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TECHNICAL ARTICLE

Geochemistry of Mine Tailings from Processing of Siderite–Cu Ores and Mobility of Selected Metals and Metalloids Evaluated by a Pot Leaching Experiment at the Slovinky Impoundment, Eastern Slovakia

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Abstract This work describes the geochemistry, mineralogy, and mobility of selected metals (Cu, Pb, Zn) and metalloids (As, Sb) in a tailings impoundment in the village of Slovinky (eastern Slovakia). The tailings were covered unevenly by slag from processing of Cu wastes. The tailings and slag both have negligible potential for acid mine drainage formation, thus neutral to alkaline conditions predominate, as shown by high paste pH values of the tailings (7.66–8.83) and neutral drainage, with pH values above 7.50. Weathering of the most abundant primary sulfides (chalcopyrite, pyrite, and arsenopyrite) releases low concentrations of As, Cu, Pb, Sb, and Zn from the tailings impoundment and in leachates from a 150 days pot leaching experiment. This is explained mostly by formation of secondary ferric oxyhydroxides (as weathering rims on the surfaces of primary sulfides or individual grains),which incorporate 4.09 wt% of As, 17.2 wt% of Cu, 1.20 wt% of Pb, 15.0 wt% of Sb, and 1.59 wt% of Zn. Elevated contents of metals and metalloids in weathering rims formed on slag components like glasses, metallic grains, and residues of blast-furnace lining indicate that secondary solid phases are controlling the mobility of the potentially toxic elements. Generally, with the exception of Cu, no separate secondary compounds of the metals or metalloids were found. The potentially toxic elements are mainly immobilized by ferric oxyhydroxides and other iron mineral phases in the tailings impoundment.

Keywords Adsorption · Antimony · Arsenic · Iron oxyhydroxide · Neutralization · Water contamination

Introduction

Mine tailings are wastes that remain after ore concentration processes such as milling operations and ore extraction. At such sites, huge quantities of tailings are typically deposited in impoundments as a fine-grained sediment-water slurry (Lottermoser 2007). Recent severe accidents at several tailings impoundments (e.g. Ajka, Hungary in 2010, Mianyang City, China in 2011), where large volumes of tailings were discharged directly into the surrounding environment, clearly draw international attention to the safety of tailings impoundments, and the need to assure the safety of these structures (Nagy et al. 2013; WISE-Uranium 2013).

Potential hazards associated with tailings impoundments include stability, rupture, surface and groundwater contamination through leaching of potentially toxic elements (PTEs) and formation of acid mine drainage (AMD) (Dold and Fontboté 2002; Grangeia et al. 2011). In the Slovak

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Republic, mining was a large industry that provided valuable raw materials and created economic benefit for local communities. However, environmental damages caused by this industry range from unsightly mine tailings to dispersion of PTEs into the surrounding environment, thereby contaminating soils and waters (Balintova et al. 2015; Hiller et al. 2012). Several tailings impoundments in Slovakia potentially represent a very high risk for people living in their vicinity and for the environment, given the large concentrations of PTEs in the tailings and improper technical conditions of the impoundments. An evaluation of environmental damages caused by mining classified 25 of 535 evaluated areas in Slovakia as hazardous and requiring decontamination (Vrana et al. 2005).

Although less spectacular than the disastrous failure of tailings dams, discharge of water from intact tailings impoundments containing elevated concentrations of dissolved sulfate and PTEs results in widespread and serious environmental problems (Sarmiento et al. 2011). The different weathering processes that occur in tailings impoundments, such as sulfide oxidation, acid generation and acid-neutralization, oxidation–reduction reactions involving Fe, metal cycling associated with efflorescent sulfate salts, secondary precipitation of hydroxides and hydroxysulfates, and associated sorption of dissolved metals and metalloids, all contribute to the mine drainage chemistry (Nordstrom and Alpers 1999).

If tailings are exposed to atmospheric O_2, the acidity in the form of sulfide minerals is transformed to H^+, generating AMD (Akcil and Koldas 2006; Simate and Ndlovu 2014) that usually contains elevated concentrations of PTEs as a result of mineral dissolution reactions (Goumih et al. 2013; Jurjovec et al. 2002; Sima et al. 2011). On the other hand, the AMD may be neutralized by the dissolution of carbonate and aluminosilicate minerals (Heikkinen et al. 2009; Lindsay et al. 2009). The occurrence of these minerals in tailings impoundments with high sulfide-bearing mineral content is particularly important because neutralization of the acidity can decrease the concentrations of the dissolved metals (Khorasanipour and Eslami 2014). Mobility of PTEs released by sulfide oxidation depends on the formation of secondary minerals such as ferric oxyhydroxides, which play an important role in the natural attenuation of PTEs through adsorption or co-precipitation (Berger et al. 2000; Lin 1997). Therefore, the chemistry of tailings porewaters and the mobility of PTEs in such heterogeneous environments are markedly dependent on their unstable physico-chemical conditions, and can be very difficult to predict.

The assessment of PTE mobility in the studied mine tailings impoundment at Slovinky (eastern Slovakia) is complex because slag from processing of Cu wastes in the Krompachy metallurgical plant were deposited in the upper 3–5 m of the impoundment, on top of the flotation tailings from siderite–Cu ore processing. Slag is produced during the pyrometallurgical recovery of base metals by smelting in a furnance (Piatak et al. 2004, 2015) and is often considered to be chemically inert (Parsons et al. 2001), but many studies have shown that high concentrations of PTEs may be released into the environment by natural weathering of slag, and that this can have deleterious effects on water and soil at historical smelting sites (Ettler et al. 2009; Gee et al. 1997; Lottermoser 2002).

Effective management of tailings impoundments requires an understanding of the processes resulting in contaminant release, transport, and attenuation (Brookfield et al. 2006). Total concentrations of PTEs in tailings solids only provide information on the degree of contamination, not on their mobility and bioavailability; only the metal fraction that is readily released from its solid state is likely to adversely affect living organisms and the environment (Bird et al. 2003). Therefore, leaching experiments targeting the water-soluble, easily mobilizable fractions of PTEs provide useful information about their mobility and possible impact on the environment.

The studied tailings impoundment: (1) is located near a sensitive aquatic environment, (2) contains a large volume of tailings, (3) is mechanically unstable and is located above the village of Slovinky, and (4) is not maintained. The main aims of this study were: (1) to determine the fundamental geochemical properties and mineralogy of the tailings and slag in the Slovinky impoundment, (2) to investigate the mobility of target PTEs (As, Cu, Pb, Sb, and Zn) using short-term leaching experiments, 150 days pot leaching experiment, and sampling of drainage waters, and (3) to evaluate the impact of tailings geochemistry and mineralogy on the release of PTEs.

Study Area

The mine is located in the village of Slovinky in the western part of the Spišsko-Gemerské Rudohorie mountains, and northeastern part of the Slovak Republic (Supplemental Figure 1). The Slovinky-Gelnica ore deposit had the highest accumulation of Cu ores (in quartz–siderite–sulfidic veins); Cu, Ag, and Fe ores were exploited. Wall rock of the Slovinky deposit are mostly quartz–sericites, black phyllites, metarhyolites, and metatuffs of the Early Palaeozoic Gelnica Group, metabasalts, metatuffs, and sericite–chloritic phyllites of the Rakovec Group, conglomerates and breccias of the Permian Krompachy Group, and shales, sandstones, and limestones of the Mesozoic Stratená Group. The most important ore veins of the metamorphic-hydrothermal siderite-sulfidic mineralization were the Hrubá and Zlatá veins, which were 16 and 24 km long, respectively, making them the longest ore vein structures in the Spišsko-Gemerské Rudohorie Mts. (Grecula et al. 1995). The veins are characterized by continuous mineralization over a length of hundreds of meters, and vertically reach a depth of more than 1 km.

Mineral filling of the veins is variable with the prevalence of quartz–sulfidic mineralization over siderite. The most abundant sulfide minerals are chalcopyrite, tetrahedrite, pyrite, and arsenopyrite. Galena, sphalerite, bornite, bournonite, jamesonite, tennantite, Cu-arsenopyrite, stibnite, Bi-sulfosalts, cobaltite, and native silver are less abundant. Siderite is characterized by elevated MgO content (9–19 wt%), ankerite is replaced partially by Fe–dolomite, and tourmaline, albite, rutile, chlorite, and sericite are also present (Radvanec et al. 2004). The Slovinky mine was active for over 600 years and produced over 100,000 t of Cu ore from 1368 to 1993; more than 56 % of the Cu ore was exploited after World War II. Initially, mining focused on the recovery of sulfidic Cu ores, mainly chalcopyrite and tetrahedrite. In the late nineteenth century, the recovery of Cu ores receded and that of siderite increased, due to the depletion of Cu–rich deposits, decline of global copper prices, and increased demand for iron. In 1925, production of copper was renewed whereby also Ag and Au were recovered from copper concentrate. The mined ores were processed by electromagnetic separation and selective flotation (Grecula et al. 1995). After closure of the mine in 1993, industrial wastes were smelted in the Krompachy metallurgical plant to recover copper.

The impoundment (also called “Kaligrund” or “New”) with a storage capacity of 6.5 million m^3 was build in 1967 and used for the deposition of tailings produced in the Slovinky mine. The impoundment is situated east of the mine site, only 400 m southeast of the village of Slovinky (Supplemental Figure 1). The impoundment has a 113 m high dam and stores about 4.7 million t of tailings with a unit weight of 19.5 kN/m^3 (Piovarcsy andRáchela 1998). Tailings in the form of sludge/mud were transported from the flotation plant into the impoundment using a 1200 m long pipeline. This hydraulically driven transport resulted in the deposition of coarse-grained material (sands) near the discharge point, grading to fine-grained material further from the discharge. Based on particle size distribution, the impoundment is divided into three depth layers. The first layer, from the surface to a depth of 22.5 m, consists of fine- to medium-grained sands and loamy sands (3–24 wt% <63 μm fraction and 0–4 wt% <2μm fraction). The second (from 22.5 to 44 m) contains silty and loamy sands (30–70 wt% <63 μm fraction and 3–10 wt% <2 μm fraction), while the bottom layer (44–51.8 m) consists of silty and clayey loams and clays (0–31 wt% <63 μm fraction and 7–35 wt% <2 μm fraction) (Hasaj and Šťastný 1983). Slag was deposited in the uppermost part of the impoundment as a 3–5 m thick layer overlying much of the tailings after 1993.

The impoundment’s drainage system consists of a massive filtration layer on the main dam where the seepage waters are diverted into the Slovinky Creek by three drainage pipes (Hasaj and Šťastný 1983). The impoundment has been idle without technical and security monitoring since an ownership change in 2003. The dam surface is trenched by water erosion, and furrows and tailings slumps form during rainy periods.

The climate in the study area is moderately cool with an average temperature of −5 °C in January and +15 °C in July. Average annual temperature is +5 °C, and annual rainfall and evaporation are 550 and 400 mm, respectively (Landscape Atlas of the Slovak Republic 2002).

Materials and Methods

Sampling of Mine Tailings and Waters

Tailings were sampled at regular depth intervals from two boreholes (B-1 and B-2). The first borehole (B-1), with a depth of 21 m, was located in the middle of the top level of the impoundment. The second borehole (B-2) was 20 m deep and located in the slope of the impoundment down from the borehole B-1, so that the top of borehole B-2 was in a horizontal plane with the bottom of borehole B-1 (Supplemental Figure 1). Samples used for mineralogical and geochemical analyses were collected from the central point of the core along its length. Drilling was done by Aqua-Geo Ltd., Bratislava. All samples were frozen for transport to the laboratories.

Aqueous samples were collected during one sampling campaign in 2013 at the impoundment from (Supplemental Figure 1): (1) the surface stream draining into the impoundment (sample W-1), (2) the flooded area of the impoundment (W-2), (3) the discharge of the impoundment equipped with three pipes (W-3 to W-6), and (4) Slovinský creek (W-7) where the water from the impoundment is discharged and above that discharge (W-8). The waters were sampled in 1 day immediately after rain occurred. This sampling was designed to assess the actual leaching of the exposed tailings material. Values of pH, Eh, and electric conductivity (EC) were measured in situ using a WTW Multi 350i instrument equipped with Sentix® 41, Sentix® ORP, and TetraCon® 325 electrodes, respectively. Water samples were collected in polyethylene bottles and filtered in the field using a 0.45 μm pore-size filter (Millipore). Aqueous samples for metal analysis were immediately preserved at $pH < 2$ using HNO_3; those for anion analysis were left unacidified.

Analysis of Mineralogical Composition

Powder x-ray diffraction (XRD) analyses were conducted on a BRUKER D8 Advance diffractometer under the following conditions: Bragg–Brentano geometry (Theta-2Theta), Cu anticathode ($\lambda\alpha_1 = 1.54060$ Å), a 40 kV accelerating voltage, and beam current of 40 mA. Ni Kβ filters were used to strip Kβ radiation on the primary and diffracted beam, and data were obtained by the BRUKER LynxEye detector. The step size was 0.01° 2θ, the step time was 1 s per one step, and the range of measurement was 4–65° 2θ. Main mineral phases were identified with the DIFFRAC^{plus} EVA software package (Bruker 2010a). The abundance of the main mineral phases in the XRD patterns was quantified by the Rietveld refinement with the DIFFRAC^{plus} TOPAS program (Bruker 2010b) using fundamental parameters. α-Corundum powder was mixed into each sample as an internal standard.

The heavy fractions of the samples were concentrated by panning in water or ethanol. Selected heavy concentrates were prepared for further study in the form of standard thin and polished sections to be inspected in transmitted and reflected polarized light, respectively.

Chemical compositions of the primary and secondary phases were determined with a Cameca SX-100 electron microprobe (EMP) in wavelength-dispersive mode (WDS) under the conditions of 15 kV, 20 nA, and a beam size of 1–5 μm. The following lines, standards, and detector crystals were used for the analyzed elements: Mg (*K*α, forsterite, TAP), Al (*K*α, Al_2O_3, TAP), Si (*K*α, SiO_2, TAP), S, Fe, Cu (*K*α, $CuFeS_2$, PET), P (*K*α, GaP, PET), Ca (*K*α, wollastonite, PET), Mn (*K*α, Mn, LIF), Co (*K*α, Co, LIF), Ni (*K*α, Ni, LIF), Zn (*K*α, ZnS, LIF), Pb (*M*α, PbS, PET), Sb (*L*β, Sb_2S_3, PET), and As (*L*β, FeAsS, TAP). The counting time on each peak was 20 s, on background 10 s (20 s for Sb).

Geochemical Analyses of Mine Tailings and Waters

Tailings samples were allowed to thaw to determine paste pH and Eh. Distilled water was added to the unfrozen tailings sample until a slurry was obtained (Richards 1954). The slurry was left to stand for 15 min and pH or Eh was measured until a constant value was obtained.

Tailings samples for the determination of neutralization potential, concentrations of major (Si, Fe, Al, Ca, Mg, K, Na, Mn, P, and S) and minor (As, Cu, Hg, Pb, Sb, and Zn) elements, and subsequent leaching were air-dried at room temperature, then crushed, quartered, homogenized, and sieved to <1.0 mm fraction. Static acid–base accounting (ABA) was performed using the modified Sobek method (Skousen et al. 1997) because the tailings contain abundant siderite (see below). The net acid generation (NAG) test, in which sulfides in a tailings sample were rapidly oxidized by hydrogen peroxide and the generated acidity was neutralized naturally by carbonates, if present (Miller et al. 1997).The saturated paste pH indicates the immediate effects of acid released from readily soluble phases, such as efflorescent sulfate minerals, whereas the NAG pH indicates the eventual effects of additional acid released by sulfide oxidation.

Major chemical elements were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian Vista AX and Varian Liberty 200 instruments) after fusion of samples with lithium metaborate and digestion with HCl. Metals (Cu, Pb and Zn) and metalloids (As and Sb) were measured by atomic absorption spectrometry (AAS, Varian SpectrAA 220) and AAS with a hydride generation system (AAS-HG, VGA 76), respectively, using samples digested at 90 °C with a mixture of *aquaregia*–HF. Total sulfur (S_{tot}) was determined by ICP-AES in samples digested with a mixture of *aquaregia*–HF. Diluted HCl (40 % *v*/*v*) was used to extract sulfates, and the solution obtained was analyzed by ICP-AES. The accuracy of the digestion/analytical procedure was better than <10 % relative standard deviation for all elements. Chemical composition of samples was analyzed by accredited testing laboratories (Ecological Laboratories, EL, Ltd., Spišská Nová Ves, Slovakia) according to STN EN ISO/IEC 17025 (2005).

Water samples and leachates were analyzed for selected major and trace cations (Ca, Cu, Fe, K, Mg, Mn, Na, Pb, and Zn) using ICP-AES (models Varian Vista AX and Varian Liberty 200). Both As and Sb concentrations were determined by AAS-HG, sulfate and chloride anions were measured by ion chromatography (IC, Dionex DX-120), and alkalinity was measured by manual titration using 0.1 M HCl. Accuracy and precision of the analytical methods were checked by analyzing duplicate samples, blanks, and certified reference material ERM-CA713 (wastewater for As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se). Precision was within a range of ±10 % or less.

Leaching of Mine Tailings

Two leaching tests were used in this study. In order to categorize mine tailings as nonhazardous/hazardous waste by the EU legislation (Van Gerven et al. 2005), short-term batch extraction tests were performed according to the standardized leaching protocol European norm EN 12457 (EN 12457-2 2002). Ten g of air-dried tailings sample were added to 100 mL of Milli-Q+ deionized water in polyethylene bottles and shaken for 24 h at a temperature of 22 ± 3 °C. After shaking, the bottles were centrifuged at 2500×*g* for 20 min and filtered through a 0.45 μm pore-size filter. Concentrations of target elements (As, Cu, Pb, Sb, and Zn) and sulfates in the leachates were determined by the same analytical methods as described above.

To investigate the release of selected metals and metalloids from mine tailings under more realistic conditions than may be provided by short-term batch extraction tests, long-term leaching experiments over 150 days (from October 2013 to March 2014) were performed outdoors in a 7.5 L plastic pot. A slag–tailings sample from a depth of 0–1.0 m and a tailings sample from a depth of 8.0–9.0 m were used in the pot leaching test because both samples were representative of an average chemical composition of slags and tailings deposited in the impoundments. Six and four kilogram of air-dried, homogenized, and sieved to <1 mm tailings and slag–tailings mixture, respectively, were placed in the plastic pot. One Rhizon pore water sampler with a pore size of 2 µm (Prenart Equipment ApS, DK) was placed in the bottom part of the pot and the other was placed in the slag–tailings layer (Supplemental Figure 2). At the beginning of the experiment, the pot was irrigated with 2.56 L of deionized water (MilliQ+, Millipore, USA) to approximately 60 % of the water-holding capacity (WHC) and first pore water samples were taken from both Rhizon samplers after 24 h. To simulate "dry" and "wet" cycles after the first step, the pot was left to dry for 5 days, then irrigated with deionized water to 60 % WHC, followed by collection of pore water. This was repeated once more, after which the time between two consecutive irrigations was prolonged to 10 and 20 days after 11 and 31 days, respectively, since the start of the experiment. Overall, 11 pore water samples were taken from each Rhizon sampler after 1, 6, 10, 20, 30, 50, 70, 90, 110, 130, and 150 days. Values of pH, Eh, and EC were recorded by a WTW Multi 350i instrument. Concentrations of major cations and anions, metals, and metalloids in pore water samples were analyzed by the methods given above.

Geochemical Calculations

Speciation-equilibrium calculations were performed using PHREEQC (Parkhurst and Appelo 1999) with the included minteq.v4.dat database. This program is used to calculate the speciation of dissolved ions in an aqueous solution and saturation indices (SI) of mineral phases as a function of pH, temperature, ionic strength, etc. A positive SI value indicates that the mineral will precipitate eventually, a negative SI value shows that the mineral will dissolve, and an SI value equal to 0 indicates equilibrium between aqueous solution and the mineral.

Results and Discussion

General Description and Mineralogical Composition

The uppermost part of borehole B-1 consisted of a ≈3 m thick layer of a slag–tailings mixture; however, no slags were present in borehole B-2. The slag–tailings mixture was different visually from the tailings. The mixture was dark gray to black and created a crust on the surface of the impoundment. Below the slag layer in B-1, tailings layer with some indications of oxidation were found up to a depth of 5 m. At deeper depths, ≈ 8 m and below, the tailings were mostly clayey layers with typically grayish colors; the water table was reached at a depth of about 15 m. The upper layers of tailings in borehole B-2 exhibited signs of oxidation to a depth of 4 m and had a reddish-brown color. This layer was underlain by dark gray, water-saturated tailings, which extended down to the base of borehole B-2 at a depth of 20 m.

The sulfide-S contents were low in both slag and tailings samples, and ranged within 0.13–0.44 wt% in B-1, with a decrease of sulfide-S content with increasing depth, and 0.07–0.29 wt% in B-2, with an increasing trend downward (Fig. 1a). The neutralization potential ratio (NPR) calculated as neutralization potential (NP)/acid generation potential (AP) for selected samples is shown in Fig. 1b. In B-1, a maximum value of 51.7 was observed in the slag–tailings layer and then NPR values decrease with increasing depth to a value of 7.9 at 19 m depth. The same trend was seen in B-2 with a maximum of 21.5 in the surface layer of the tailings and lower NPR values in deeper layers of the tailings profile. These relatively high NPR ratios indicate that there is a significant neutralization capacity throughout all depths in both investigated boreholes. This is consistent with the neutral to slightly alkaline paste pH values, which ranged from 7.66 to 8.74 and from 7.77 to 8.83 in B-1 and B-2, respectively (Fig. 1c). Moreover, since the NAG pH was well above the critical value of 4.50 (Fig. 1d), the slag and tailings can be regarded as non-acid generators (Miller et al. 1997).

The mineralogical composition of the tailings in boreholes B-1 and B-2 is given in Supplemental Table 1. The most abundant primary minerals in the tailings were quartz, siderite, and muscovite; chlorite, dolomite, and gypsum were less abundant. The quartz, siderite, and muscovite content in B-1 seems to increase with increasing depth (data not shown); however, the increase was not continuous, e.g. quartz content increased continuously from approximately 8 wt% up to a maximum of ≈26 wt% at 10 m, and then decreased to ≈20 wt% at 19 m. The quartz, siderite, and muscovite content in the B-2 tailings did not change significantly with depth.

As previously mentioned, the uppermost part of borehole B-1 consists of a mixture of copper slag and tailings; therefore, its mineralogy differed from the tailings. This mixture consisted mainly of amorphous glasses with variable chemical composition, of the same minerals as identified in the tailings samples, crystalline slag fragments represented mainly by ortho- and clino-pyroxenes enstatite

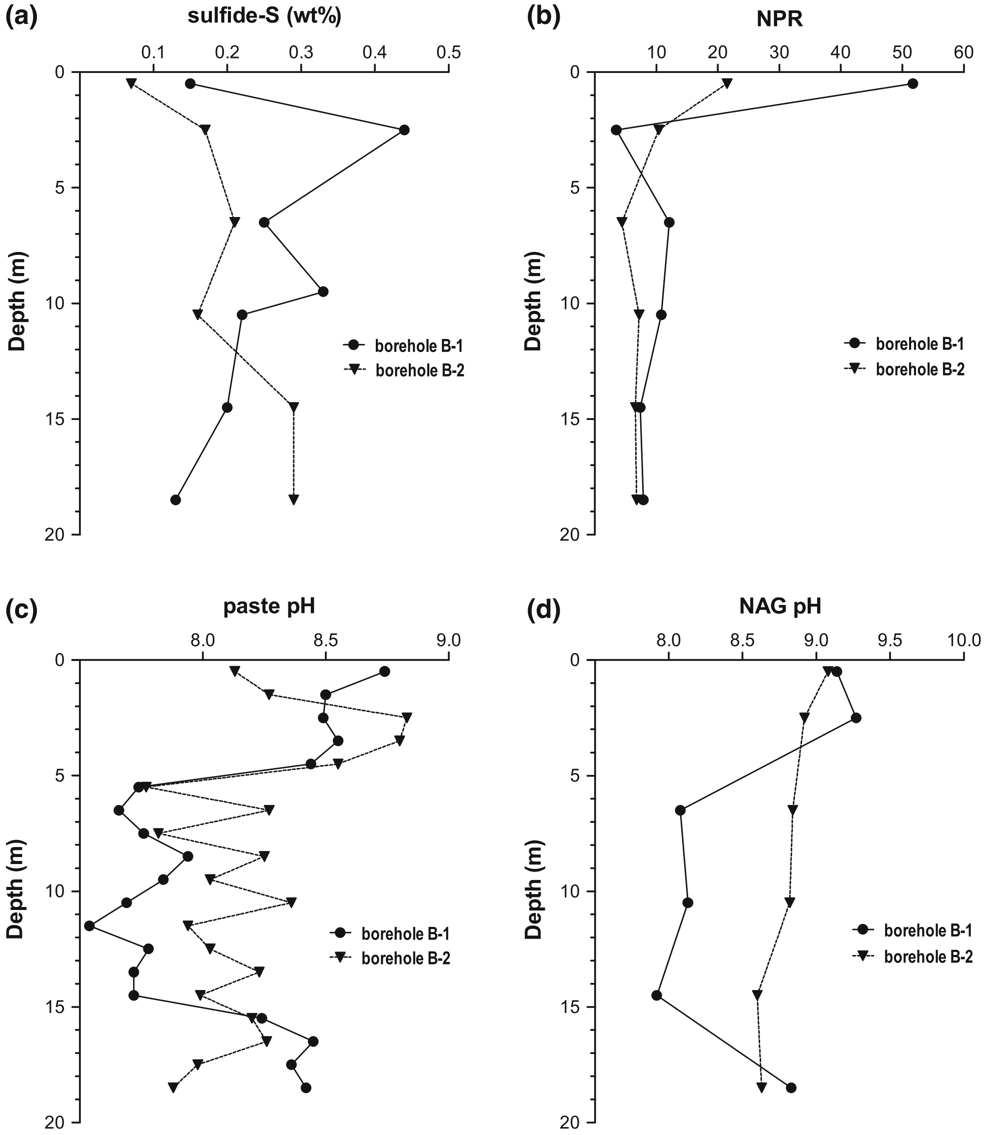


Fig. 1 Profiles of **a** content of sulfide-S, **b** neutralization potential ratio NPR, **c** paste pH values, and **d** NAG pH values in two boreholes B-1 and B-2

and diopside, respectively, and some forsterite. Moreover, the slag–tailings mixture contained elemental Fe, metallic phases consisting mainly of elemental Fe and Mn (Fig. 2a), and residues of the blast-furnace lining (Fig. 2f). These phases were frequently weathered, as evidenced by the occurrence of massive weathering rims developed on their surfaces (Fig. 2a, f).

The most common sulfide minerals identified in heavy fractions of the solid samples were chalcopyrite and pyrite, followed by tetrahedrite and rare arsenopyrite. In a previous study by Kučerová et al. (2013), delafossite was also identified in the tailings using micro-Raman spectroscopy. Covellite in the form of blue coatings on chalcopyrite and native copper was also rarely identified using optical microscopy.

Secondary products originating from sulfide weathering included rims on the primary sulfide minerals and individual grains. The representative chemical composition of weathering products measured by EMP is shown in Supplemental Table 2. Weathering rims developed on the chalcopyrite grains consisted mostly of amorphous Fe(III) oxyhydroxides (Fig. 2b). They exhibited variable contents of Fe (35.5–45.9 wt%), As (0.25–1.63 wt%), Ca (0.35–1.35 wt%), Cu (5.71–14.6 wt%), Sb (0.89–15.0 wt%), and Zn (0.04–1.07 wt%). The chemical composition of weathering rims on the pyrite grains (Fig. 2c) was also variable (Supplemental Table 2); they were predominantly amorphous Fe(III) oxyhydroxides and rarely goethite of low crystalinity (Kučerová et al. 2014). Individual grains of secondary minerals consisted mainly of amorphous Fe(III)

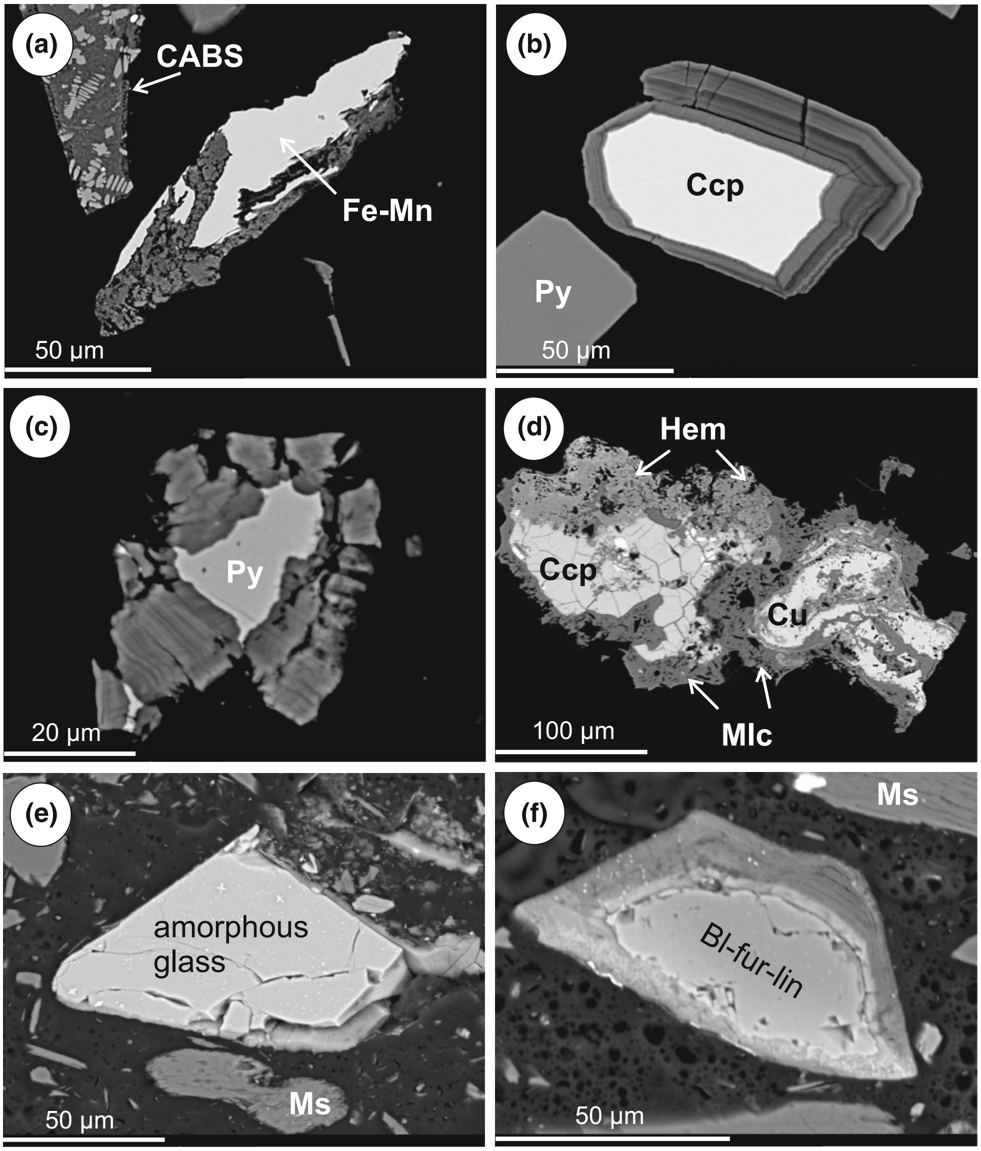


Fig. 2 Selected back-scattered electron (BSE) images of mineral phases from the tailings and slags: **a** grain of metallic Fe–Mn phase (*white color*) with oxidation rim (*gray color*) and crystalline air-cooled slag fragment (CABS), **b** weathering rim on chalcopyrite (Ccp) and grain of pyrite (Py), **c** weathering rim (*dark gray*) on pyrite (Py), **d** chalcopyrite (Ccp), native copper (Cu) and hematite (Hem) with cementing malachite (Mlc), **e** weathering rim (*dark gray*) developed on amorphous glass (*bright gray*) and muscovite (Ms), **f** blast-furnace lining residue (Bl-fur-lin) with weathering rim

oxyhydroxides and goethite with elevated contents of some elements, like Cu, Mg, Mn, Pb, Sb, Si, and Zn (Supplemental Table 2). These Fe(III) oxyhydroxides originated from the weathering of siderite and sulfide minerals as well as by precipitation from the pore solutions. The elevated Mg and Mn content of some individual grains of Fe(III) oxyhydroxides and in weathering rims may be due to dissolution of dolomite and siderite, which may contain up to 19 wt% of MgO (Chovan et al. 1994). A rare occurrence of hematite was also observed in the tailings (Fig. 2d; Kučerová et al. 2014). Previous studies that focused on tailings mineralogy (e.g. Blowes et al. 1998; Hiller et al. 2013; Lalinská-Voleková et al. 2012; Souissi et al. 2013) have documented that ferric oxyhydroxides, either amorphous or crystalline, mainly ferrihydrite, goethite, and hematite, are the most common weathering products of primary minerals in many tailing impoundments with high neutralization capacity. In the first 0.50 m from the tailings surface, copper oxides/carbonates were also identified. These Cu-bearing mineral phases mostly cemented other minerals, e.g. sulfides, carbonates, or silicate minerals (Fig. 2d), but also occurred as individual grains. Using micro-XRD, Kučerová et al. (2014) confirmed that these secondary Cu oxides/carbonates were cuprite and malachite.

Bulk Chemical Composition

Concentrations of major and trace elements in solid samples of boreholes B-1 and B-2 are shown in Table 1. There was large difference in chemical composition between the slag–tailings mixture and the tailings (Table 1). In general,

Table 1 Concentrations of major and trace chemical elements in the slag and tailings samples collected from two boreholes B-1 and B-2

Element	Unit	Tailings B-1	Slag–tailings B-1	Tailings B-2
N		8	3	11
Si	wt%	28.67 ± 1.09[a]	16.77 ± 2.04	29.06 ± 0.81
Fe	wt%	8.88 ± 0.99	22.60 ± 4.23	9.44 ± 0.93
Ca	wt%	0.98 ± 0.29	4.21 ± 0.99	1.08 ± 0.25
Mg	wt%	1.96 ± 0.35	2.24 ± 0.70	2.52 ± 0.35
Al	wt%	4.27 ± 0.37	3.15 ± 0.20	2.62 ± 0.15
K	wt%	1.23 ± 0.99	0.53 ± 0.31	1.16 ± 0.08
Na	wt%	0.18 ± 0.13	0.37 ± 0.12	0.23 ± 0.04
Mn	wt%	0.37 ± 0.05	0.26 ± 0.03	0.49 ± 0.06
Ti	wt%	0.19 ± 0.02	0.15 ± 0.01	0.14 ± 0.01
P	wt%	0.04 ± 0.007	0.06 ± 0.009	0.03 ± 0.004
As	mg/kg	375 ± 191	310 ± 115	261 ± 115
Cu	mg/kg	1685 ± 849	7296 ± 1969	1051 ± 667
Pb	mg/kg	247 ± 218	2300 ± 1331	165 ± 167
Sb	mg/kg	213 ± 267	1725 ± 1791	47.2 ± 30.0
Zn	mg/kg	2207 ± 2058	28,251 ± 4764	1204 ± 1422

N number of samples

[a] Concentrations are given as mean value and standard deviation

the mixture contained less Si, but more Fe and Ca than the tailings. Moreover, concentrations of Cu, Pb, Sb, and Zn in the slag–tailings mixture were much higher than in the tailings. This was obviously due to the different nature of slags and weathering reactions occurring in the uppermost oxidized layers. Chemical composition of the studied copper slags, despite being mixed with the tailings, is within the range of chemical compositions of other copper slags compiled by Alter (2005) and Gorai et al. (2003).

The abundance of major elements in the tailings reflected the occurrence of gaunge minerals (quartz, siderite, chlorite, and muscovite) and decreased in the order: Si > Fe > Al > Mg > Ca > K > Mn > Na ≈ Ti > P. Among the investigated metals and metalloids, the highest concentrations in the B-1 and B-2 tailings were recorded for Zn (215–6048 mg/kg), followed by Cu (689–3475 mg/kg), As (93.0–649 mg/kg), Pb (36.3–678 mg/kg), and Sb (17.3–859 mg/kg). The Cu, Pb, Sb, and Zn concentrations in both boreholes varied with depth in a similar way and were strongly correlated with each other (Supplemental Figure 3). The highest concentrations of these elements in B-1 were in the slag–tailings layer, whereas in B-2, they were preferentially concentrated in oxidized layers of the tailings, at a depth of 1–2 m. This preferential accumulation of Cu, Pb, Sb, and Zn was accompanied with the highest concentration of Fe at this depth (≈15 wt%). This could be explained by the precipitation of secondary phases, such as ferric oxyhydroxides, after the weathering of sulfides under the oxidizing conditions predominating near the surface. These secondary phases retain metals and metalloids released from weathered sulfides and lead to metal enrichment (McGregor et al. 1998). Arsenic profiles were irregular, with no apparent enrichment in the slag–tailings layer and the oxidized zone of boreholes B-1 and B-2.

Water Geochemistry

Water samples collected in 2013 from the tailings impoundment and associated nearby sites, including Slovinský Creek (Supplemental Figure 1), were used to assess the potential for the mine waste leachate to affect water quality. Although water flow conditions can affect the chemical composition of waters (Balintova et al. 2015; Frau et al. 2009; Salvarredy-Aranguren et al. 2008), it seems, based on previously obtained results (Bajtoš 2012; Final report 2012), that their role is small in the study area. The physico-chemical parameters are shown in Table 2. All of the samples had a neutral to slightly alkaline pH (7.51–8.55), confirming that the mine wastes were able to efficiently neutralize the acidity generated by sulfide oxidation. Most of the water samples were of the Mg–Ca–HCO_3–SO_4 type with a Ca/Mg molar ratio between 0.38 and 1.38. These Ca/Mg molar ratios are indicative of dolomite and silicate dissolution (Prasanna et al. 2010). Moreover, the molar concentrations of $Ca^{2+} + Mg^{2+}$ in both impoundment-influenced water samples and leachates correlated significantly with those of $SO_4^{2-} + HCO_3^-$ ($p < 0.001$), and fell along the equiline where $Ca^{2+} + Mg^{2+} = SO_4^{2-} + HCO_3^-$. This is a consequence of various interrelated physico-chemical processes. Weathering of pyrite and other sulfides in the impoundment releases SO_4^{2-} and acidity, which is consequently neutralized by the dissolution of dolomite (the source of Mg^{2+}, Ca^{2+}, and HCO_3^-), siderite, and likely also aluminosilicates like chlorite.

Despite the fact that the mine wastes had high concentrations of PTEs, mainly As, Cu, Pb, Sb, and Zn (Table 1), their concentrations in the waters draining directly from the tailings impoundment (samples W-3–W-6) were very low. Lead was below the detection limit of the method (<10 µg/L) in all water samples, whereas Cu and Zn concentrations were only 6.0 µg/L and 9.0–11.0 µg/L, respectively, in the flooded area of the impoundment (sample W-2) as well as in surface water entering the impoundment (sample W-1). Copper was only 5.0 µg/L in sample W-7 at the confluence of drainage waters and the Slovinský creek. Metalloids (As and Sb) occurred in the water samples more frequently and at higher concentrations than metals (Table 2), but still far below the concentrations at which any environmetal risk to the aquatic fauna and flora would be expected. These results agree well with those obtained by Bajtoš (2012), who determined As and Sb concentrations in water

Table 2 Main physico-chemical parameters and concentrations of major ions, selected trace metals and metalloids in water samples

Sample	pH	EC (µS/cm)	Eh (mV)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	As (µg/L)	Cu (µg/L)	Fe (µg/L)	Pb (µg/L)	Sb (µg/L)	Zn (µg/L)
W-1	8.29	465	+462	37.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<1.0	<5.0	23	<10	2.0	9.0
W-2	8.55	394	+429	33.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.0	6.0	601	<10	73	11
W-3	7.97	850	+421	232	284	3.6	58.4	76.7	18.2	8.8	9.0	<5.0	53	<10	28	<5.0
W-4	7.80	857	+406	202.8	282	16.2	94.7	41.7	21.9	7.8	2.0	<5.0	65	<10	12	<5.0
W-5	7.59	391	+438	50.2	184	2.9	30.9	26.1	11.6	4.3	14	<5.0	16	<10	37	<5.0
W-6	7.60	416	+455	349	372	5.8	75.1	119	14.0	8.7	14	5.0	27	<10	13	<5.0
W-7	7.54	390	+445	42.8	225	<2.0	26.4	40.6	3.3	1.2	41	5.0	29	<10	13	<5.0
W-8	7.51	323	+467	52.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<1.0	<5.0	21	<10	1.0	7.0

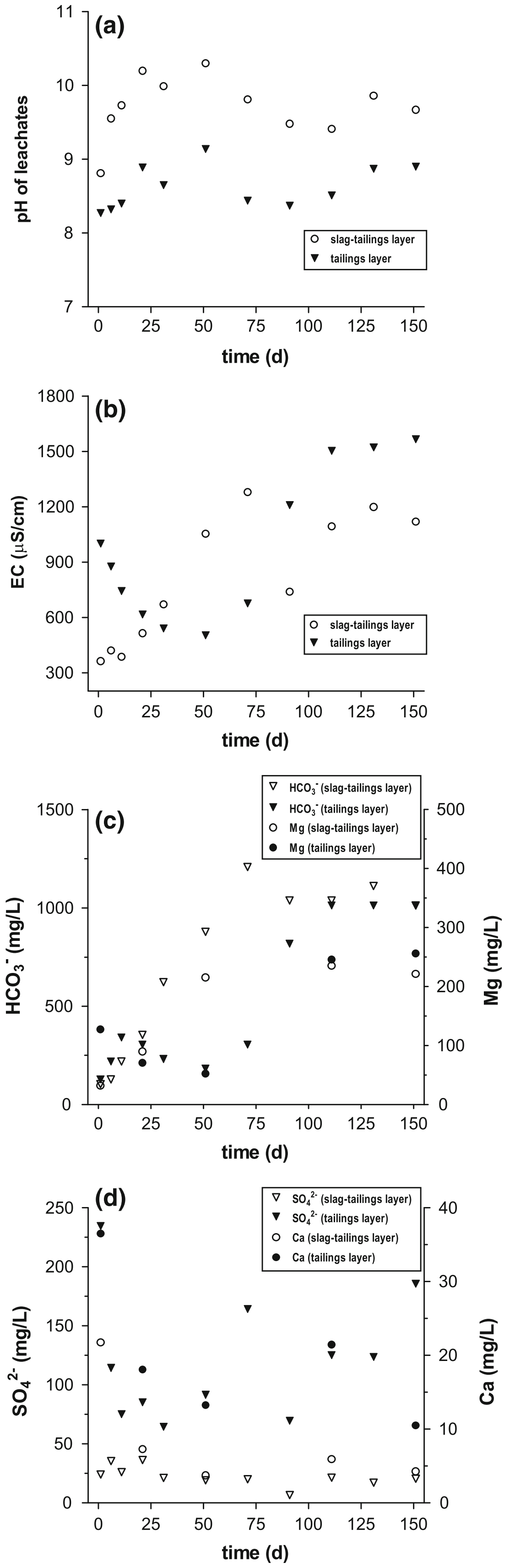
n.d. not determined

draining from the impoundment (7.0–18 µg/L for As and 8.0–12 µg/L for Sb) and in Slovinský creek (19–44 µg/L for As and 6.0–14 µg/L for Sb) between 2008 and 2012. Moreover, he observed a small inverse effect of flow rate in Slovinský Creek on dissolved concentrations of both metalloids, showing that As and Sb are partially diluted by meteoric waters. Comparison of the concentrations of PTEs, Fe, and SO_4^{2-} in Slovinský creek (samples W-7 and W-8) with their average concentrations (3.4, 5.0, 1.7, 8.5, and 19.0 µg/L for As, Cu, Pb, Sb, and Zn, respectively, and 0.106 mg/L for Fe, and 44.08 mg/L for SO_4^{2-}) in surface waters of the Spišsko–Gemereské Rudohorie Mts. (Rapant et al. 2009) shows similar values. This means that levels of PTEs in the stream water are controlled by the lithology of the area rather than by the impoundment water that enters Slovinský Creek, i.e. the impact of tailings on the creek's water quality seems to be of minor importance.

Leaching Tests and Controls on the Mobility of Dissolved Constituents

Major Cations and Anions

Leaching of the target PTEs in the impoundment during 150 days was simulated using a plastic pot containing the flotation tailings covered with a layer of the slag–tailings mixture as was observed in parts of the impoundment. The solutions collected by Rhizon pore water samplers at the end of each lixiviation cycle were analyzed for the main physico-chemical parameters (pH, Eh, and EC), the major cations and anions (Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^2), and PTEs (As, Cu, Pb, Sb, and Zn). All of the leachates recovered from the slag–tailings mixture had alkaline pH values (8.81–10.34), which decreased to pH values of 8.27 to 9.14 after percolation of pore waters through the tailings (Fig. 3a). The alkaline leachate produced from the slag–tailings mixture is mainly due to the dissolution of Ca and Mg oxides/hydroxides and carbonates like brucite and dolomite, respectively, that were identified in the slag–tailings mixture. Additionally, dissolution of olivines and pyroxenes present in the slag–tailings mixture may contribute to high pH values of the leachates (Jambor et al. 2002), although these aluminosilicates dissolve much slower than carbonate minerals. The Eh values exhibited low variability and were between +385 and +531 mV, indicating a fairly oxidizing conditions during the entire experimental time period. Electrical conductivity (EC) of the leachates from the slag–tailings mixture increased with increasing number of leaching cycles (Fig. 3b) and the same trend was observed in the leachates collected in the tailings layer. It was interesting to note that the EC values correlated with the Mg^{2+} and HCO_3^- concentrations (Fig. 3b vs. c, d) but not with Ca^{2+} and SO_4^{2-}



◀**Fig. 3** Main physico–chemical parameters **a** pH and **b** electrical conductivity (EC) and concentrations of **c** Mg^{2+} and HCO_3^-, and **d** Ca^{2+} and SO_4^{2-} in the leachates recovered from slag–tailings and tailings layers at the end of each lixiviation cycle over 150 days period

concentrations. These results suggest that the dissolution of Mg-bearing phases was the main factor controlling the EC of the leachates. Additionally, a gradual increase of Mg concentrations in the leachates from the slag–tailings layer in each subsequent leaching cycle was observed (Fig. 3c) and this increase was also observed in the tailings leachates, partially due to transport of pore waters from the slag–tailings layer into the tailings layer. It is suggested that elevated leaching of Mg later in the experiment is due to partial dissolution of dolomite, siderite with an elevated Mg content, and the amorphous glass in the slag, which contained up to 9.22 wt% of Mg (Supplemental Table 2). Such glass is not readily soluble during short-term leaching experiments but its dissolution may be accelerated at a pH above 9 (Gitari et al. 2009). Mineralogical inspection of residues after leaching using EMP/WDS analysis revealed frequently occurring weathering rims on the surface of the glass particles and blast-furnace lining (Fig. 2e, f), which had elevated Mg contents (up to 44.3 wt%), Fe (up to 35.5 wt%), and other chemical elements such as Cu (a maximum of 28.6 wt%), Pb (to 1.43 wt%), and Zn (up to 5.07 wt%) (Supplemental Table 2). This confirmed that the glass and other solids rich in Mg partially dissolved in the later phase of leaching, i.e. after 1 month.

Geochemical calculations using PHREEQC predicted near-saturation of the leachates recovered from the slag–tailings layer with brucite [$Mg(OH)_2$] (Supplemental Table 3), which was identified by XRD in the samples. Therefore, brucite was considered to be another solid phase controlling the mobility of Mg in the tailings impoundment. Although pot leaching experiments are only simplifications of the complex natural conditions, concentrations of the major ions (Ca^{2+}, Mg^{2+} and SO_4^{2-}) and values of pH, Eh and EC in the waters draining from the impoundment base (samples W-3–W-6; Table 2) were comparable to those found in the leachates at the base of the tailings layer (Fig. 3a–d). Based on the chemical similarity with the drainage water samples, it seems that the pot leaching experiment provides an adequate approximation of the chemistry of potential runoff from the slag and tailings materials.

Potentially Toxic Elements

The evolution of metal and metalloid concentrations in leachates from the slag–tailings layer and the tailings over time is shown in Fig. 4. Leachates from the slag–tailings

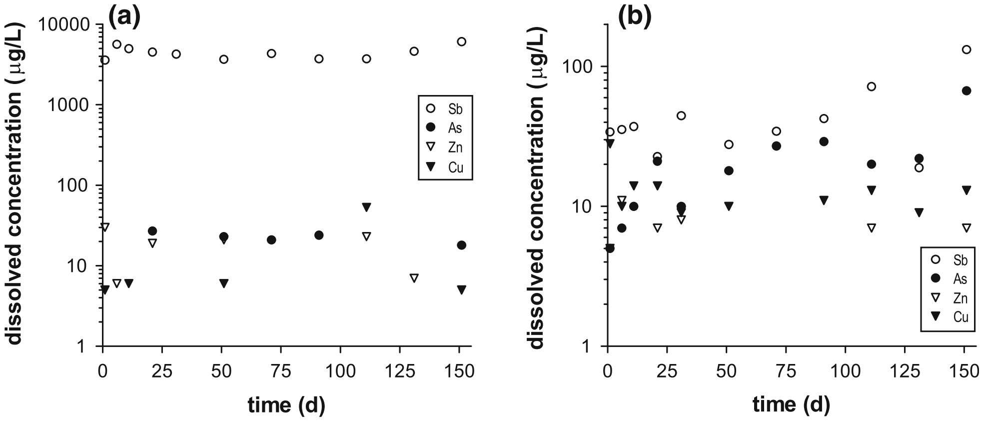


Fig. 4 Dissolved concentrations of potentially toxic elements in the leachates recovered from **a** slag–tailings layer and **b** tailings layer at the end of each lixiviation cycle over 150 days period. Concentrations of lead are not shown because they were above the detection limit only in one leachate sample collected after 110 days since the start of the pot leaching experiment

layer yielded elevated dissolved concentrations of Sb (up to 6100 µg/L), which remained relatively constant over time, whereas concentrations of As, Cu, and especially Pb and Zn, were low and generally below the detection limit of the analytical methods used (Fig. 4a). After the percolation of leachates through the tailings layer, Sb concentrations dropped sharply below 100 µg/L and other dissolved PTEs remained unchanged, with the exception of As and Cu, which were frequently detected in the leachates at concentrations above their corresponding detection limits of <1.0 and <5.0 µg/L, respectively (Fig. 4b). The concentrations of metals and metalloids in the leachates from the bottom tailings layer were comparable with those in the waters draining the impoundment (Table 2), showing the usefulness of the pot experiment as a tool for simulating contaminant release from the mine wastes. Total amounts of Sb, As, Cu, and Zn released from the solids during the entire experiment were very low compared to the corresponding total concentrations in the tailings material. Approximate calculations indicated that only 9.6 mg of Sb, 0.5 mg of As, and 0.3 mg of Cu were removed from the tailings, which corresponded to about 0.05 % Sb, 0.02 % As, and 0.0005 % Cu of the total content in the tailings. The leaching of both Zn and Pb was negligible. These results suggest that the slag and tailings stored in the impoundment are geochemically stable over time and very effective in controlling the mobilization of metals and metalloids.

The limited mobility of Cu, Pb, and Zn in the tailings is related mainly to their strong retention by abundant amorphous Fe(III) oxyhydroxides in the form of coatings and individual grains, and incorporation into the rims rich in Fe developed on the surfaces of the amorphous glass particles, blast-furnace lining, and metallic phases. Copper mobility may also be controlled by malachite, which was identified in the tailings, but the role of malachite is expected to be minor because of its rare occurrence. Inspection of the chemical composition of weathering rims using EMP analyses after the pot leaching experiment revealed that the rims were enriched with Cu, Pb, and Zn and contained to 4.05 wt% of Cu, 4.39 wt% of Pb, and 13.4 wt% of Zn (Supplemental Table 2). Additionally, speciation calculations performed with PHREEQC predicted that Cu was present mostly as carbonate and hydroxy complexes and that the prevailing species of Zn were carbonate and hydroxy complexes as well as free Zn^{2+} (Supplemental Table 3). Therefore, these metals may be effectively retained by amorphous Fe(III) oxyhydroxides through surface adsorption under slightly alkaline conditions due to their large surface area and point of zero charge between 7 and 9 (Gaboriaud and Ehrhardt 2003; Hiemstra and Van Riemsdijk 2009). In line with mineralogical observations, precipitation of several ferric oxyhydroxides and malachite was predicted by PHREEQC calculations (Supplemental Table 3); however, common secondary Zn minerals like smithsonite and goslarite were not observed in the tailings nor predicted to be the main solubility-controlling phases for Zn. Based on the pot leaching test and the geochemical, mineralogical, and modeling results, adsorption and coprecipitation by Fe(III) oxyhydroxides and other solid components rich in Fe were the most important solid phases preventing the mobilization of Cu, Pb, and Zn in the tailings. Our results agree with those of previous studies (Hiller et al. 2013; Lindsay et al. 2009; Othmani et al. 2015; Sracek et al. 2010), which confirmed the important role of ferric oxyhydroxides in the natural attenuation of dissolved metal concentrations in tailings generating neutral drainage.

Concentrations of As and Sb were low but distinctively higher than those of Cu, Pb, and Zn. As was found with the metals, the main solid phases controlling the mobilization of both metalloids appear to be the abundantly occurring amorphous Fe(III) oxyhydroxides and other secondary Fe phases in the form of weathering rims, because no separate secondary minerals of As and Sb were identified in the tailings. For example, chemical composition of rims on the grains of metallic phases measured by EMP after the experiment indicated higher contents of Sb (a mean of 1.70 wt%) and As (a mean of 0.42 wt%) than those determined in unweathered parts of these metallic phases with a mean content of 0.01 wt% Sb and 0.03 wt% As (Supplemental Table 2). It is known from previously published studies that both amorphous or crystalline Fe(III) oxyhydroxides have a high capability to incorporate both metalloids into their structures through adsorption or co-precipitation (Dixit and Hering 2003; Leuz et al. 2006; Majzlan et al. 2011), and that their desorption is highly dependent on the pH and the speciation of the element. These elements occurred as negatively charged species under slightly alkaline and oxidizing conditions (Supplemental Table 3), where surfaces of most Fe(III) oxyhydroxides have a negative charge (Hiemstra and Van Riemsdijk 2009). As a consequence, the repulsion between the negatively charged oxyanions of As and Sb and the net negative charge of Fe(III) oxyhydroxides favours the desorption of these metalloids at higher pH (Leuz et al. 2006). This might explain the higher mobility of As and Sb in the tailings than that of Cu, Pb, and Zn. It is also hypothesized that adsorption of the investigated PTEs on siderite might be an alternative process suppressing their mobilization because siderite was the second most abundant mineral in the tailings. Scarce studies dealing with the adsorption of metals and metalloids on natural siderite have shown that siderite effectively adsorbs Pb^{2+} ions (Erdem and Özverdi 2005) and both arsenite and arsenate oxyanions under neutral conditions (Guo et al. 2007a, b). Evaluation of adsorption of PTEs on siderite, which was one of the main minerals in the tailings, was beyond the scope of this study but if the mobilization of As, Cu, Pb, Sb, and Zn is to be understood in detail, it should be investigated in future work.

In order to classify the tailings as hazardous or nonhazardous waste according to the EU legislation (Van Gerven et al. 2005), static leaching test EN 12457 (EN 12457-2 2002) was performed in duplicates with 10 tailings samples of boreholes B-1 and B-2 taken from depth intervals of 0–1, 2–3, 4–5, 6–7, 8–9, 10–11, 12–13, 14–15, 16–17, and 18–19 m. The results of short-term leaching of selected metals (Cu, Pb, and Zn) and metalloids (As and Sb) and comparison with limit values are shown in Fig. 5. Comparison of the concentrations of metals and metalloids leached from the tailings samples with the limit values shows that both slag–tailings and tailings may be classified as nonhazardous waste with the exception of Sb. Antimony in three samples and in all samples of borehole B-1 exceeded the corresponding limits for hazardous (0.5 mg/L) and nonhazardous (0.07 mg/L) wastes, respectively, and it was above the limit for nonhazardous waste in three samples of borehole B-2. Thus, the results of leaching suggested that only Sb might be considered to be of an environmental concern in the vicinity of the impoundment. However, comparison of the leaching results from the static test EN 12457 (Fig. 5) with those from the pot leaching experiment (Fig. 4) and with analyses of natural waters draining the impoundment (Table 2) showed that the static test indicated much higher concentrations of all studied metals and metalloids in the leachates than occurred in reality. This is mostly due to the continuous agitation used in the static leaching test, which increases the direct contact of solid particles with water. Therefore, the long-term pot leaching method used in this study was more useful than the static test method for the determination of actual release of metals and metalloids from the tailings impoundment.

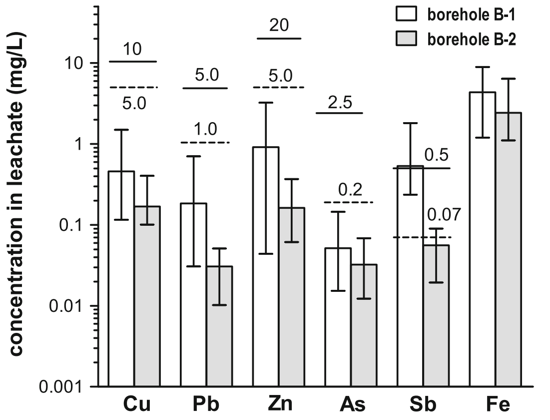


Fig. 5 Results of short-term leaching test according to EN 12457 and comparison with EU regulatory concentration levels for nonhazardous and hazardous wastes. *Dashed horizontal lines* denote regulatory concentration levels for nonhazardous waste materials and *solid horizontal lines* show regulatory concentration levels for hazardous wastes. Regulatory concentration levels for Fe are not defined. *Error bars* show the range of concentrations in the leachates

Conclusions

The main aims of this study were to determine the geochemistry and mineralogy of the siderite–Cu tailings deposited in the voluminous impoundment situated above the village of Slovinky in eastern Slovakia and the identification of fundamental processes that regulate the mobility of selected metals (Cu, Pb, Zn) and metalloids (As, Sb). The studied impoundment has a unique feature in comparison with the other impoundments described previously in literature because the stored tailings are covered sporadically by a 3–5 m thick layer of a mixture consisting of original flotation tailings and slags from the smelting of Cu-wastes of unknown sources in the Krompachy metallurgical plant to recover copper. Quartz, siderite, and muscovite were the most abundant primary minerals in the tailings followed by chlorite and dolomite. Sulfide minerals, mainly chalcopyrite, pyrite, tetrahedrite, and arsenopyrite, are still present but constitute only a minor proportion of the tailings mineral assemblage, as it is evidenced by its low sulfide-S content, with a maximum of 0.44 wt%. In addition, the slag–tailings mixture contains amorphous glass particles rich in Fe, metallic phases of elemental Fe and Mn, residues of blast-furnace lining, as well as pyroxenes and olivines. The abundance of carbonates in the tailings ensures their high neutralization capacity, which is significantly greater than the acidity generated by the oxidation of the sulfide minerals. The NPR values of the tailings (from 3.5 to 51.7), their neutral to slightly alkaline paste pH (7.66–8.83), and high pH values of the waters draining the impoundment (7.51–8.55) confirm that there is no development of AMD in the impoundment. Geochemical analyses showed elevated concentrations of As, Cu, Pb, Sb, and Zn in the solid samples with their significantly higher concentrations determined in the mixed slag–tailings layer (3.37 wt% of Zn, 0.85 wt% of Cu, and 0.38 wt% of Pb and Sb). The principal secondary solid phases were amorphous Fe(III) oxyhydroxides and rarely goethite. These amorphous Fe(III) phases were shown to form coatings on the surface of sulfide minerals and siderite, as well as individual grains, and to be enriched in the studied metals and metalloids (up to 4.09 wt% of As, 17.2 wt% of Cu, 1.20 wt% of Pb, 15.0 wt% of Sb, and 1.59 wt% of Zn). It was found that only Cu formed separate secondary minerals like malachite and cuprite, with a Cu content up to 84.4 wt%. Weathering rims were also common on the surfaces of slag components (amorphous glass, metallic phases, blast-furnace lining residues) and their chemical compositions were highly variable.

Slag–tailings material stored in the impoundment contains high amounts of metals and metalloids that may be available for leaching, but the amounts released into aqueous solution were very low, not exceeding 0.05 % of the total content according to the results of a long-term pot leaching experiment performed over 150 days. Conditions in the tailings are mostly alkaline ($pH > 7.50$) and oxidizing ($Eh > 250$ mV), and are favorable for elevated As and Sb mobility; however their concentrations in the leachates and drainage waters (<1.0–41 μg/L As and 12–37 μg/L Sb) were low, probably due to adsorption of both metalloids on oxyhydroxide and siderite.

Results of this study showed that the chemistry of neutral mine drainage was regulated mostly by the occurrence of neutralizing minerals and secondary ferric minerals in the Slovinky tailings, which prevented development of AMD and mobilization of potentially toxic elements to the surrounding environment.

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References

Akcil A, Koldas S (2006) Acid mine drainage (AMD): causes, treatment and case studies. J Clean Product 14:1139–1145. doi:10.1016/j.jclepro.2004.09.006

Alter H (2005) The composition and environmental hazard of copper slags in the context of the Basel Convention. Resour Conserv Recy 43:353–360. doi:10.1016/j.resconrec.2004.05.005

Bajtoš P (2012) Mass flux balance of contaminants at mountain regions influenced by mining activity on example of the Dubrava Sb deposit and the Slovinky Cu deposit. Podzemná Voda 18:110–122 **(In Slovak with English abstract and summary)**

Balintova M, Singovszka E, Vodicka R, Purcz P (2015) Statistical evaluation of dependence between pH, metal contaminants, and flow rate in the AMD-affected Smolnik Creek. Mine Water Environ. doi:10.1007/s10230-014-0324-2

Berger AC, Bethke CM, Krumhansl JL (2000) A process model of natural attenuation in drainage from a historic mining district. Appl Geochem 15:655–666. doi:10.1016/S0883-2927(99)00074-8

Bird G, Brewer PA, Macklin MG, Balteanu D, Driga B, Serban M, Zaharia S (2003) The solid state partitioning of contaminant metals and As in river channel sediments of the mining affected Tisa drainage basin, northwestern Romania and eastern Hungary. Appl Geochem 18:1583–1595. doi:10.1016/S0883-2927(03)00078-7

Blowes DW, Jambor JL, Hanton-Fong CJ, Lortie L, Gould WD (1998) Geochemical, mineralogical and microbiological characterizationof a sulphide-bearing carbonate-rich gold-mine tailings impoundment, Joutel, Québec. Appl Geochem 13:687–705. doi:10.1016/S0883-2927(98)00009-2

Brookfield AE, Blowes DW, Mayer KU (2006) Integration of field measurements and reactive transport modelling to evaluate contaminant transport at a sulfide mine tailings impoundment. J Contam Hydrol 88:1–22. doi:10.1016/j.jconhyd.2006.05.007

Bruker (2010a) DIFFRACplus EVA. http://www.brukeraxs.com/eva.html. Accessed 6 October 2013

Bruker (2010b) DIFFRACplus TOPAS. http://www.bruker-axs.de/topas.html. Accessed 6 October 2013

Chovan M, Háber M, Jeleň S, Rojkovič I (1994) Ore textures in theWestern Carpathians. Slovak Academic Press, Bratislava

Dixit S, Hering JG (2003) Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ Sci Technol 37:4182–4189. doi:10.1021/es030309t

Dold B, Fontboté L (2002) A mineralogical and geochemical study of element mobility in sulfide mine tailings of Fe oxide Cu–Au deposits from the Punta del Cobre belt, northern Chile. Chem Geol 189:135–163. doi:10.1016/S0009-2541(02)00044-X

EN 12457-2 (2002) Characterisation of waste-leaching-compliance test for leaching of granular waste materials and sludges—part 2: one stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm (without or with size reduction). The European Committee for Standardization (CEN), Brussels

Erdem M, Özverdi A (2005) Lead adsorption from aqueous solution onto siderite. Sep Purif Technol 42:259–264. doi:10.1016/j.seppur.2004.08.004

Ettler V, Johan Z, Křîbek B, Šebek O, Mihaljevič M (2009) Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. Appl Geochem 24:1–15. doi:10.1016/j.apgeochem.2008.10.003

Final report (2012) Influence of mining of mineral resources on the environment. State Geological Institute of Dionyz Stur, Bratislava **(in Slovak)** http://dionysos.gssr.sk/cmsgf/files/Hodn_monitor_2012/04_Vplyv_tazby_2012.pdf. Accessed 15 June 2015

Frau F, Ardau C, Fanfani L (2009) Environmental geochemistry and mineralogy of lead at the old mine area of Baccu Locci (south-east Sardinia, Italy). J Geochem Explor 100:105–115. doi:10.1016/j.gexplo.2008.01.005

Gaboriaud F, Ehrhardt J-J (2003) Effects of different crystal faces on the surface charge of colloidal goethite (α-FeOOH) particles: an experimental and modeling study. Geochim Cosmochim Acta 67:967–983. doi:10.1016/S0016-7037(02)00988-2

Gee C, Ramsey MH, Maskall J, Thornton I (1997) Mineralogy and weathering processes in historical smelting slags and their effect on the mobilization of lead. J Geochem Explor 58:249–257. doi:10.1016/S0375-6742(96)00062-3

Gitari WM, Fatoba OO, Petrik LF, Vadapalli VRK (2009) Leaching characteristics of selected South African fly ashes: effect of pH on the release of major and trace species. J Environ Sci Health A 44:206–220. doi:10.1080/10934520802539897

Gorai B, Jana RK, Premchand M (2003) Characteristics and utilisation of copper slag—a review. Resour Conserv Recy 39:299–313. doi:10.1016/S0921-3449(02)00171-4

Goumih A, El Adnani M, Hakkou R, Benzaazoua M (2013) Geochemical behavior of mine tailings and waste rock at the abandoned Cu–Mo–W Azegour mine (Occidental High Atlas, Morocco). Mine Water Environ 32:121–132. doi:10.1007/s10230-013-0221-0

Grangeia C, Ávila P, Matias M, Ferreira da Silva E (2011) Mine tailings integrated investigations: the case of Rio tailings (Panasqueira Mine, Central Portugal). Eng Geol 123:359–372. doi:10.1016/j.enggeo.2011.10.001

Grecula P, Abonyi A, Abonyiová M, Antáš J, Bartalský B, Bartalský J, Dianiška I, Drnzík E, Ďuď'a R, Gargulák M, Gazdačko Ľ, Hudáček J, Kobulský J, Lörincz L, Macko J, Návesňák D, Németh Z, Novotný L, Radvanec M, Rojkovič I, Rozložník O, Varček C, Zlocha J (1995) Mineral deposits of the Slovak Ore Mts. Geokomplex, Bratislava **(in Slovak with an English summary)**

Guo H, Stüben D, Berner Z (2007a) Removal of arsenic from aqueous solution by natural siderite and hematite. Appl Geochem 22:1039–1051. doi:10.1016/j.apgeochem.2007.01.004

Guo H, Stüben D, Berner Z (2007b) Adsorption of arsenic(III) and arsenic(V) from groundwater using natural siderite as the adsorbent. J Colloid Interf Sci 315:47–53. doi:10.1016/j.jcis.2007.06.035

Hasaj J, Šťastný V (1983) Slovinky—stabilization and reclamation of the impoundment, supplementing engineering–geological research. IGHP, Košice **(in Slovak)**

Heikkinen PM, Räisänen ML, Johnson RH (2009) Geochemical characterisation of seepage and drainage water quality from two sulphide mine tailings impoundments: acid mine drainage versus neutral mine drainage. Mine Water Environ 28:30–49. doi:10.1007/s10230-008-0056-2

Hiemstra T, Van Riemsdijk WH (2009) A surface structural model for ferrihydrite I: sites related to primary charge, molar mass, and mass density. Geochim Cosmochim Acta 73:4423–4436. doi:10.1016/j.gca.2009.04.032

Hiller E, Lalinská B, Chovan M, Jurkovič Ľ, Klimko T, Jankulár M, Hovorič R, Šottník P, Fľaková R, Ženišová Z, Ondrejková I (2012) Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia. Appl Geochem 27:598–614. doi:10.1016/j.apgeochem.2011.12.005

Hiller E, Petrák M, Tóth R, Lalinská-Voleková B, Jurkovič Ľ, Kučerová G, Radková A, Šottník P, Vozár J (2013) Geochemical and mineralogical characterization of a neutral, low-sulfide/high-carbonate tailings impoundment, Markušovce, eastern Slovakia. Environ Sci Pollut Res 20:7627–7642. doi:10.1007/s11356-013-1581-5

Jambor JL, Dutrizac JE, Groat LA, Raudsepp M (2002) Static tests of neutralization potentials of silicate and aluminosilicate minerals. Environ Geol 43:1–17. doi:10.1007/s00254-002-0615-y

Jurjovec J, Ptacek CJ, Blowes DW (2002) Acid neutralization mechanisms and metal release in mine tailings: a laboratory column experiment. Geochim Cosmochim Acta 66:1511–1523. doi:10.1016/S0016-7037(01)00874-2

Khorasanipour M, Eslami A (2014) Hydrogeochemistry and contamination of trace elements in Cu–porphyry mine tailings: a case study from the Sarcheshmeh mine, SE Iran. Mine Water Environ 33:335–352. doi:10.1007/s10230-014-0272-x

Kučerová G, Ozdín D, Lalinská-Voleková B (2013) Primary low–temperature delafossite $CuFeO_2$ from mine tailing Slovinky (Slovakia). Bull Mineral Petrolog Odd Nár Muz (Praha) 21:78–83 **(in Slovak, with English summary)**

Kučerová G, Majzlan J, Lalinská-Voleková B, Radková A, Bačík P, Michňová J, Šottník P, Jurkovič Ľ, Klimko T, Steininger R, Göttlicher J (2014) Mineralogy of neutral mine drainage in the tailings of siderite–Cu ores in eastern Slovakia. Can Mineral 52:779–798. doi:10.3749/canmin.1400020

Lalinská-Voleková B, Majzlan J, Klimko T, Chovan M, Kučerová G, Michňová J, Hovorič R, Göttlicher J, Steininger R (2012) Mineralogy of weathering products of Fe–As–Sb mine wastes and soils at several Sb deposits in Slovakia. Can Mineral 50:481–500. doi:10.3749/canmin.50.2.481

Landscape Atlas of the Slovak Republic (2002) Ministry of Environment of the Slovak Republic and Slovak Environmental Agency, 1st edn. Bratislava

Leuz AK, Mönch H, Johnson CA (2006) Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization. Environ Sci Technol 40:7277–7282. doi:10.1021/es061284b

Lin Z (1997) Mineralogical and chemical characterization of wastes from the sulfuric acid industry in Falun, Sweden. Environ Geol 30:152–162. doi:10.1007/s002540050142

Lindsay MBJ, Condon PD, Jambor JL, Lear KG, Blowes DW, Ptacek CJ (2009) Mineralogical, geochemical, and microbial investigation of a sulfide-rich tailings deposit characterized by neutral drainage. Appl Geochem 24:2212–2221. doi:10.1016/j.apgeochem.2009.09.012

Lottermoser BG (2002) Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia. Mineral Mag 66:475–490. doi:10.1180/0026461026640043

Lottermoser BG (2007) Mine wastes. Characterization, treatment, environmental impacts, 2nd edn. Springer, Berlin

Majzlan J, Lalinská B, Chovan M, Bläß U, Brecht B, Göttlicher J, Steininger R, Hug K, Ziegler S, Gescher J (2011) A mineralogical, geochemical, and microbiological assessment of the antimony- and arsenic-rich neutral mine drainage tailings near

Pezinok, Slovakia. Am Mineral 96:1–13. doi:10.2138/am.2011.3556

McGregor RG, Blowes DW, Jambor JL, Robertson WD (1998) The solid-phase controls on the mobility of heavy metals at the Copper Cliff tailings area, Sudbury, Ontario, Canada. J Contam Hydrol 33:247–271. doi:10.1016/S0169-7722(98)00060-6

Miller S, Robertson A, Donahue T (1997) Advances in acid drainage prediction using the net acid generation (NAG) test. Proceedings of 4th international conference on acid rock drainage, vol II, Vancouver, pp 535–549

Nagy AS, Szabó J, Vass I (2013) Trace metal and metalloid levels in surface water of Marcal River before and after the Ajka red mud spill, Hungary. Environ Sci Pollut Res 20:7603–7614. doi:10.1007/s11356-013-2071-5

Nordstrom DK, Alpers CN (1999) Geochemistry of acid mine waters. In: Plumlee GS, Logsdon MJ (eds) The environmental geochemistry of mineral deposits. Part A. Processes, methods and health issues. Rev Econ Geol, vol 6A. Soc of Economic Geologists, Littleton, CO, USA, pp 133–160

Othmani MO, Souissi F, Bouzahzah H, Bussière B, da Silva EF, Benzaazoua M (2015) The flotation tailings of the former Pb-Zn mine of Touiref (NW Tunisia): mineralogy, mine drainage prediction, base-metal speciation assessment and geochemical modeling. Environ Sci Pollut Res 22:2877–2890. doi:10.1007/s11356-014-3569-1

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC: a computer program for speciation, reaction-path, 1-D transport, and inverse geochemical calculations. US Geological Survey Water-Resources Investigations Report 99-4259

Parsons MB, Bird DK, Einaudi MT, Alpers CN (2001) Geochemical and mineralogical controls of trace element release from the Penn Mine base–metal slag dump. Appl Geochem 16:1567–1593. doi:10.1016/S0883-2927(01)00032-4

Piatak NM, Seal RR II, Hammarstrom JM (2004) Mineralogical and geochemical controls on the release of trace elements from slag produced by base- and precious-metal smelting at abandoned mine sites. Appl Geochem 19:1039–1064. doi:10.1016/j.apgeochem.2004.01.005

Piatak NM, Parsons MB, Seal RR II (2015) Characteristics and environmental aspects of slag: a review. Appl Geochem 57:236–266. doi:10.1016/j.apgeochem.2014.04.009

Piovarcsy K, Ráchela R (1998) Slovinky-Gelnica ore deposit-complex evaluation of Cu, an exploration (final report). Ministry of Environment of the Slovak Republic, Bratislava **(in Slovak)**

Prasanna MV, Chidambaram S, Senthil Kumar G, Ramanathan AL, Nainwal HC (2010) Hydrogeochemical assessment of groundwater in Neyveli Basin, Cuddalore District, South India. Arab J Geosci 4:319–330. doi:10.1007/s12517-010-0191-5

Radvanec M, Grecula P, Žák K (2004) Siderite mineralization of the Gemericum superunit (Western Carpathians, Slovakia): review and a revised genetic model. Ore Geol Rev 24:267–298. doi:10.1016/j.oregeorev.2003.07.004

Rapant S, Cvečková V, Dietzová Z, Khun M, Letkovičová M (2009) Medical geochemistry research in Spišsko-Gemerské Rudohorie Mts., Slovakia. Environ Geochem Health 31:11–25. doi:10.1007/s10653-008-9152-2

Richards LA (1954) Diagnosis and improvement of saline and alkali soils. Agricultural Handbook No 60. US Dept of Agriculture, Washington DC

Salvarredy-Aranguren MM, Probst A, Roulet M, Isaure MP (2008) Contamination of surface waters by mining wastes in the MilluniValley (Cordillera Real, Bolivia): mineralogical and hydrological influences. Appl Geochem 23:1299–1324. doi:10.1016/j.apgeochem.2007.11.019

Sarmiento AM, DelValls A, Nieto JM, Salamanca MJ, Caraballo MA (2011) Toxicity and potential risk assessment of a river polluted by acid mine drainage in the Iberian Pyrite Belt (SW Spain). Sci Total Environ 409:4763–4771. doi:10.1016/j.scitotenv.2011.07.043

Sima M, Dold B, Frei L, Senila M, Balteanu D, Zobrist J (2011) Sulfide oxidation and acid mine drainage formation within two active tailings impoundments in the Golden Quadrangle of the Apuseni Mountains, Romania. J Hazard Mater 189:624–639. doi:10.1016/j.jhazmat.2011.01.069

Simate SG, Ndlovu S (2014) Acid mine drainage: challenges and opportunities. J Environ Chem Eng 2:1785–1803. doi:10.1016/j.jclepro.2004.09.006

Skousen J, Renton J, Brown H, Evans P, Leavitt B, Brady K, Cohen L, Ziemkiewicz P (1997) Neutralization potential of overburden samples containing siderite. J Environ Qual 26:673–681. doi:10.2134/jeq1997.00472425002600030012x

Souissi R, Souissi F, Chakroun HK, Bouchardon JL (2013) Mineralogical and geochemical characterization of mine tailings and Pb, Zn, and Cd mobility in a carbonate setting (Northern Tunisia). Mine Water Environ 32:16–27. doi:10.1007/s10230-012-0208-2

Sracek O, Mihaljevič M, Kříbek B, Majer V, Veselovský F (2010) Geochemistry and mineralogy of Cu and Co in mine tailings at the Copperbelt, Zambia. J Afr Earth Sci 57:14–30. doi:10.1016/j.jafrearsci.2009.07.008

STN EN ISO/IEC 17025 (2005) General requirements for the competence of testing and calibration laboratories. Slovak Office of Standards, Metrology and Testing, Bratislava (in Slovak)

Van Gerven T, Geysen D, Stoffels L, Jaspers M, Wauters G, Vandecasteele C (2005) Management of incinerator residues in Flanders (Belgium) and neighbouring countries. A comparison. Waste Manag 25:75–87. doi:10.1016/j.wasman.2004.09.002

Vrana K, Vojtaško I, Žák D, Piovarči M, Kúšiková S, Puchnerová M, Lanc J, Naštický J (2005) System for the determination and the monitoring of environmental damages caused by mining activities, informative engineering—geological research. Geokomplex Inc., Bratislava **(in Slovak)**

WISE Uranium Project (2013) Chronology of major tailings dam failures. http://www.wise-uranium.org/mdaf.html. Accessed 15 January 2015