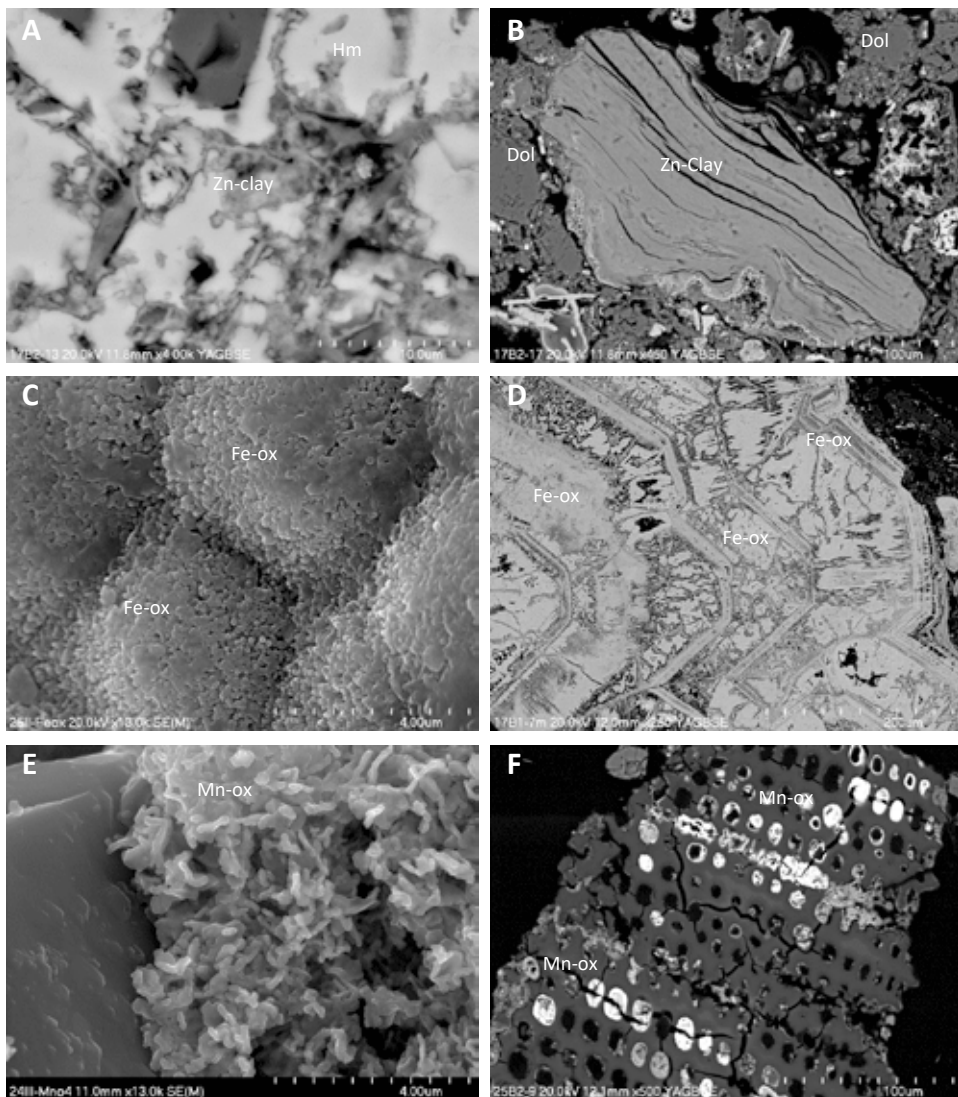


Fig. 4. Scanning electron microphotographs (SEM) of soil samples of mine waste heaps: A – cavities in hemimorphite filled with zinc-containing sheet silicates, B – zinc containing sheet silicate plate, C – an aggregate of iron oxides, D – etched iron-oxide aggregate, E – an aggregate of manganese oxides, F – pores in organic matter particle filled with lead rich manganese oxides. Back scattered electron images (BSE): A, B, F; secondary electron images (SE): C, D, E (from Jerzykowska 2013). Zn-clay – zinc containing sheet silicate plate, Fe-ox – iron oxides, Mn-ox – manganese oxides, Dol – dolomite

Ryc. 4. Mikrofotografie preparatów z gleb wykonane przy pomocy skaningowego mikroskopu elektronowego (SEM): A – szczeliny w rozpuszczonym hemimorficie wypełnione glinokrzemianami warstwowymi z cynkiem, B – blaszka glinokrzemianu warstwowego z cynkiem, C – skupienie tlenków żelaza, D – konkrecja tlenków żelaza nosząca ślady rozpuszczania, E – skupienie tlenków manganu, F – pory w fragmencie materii organicznej wypełnione tlenkami manganu bogatymi w ołów. Obraz elektronów wstecznie rozproszonych (BSE): A, B, F; obraz elektronów wtórnych (SE): C, D, E (za Jerzykowska 2013). Zn-clay – glinokrzemiany warstwowowe z cynkiem, Fe-ox – tlenki żelaza, Mn-ox – tlenki manganu, Dol – dolomit

of soils. Zinc-bearing aluminosilicates, or iron oxides sometimes fill etching cracks.

Hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot (H_2O)$) occurs in some soils, and infrequently in the waste heap material. The most common forms are rosette clusters of tabular crystals (Fig. 3E, F). In some places, hemimorphite crystals have been observed coating the rounded grains of quartz, iron oxides, dolomite and clay minerals in soil aggregates which consist of small grains of aluminosilicates with zinc and iron, dolomite and feldspar. These crystals are also found among acicular iron oxides, which may indicate that they were formed during pedogenesis. The analysis of BSE images (taken using a type of SEM imaging explained later) showed few marks of hemimorphite etching. In pits and cracks in the etched hemimorphite there are some phases of similar structure and chemical composition as iron oxides and zinc-bearing aluminosilicates (Fig. 4A).

Zinc-bearing sheet aluminosilicates were found in all the investigated grassland soils. They form aggregates of platy crystals, often with iron oxides and organic matter (Fig. 4A), or less commonly, single plates (Fig. 4B). Diffraction analyses of the clay fraction show the presence of minerals from the smectite and kaolinite group (Jerzykowska et al. 2014). The high content of zinc, as shown in most analyses of platy minerals, may suggest that the samples contain minerals similar to saunonite ($Na_{0,3}Zn_3(Si,Al)_4O_{10}(OH)_2 \cdot 4(H_2O)$) – trioctahedric zinc-smectite, and fraipontite ($((Zn,Al)_3(Si,Al)_2O_5(OH)_4)$ – trioctahedric mineral belonging to the serpentine-kaolinite group, originating from smithsonite through weathering processes (Jerzykowska 2013, Jerzykowska et al. 2014).

Iron oxides commonly occur in the soil, and less abundantly in the substrate (material from the heap). They form veins, coatings, and aggregates of different types (e.g acicular,

or botryoidal (Fig. 4C)), commonly with clay minerals and organic matter in the soil. In places, they fill pores or replace organic fragments. The microdiffraction analyses (μ XRD), using synchrotron radiation, has shown that most iron oxides occur as fine-crystalline goethite ($\alpha\text{-Fe}^{3+}O(OH)$) (Jerzykowska et al. 2014). Marks of iron oxides dissolving are scarce (Fig. 4D).

Manganese oxides occur mainly in the soil, and in small amounts in the waste material. They form porous aggregates of lamellar, acicular or ‘worm-like’ structures (Fig. 4E), coatings, veins, and pore-fillings

Table 1. The mean content [wt. %] of zinc (Zn), lead (Pb), arsenic (As) and cadmium (Cd) in selected minerals from soil on mine waste heaps, calculate on the basis of the chemical composition of soil determined by electron microprobe analyses (EPMA) (base on Jerzykowska 2013)

Tabela 1. Średnia zawartość [% wag.] cynku (Zn), ołowiu (Pb), arsenu (As) i kadmu (Cd) w wybranych minerałach gleb na hałdach odpadów górniczych, obliczona na podstawie składu chemicznego określonego za pomocą mikroskopy elektronowej (EPMA) (za Jerzykowska 2013)

Mineral Minerał	n	Zn	Pb	As	Cd
		[wt. %] [% wag.]			
Dolomite Dolomit	18	0.29	0.13	n.d.	0.03
Smithsonite Smithsonit	18	50.49	1.23	0.02	0.18
Hemimorphite Hemimorfit	27	57.21	0.07	0.03	0.01
Zinc-rich sheet aluminosilicates Glinokrzemiany cynku	28	18.05	0.54	0.02	0.004
Iron oxides Tlenki żelaza	212	5.02	1.29	0.15	0.03
Manganese oxides Tlenki manganu	20	5.73	12.87	0.03	0.05

n – number of measurements

n – liczba pomiarów

n.d. – not detected

n.d – nie wykryto

in organic matter (Fig. 4F). Their composition and forms in which they occur indicate that they represent biogenic birnessite $((\text{Na,Ca,K})_x(\text{Mn}^{4+},\text{Mn}^{3+})_2\text{O}_4 \cdot 1.5(\text{H}_2))$ whose formation is catalysed by bacteria and fungi (Kwon et al. 2010). Of all manganese oxides, birnessite has the highest capacity for lead accumulation (O'Reilly 2002). The analyses of chemical composition in the microarea have shown that the aggregates of manganese oxides contain high amounts of lead (Table 1).

The described minerals contain many toxic elements, including zinc, lead, arsenic, and cadmium, which are the most notable environmental pollutants (Table 1). The main sources of zinc are smithsonite, clay minerals, and hemimorphite. Cadmium occurs mostly as an admixture in smithsonite. Arsenic is found with iron oxides. Whereas lead is mostly found with manganese oxides and, in smaller amounts, with iron oxides. Dolomite is also an important carrier of harmful elements. It contains only a small admixture of these elements, but it constitutes almost half of the mineral mass of soils.

Pollution

The main sources of soil pollution in the post-mining area are wastes from the mining and processing of ores, uncontrolled emissions (i.e. dusting from places where waste is deposited, such as spoil heaps and flotation tailings heaps), and emissions from smelters processing zinc-lead ores (e.g. Verner et al. 1996, Lis and Pasieczna 1999). All types of waste contain high amounts of heavy metals (zinc, lead, arsenic, cadmium).

Zinc, lead, arsenic and cadmium are elements that pose a threat to plants, animals, and humans (e.g. Kabata-Pendias 2011). Table 2 shows the total content of these elements in the soils of mine waste heaps. These concentrations

are much higher than the geochemical background of the Silesian-Cracow area (Table 2). According to the Regulation of the Ministry of Environment on soil quality standards in Poland, as of 5 September 2016 (Journal of Law 2016, item 1395) soil is considered to be polluted when the concentration of at least one substance exceeds the acceptable value. The soils of mine waste heaps are strongly polluted. Concentrations of all metals in these soils exceed the standards for soils of industrial and mine

Table 2. The mean total content [mg/kg] of zinc (Zn), lead (Pb), arsenic (As) and cadmium (Cd) in mining wastes and soil horizons (I, II, III) of heaps. I – heap material, II – mineral horizon, III – organic horizon. Geochemical background in soils of the Silesian-Cracow region from Lis and Pasieczna (1999), limit values for concentrations of elements in soils and grounds of industrial areas, fossil lands and communication areas according to the Act of the Ministry of the Environment, 5th September 2016 (Journal of Laws 2016 item 1395)

Tabela 2. Średnia całkowita zawartość [mg/kg] cynku (Zn), ołowiu (Pb), arsenu (As) i kadmu (Cd) odpadach górniczych i poziomach glebowych (I, II, III) hałd. I – materiał hałd, II – poziom mineralny, III – poziom organiczny. Tło geochemiczne w glebach regionu śląsko-krakowskiego za Lis i Pasieczna (1999), wartości dopuszczalne stężeń pierwiastków w glebie lub ziemi terenów przemysłowych, użytków kopalnych i terenów komunikacyjnych według Rozporządzenia Ministra Środowiska z dnia 5 września 2016 r. (Dz.U. 2016 poz. 1395)

Soil Horizon Poziom glebowy	n	Zn	Pb	As	Cd
		[mg/kg]			
I	8	26460	1372	111	154
II	9	26769	989	109	153
III	8	28049	838	88	166
Geochemical background Tło geochemiczne	1564	104	44	<5	1.3
Standard for soil contamination Norma zanieczyszczenia gleby	–	2000	600	100	15

n – number of measurements
n – liczba prób

areas. Also, according to the scale used by the Institute of Soil Science and Plant Cultivation (IUNG) in Puławy these soils are very polluted. Soils strongly contaminated by zinc, cadmium and lead are often called metalliferous soils, or calamine soils (e.g. Baker et al. 2010).

It is not, however, the total (absolute) content of a harmful element in the soil which determines its toxicity to the environment. The

mobility and bioavailability of the element is important. The immobility or mobility of an element in the soil, its accumulation in plants, and further uptake by animals and humans depends primarily on the form in which it occurs and physicochemical conditions in the weathering environment (e.g. pH, redox potential, temperature). In the soil, heavy metals and other toxic elements may occur

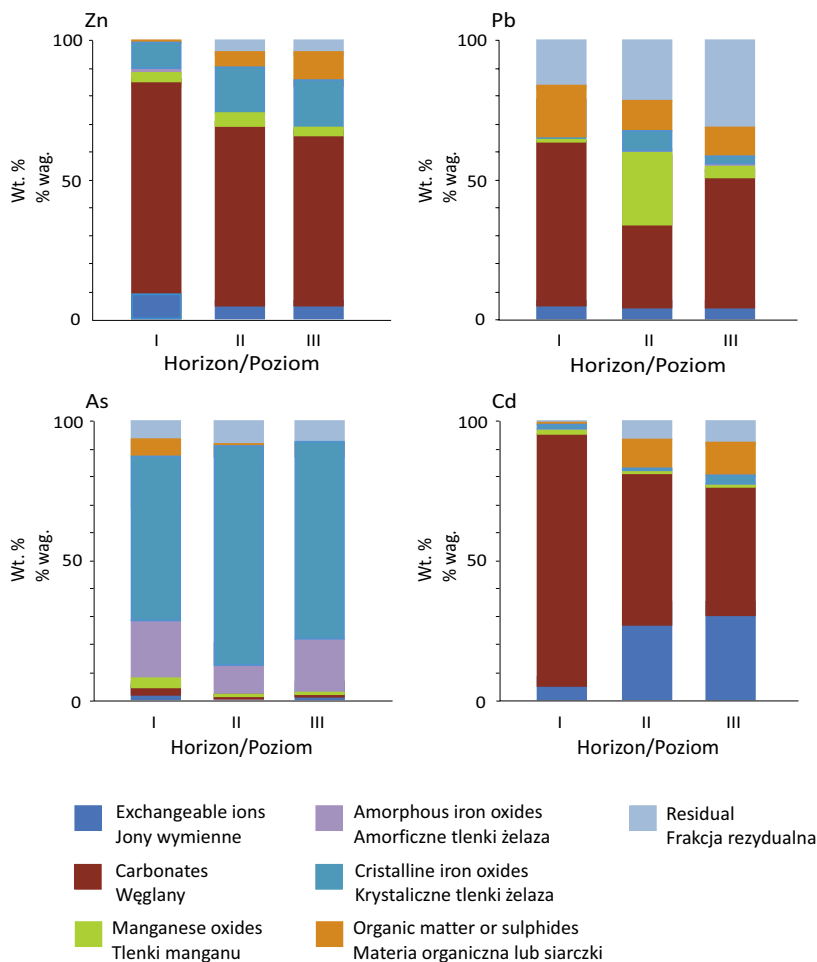


Fig. 5. Percentage [wt. %] of zinc (Zn), lead (Pb), cadmium (Cd) and arsenic (As) in fractions of sequential extractions of soil horizons (I, II, III) of soils on mining waste heaps. I – waste materials, II – mineral horizon, III – organic horizon (from Jerzykowska 2013)

Ryc. 5. Zawartość procentowa [% wag.] cynku (Zn), ołowiu (Pb), kadmu (Cd) i arsenu (As) w poszczególnych etapach (frakcjach) ekstrakcji sekwencyjnej gleby w warstwach (I, II, III) wyodrębnionych w profilu glebowym gleb na hałdach odpadów górniczych. I – materiał odpadów, II – poziom mineralny, III – poziom organiczny (za Jerzykowska 2013)

in the structure of primary ore minerals, or secondary phases that are formed during the process of weathering and pedogenesis such as minerals, organic-mineral complexes, and dissolved, or adsorbed ions. Dissolved ions and some of the adsorbed ions are readily available to plants (Cabała 2009). Also, in the long term, elements occurring in theoretically more stable forms can be made available as a result of changes in the environmental conditions (e.g. a decrease in pH).

Figure 5 shows the forms of zinc, lead, cadmium and arsenic in the waste and in the two horizons of calamine soils, identified using one of the applicable methods, specifically the seven-step sequential extraction procedure. Zinc, lead and cadmium are found mostly in the carbonate fraction and arsenic is mostly found in crystalline and amorphous iron oxides. Zinc is also associated with the fraction of crystalline iron oxides. Lead occurs in the soil alongside manganese oxides and sulfides, and considerable amounts of cadmium which are present in the form of exchangeable ions.

Using the results of extraction, one can assess the mobility of particular elements by calculating the mobility index, i.e. the ratio of the element concentration in mobile fractions to the total content of this element in all fractions. The classic mobility index (MI) (Gworek and Mocek 2003, Kashem et al. 2011), referred to from now on as potential mobility, implies that the first two fractions (exchangeable and carbonate) contain mobile elements, while the remaining fractions are treated as immobile. In soils with neutral or alkaline pH, only the first fraction of exchangeable ions should be treated as mobile. Therefore, in addition, it is important to calculate the index of temporary mobility – MI* (Jerzykowska 2013). A decrease in environmental pH (increasing acidity) may result in the activation of elements from carbonate fraction, therefore both indices

are useful to assess the temporary and potential mobility of a given element. The mobility indices, calculated for soils of calaminarian grasslands, show that cadmium is the most readily available element in these soils. However, zinc and lead are also potentially easily released (Table 3). Arsenic is least mobile.

The sequential extraction procedure is relatively simple and not expensive; therefore, it is widely used to determine the mobility of heavy metals in the environment. It has, however, some drawbacks. The main disadvantages of sequential extraction are non-selective reagents, and the redistribution and re-adsorption of metals (Gleyzes et al. 2002, Cappuyns et al. 2007). Redistribution of elements to other forms occurs most often in samples with high concentrations of metals (Cappuyns et al. 2007). Fractions that are determined using this method do not correspond to the specified mineral phases (Anju and Banerjee 2010, Hayes et al. 2009). Therefore, to determine zinc, lead, cadmium, and arsenic mobility in the soils on mine waste, the results of extraction

Table 3. Potential and temporary mobility indexes of zinc (Zn), lead (Pb), arsenic (As) and cadmium (Cd) calculated on the base of results of sequential extraction of heap soils

Tabela 3. Indeksy mobilności potencjalnej (MI) i chwilowej (MI*) dla cynku (Zn), ołowiu (Pb), arsenu (As) i kadmu (Cd) obliczone na podstawie wyników ekstrakcji sekwencyjnej gleb nawałdach

Index Indeks	Zn	Pb	As	Cd
MI %	68.56	61.70	4.54	87.11
MI* %	6.13	4.10	0.95	22.03
Mobility order Szereg mobilności	Cd > Zn > Pb > As			

MI, MI* calculated according the formula:
MI, MI* liczone według wzorów:

$$MI = (FI + FII) / [(FI + FII + FIII + FIV + FV + FVI + FVII) \cdot 100\%]$$

$$MI* = FI / [(FI + FII + FIII + FIV + FV + FVI + FVII) \cdot 100\%]$$

procedure were compared with the results of mineralogical analyses.

The results of sequential extraction (Table 3) partly confirm the microscope observations of grassland soils on mine waste (see Figs 2–4). In these soils, the occurrence of zinc is often associated with the occurrence of cadmium. Both of them replace calcium in the structure of dolomite, and cadmium replaces zinc in the structure of smithsonite, which is common in mine waste and soils on waste material, hence they prevail in carbonate fractions. Hemimorphite and sheet aluminosilicates are dissolved most likely with carbonates as well as with crystalline and amorphous fractions of iron oxides. This observation has not been directly confirmed and needs further verification. In the soils of waste heaps, zinc is also adsorbed by amorphous and crystalline iron oxides. The occurrence of arsenic in the fraction of iron oxides is confirmed by the results of microscopic analyses. Analyses of the chemical composition of minerals in the microarea (EMPA) (see Table 1) showed that the highest lead concentrations are in manganese oxides. This is somewhat inconsistent with the results of sequential extraction, which showed that lead prevails in carbonate fraction. There may be two explanations for this: either (1) the reagent solvating carbonates causes partial desorption of lead from manganese oxides, or (2) the samples contain fine-grained lead carbonate which was overlooked during microscope observations and chemical analyses in the microarea.

Mineral transformations and their impact on the bioavailability of metals

Soil is a natural, three-phase weathering environment where intense chemical processes, called pedogenesis, are at work in the interface

between lithosphere, hydrosphere, biosphere, and atmosphere. The main factors governing weathering processes and soil formation are temperature, pH, redox potential, and the presence of ions in soil solutions. The most intense weathering processes occur in soils with an acidic pH, but they may also occur in a neutral environment. The most important physicochemical processes occurring in the soil are dissolution and precipitation, sorption and desorption, acidification and alkalization, oxidation and reduction, peptization and coagulation, and diffusion (Dziadek and Waclawek 2005). Most processes that are important from the point of view of soil contamination occur in the contact area between the solid phase (mineral and organic components of soil) and liquid phase (soil solution).

Evidence of the mobility of heavy metals, and consequently their availability to plants has been demonstrated in the soils of calaminarian grasslands, formed on old mine waste heaps. Direct evidence of the mobility of elements (including heavy metals) in the soils is provided by scanning electron microscope (SEM) imaging which shows the effect of dissolution of minerals i.e. corrosion crevices and pits on the surface of minerals (see Figs 3, 4). The released elements get into the soil solutions where part of them is immediately precipitated in the form of secondary minerals, or adsorbed by mineral or organic mineral compounds, while part of them remain in the form of exchangeable ions (bioavailable) in soil solution.

Processes occurring in the soils on mine waste heaps are shown in Figure 6. The accumulated mine waste with residues from zinc ores occur in the form of gravel fraction grains. Soil forming processes result in the granular disintegration of rock and minerals (Fig. 6A), the size of grains in the upper soil horizons decreases, and consequently, the active surface of minerals (surface affected by weathering

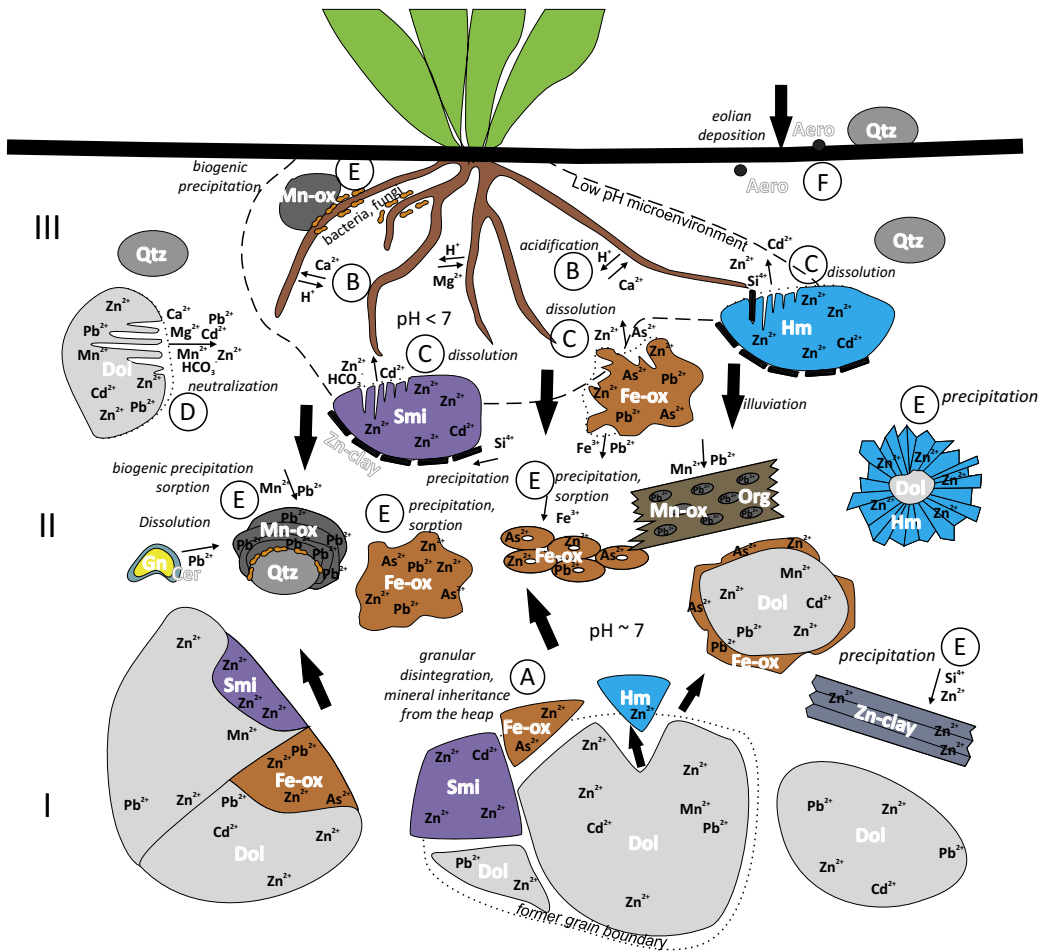


Fig. 6. An outline of processes occurring in soil profiles on mine waste heaps. Explanations of A, B, C, D, E, F in the text. Soil horizons: I – waste materials, II – mineral horizon, III – organic horizon. Aero – aerosol particles, Cer – cerussite, Dol – dolomite, Fe-ox – iron oxides, Gn – galena, Hm – hemimorphite, Mn-ox – manganese oxides, org – organic matter particles, pH – reaction, Qtz – quartz, Smi – smithsonite, Zn-clay – zinc containing sheet silicates, Ions: As^{2+} – arsenic, Ca^{2+} – calcium, Cd^{2+} – cadmium, Fe^{3+} – iron, H^+ – hydrogen, HCO_3^- – bicarbonate, Mg^{2+} – magnesium, Mn^{2+} – manganese, Pb^{2+} – lead, Zn^{2+} – zinc

Ryc. 6. Schemat procesów zachodzących w glebach wykształconych na hałdach odpadów górniczych. Objasnienia do A, B, C, D, E, F w tekście. Warstwy w profilu glebowym: I – warstwa odpadów, II – warstwa mineralna, III – warstwa organiczna. Aero – aerozole, Cer – cerusyt, Dol – dolomit, Fe-ox – tlenki żelaza, Gn – galena, Hm – hemimorfit, Mn-ox – tlenki manganu, org – szczątki organiczne, pH – odczyn, Qtz – kwarc, Smi – smithsonit, Zn-clay – glino-krzemiany warstwowe z cynkiem. Jony: As^{2+} – arseniu, Ca^{2+} – wapnia, Cd^{2+} – kadmu, Fe^{3+} – żelaza, H^+ – wodoru, HCO_3^- – wodorowęglanowe, Mg^{2+} – magnezu, Mn^{2+} – manganu, Pb^{2+} – ołowiu, Zn^{2+} – cynku

Descriptions in Polish:

acidification – zakwaszenie, bacteria – bakterie, biogenic precipitation – biogeniczne strącanie, dissolution – rozpuszczanie, eolian deposition – depozycja eoliczna, former grain boundary – wcześniejsza granica ziarna, fungi – grzyby, granular disintegration – dezintegracja ziarnowa, mineral inheritance from the heap – dziedziczenie minerałów z hałdy, illuviation – wmywanie, low pH microenvironment – mikrośrodowisko o niskim pH, neutralization – zobojętnianie, precipitation – strącanie, sorption – sorpcja

processes) increases. In the uppermost soil layer, the weathering of minerals and mobilization of elements are greatly influenced by rhizosphere, and particularly by mycorrhized roots (Cabała 2009). The activity of roots and microorganisms stimulates mineral transformation processes (e.g. Cabała et al. 2004, Cabała 2009). As a result of the uptake of nutrients by roots, hydrogen ions (H^+) are released, acidifying the soil zone around roots, rhizosphere (Dakora and Phillips 2002) (Fig. 6B). The occurrence of weathering microenvironments whose properties are different from those of the whole soil volume, has been well characterized (e.g. Morton and Hallsworth 1999, Lång 2000, Skiba 2003, Cabała et al. 2004, Jerzykowska et al. 2006).

Although the range of root activity is limited to a 5 mm radius, the soil environment conditions can change considerably because of the dense network of roots (Cabała 2009, Dotaniya and Meena 2015). A local decrease in pH to pH 7 (neutral) may cause the dissolution of solid minerals. An acidic medium (pH < 7) results in the dissolution of smithsonite and hemimorphite (Fig. 6C), which releases zinc and cadmium, and the dissolution of dolomite, which releases zinc, cadmium and lead to soil solutions. Observations using a microscope have given lots of evidence for the dissolution of these minerals (cf. Figs 3, 4). The dissolution of dolomite results in the neutralisation of the acidic pH and stops further dissolution processes (Fig. 6D).

Neutral pH in most of the soil volume and the availability of carbonate ions (CO_3^{2-}) and others may cause quick precipitation of the released ions of zinc, lead and cadmium in the form of carbonates or silicates and their sorption on iron oxides. Lead sorbs mostly on manganese oxides (Fig. 6E) when lead carbonates, which according to Cabała (2009) stabilize lead most quickly in these soils, are scarce. In

the soils of waste heaps, numerous secondary minerals have been observed, for example, hemimorphite forming rosette clusters on quartzite, clay minerals (sheet aluminosilicates) (see Fig. 4A, B) forming organic-mineral aggregates in the soils, and secondary iron and manganese oxides, which are precipitated in porous organic matter in the soil, for example (Fig. 6E). The weakest sorption was found in the case of cadmium, as demonstrated also by the results of extraction analyses (see Fig. 5), indicating its high mobility.

Iron oxides (mostly goethite) occur commonly in the soils of mine waste heaps in the forms of veins, aggregates, coatings, and substitutes of organic fragments (see Fig. 4F). Part of them may come from ores, and part is formed in the course of pedogenesis. All of them have high capacity to sorb different elements, above all arsenic but also zinc, lead, and cadmium. Goethite is a mineral which dissolves slowly and sparingly in typical soil solutions of neutral and alkaline pH (Cornell and Schwertmann 2003). However, its poor crystallinity and the added presence of microenvironments with lower pH (within the rhizosphere) may result in the dissolution of this mineral and mobilization of zinc, cadmium and arsenic (Fig. 6C). Processes occurring in the root-soil interface may also lead to changes in redox conditions (Hinsinger 2001) and contribute to the dissolution of iron and manganese oxides (Fig. 6C). However, arsenic is very quickly resorbed by iron oxides, which results in its low mobility, as shown by extraction analyses (see Table 3).

A very interesting phase or aggregate of minerals occurring in the soils of calaminarian grasslands are manganese compounds which form fine acicular structures (see Fig. 4E) that are capable of sorbing high amounts of lead (see Table 1). Their form and chemical composition show that they may be birnessite, whose formation in the soil is catalysed by bacteria

(Tebo et al. 2004). Cabała (2009) noticed that organic components of the rhizosphere were enriched in manganese. Specifically, these grains of manganese compounds often occurred in the form of coatings and encrustations in the rhizosphere and on the epidermis of roots (particularly micorrhized roots) of Carthusian pink *Dianthus carthusianorum* L., one of the plants occurring in calaminarian grasslands. According to Cabała (2009), this indicates that precipitation of manganiferous phases in soils of the grasslands on mine waste may be an effect of the biochemical activity of fungi or symbiotic bacteria.

Sheet aluminosilicates play an important role in the stabilization of zinc, and to a lesser extent, of cadmium. Sheet aluminosilicates (described in former subsections) from the soils of waste heaps probably belong to the group of zinc smectites (Jerzykowska 2013), which are characterized by a high capacity to adsorb different pollutants between their layers. The presence of quartz in these soils, particularly in superficial soil horizons, is connected with the aeolic (wind) deposition of quartz grains (Fig. 6F).

To summarize, the mobilization of zinc in soils is caused by a local decrease in pH and the dissolution of smithsonite, hemimorphite and dolomite. These minerals often show traces of etching such as corrosion cracks and pits. The mobility of zinc is reduced by its sorption on iron oxides, which are stable in the soil environment. Cadmium is mobilized together with zinc from dissolved smithsonite, dolomite, and to a lesser degree from zinc-bearing aluminosilicates. During weathering, the geochemical separation of zinc and cadmium takes place. Cadmium is adsorbed by iron oxides more weakly than zinc, and only small amounts of cadmium are incorporated in the structure of aluminosilicates. It usually remains in soil solutions. Lead, released from dolomite and small grains of galena, is strongly adsorbed by

manganese oxides, and to a lesser degree by iron oxides. Elements bonded to iron oxides, such as arsenic, or zinc, are released to soil solutions, for example in the processes of desorption. Arsenic, however, is quickly precipitated with secondary iron oxides.

Conclusions

Weathering processes still take place in the soils formed on waste from oxidized zinc ores mining and processing, despite their natural pH, which results in mineral transformations and release of heavy metals to the environment, and their subsequent uptake by plants. In the weathering environments described, the greatest threat is posed by cadmium, particularly in superficial soil horizons. Also, zinc and lead are potentially readily released from minerals, and when pH decreases (e.g. as a result of plant succession and the impact of plant roots) these metals may be released in large amounts to soil solution. Arsenic shows the least mobility. A change in soil conditions from oxic to anoxic (e.g. caused by excess water) may cause the mobilization of metals (mainly zinc, arsenic and lead) which are also bound to manganese and iron oxides.

Description of some methods used in the study

Soil samples were collected from four mine waste heaps located between Bolesław and Bukowno (Fig. 7). From each waste heap two soil profiles were described. Within the profiles there were three to four distinct horizons, differing in colour and fraction (cf. Fig. 1).

In the soil samples pH was measured in aqueous suspension using a pH electrode. To estimate the mobility of zinc, lead, arsenic and cadmium in the soils, the seven-step sequential extraction procedure was used

(modified according to Tessier et al. 1979). The mineral composition of the material from each horizon was verified using the method of X-ray diffraction. The clay fraction was separated according to Mehra and Jackson (1960). Next, X-ray diffractograms from clay preparations were analysed. Using the scanning electron microscope (SEM), (SE and BSE images) photographs of fine-grained material specimens from soils and thin sections were taken. The chemical composition of minerals was examined with an electron microprobe (EMPA). The micro-X-ray diffraction (μ XRD) and X-ray absorption spectroscopy (XAS) analyses of iron oxide aggregates were performed

Table 4. Steps of sequential extractions: extracted fractions and reagents used (from Jerzykowska 2013)

Tabela 4. Etapy ekstrakcji sekwencyjnej: usuwane frakcje i wykorzystane odczynniki (za Jerzykowska 2013)

Fraction Frakcja	Chemical reagents Odczynniki chemiczne
Exchangeable ions Wymienna	1 M $C_2H_7NO_2$
Carbonates Węglanowa	74 ml of 0.2 M $C_2H_4O_2$ + 176 ml 0.2 M $C_2H_3NaO_2 \cdot 3 H_2O$
Manganese oxides Tlenki manganu	0.1 M H_4ClNO + HCl
Amorphous iron oxides Amorficzne tlenki żelaza	0.2 M $(NH_4)_2C_2O_4 \cdot H_2O$ + 0.2 M $C_2H_2O_4 \cdot 2H_2O$
Crystalline iron oxides Krystaliczne tlenki żelaza	40 ml 0.3 M $C_6H_5Na_3O_7$ + 5 ml 1 M $NaHCO_3$, 3 × 0,5 g $Na_2S_2O_4$
Organic matter-sulphides Organiczno-siarczkowa	20 × 10 ml 30% H_2O_2 + 1 M HNO_3 , $C_2H_7NO_2$
Residual Rezydualna	25 ml HF, 3 drops/krople $HCClO_4$, HCl



Fig. 7. Localization of mine waste heaps (1–4) on which soil samples were collected. A – ZGH Bolestaw zinc smelter, B – ZGH Bolestaw settling ponds [Orthophotomap originate from the National Geodetic and Cartographic Resources (PZGiK)]

Ryc. 7. Lokalizacja hałd odpadów pogórnich (1–4) na których pobrano próbki gleby. A – huta cynku ZGH „Bolestaw”, B – stawy osadowe ZGH „Bolestaw” [Ortofotomapa pochodzi z Państwowego Zasobu Geodezyjnego i Kartograficznego (PZGiK)]

using synchrotron radiation (for details of the method see Jerzykowska et al. 2014).

The method of selective sequential extraction is commonly used to determine the form metal in different environments. The extraction of metals occurs in so-called fractions, from easily accessible to stable ones, from a sample, using different chemical reagents. There are different variants of this method, from simple three-step to the more difficult five- or even seven-step one (e.g. Tessier et al. 1979). In this study, the seven-step method was applied, and reagents and extracted fractions were listed in Table 4.

X-ray powder diffraction analysis (XRD) uses X-ray radiation to determine the mineral composition of powdered samples of rock or soil. Analyses of soil samples from waste heaps were performed using a Philips X'pert APD diffractometer (with a PW 1870 generator

and a PW 3020 goniometer), copper lamp and a graphite monochromator. The applied voltage was 40 kV.

Scanning electron microscopy is a high-resolution method to produce images of rock, mineral, or soil samples. The surface of samples is scanned using a focused beam of electrons. By examining secondary electrons ejected from the surface of minerals (SE), one can obtain information about the surface topography of a sample. By examining backscattered electrons (BSE) ejected from the deeper parts of the studied material, one can obtain information about the average mass of elements present in a sample. BSE and SE images of soil samples from mine waste dumps were obtained using the HITACHI S-4700 field emission scanning electron microscope (FE-SEM) integrated with the EDS microanalysis system of dispersion energy (NORAN Vantage). The source of electrons in the microscope is a cold wolfram cathode. The magnification power of the microscope is 500,000×. It is equipped with a backscattered electron detector of the YAG type. Images were produced at an accelerating voltage of 20 KeV, a beam diameter of 10 μA, and a working distance (WD) of 12 mm. This configuration produced an image resolution of up to 1.5 nm.

The electron microprobe analyzer (EMPA) is an analytical tool integrated with the scanning electron microscope which enables the chemical composition of a sample to be determined in situ by measuring the wavelength of X-ray radiation emitted from a sample. 323 measurements were made with Jeol JXA-8530F HyperProbe for the soils in this investigation.

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