Mineralogy and speciation of Zn and As in Fe-oxide-clay aggregates in the mining waste at the MVT Zn–Pb deposits near Olkusz, Poland

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A B S T R A C T

Oxidation zones of ore deposits offer valuable insights into the long-term fate of many metals and metalloids. In this work, we have studied a paleo-acid rock drainage (ARD) system – the oxidation zone of Mississippi-valley type Zn–Pb deposits near Olkusz in southern Poland. The ARD systems exhausted their acid-generating capacity and have come almost to the conclusion of the mineral and geochemical transformations. Primary pyrite, marcasite, galena and sphalerite have been decomposed but the acidity was neutralized by the abundant carbonate host rocks. Zinc is stored in smithsonite, hemimorphite, and Zn-rich sheet aluminosilicates. Some of these minerals formed simultaneously with the oxidation zone but some precipitated in the soils in situ, thus documenting the mobility of Zn, Al, and Si in the soils. Iron oxides are represented mostly by goethite, either well-crystalline or nanocrystalline, as determined by a combination of powder X-ray diffraction, micro-X-ray diffraction, and Mössbauer spectroscopy. Iron oxides bind a substantial amount of arsenic, to a lesser extent also zinc, lead, and cadmium, as shown by electron microprobe analyses and sequential extractions. The X-ray absorption spectroscopy data of the local environment of arsenic in goethite suggest the existence of bidentate mononuclear complex, in addition to the more common bidentate binuclear complex. These results suggest that arsenic is incorporated in the crystal structure of goethite, in addition to adsorbed to the surface of the particles or occluded in the voids and pores. Zinc is bound in goethite as a mixture of tetrahedrally and octahedrally coordinated cations. This study shows that the mature system binds the metals from the primary sulfides relatively strongly. Yet, some release of the metals was observed in this study, either in the laboratory (by sequential extractions) and in nature (e.g., neofomed Zn phyllosilicates). The physical conditions in the oxidation zone and on the surface are largely similar but the metals, to a certain extent, are still mobile in the soils. We may speculate that their mobility near the surface, in the mining waste, may be enhanced by a higher water/rock ratio than in the oxidation zone. This result implies that although the studied material is relatively benign, it still has a potential to cause local environmental problems.

1. Introduction

Oxidation zones of ore deposits offer valuable insights into the long-term fate of many metals and metalloids. They are a window through which we can peek into the future and examine the fate of metal-rich waste forms over long-term periods. Mineralogy of the oxidation zones provides abundant evidence of many sinks of metals and metalloids; for example, the well-developed oxidation zone in Tsumeb has yielded so far more than 250 minerals, many of them secondary (Lombaard et al., 1986). In comparison to the superb example of Tsumeb, other oxidation zones appear less rich and interesting but they are, in their own right, an exciting source of information about mineral transformations and element migration patterns.

In this contribution, we have examined the mine waste from the oxidation zone of Mississippi-valley type (MVT) Zn–Pb deposits near Olkusz in southern Poland (Sass-Gustkiewicz and Dżułyński, 1998; Cabala, 2001). The objectives of the present study were to...
(i) identify the secondary minerals, (ii) evaluate the leachability of metals and metalloids from them, and (iii) determine speciation of As and Zn, two major pollutants, in these minerals. We have used a combination of bulk (XRF analysis, sequential extraction) and micro-methods (electron microprobe, X-ray microdiffraction, X-ray absorption microspectroscopy) to achieve these goals.

2. Geological settings and history of the deposit

Sulfide MVT deposits in the Cracow–Silesia region are hosted by the Triassic carbonate rocks of the Cracow–Silesian Monoclise (Bula and Zaba, 2008). Beneath the Permio-Mesozoic rocks, the Cracow–Lubliniec fault zone divides Precambrian to Paleozoic tectonic units – Upper Silesian Block (Brunovistulicum) and Malopolska Blok. Host rocks of the ores are the so-called ore-bearing dolomites (OBD) that occur down to 300 m below the ground level as tabular bodies in the sequence of middle Triassic carbonate rocks (Bogacz et al., 1975; Sass-Gustkiewicz and Dźulzyński, 1998). Several stages of hydrothermal sulfide mineralization resulted in the formation of a few generations of sulfides. The dominant minerals are sphalerite (ZnS), marcasite (FeS2), pyrite (FeS2), and galena (PbS) (Haraczynz, 1962; Sass-Gustkiewicz and Kucha, 2005). As and Pb sulfosalts are less common (Kucha and Viane, 1993).

From late Cretaceous to middle Miocene, with most favorable weathering conditions from early Paleogene to middle Miocene (Coppola et al., 2009; Strzelska-Smakowska, 2010), an oxidation zone has developed in the tectonic horsts and places without clay cover over sulfide deposits. Supergene non-sulfide deposits form tabular bodies, nests, and lenses in OBD (Zabiński, 1960). Most of the non-sulfide deposits were exploited until the mid-1980s. The remaining ~57 million tons of ores contain around 5.6 wt.% Zn and 1.4 wt.% Pb (Coppola et al., 2009). Main components of the non-sulfide deposits are Zn carbonates (mainly smithsonite, ZnCO3), goethite (FeOOH), remnants of sulfides and cerussite (PbCO3) (Zabiński, 1960). Hemimorphite [Zn2SiO4(OH)2·H2O], jarosite [KFe3( SO4)2(OH)6], manganiferous FeSO4·7H2O, epsomite (MgSO4·7H2O), gypsum (CaSO4·2H2O), hydrozincite [Zn5(CO3)2(OH)4], anglesite (PbSO4), pisolomelane (a mixture of Mn oxides), pyrolusite (MnO2), Zn-dolomite [Ca(Mg,Zn)(CO3)2], greenockite (CdS) (Zabiński, 1960; Gałkiewicz, 1983; Cabala, 2009) and Zn-smectites (Zn–Al silicate clays, see below) (Coppola et al., 2009) occur rarely.

Mining activity in the region Olkusz was carried out with brief interruptions from the Middle Ages to the present day (Cabala, 2009). It resulted in a significant transformation and pollution of various components of the environment, including water and river sediments (Helios-Rybińka, 1996a,b; Ciszewski and Malick, 2003, 2004; Van Roy et al., 2006; Aleksander-Kwaterczak and Helios-Rybińka, 2008; Aleksander-Kwaterczak et al., 2010; Ciszewski, 2010) and soil (Chlopecka, 1996; Chlopecka et al., 1996; Trafas, 1996; Verner et al., 1996; Mayer et al., 2001; Krazkiewski et al., 2004; Cabala et al., 2004, 2008, 2009; Gruszeczka and Helios Rybińka, 2006; Cabala and Tepner, 2007; Chrustny et al., 2011). The main sources of soil pollution are smelter emissions and the old mining dumps (e.g., Chrastny et al., 2011).

3. Materials and methods

Samples were collected at three sites (14, 17, 24, and 25) where supergene non-sulfide mining wastes from four open pits ‘Boleslaw’ (site 14), ‘Krępki’ (sites 24 and 25), ‘Ujkwó Stary’ (site 17) were deposited between the end of 19th century and 1985 (Cabala, 2009). Dump site 14 is the oldest among the studied ones. Sites 14 and 17 are covered by spontaneously overgrown thermophilous grassland called calamine grassland and the sites 24 and 25 by afforested Scots pine (Kapusta et al., 2011; Grodzińska et al., 2010). Investigated soils are shallow (20–30 cm) and skeletal Technosols (FAO World Reference Base for Soil Resources) resembling initial rendzinas (Lis and Pasieczna, 1999; Kapusta et al., 2011) with poorly developed soil profiles. At each site, around 2 kg samples were collected from two soil profiles (a and b), each profile comprising 3 or 4 horizons (Fig. 1), distinguishable from each other by color. From the lowermost horizons, dump rocks samples were taken. Collected samples were stored in open plastic bags in dry air conditions. For further investigation, selected samples were prepared in a form of thin sections, suitable for the methods with microscopic resolution.

Soil samples were sieved to a fraction <1 mm and then mixed in ratio 1:2.5 with deionized water or 1 M KCl solution. pH of soil–solution mixture was measured after 24 h, using a pH electrode Elmetron CP–401. For bulk chemical composition, samples were ground in an WC ball mill and analyzed using inductively coupled plasma atomic emission spectrometry (ICP AES) and inductively coupled plasma mass spectrometry (ICP MS) methods (at the Acme Analytical Laboratories, Canada). Samples were fused with lithium metaborate (LiB2O3) and lithium tetraborate (Li2B4O7) and dissolved in HNO3, for ICP AES analyses of the main components and ICP MS analyses of Zn, Pb, As, Cd and trace elements. The content of Zn, Pb, As and Cd was measured again using ICP AES for which samples were heated and mineralized in acids: HF, HClO4, HNO3, and distilled water in the ratio 2:2:1:1.

Sequential step extraction was carried out in duplicate for 0.5 g of each of the soil samples (<1 mm) and dump material (ground in an agate-mortar), according to modified procedure of Kersten and Forstner (1986) and Tessier et al. (1979). The sample/solution ratio, solution molarities, time and conditions of treatment are summarized in Table 1.

Samples were weighed before each step, centrifuged after reaction (>10,000 rpm, 10 min), and weighed with the remaining solution after decanting the supernatant. Extracts after each step were filtered, acidified with a few drops of HNO3, stored in 4 C and sent for elemental analyses immediately after the completion of the whole experiment. Control samples with Merck ICP standards (traceable to NIST-SRM CertiPUR®) were examined simultaneously with each analysis. The amount of trace elements in chemical reagents was also checked.

Concentration of Zn, Pb, As and Cd in extracts was examined using ICP AES instrument Perkin Elmer Thermo Scientific method in the laboratory of the Voivodship Inspectorate for Environmental Protection in Cracow. After the chemical analysis, correction for Zn, Pb, As and Cd in the solution remaining after each step was counted based on sample weight, weight of the remaining solution, and reagent density. Average recovery, which represents sum of each element from all the steps of sequential extraction and the bulk chemical analysis, is 87% which is in a good agreement with previous studies (e.g., Anju and Banerjee, 2010). Sequential extraction method compared with detailed mineralogical analyses is a suitable tool to quantitatively determine the forms of elements occurrence in polluted soils. Observed discrepancies in the results can be improved by examining the residue after each step of extraction (Kierczak et al., 2008).

Mineral composition of samples was determined using optical microscopy (polished thin sections), SEM-EDS analysis (Hitachi S-4700 field emission microscope

Fig. 1. Photograph of the profile 14b with indication of the individual sampled horizons.
**Table 1**

<table>
<thead>
<tr>
<th>Step</th>
<th>Chemical reagents</th>
<th>Conditions</th>
<th>Sample:reagent ratio</th>
<th>Time [min]</th>
<th>Measured fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1M HCl, 50% HNO₃, 176 ml O₂, 176 ml H₂O₂</td>
<td>Shaking, 60 °C</td>
<td>1:120</td>
<td>1.5</td>
<td>85°C, stirring</td>
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<tr>
<td>II</td>
<td>2H₂O₂ + 3H₂O₂</td>
<td>Shaking, the dark</td>
<td>1:50</td>
<td>1.15</td>
<td>85°C, stirring</td>
</tr>
<tr>
<td>III</td>
<td>2H₂O₂ + 3H₂O₂</td>
<td>Heating</td>
<td>1:20</td>
<td>0.85</td>
<td>85°C, stirring</td>
</tr>
<tr>
<td>IV</td>
<td>2H₂O₂ + 3H₂O₂</td>
<td>Evaporating</td>
<td>1:50</td>
<td>0.74</td>
<td>85°C, stirring</td>
</tr>
</tbody>
</table>

**Text:**

fitted with energy dispersive spectrometer, and a powder X-ray diffraction (PHILIPS Xpert APD) in the Institute of Geological Sciences, Jagiellonian University, Poland. SEM-EDS analyses were performed with analytical spot ca. 1 μm, accelerating voltage 20 kV, beam current 10 nA, and counting time 60 s. During XRD analyses, the samples were irradiated by Cu Kα radiation at room temperature and the data were collected in the range of 2–64 2θ, with a step of 0.02 2θ and dwell time of 1 s. Clay fraction was separated according to Jackson (1974) and Mehra and Jackson (1960). Samples were saturated with Na and Mg. Oriented specimens were analyzed in dry air conditions, after glycol saturation and after heating to 330 °C and 550 °C.

Samples from sites 17a and 24a were also studied with electron microprobe (EMP) Jeol JXA-8380F HyperProbe in Centre for Experimental Mineralogy, Petrology and Geochemistry (CEMPEC), University of Upsala. The analyses were carried out in wavelength-dispersive mode. Fourteen elements: As (with the standard GaAs), Pb (Pb₅(VO₄)₂Cl) Zn, S (ZnS), Cd (Cd), Fe (Fe₂O₃), Ca, Si (CaSO₄), Mn, Ti (MnTiO₃), Ba (BaSO₄), Mg (MgO), Al (Al₂O₃), K (K₂SO₄), or (ZnSO₄), Si and Ca (wollastonite), Ti (rutile), Pb (PbS), K (orthoclase), S (pyrite), Zn (metal), Mn (Mn metal), and Fe (hematite). The analytical conditions were 15 kV, 5 nA, beam diameter 1–5 μm. Time at the peak was 10 s and at the background 5 s. The back-scattered electron (BSE) images were also acquired with this instrument.

Aggregates of Fe oxides from the samples 17a and 24a were selected using a binocular and subjected to a Mössbauer spectrometry analysis. About 100 mg of the aggregates were ground in an agate mill and mixed with BaC. Mössbauer spectra were obtained at room temperature (RT) for all selected samples and for 24a and 24b also at 80 K using conventional Moessbauer spectrometer REV 3P3a-3 in transmission mode. Low temperature was maintained by the Janis SVP-400M cryostat. Fits to the data were performed using the software package Mosgraf-2009 (Ruebenbauer and Dural, 2009).

The micro-X-ray diffraction (µ-XRD) and micro-X-ray absorption spectroscopy (µ-XAS) data were collected at the beamline of the Synchrotron Radiation Laboratory for Environmental Studies (SUL-X, Angströmquelle Karlsruhe, Germany) in the synchrotron radiation source ANKA. For this work, the samples polished to a thin section were detached from the supporting glass resulting in self-supporting foils which maintained the grains of secondary minerals in a position for the measurement without the interference of X-ray scattering of the supporting material. A silicon (1 1 1) crystal pair with a fixed beam exit was used as a monochromator. The X-ray beam was aligned to an intermediate focus, and then collimated by slits located at the distance of the intermediate focus to about 100 μm × 100 μm and subsequently focused with a Kirkpatrick-Baez mirror pair to about 50 μm × 50 μm at the sample position.

The µ-XRD data were acquired in transmission mode with a CCD detector (Pho
tonic Science XDI VHR-2 150). For our experiments, the beamline was operated at 14 keV (λ = 0.886 A). Powdered Si (NIST 5464) was used to calibrate the diffraction angles. The images were integrated with the program FIG2D (Hammerley et al., 1996) and the 1D XRD patterns were further used for Rietveld refinement with the program GSAS (Larson and van Dreele, 1994) after background subtraction.

The µ-XAS spectra at As K edge and Zn K edge were measured in fluorescence mode in energy steps of 5 eV in the region from –50 eV to 50 eV relative to the absorption edge, of 2 eV in the region from –50 eV to –20 eV, of 0.4 eV from –20 eV to +20 eV, and with a step of 0.05 from +20 eV to +50 eV (about k=15, usable up to about k=13 for As, and up to about k=14 for Zn). Energy has been calibrated to 11.915 eV (maximum of first derivative) with a Au foil for the As K-edge and to 9629 eV (maximum of the first derivative) with a Zn foil for the Zn K-edge. The intensity of the primary beam was measured by an ionization chamber. Fluorescence intensities were collected with a 7 element Si(Li) solid state detector (SCX sensor technology, formerly Gresham) with the energy window set to the As Kα or Zn Kα fluorescence emission line. Data were dead time-corrected, summed up for all seven channels and divided by the input intensity, which was measured in an ionization chamber prior to the sample analysis. The collected data were processed by Athena and Artemis software suite (Ravel and Newville, 2005).

4. Results and discussion

4.1. General description and chemical composition of the studied material

The examined soils are skeletal, characterized by sandy-loam texture (USDA Soil Texture) and pH close to neutral (pH₅.₆ 6.8–8.3; Table 2). The uppermost horizons contain numerous fragments of organic matter in different stages of decomposition and small spherical particles deposited from atmospheric pollution from smelters or power plants (Cabala and Teper, 2007; Cabala et al., 2009) and quartz grains. The results of bulk chemical analyses are
Table 2: Results of mineralogical and chemical analyses of the samples from the profiles 14 and 17. The semi-quantitative mineralogical results show the abundance of each mineral, from absent (–) through rare (*), common (**, *** to frequent (****, *****)) and dominant (******). All chemical data in weight % with the exception of As and Cd (in ppm). LOI = loss on ignition.

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<th>14bl</th>
<th>14bIII</th>
<th>14bIV</th>
<th>14blII</th>
<th>17al</th>
<th>17all</th>
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<th>17bll</th>
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<td>As (ppm)</td>
<td>119.9</td>
<td>345.5</td>
<td>299.2</td>
<td>260.6</td>
<td>414.9</td>
<td>573.6</td>
<td>605.8</td>
<td>41.7</td>
<td>311.5</td>
<td>358.8</td>
<td>44.1</td>
</tr>
<tr>
<td>Cd (ppm)</td>
<td>164.8</td>
<td>257.4</td>
<td>187.9</td>
<td>62.3</td>
<td>211.7</td>
<td>364.2</td>
<td>328.7</td>
<td>122.5</td>
<td>133.9</td>
<td>180.9</td>
<td>96.0</td>
</tr>
</tbody>
</table>

The minor and trace elements Zn, Pb, As, and Cd correlate well with Fe₂O₃ (Fig. 2) and hence, just as Fe₂O₃, they are particularly enriched in the soil horizon II. The amount of Zn varies from 3 wt% in the quartz-rich sample 25all, 4 wt% in samples from dump material on the site 17 to 11 wt% in the smithsonite-rich sample 25bl. Pb amount reaches 6 wt% in sample 24all, the lowest Pb content of 334 ppm was found in sample 17bl. Arsenic varies between 33 ppm (25all) and 979 ppm (24bl), cadmium from 17 ppm (25all) to 424 ppm (25bl). In most cases, studied elements are enriched in the soil horizons III and II in comparison to the horizon I (i.e., dump

listed in Table 2. The amount of SiO₂ varies between 1 wt% in some samples from dump material to 85 wt% in the sample 25all which contains large amounts of quartz grains. High proportion of SiO₂ in uppermost horizons in comparison to the dump material is the evidence of aeolian origin of quartz (windblown from fluvioglacial sands mined nearby). Fe₂O₃ content is low from about 0.1 wt% up to 6.5 wt% and generally increases to the top of the soil profiles. The content of Fe₂O₃ varies between 1 wt% and 21 wt% and is generally higher in soil horizons II than I and III and is associated with a higher content of Fe-oxides.
material, Table 2). Therefore, the analytical work concentrated on the horizons II and III.

4.2. Mineral composition

Mineral composition of the material from the dumps and soil samples generally resembles the composition of the non-sulfide Zn–Pb deposits in this region. Using XRD analyses, carbonates (dolomite, smithsonite, calcite), silicates (quartz, hemimorphite, sheet silicates), goethite and sulfides (margarite, sphalerite, galena) were identified; Mn oxides were detected only by SEM-EDS and EPM analyses. Semiquantitative abundance of minerals is listed in Table 2. The most common minerals in all samples are dolomite and quartz. There is a distinct difference in mineralogical Zn speciation between the profiles 14, 24, 25 and 17: the first three contain abundant smithsonite and no hemimorphite. Profile 17, on the other hand, contains scarce hemimorphite and no smithsonite. Sheet silicates were identified in the profiles 14, 17, and 24 but are missing in the profile 25. Sulfides occur in trace amounts, and when detected, probably represent relics of the primary mineralization. Goethite was detected in all but two (17a and 17b) samples.

The semiquantitative mineral composition (Table 2) correlates well with the bulk chemical composition (Table 2). Principal-component analysis (PCA) of the bulk-chemical data identified three principal components. The first one is correlated positively with SiO2 and negatively with MgO, CaO and loss on ignition (LOI), which can be interpreted as a mixture of the major minerals dolomite and quartz. The second component correlates with Zn, Cd, and Mn and can be related to the presence of smithsonite and Mn oxides with incorporated or adsorbed Cd. The third component correlates Al2O3, Fe2O3, Na2O, K2O, Pb and As and represents the common fine-grained mixture of Fe oxides and clay minerals.

4.2.1. Zn carbonates, silicates, and aluminosilicates

Smithsonite occurs as fillings of cavities in dolomite (Fig. 3a), as separate massive or botryoidal aggregates of variable size or pseudomorphs after sphalerite crystals (Fig. 3b). Smithsonite surface is often etched, especially in the uppermost soil horizons. Apart from Zn, smithsonite contains trace amounts of CdO (average 0.2 wt%), PbO (0.6), FeO (0.2), CaO (0.7), and MgO (0.2). The average concentration of arsenic (0.08 wt%) is near the detection limit of the EMP. Several representative EMP analyses are listed in Table 3.

Hemimorphite is common in soil horizons from the site 17, infrequent in the dump material of this site, and rare as overgrowths of smithsonite at the site 24. It forms radial aggregates of elongated

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**Fig. 2.** A schematic map of the studied area with the positions of the sampling points.

**Fig. 3.** Scanning electron microphotographs of (a) an association of smithsonite, dolomite, Fe oxides, and sheet silicates. Note that smithsonite fills cavities in dolomite; (b) an aggregate of smithsonite crystals with etch pits and crusts of Mn oxides; (c) a crystal of Zn-containing sheet silicates with dolomite and Mn oxides; (d) Zn-containing sheet silicates as filling of cavities in an aggregate of hematite crystals.
crystals or massive aggregates. Hemimorphite crystallizes on the soil particles, on the Zn-aluminosilicates and occasionally on the quartz grains, indicating that it formed in the soils. In mineral soil horizons 17Al and 17Bl, most of the hemimorphite grains are slightly etched. Apart from Zn and Si, only the average concentration of FeO exceeds 0.1 wt%. A few representative analyses are listed in Table 3.

Zn-rich sheet aluminosilicates were found in all soil profiles, but in larger amounts at the site 17. They form large (up to 500 μm) platy crystals (Fig. 3c) or aggregates of small particles; they may also occur together with Fe oxides in rims around various grains in soils (Fig. 3a and d). Characteristic is the occurrence of Zn-aluminosilicates in etch pits in smithsonite and hemimorphite which indicates that the released Zn precipitated as aluminosilicates. XRD analysis revealed three types of minerals in the clay fraction. The first mineral is characterized by the basal peak at d ~ 15 Å in air-dried conditions which shifts to d ~ 17 Å after saturation with glycol and collapses to d ~ 10 Å after heating to 220°C. This behavior is typical for smectite-group minerals but the absence of rational series of reflections indicates that the presence of mixed-layered clay minerals cannot be excluded (illite-smectite or kaolinite-smectite, R = 0; Srodoń, 2006). The minerals of the serpentine-kaolinite group are characterized by the interlayer distance of 7.12 – 7.18 Å in air-dried conditions; the corresponding XRD peak disappears at 550°C. The structure of the mineral does not swell after glycol saturation. Mica-group minerals were recognized on the basis of the peak at 10 Å which does not change position after glycol saturation. The clay fraction is dominated by smectite-group minerals and kaolinite-group minerals, mica-group minerals occur in minor amount.

The results of EMP analyses of the sheet silicates are rather scattered (Fig. 4, Table 3). The amount of Zn in most of the analyses is too low for stoichiometric saucitone [Zn trioctahedral smectite Na₄₋₃Zn₃(Si,Al)₄O₁₀(OH)₂·4H₂O]. The formula normalized to Si + Al = 4 is (K,Ca)₀.₁₈(Zn,Fe,Mg,Mn,Al)₁₂.₈₅(Si,Al)₂O₁₀(OH)₂·4H₂O. Pure kaolinite was not observed, either by EDS- or WDS-EMP analyses, implying that kaolinite in the clay fraction also contains Zn in its structure. Some of the analyses are close to fraipontite – Zn trioctahedral mineral [(Zn,Al)₂(Si,Al)₂O₅(OH)₄] of serpentine-kaolinite group. It is likely that the analyzed material consists of a fine-grained mixture of saucitone and fraipontite and the spatial resolution of the EMP does not allow to separate the contribution of these two minerals to the analytical results. An explanation for the co-existence of such phases was provided by Paquet et al. (1986) who claim that trioctahedral Zn-smectites are unstable under
weathering conditions and transform to dioctahedral smectites with time. On pedogenic time scales (up to 10,000 years), the smectites further change to Zn-kaolinite and Zn-goethite. Such a process could have also operated at the site studied in this work.

The Zn K edge EXAFS spectra, collected on the clay fraction, confirm that Zn is incorporated in the structure of the sheet silicates (Fig. 5). According to the refinement, each Zn atom has ∼4 Zn neighbors in the second shell, meaning that the clays, be they from the smectite or serpentine-kaolinite group, are Zn rich or that Zn clusters in their structures (Table 4).

4.2.2. Fe and Mn oxides

Fe oxides concentrate in the soil horizons II where they form massive and porous aggregates of different sizes. Internally, these aggregates are often zoned (Fig. 6a) or they are pseudomorphs after the primary iron sulfides (Fig. 6b and c). Fe oxides may be very fine-grained (Fig. 6d) and also replace organic fragments. According to the μ-XRD results, Fe oxides consist mainly of goethite, with occasional admixture of hematite or rarely other minerals.

Fig. 5. FT EXAFS data for the Zn-containing sheet silicates, collected at the Zn K edge. Circles represent the measured and processed data, solid line is the fit. For quantitative interpretation of the data, see Table 4 and text.

Fig. 6. Scanning electron microphotographs of (a) a zoned grain of Fe oxides; (b) a pseudomorph of Fe oxides after Fe sulfides; (c) a pseudomorph of Fe oxides after marcasite. Relics of the primary marcasite are still present; (d) a fine-grained, porous aggregates of Fe oxides; (e) a similar morphology of Mn oxides, suggestive perhaps of a biological contribution in their formation; (f) masses of Mn oxides in the voids of organic material.
Moessbauer spectroscopy revealed that Fe oxides aggregates contain 80–100% of high-spin Fe$^{3+}$ (in nanoparticles) and up to 20% high-spin Fe$^{2+}$ (Table 5). The most probable location of the high spin Fe$^{3+}$ is within goethite nanoparticles as low temperature spectra are consistent with the corresponding goethite spectra (Brož et al., 1990; Berquó et al., 2007). This hypothesis is supported by the lack of magnetic order at room temperature. The high-spin Fe$^{2+}$ has the same hyperfine parameters as iron located in ankerite (De Grave and Wochten, 1985; De Grave, 1986). Moreover, the high amount of Fe$^{2+}$ in the samples 17al and 24al (dump material) correlates well with the abundance of carbonates of the dolomite-ankerite series (as determined by XRD). There is 14% of Fe in the form of Fe$_3$O$_4$ in the sample 17all, probably from dust particles.

We also identified lepidocrocite ($\gamma$-FeOOH) as a minor component (7%) in the sample 24all (Table 5). Lepidocrocite was not identified during $\mu$-XRD studies but its presence in Polish non-sulfide Zn deposits was mentioned by Cabala (2001). Fe oxide aggregates contain considerable amounts of Zn, Pb, As and Cd (Table 6), with the mean values of 5.02 wt% Zn, 1.25 wt% Pb, 0.15 wt% As, and 0.03 wt% Cd.

Mn oxides occur mainly in soils horizons II from sites 14 and 17. They form porous (Fig. 6e), often layered aggregates filling cracks in dolomite, overgrowing soil grains, or replacing and filling organic fragments (Fig. 6f). Mn oxides contain high amount of PbO with a mean value of 12.87 wt% Pb. The co-occurrence of Mn oxides and Pb has been observed in many similar weathering environments (e.g., Eusden et al., 2002; Rollinson et al., 2011; Miller and Gosar, 2012). Soil Mn-oxides, especially biogenic binirse, have a high capacity for Pb accumulation (Nelson et al., 1999; O’Reilly and Hochella, 2003). Other minor elements in the Mn oxides are on average 5.73 wt% Zn, 0.03 wt% As, and 0.05 wt% Cd. Grains containing smaller amounts of Pb contain often Ba. Fe oxides often occur in mixtures with clay minerals and Mn oxides enriched in Pb. A PCA analysis of the EPMA results identified four components. The first one is correlated with SiO$_2$, MgO, Al$_2$O$_3$ and K$_2$O and corresponds to clay minerals. The second component includes MnO and PbO and corresponds likely to Mn oxides. The third component is Fe$_2$O$_3$ and represents the Fe oxides and the last component is ZnO. ZnO is probably a separate component because it may be associated with both sheet silicates and Fe oxides.

### Table 4
Results of the refinement of the structural model for the Zn-clays from the EXAFS measurements on the Zn K edge (Fig. 5). $\Delta E_0 = 1.2(2.2)$. Data for the fit were taken between $k = 2.5$ and $k = 12.4 \text{Å}^{-1}$ and $(R + \Delta R) = 1.0$ to $(R + \Delta R) = 3.5 \text{Å}$. Number of independent data points 2174, number of refined variables 8 (the variables were refined successively, not all simultaneously). Statistics of the fit: reduced $\chi^2 = 1301$. All parameters computed or refined by the software package Artemis (Ravel and Newville, 2005).

<table>
<thead>
<tr>
<th>Path (s)</th>
<th>CN (s)</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn–O</td>
<td>4.6(1)</td>
<td>2.08(2)</td>
<td>0.009(4)</td>
</tr>
<tr>
<td>Zn–Zn and Zn–Si$^\ddagger$</td>
<td>4.6(1)</td>
<td>3.09(2)</td>
<td>0.009(3)</td>
</tr>
</tbody>
</table>

* Both paths refined with one set of parameters (CN, $\Delta r$, $\sigma^2$).

### Table 5
Results of the Moessbauer spectroscopy analysis of the studied samples, with the fitting parameters and the assignment of the absorption bands.

<table>
<thead>
<tr>
<th>Sample/Fe form</th>
<th>Content (%) (±1%)</th>
<th>$S$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>$R$ (T)</th>
<th>$\Gamma$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17al RT</td>
<td>Fe$^{3+}$</td>
<td>80</td>
<td>0.36(1)</td>
<td>0.61(1)</td>
<td>0.35(1)</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$</td>
<td>20</td>
<td>1.26(2)</td>
<td>1.46(2)</td>
<td>0.43(4)</td>
</tr>
<tr>
<td>17all RT</td>
<td>Fe$^{3+}$</td>
<td>82</td>
<td>0.35(1)</td>
<td>0.59(1)</td>
<td>0.35(1)</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$</td>
<td>4</td>
<td>1.61(2)</td>
<td>0.91(3)</td>
<td>0.43(5)</td>
</tr>
<tr>
<td></td>
<td>Fe$_3$O$_4$</td>
<td>14(9 + 5)</td>
<td>0.36(1)</td>
<td>–0.13(3)</td>
<td>50.4(1)</td>
</tr>
<tr>
<td></td>
<td>Zn–O</td>
<td>0.54(2)</td>
<td>0.04(4)</td>
<td>45.5(2)</td>
<td></td>
</tr>
<tr>
<td>24al RT</td>
<td>Fe$^{3+}$</td>
<td>87</td>
<td>0.36(1)</td>
<td>0.58(1)</td>
<td>0.35(1)</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$</td>
<td>13</td>
<td>1.39(2)</td>
<td>1.22(2)</td>
<td>0.43(5)</td>
</tr>
<tr>
<td>24all 80K</td>
<td>Fe$^{3+}$</td>
<td>34</td>
<td></td>
<td>46.6(1)</td>
<td>0.36(3)</td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$</td>
<td>25</td>
<td>0.49(2)</td>
<td>–0.22(2)</td>
<td>48.5(1)</td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$</td>
<td>16</td>
<td>1.36(1)</td>
<td>1.94(2)</td>
<td>0.45(5)</td>
</tr>
<tr>
<td>24all RT</td>
<td>Fe$^{3+}$ nanoparticles</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>24all 80K</td>
<td>Fe$^{3+}$ nanoparticles</td>
<td>92</td>
<td>0.49(1)</td>
<td>–0.23(2)</td>
<td>47.5(4)</td>
</tr>
<tr>
<td>$\gamma$-FeOOH</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</table>

### Table 6
Representative electron microprobe analyses of Fe oxides. All data in wt.%

<table>
<thead>
<tr>
<th>Analysis</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>ZnO</th>
<th>MnO</th>
<th>PbO</th>
<th>K$_2$O</th>
<th>SO$_3$</th>
<th>As$_2$O$_3$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>14II-F2</td>
<td>1.65</td>
<td>0.00</td>
<td>86.32</td>
<td>0.01</td>
<td>0.16</td>
<td>0.00</td>
<td>3.00</td>
<td>0.00</td>
<td>2.10</td>
<td>0.02</td>
<td>0.22</td>
<td>1.07</td>
<td>94.55</td>
</tr>
<tr>
<td>14II-B5</td>
<td>2.46</td>
<td>0.00</td>
<td>73.66</td>
<td>0.01</td>
<td>0.16</td>
<td>0.14</td>
<td>5.41</td>
<td>0.05</td>
<td>0.54</td>
<td>0.01</td>
<td>0.19</td>
<td>0.42</td>
<td>83.06</td>
</tr>
<tr>
<td>14II-F4</td>
<td>8.24</td>
<td>0.04</td>
<td>75.93</td>
<td>0.71</td>
<td>0.63</td>
<td>0.30</td>
<td>8.80</td>
<td>0.03</td>
<td>1.20</td>
<td>0.02</td>
<td>0.09</td>
<td>0.43</td>
<td>96.42</td>
</tr>
<tr>
<td>17II-A2</td>
<td>4.19</td>
<td>0.00</td>
<td>52.15</td>
<td>0.44</td>
<td>0.25</td>
<td>0.17</td>
<td>5.04</td>
<td>0.00</td>
<td>0.30</td>
<td>0.00</td>
<td>0.07</td>
<td>0.39</td>
<td>63.02</td>
</tr>
<tr>
<td>17II-D3</td>
<td>3.37</td>
<td>0.00</td>
<td>80.52</td>
<td>0.37</td>
<td>0.12</td>
<td>0.03</td>
<td>6.53</td>
<td>0.03</td>
<td>1.61</td>
<td>0.00</td>
<td>0.17</td>
<td>0.00</td>
<td>92.74</td>
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<tr>
<td>17II-G1</td>
<td>20.28</td>
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<td>54.45</td>
<td>0.35</td>
<td>1.31</td>
<td>9.07</td>
<td>0.01</td>
<td>0.30</td>
<td>1.20</td>
<td>0.04</td>
<td>0.00</td>
<td>94.66</td>
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<tr>
<td>24II-B3</td>
<td>11.02</td>
<td>0.12</td>
<td>61.89</td>
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<td>0.42</td>
<td>0.49</td>
<td>6.12</td>
<td>0.03</td>
<td>1.31</td>
<td>0.45</td>
<td>0.23</td>
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<tr>
<td>24II-G1</td>
<td>7.30</td>
<td>0.53</td>
<td>69.54</td>
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<td>0.37</td>
<td>0.38</td>
<td>7.55</td>
<td>0.04</td>
<td>1.61</td>
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<td>0.17</td>
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<td>0.07</td>
<td>5.24</td>
<td>0.00</td>
<td>1.11</td>
<td>0.05</td>
<td>0.33</td>
<td>0.77</td>
<td>95.41</td>
</tr>
<tr>
<td>24II-D2</td>
<td>8.19</td>
<td>0.03</td>
<td>73.32</td>
<td>4.71</td>
<td>0.17</td>
<td>0.51</td>
<td>5.66</td>
<td>0.01</td>
<td>0.70</td>
<td>0.54</td>
<td>0.47</td>
<td>0.00</td>
<td>94.51</td>
</tr>
</tbody>
</table>
4.3. Speciation of Zn, As, Cd, and Pb in the mining waste

4.3.1. Sequential extractions

Results of sequential extractions are summarized in Fig. 7. The most striking feature is the difference in the speciation between As and Zn, Cd, Pb. Arsenic is extracted mostly in the reducible fraction, indicating its association with iron oxides, mostly crystalline, to a lesser extent X-ray amorphous. The μ-XRD and Mössbauer data showed that the Fe oxides consist mostly of crystalline goethite, rarely hematite, and therefore most of the arsenic should be associated with goethite. The amount of As in fractions other than reducible (i.e., oxidizable, acid-soluble) is higher in the dumps than in the soil profiles.

Zinc, cadmium and lead, on the other hand, are released mostly in the acid-soluble fraction, to a lesser extent, in the case of cadmium, in the exchangeable fraction. This observation can be explained well from the association of Zn with carbonates (smithsonite or dolomite). An exception are the samples from site 17 where Zn is released in acid-soluble and reducible fractions but the mineralogical analysis pointed at the absence of smithsonite there (cf. Table 2). Therefore, Zn stored in hemimorphite and Zn-rich sheet silicates is extracted in the same solutions as the carbonates; it is also possible that some Zn resides in dolomite. This extraction behavior is interesting and highlights the inefficiency of the sequential extractions to distinguish different reservoirs of an element, although they may appear to be chemically distinct (i.e., carbonates versus silicates). The amount of Zn bound to reducible and oxidizable fraction increases toward the top of the profiles while the acid-soluble fraction decreases toward the top. This trend can be rationalized by the greater abundance of Fe oxides in the soils than in the dumps and by the dissolution of smithsonite and hemimorphite in the soils. The Fe oxides bind not only As but also Zn (see Fig. 8).

Cadmium, as mentioned above, is probably geochemically coupled to zinc. The largest difference in the behavior between Cd

Fig. 7. Graphical summary of the sequential extractions.

Fig. 8. Triangle diagram of the bulk analysis of the studied material (diamonds, ICP data) and the spot analyses of iron oxides (circles, EMP analyses).
Zn is the abundant release of Cd in the exchangeable fraction. This behavior is observed particularly in the horizons II and III and could be related to the binding strength and capacity of Fe oxides. The results could be interpreted by a weaker sorption of Cd to the Fe oxides in comparison to Zn.

Zinc and cadmium in the samples 14 and 17 show affinity for organic matter. This association was not further investigated as this work targeted the inorganic constituents of the system, i.e., minerals.

The speciation of lead is somewhat more difficult to explain. The extraction in the acid-soluble fraction (30–95% of total Pb) could suggest that lead occurs in the form of carbonates but our EMP results indicate that lead appears to be associated mostly with Mn oxides and part of it may be released in the acidic buffer solution. The enhanced extraction of Pb in the reducible fraction from the horizon II from the sites 14 and 17 correlates well with the higher abundance of Mn oxides in these samples. In some samples (especially 14 and 17), lead associates to a larger degree with organic matter.

4.3.2. Electron microprobe (EMP) elemental mapping and analyses

Mapping and analytical work with an electron microprobe reveals association and correlation of elements with certain types of matrices. Fe oxides, as mentioned above, occur either as pseudomorphs after the primary Fe sulfides (pyrite, marcasite) or as zoned grains which probably precipitated from the supergene fluids. In the pseudomorphs, we observed zones with elevated content of As and Zn (Fig. 9). Arsenic and zinc correlate well but there is no correlation of these two elements with either Si or Pb. These correlations suggest that the Fe oxides act as a sink of many, but not all elements which may be mobile in the supergene zone. Interestingly, both As (usually present as arsenate anions) and Zn (usually present as a cation) are retained by the Fe oxides, in agreement with the results of sequential extraction. The spatial association of Zn and As cannot be explained by impurities in the primary sulfides. Pyrite and marcasite do often contain elevated concentrations of arsenic (e.g., Kolker and Nordstrom, 2001) but they do not contain Zn, apart from negligible traces. Therefore, the zones in the pseudomorphs

Fig. 9. Distribution of major, minor, and trace elements in an aggregate (pseudomorph) of Fe oxides (EMP mapping, the relative concentration is shown in a scale of number of counts).
as well as the zones in the newly formed grains document episodes of element mobility under the supergene conditions.

4.3.3. X-ray absorption spectroscopy (XAS)

The close spatial correlation between the elements As and Zn and goethite led us to a more detailed investigation of the speciation of these two elements. We have applied X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) spectroscopy at the As K or Zn K edge to determine the local environment of these elements in goethite. The XANES spectra at the As K edge showed that As is present in the pentavalent oxidation state.

To strengthen the interpretation of the As XAS data, the spectra of lollingite, arsenolite, scorodite, and As-rich hydrous ferric oxides were collected together with the data of our samples. The EXAFS spectra of the four standards were processed and agreed with the crystallographic structure of the three minerals and the bidentate-binuclear arsenate complex for the As-rich hydrous ferric oxide.

The first shell of As atoms consists of 4 oxygen atoms with a distance of 1.70(1) Å, both parameters typical for As\(^{5+}\) in tetrahedral coordination. The second shell deviates from the second shell of ferrihydrite or hydrous ferric oxide with sorbed As\(^{5+}\) (cf. Fig. 10) or scorodite. We tried to refine a number of models for the spectra of our samples. Statistically, the best models, as indicated by the goodness-of-fit variable returned by the Artemis software, required the presence of multiple-scattering paths where the CN was fixed to 12. The CN of 12 is the theoretical number of multiple-scattering paths derived from the consideration of the geometry of the arsenate anion. Additionally, the prominent feature at 2.3 Å (uncorrected for phase shift) had to be taken into account. Incorporation of a bidentate-mononuclear complex into the model improved the fit and describes this feature satisfactorily (Fig. 11). The refined parameters are listed in Table 7 and warrant some discussion. The bidentate-mononuclear complex corresponds to an edge-sharing configuration between an octahedron and a tetrahedron, a rather unusual one in solid state. Tetrahedra, especially the smaller ones, are thought to be reluctant to allow such type of a complex because of a strong electrostatic repulsion of the two neighboring cations. Such type of a complex, however, has been proposed or observed, for example between selenate and the surface of goethite (Manceau and Charlet, 1994) or between arsenate and chromate and the surface of goethite (Fendt et al., 1997; Farquhar et al., 2002). Edge-sharing Fe\(^{3+}\) octahedra and phosphate tetrahedra are known from the crystal structures of sarcopside, (Fe\(^{2+}\)Mn\(_2\))\(_2\)PO\(_4\) (Moore, 1972) and heterosite, FePO\(_4\) (Eventoff et al., 1972). Edge-sharing between octahedra and related polyhedra and arsenate tetrahedra was also observed in arsenoclasite, Mn\(_2\)O\(_4\)As\(_2\)O\(_7\) (Moore and Molin-Case, 1971), lammerite, Cu\(_2\)As\(_2\)O\(_7\) (Hawthorne, 1986), and parwelite, Mn\(_5\)Sb\(_2\)O\(_9\)\(_2\)As\(_2\)O\(_7\) (Moore and Araki, 1977). With the exception of heterosite, in all these cases is the central octahedral cation divalent. Such configuration appears to be more likely than edge-sharing between arsenate and an octahedron of a trivalent cation. For our samples, an alternative explanation would be edge sharing between arsenate tetrahedra and the octahedra of the abundant Zn\(^{2+}\). The two possibilities (octahedra occupied by Zn\(^{2+}\) or Fe\(^{3+}\)) are difficult to distinguish because of the similar scattering power of Zn and Fe. The other As–Fe distance seen in the EXAFS spectra can be interpreted as a bidentate-binuclear complex commonly found for arsenate adsorbed onto iron oxides.

The existence of the bidentate-mononuclear complexes, either with Zn\(^{2+}\) or Fe\(^{3+}\), opens the possibility of speculation that the arsenate groups are incorporated in the structure of goethite and do not only reside on the surface of the particles. The mechanism of incorporation is unknown. What could be said is that an oxidation zone, with its long geological time of ripening, would be an ideal site for the occlusion and incorporation of foreign cations into the structures of supergene products. Recently, we have observed a significant amount of As\(^{5+}\) and Sb\(^{5+}\) in the structure of goethite (Majzlan et al., 2011) where an inspection of the samples in high-resolution transmission electron images did not reveal any additional phase. These samples came from a tailing pond with much shorter history (less than 100 years) and document the ability of goethite to pick up and to store many elements, even if their coordination polyhedra may not readily fit into its structure.

The first shell in the Zn K edge spectra was satisfactorily fit with a mixture of tetrahedrally and octahedrally coordinated Zn. Because of the presence of both coordination polyhedra, we did not perform shell-by-shell fitting of the Zn EXAFS spectra. A number of paths could be expected with a severe overlap of the EXAFS oscillations. Positions of the features in the second shell

Table 7

<table>
<thead>
<tr>
<th>Path(s)</th>
<th>CN</th>
<th>R (Å)</th>
<th>(\sigma^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As–O</td>
<td>4.1(2)</td>
<td>1.7(0)</td>
<td>0.003(1)</td>
</tr>
<tr>
<td>As–Fe</td>
<td>0.4(2)</td>
<td>2.7(3)</td>
<td>0.005(2)</td>
</tr>
<tr>
<td>As–O–O–As</td>
<td>[12]</td>
<td>3.16(4)</td>
<td>[2(\sigma^2)As–O]</td>
</tr>
<tr>
<td>As–Fe</td>
<td>0.9(3)</td>
<td>3.31(2)</td>
<td>[(\sigma^2)As–Fe]</td>
</tr>
</tbody>
</table>
Fig. 11. EXAFS (left) and FT EXAFS (right, magnitude and real part) of the XAS data for Fe oxides, collected at the As K edge. Circles represent the measured and processed data, solid line is the fit. For quantitative interpretation of the data, see Table 7 and text.

Fig. 12. (a) Zn K-edge k^2-weighted χ spectra of reference minerals and the samples (all spectra for the sample spots measured were merged); (b) Zn K-edge Fourier-transformed (FT) EXAFS spectra for the measured samples and the Zn-goethite for comparison. All measured sample spots were identified as goethite by X-ray microdiffraction.

can be qualitatively compared to the EXAFS spectra of a number of reference compounds (Fig. 12a). Some reference compounds (zincite, franklinite, sphalerite) which deviate too much from the data from our samples were not considered at all. The sample spectra are similar to the spectrum of goethite prepared from ferrihydrite coprecipitated in the presence of Zn^{2+} in the solution. The two features are located at very similar positions (cf. Fig. 12b) but their intensity does not match. In our samples, the feature at ~2.6 Å has a greater magnitude than the feature at ~3.0 Å (both not corrected for phase shift), unlike in the goethite sample.

5. Concluding remarks

The results of weathering, mineral and geochemical transformation of the studied material near Olkusz provide a fascinating and intriguing case study for a simple reason: We have studied a paleo-acid rock drainage system which exhausted its acid-generating capacity and has come almost to the conclusion of the primary step of transformations. It is clear that weathering and decomposition of the large amounts of pyrite and marcasite had to produce a significant amount of acid, albeit it probably could have been neutralized by the abundant carbonate host rocks. Hence, we have an opportunity to investigate the future state of mine drainage systems with similar mineralogy and geochemistry, for example tailing ponds and dumps from hydrothermal veins with abundant carbonates.

Indeed, the studied material reached the mature stages of the drainage systems characterized by abundant crystalline iron oxides, mostly goethite (cf. Jambor, 2003). Zinc, the second most abundant metal, was stored in separate secondary phases (smithsonite, hemimorphite) but also in large amount in goethite. An interesting aspect shown by this study is the remobilization of zinc under the surface conditions. The evidence for these processes is etching of smithsonite and hemimorphite and neo-crystallization of the zinc-containing sheet silicates. Arsenic is stored relatively strongly in goethite, as indicated by the sequential extractions. The analysis of the local environment of arsenic in goethite suggests
the existence of bidentate mononuclear complex, in addition to the more common bidentate bincular complex. We interpret these findings as incorporation of arsenic into the crystal structure of goethite, something worth further studies. Recently, we have shown that the tetrahedrally coordinated As(V) can be efficiently incorporated into the structure of hematite (Bolanz et al. 2013) and perhaps a similar mechanism can be found in goethite.

Overall, this study shows that the mature system binds the metals from the primary sulfides relatively strongly. Yet, some release of the metals is observed in laboratory (Fig. 7) and in nature (e.g., Zn phyllosilicates). This aspect is also of interest – the conditions in the oxidation zone and on the surface are largely similar but the metals, to a certain extent, are mobile. We may speculate that their mobility near the surface, in the mining waste, may be enhanced by a higher water/rock ratio than in the oxidation zone. This result can imply that although the studied material is relatively benign, especially when compared to active mine drainage systems with high loads of toxic elements (e.g., Majzlan et al., 2011), it still has a potential to cause local environmental problems. They are known from the broad area of the Polish MVT-type deposits (e.g., Czop et al., 2007) and include contamination by heavy metals and sulfate. The work by Czop et al. (2007) and by others, however, describe the water quality in the discharge from the mining works, not water quality affected by leaching of the mining waste and mining residuum. The two cases must be strictly distinguished, even though they may appear geochemically very similar.

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References


Przegląd Oceanograficzny, No. 24, pp. 129 (in Polish).


