

Characterization of ochre precipitate loaded with arsenic from mine water and study of its stability by using of leaching tests and sequential extraction analysis

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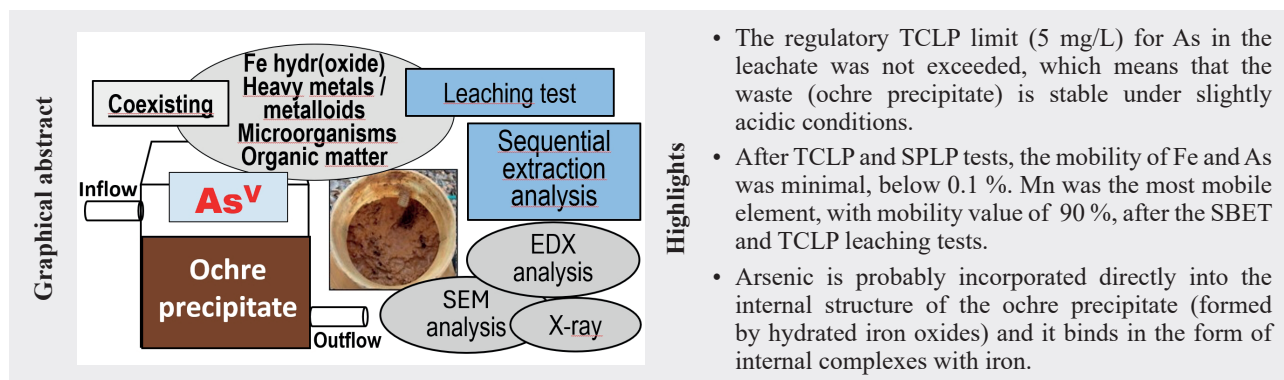
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Abstract: This study is focused on the mobility of potential toxic elements release from the ochre precipitate sample after the leaching by using selected methods. The sequential extraction method was performed to characterize the stability of the sample after the leaching tests. The TCLP regulatory limit for arsenic of 5 mg/L in the ochre precipitate was not exceeded, thus meet the legislative regulations. The highest concentrations of As were achieved in the residual fraction (5) even after leaching tests. The lowest concentration values of As were found in the mobile fractions: water-soluble fraction (1) and ion-exchangeable and carbonate fraction (2). These results indicate the low mobility of arsenic and the tight bonding between As and Fe in formed ochre precipitates.

Key words: ochre precipitate, arsenic, leaching test, sequential extraction analysis



1 Introduction

The Hauser adit is the deepest horizontal adit in the entire Zlatá Idka ore district. Mine water is characterised by a high arsenic content. This content significantly correlates with the content of divalent iron, which allows us to assume that this highly toxic micro-component of chemistry also originates from the primary environment of formation of the chemical composition of mine water – from the depth of the rock mass (the presence of arsenopyrite in the vein system of the locality Zlatá Idka), (Bačová, 2006). Outflows from the adit presented a permanent source of contamination (adit discharges, drainage water and mine heap leachate) and will recharge the surface waters of streams with elements of concern

over the long term (Cicmanová & Baláž, 2007). Mine water discharge creates a pond – with no runoff – below the backfilled mouth of the adit. The mine water probably seeps into the Quaternary sediments of the Ida Valley.

The pH is a critical parameter for the mobility of metals, and thus their bioavailability. Dissolution of carbonates and silicates is an important type of reaction that shapes the pH of waters. In terms of the potency of arsenic present in waters, it has been found to be present only in the less toxic form of pentavalent ions. This points to a significant application of oxidizing conditions of the aquatic environment – probably in the final phase of mine water discharge (Cicmanová & Baláž, 2007). In an oxidizing environment, the arsenate species predominates,

and at a pH between 6 and 9, it exists as oxyanions of arsenic acid in the form of $H_2AsO_4^-$ and/or $HAsO_4^{2-}$ (average pH of mine water from the Hauser adit = 7.3).

The ochre phases are precipitated directly from mine waters (or tailings pond leakage). They are characteristic of mine sites, adit discharges and their surroundings due to oxidation of soluble Fe^{2+} to insoluble Fe^{3+} phases. HFO, also called hydrous iron oxides and iron (III) oxide-hydroxides, include several minerals, such as ferrihydrite, akaganeite, feroxyhyte, goethite, lepidocrocite and limonite. They are poorly crystalline, highly porous, have large surface areas and they are excellent sorbents of various potentially toxic elements. Hydrous ferric oxides (HFO) harbor a remarkable ability to sequester As and Sb from the environment by adsorbing arsenate [As(V)], arsenite [As(III)], antimonate [Sb(V)] and antimonite [Sb(III)] ions

on its surface (in some cases even into the structure) under the neutral and low acidic conditions, which is the case of most groundwater and soil water conditions (Scheinost et al., 2006; Majzlan et al., 2007; Mitsunobu et al., 2006; Guo et al., 2014). Adsorption of As(V) species onto porous iron oxyhydroxides is known to take place via Coulombic and/or Lewis acid base interactions (ligand exchange reactions) and to form monodentate and bidentate inner sphere complexes (Zhang & Stanforth, 2005; Banerjee et al., 2008). Generally, it is believed that the porous nature of iron (oxy)hydroxides leads to As(V) adsorption at internal iron complexation sites (Sinha et al., 2002; Badruzzaman et al., 2004). Arsenic ions bound by the inner complexes are more strongly adsorbed than arsenic ions bound by the outer complexes (Stollenwerk, 2003).

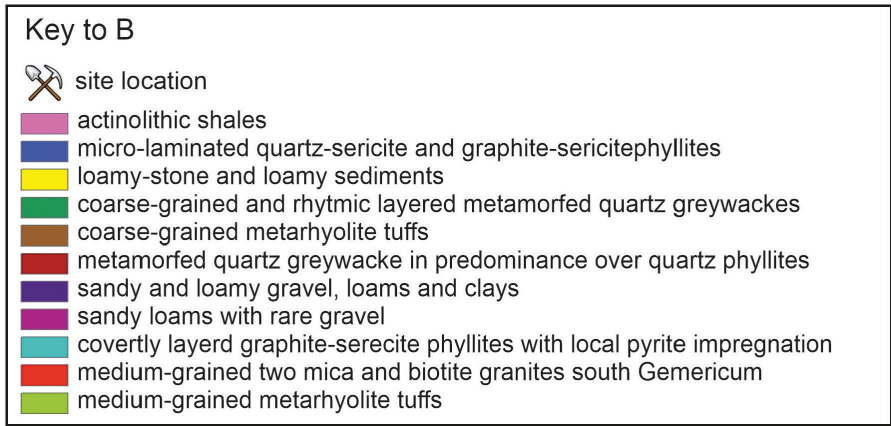
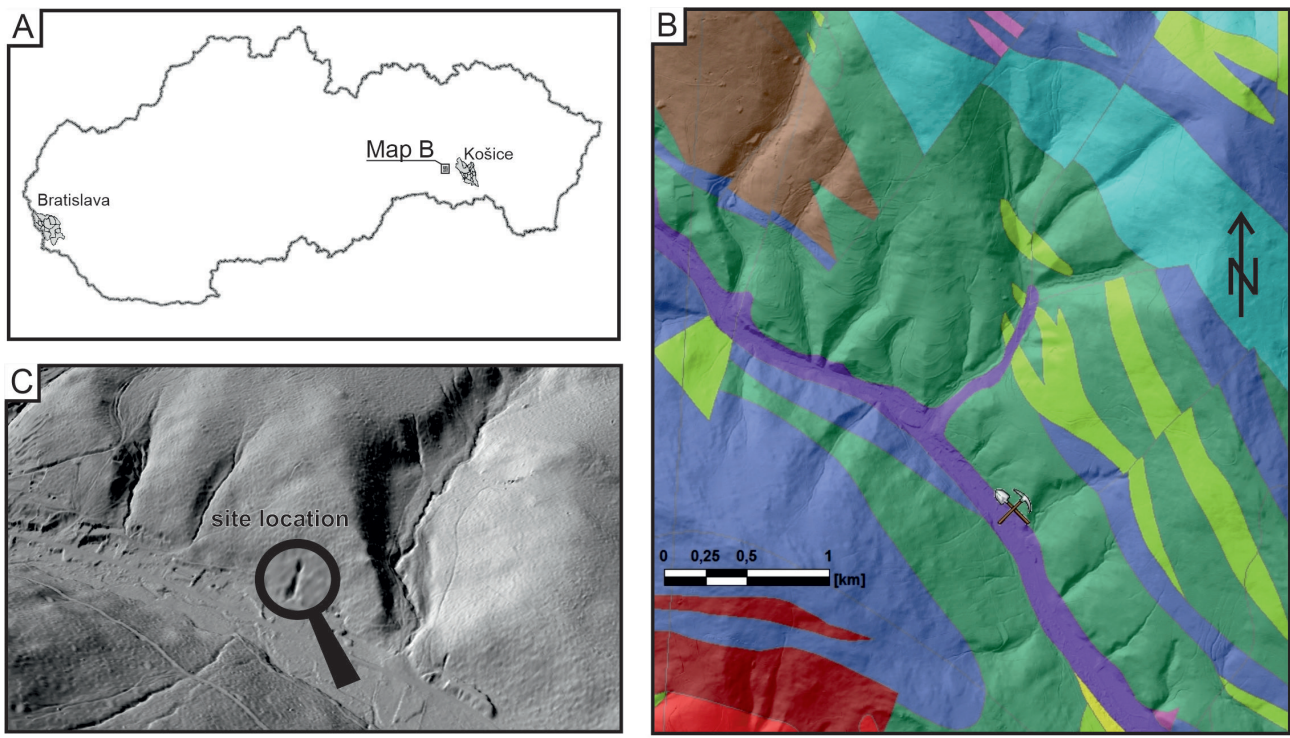


Fig. 1. (A) Simplified map of Slovak Republic: location of Zlatá Idka near Košice town (B) location of Hauser adit and geological map of the site studied (C) detailed site location.

A previous study focused on the elimination of As concentration from mine run-off water of

Hauser adit under flow conditions at the locality Zlatá Idka (Bekényiová et al., 2023), Fig. 1. The in situ field experiments consisted of designing a continuous mine water overflow system by placing two 50 L containers directly in the field, through which mine water flowed continuously by gravity flow. The mine water flowed through the two containers: a retention container and a filter container, in which different fractions of natural sorbents were deposited in layers. In the retention container, ochre precipitates naturally formed during the in situ experiment (4 months), binding a significant amount of arsenic.

The present study is focused on formed ochre precipitates and their characterization by X-ray diffraction, SEM and EDX analysis. The microbiology was discussed based on the results from the SEM analysis spectra, too. Furthermore, the main objective of the study was to determine the stability of the ochre precipitates. Leaching tests, namely SPLP, TCLP and SBET methods were used to assess the mobility of the investigated potentially toxic elements. Mobility and transport sequential extraction analysis (SEA) method was used to determine the content of potentially toxic elements in the bioavailable and unavailable fractions and to refine and understand the physicochemical processes of metal fixation.

2 Materials and Methods

2.1 Ochre precipitates

The ochre precipitates used in this study were obtained from previous in situ experiments, where they are naturally formed in 50 L container and binding a significant amount of arsenic (Bekényiová et al., 2023). Next they were used for the chemical and mineralogical analyses. Samples were collected using a field scoop into plastic bags. During collection, they were filtered through a 0.16 mm sieve to remove any residual organic matter (leaves, roots, etc.) and then washed with water. Then the precipitates were dried in a laboratory oven at a constant temperature of 60 °C to a stable mass during 3 days.

2.2 Ochre precipitate characterization

The powder X-ray diffraction (XRD) patterns of ochre precipitate sample was recorded using a diffractometer D2 Phaser (Bruker, Germany), equipped with a CuK α radiation source (30 kV, 10 mA) and Lynxeye detector. The data were qualitatively and quantitatively analysed using Software DIFFRAC.EVA with PDF-2 Database.

The ochre precipitates were studied by scanning electron microscopy FE MIRA 3 (Tescan, Czech Republic) equipped by energy-dispersive (EDX) analyser of chemical composition (Oxford Instruments).

2.3 Mobility of toxic elements and bioassessability testing

Mobility of potential toxic elements present in the ochre sample was tested using Synthetic Precipitation Leaching Procedure (SPLP), US EPA Method 1312 based on the acid rain leaching; pH 4.2 (Fey et al., 2011). The ochre sample of 5 grams was extracted by solution of H₂SO₄ and HNO₃ (weight ratio 3 : 2). The ochre sample and extraction solution were placed into the extraction bottle and shaken for 18 hours on the laboratory shaker. Then the leachate was filtered and analysed.

Toxicity Characteristic Leaching Procedure (TCLP) was performed using the method (US EPA 1311) as follows: a 50 g sample was extracted with a 1 N solution of NaOH and acetic acid, pH 2.8, with stirring for 18 hours.

The bioassessability of the toxic elements present in the ochre sample Fe-HB-Š was tested by Simply Bioavailability Extraction Test (SBET). The sediment sample of 5 grams was extracted by solution of 0.4 M glycine of pH 1.5 (adjusted by HCl) under the vigorous stirring for 1 hour at 37 °C (Report No.: 1542820-003-R-Rev0, 2016; Kim et al., 2009).

2.4 Sequential extraction analysis

The ochre sample was subjected to sequential extraction analysis with the aim to determine the content of toxic elements in biologically available and unavailable fractions. The sequential extraction analysis was provided according to the method described by Mackových et al. (2000). The extraction in each step was carried out in 3 measurements, the sample was shaken in suspension on a laboratory multirotator for 16 hours at laboratory temperature. After the extraction was completed, the solution was centrifuged at 3000 rpm for 20 minutes, the extraction leachate was filtered and fixed by the addition of HNO₃.

3 Results and discussion

3.1 Characteristics of the formed ochre precipitates

The resulting ochre precipitates (hydrated iron oxides, referred as HFO) contain high amount of arsenic, but under normal surface conditions are generally poorly soluble As compounds. They are commonly precipitated directly from mine waters as a result of the oxidation of soluble divalent iron to insoluble ferric iron phases and are characteristic of mine sites, adit outfalls and their surroundings. The water flows from the adit is neutral to slightly alkaline mine water with pH of 7.3 (an average) and with high arsenic content 360 µg/L (an average).

Sorptive properties of hydrous ferric oxides (HFO) depend on the pH of the surrounding water, the chemical composition of the water, and the ratio of the amount of dissolved trace metals to the amount of hydrous iron oxides

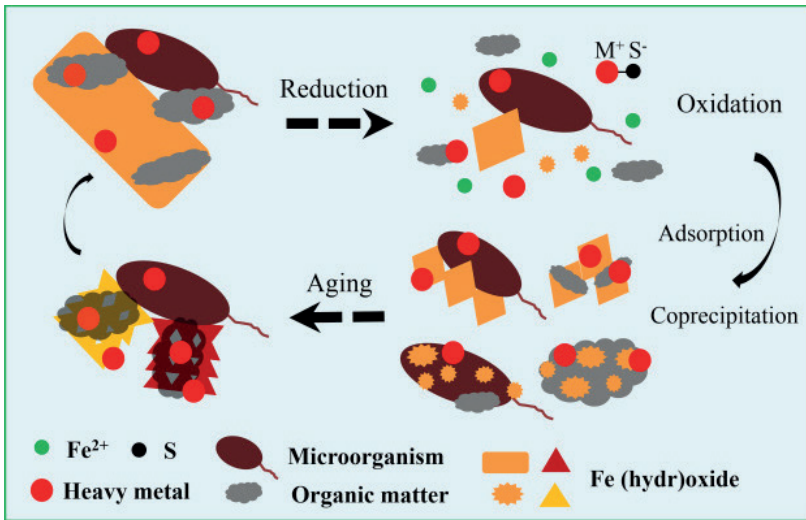


Fig. 2. Proposed scheme showing the influences of redox and aging on the behavior of heavy metals associated with Fe (hydr)oxides-organo complexes (Chenchen et al., 2019).

(Dzombak et al., 1987; Davis & Kent, 1990; Stumm, 1992). Behaviour of heavy metals in complex system of HFO is illustrated in Fig. 2.

After collection and processing ochre precipitates in the laboratory, they were further studied by using X-ray diffraction method, the morphology was studied by scanning electron microscopy with the EDX analysis.

The stability of Fe precipitates was studied by leaching tests (SBET, TCLP, SPLP). Sequential extraction (SEA) methodology was used to assess the mobility of potentially toxic elements bound in Fe precipitates before and after leaching tests, that would be released back into the water, and to refine and understand the physicochemical processes of metal fixation, mobility and transport.

The concentrations of Fe and As in the ochre precipitates formed in the container (after 4 months of filtration) are presented in Tab. 1. The data of As concentration were compared with the indication and intervention criteria of the Directive of the Ministry of Environment of the Slovak Republic No. 1/2015-7 of 28 January 2015 for the preparation of risk analysis, listed in Annex 12a to the Directive (Indication and Intervention Criteria for the Rock Environment and Soil). The chemical analyses show that the concentrations for As expressively exceed the IT criteria for industry, Tab. 1.

The fine fibrous structure observed in some places may be related to the

Tab. 1

Concentration of selected elements in ochre precipitate and comparison of As concentration with the permissible and critical limits according to the guideline

Element	Permissible limit (ID)	Critical limit (IT)		Fe – HB – Š input
		Residential districts	Industrial districts	
	[mg.kg ⁻¹]	[mg.kg ⁻¹]	[mg.kg ⁻¹]	[mg.kg ⁻¹]
As	65	70	140	56 945
Fe	x	x	x	471 000

ID – Permissible limit of contaminant concentration in soils according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7

IT – Critical limit of contaminant concentration in soils according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7



Fig. 3. Formation of ochre precipitates in a 50 L sedimentation container, ochre sampling.

presence of Fe oxidizing bacteria, which may play an important role in the mobility of the elements. Formation of ochre precipitate during monitoring period and its sampling is illustrated in Fig. 3.

Processed Fe precipitate was subjected to X-ray analysis. The results showed a predominantly amorphous phase of ferric oxyhydroxides, consisted of weakly crystalline ferrihydrite, as can be seen in Fig. 4. Ferrihydrite is usually formed from mine drainage solutions that are rich in organic matter and/or have pH values greater than 5 (Bigham et al., 1992).

From X-ray and EDX analyses it can be assumed that the rusty red colour of the sediment as well as the surface coatings of the rocks around the lake is caused by amorphous phases of iron compounds (hydroxides, oxyhydroxides), binding a significant proportion of As from the outflowing mine water. The EDX analysis of rusty red precipitates from mine water collected on the filter confirmed the presence of both iron and arsenic in amount 52 wt. % and 13.2 wt. %, respectively (Fig. 5). Fig. 6 (A),

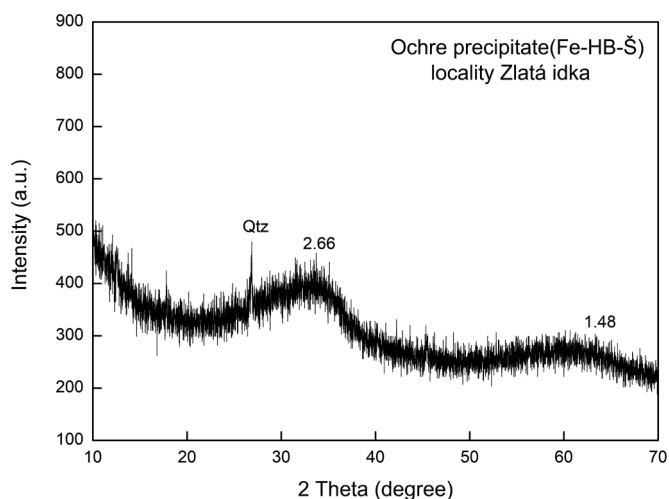


Fig. 4. X-ray diffraction of ochre precipitate.

shows Fe oxide aggregates (probably ferrihydrite) in the immediate neighbourhood of the two Fe-oxidizing bacterial species, *Gallionella ferruginea* (G) and *Lepthotrix ochracea* (L), according to Cornell and Schwertmann

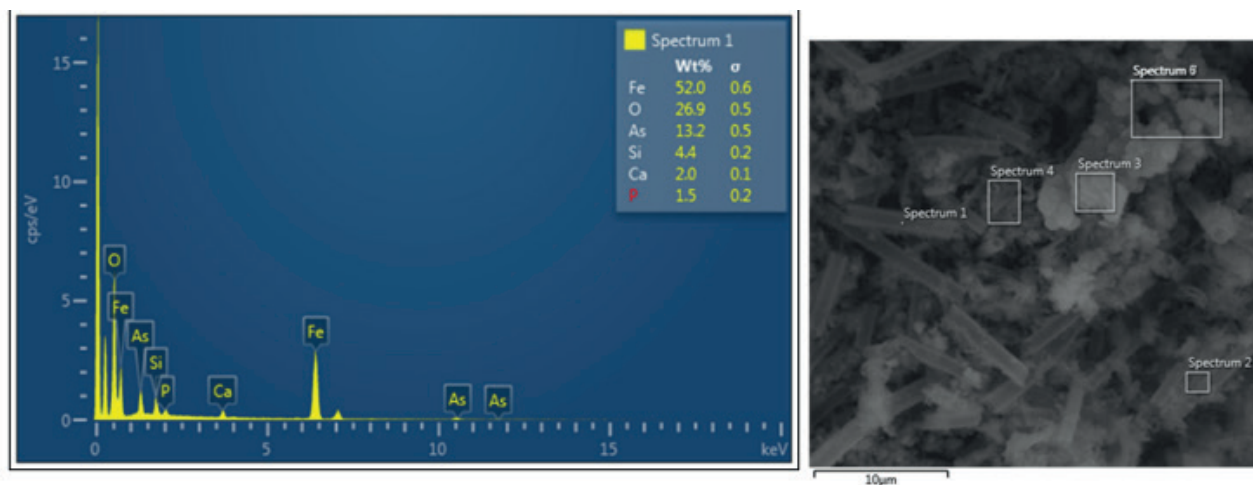


Fig. 5. EDX analysis of the ochre precipitate Fe-HB-Š.

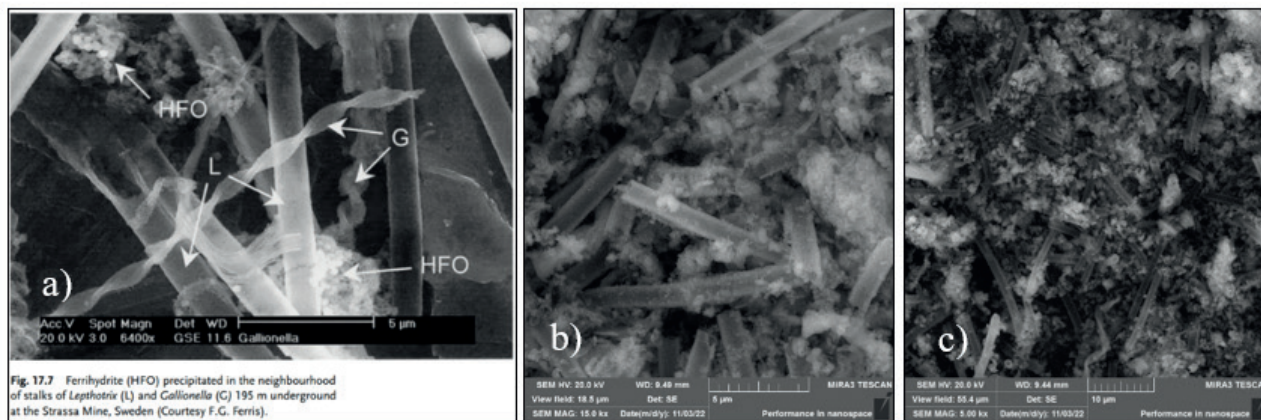


Fig. 6. Surface spectrum of HFO (Cornell & Schwertmann, 2003) (a), Fe-HB-Š sample – 15 000x magnification (b), Fe-HB-Š sample – 5 000x magnification (c).

(2003). From our observed scanning electron microscopy spectra at 15 000x and 5 000x magnification, hollow tubes are clearly visible, which probably correspond to bacterial species *Leptothrix ochracea* (Fig. 6B, C). It is well known Fe-oxidizing bacteria that occurs in higher abundance in ochres, in addition to other facultatively aerobic or microaerophilic Fe-oxidizing bacteria (*Gallionella*, *Rhodobacter*, *Sphingopyxis*, *Dechloromonas*, *Azospira*, and others). These metal-oxidizing bacteria form robust populations, with significant effects on crystallization rate of hydrated iron oxides and adsorption of metal ions/metalloids (Volekova, 2022).

Fe oxidizing bacteria of the genus *Leptothrix* form iron-precipitating shells and oxidize divalent iron to trivalent iron hydroxide. These bacteria can either adaptively use metals (or other compounds) as electron acceptors (Roden, 2012; Bryce et al., 2018; Liu et al., 2019a). This allows them to live in changing conditions, e.g. the transition zone between aerobic and anaerobic environments, and adapt to changing oxygen availability.

To better understand the biochemical processes at the locality, the PCR analysis of the Fe-HB-Š sample to determine the specific bacterial species present in the precipitates is planned to be complemented.

3.2 Leaching tests

The leaching tests (SBET, TCLP, SPLP) were aimed to assess the mobility of the investigated potentially toxic elements (As, Sb, Fe and Mn) in the Fe precipitate sample. The bioavailability test by the SBET (Simply Bioavailability Extraction Test) method characterizes the proportion of toxic elements that are absorbed from the sample (soil, sediment) into the organism via the digestive tract. The method simulates an acidic gastric environment (pH = 1.5). These tests also indicate the possible effect of soil exposed to acid mine water to pH below 2.

The toxicity characteristic leaching procedure (TCLP) using US EPA Method 1311 assesses the mobility of hazardous substances from the solid phase into the aquatic environment. It simulates landfill leaching or simulated wetting (waste/solids exposed for 100 years in a landfill, pH = 2.8). It is a standardized method for determining whether a waste is hazardous or non-hazardous for disposal purposes. Concentration limits for individual elements according to the TCLP evaluation are given in Tab. 2.

Tab. 2
TCLP limits (US EPA 1311)

Element	Fe	As	Mn	Sb
TCLP limit [mg.L ⁻¹]	–	5	–	–

The SPLP (Synthetic Precipitation Leaching Procedure) mobility test by US EPA Method 1312 simulates acid rain (waste exposed to 100 years of acid rain, pH = 4.2). The degree of waste/landfill stabilization is critical to the quality or composition of the leachate from the waste, which in turn affects the degree of groundwater contamination. The SPLP method is of limited use for the detection of metals that are present on the surface; therefore, it is considered to be not a fully suitable method for comprehensive toxicity testing. On the other hand, it simulates the effects of “normal” precipitation on waste.

When evaluating the results from the TCLP method, the total concentration is divided by 20 (the sample was diluted with extraction liquid weighing 20 times the sample weight) and compared to the TCLP regulatory limits. If the number is less than the TCLP limit, then the waste cannot leach enough of the chemical into the soil and groundwater to be considered a hazardous waste. If the initial concentrations of potentially toxic elements are not present or they are at such low levels that the TCLP limits cannot be exceeded – in this case a TCLP test may not be necessary.

The redox state of the metals found in the Fe complexes of the precipitates is important and the adsorption of As to the hydrated iron oxide (HFO) minerals may not be stable and may change continuously, either due to various geochemical interactions, or due to interactions with various living organisms, in particular bacteria, algae and fungi.

Iron oxidation by bacteria is a spatially and temporally tightly regulated process that ultimately leads to the formation of diverse biogenic Fe oxides, including HFOs, and thus form a perfect substrate for the adsorption of potentially toxic elements such as As(V) (Muehe et al., 2013; Xiu et al., 2019).

Ochre precipitates formed in a 50 L container

The longer time of water accumulation in the container and its slower outflow, led to the precipitation of Fe²⁺ into insoluble Fe³⁺ oxihydroxide phases, and the presence of potentially toxic elements bound in these Fe precipitates pose a risk of their release and mobilization. They can be highly toxic even at low concentrations and can have a negative impact on the environment.

The mobility of potentially toxic elements varied depending on the type of leaching method; the pH of buffering solution. While the bioavailability method simulates an acidic stomach environment with pH 1.5, the TCLP method leaches in a landfill with pH 2.8 and the SPLP method acidic precipitation with pH 4.2. Ochre precipitate (denoted as Fe-HB-Š) was subjected to leaching by all leaching methods. The results show that the mobility of both As and Fe were very low for both SPLP and TCLP

leaching methods. The mobility of As ranged from 0.01 % to 0.04 % for the SPLP and TCLP methods, respectively.

The highest mobility presented Mn above 90 % for the SBET and TCLP method and the least mobile was As. The concentration of As was under the limited values according to the regulatory TCLP limits in the leachate (5 mg/L).

The leachability of each element also depended on the input concentration of the selected element (Fig. 7 ,

Tab. 3). In the case of the SBET method used, although the mobility of arsenic was only 1.03 %, but due to the extremely high input concentration of As in the sample, the concentration in the leachate was relatively high for As (6.09 mg/L), Fig. 8. The Fe concentration in the leachate after the SBET method also presented a high value of concentration of 621 mg/L but the Fe mobility was minimal for the TCLP and SPLP methods.

It can be concluded, that both As and Fe mobility were highest when the SBET method was used simulating acid aggressive environment at pH 1.5 and very low mobility was detected for the SPLP method using simulating acid precipitation at pH 4.2. Sb was the most mobile after the SBET method and the same 2 % mobility was shown after the TCLP and SPLP methods. The results indicate stable chemical bonds between Fe and As.

3.3 Sequential extraction analysis (SEA)

Chemical elements can be mobilized and retained in the rock environment by various processes, such as binding to primary and secondary minerals, formation of stable complexes with organic ligands, clays and metal oxyhydroxides (Bourg, 1995). Iron, manganese and aluminium oxyhydroxides are generally stable at neutral to alkaline environmental pH values, and their dissolution occurs under acidic or strongly alkaline conditions (Cheng & Yeh, 1998).

A sample of the resulting ochre precipitate (Fe-HB-Š) from a 50 L container was subjected to sequential extraction analysis to determine the content of potentially toxic elements in the bioavailable and non-available fractions. Each extraction step represents the leaching of a form of the element bound to a specific soil or sediment phase (Žemberyová et al., 2006). The fractions are indicated by the numbers 1–5, which according to the methodology (Mackových et al., 2000) means:

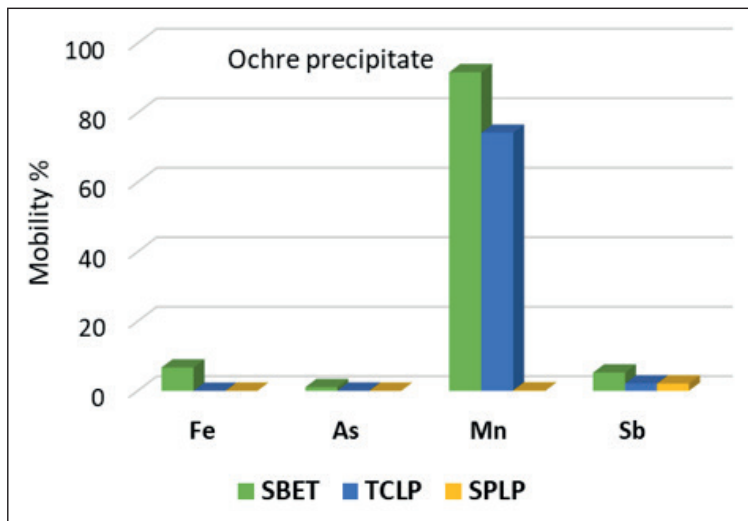


Fig. 7. Mobility of the potentially toxic elements after individual leaching tests in ochre precipitate Fe-HB-Š.

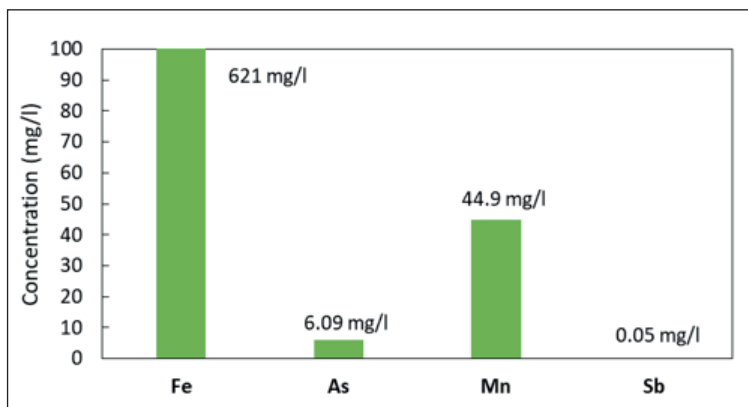


Fig. 8. Concentrations of potentially toxic elements in leachate after SBET bioavailability test in ochre precipitate Fe-HB-Š.

Tab. 3

Concentrations of potentially toxic elements in the ochre precipitate Fe-HB-Š before and after leaching tests

Sample	Element	Input [mg.kg ⁻¹]	C _{SBET} [mg.kg ⁻¹]	CV [mg.L ⁻¹]	SBET [%]	C _{TCLP} [mg.kg ⁻¹]	CV [mg.L ⁻¹]	Mobility TCLP [%]	C _{SPLP} [mg.kg ⁻¹]	CV [mg.L ⁻¹]	Mobility SPLP [%]
Fe-HB-Š	Fe	462 190	31 050	621	6.72	9.10	0.46	0.00	6.79	0.34	0.00
	As	29 407	304	6.09	1.03	10.50	0.53	0.04	3.20	0.16	0.01
	Mn	2 449	2 245	44.9	91.7	1 818	90.9	74.2	2.56	0.13	0.10
	Sb	47.67	2.50	0.05	5.24	1.00	0.05	2.10	1.00	0.05	2.10

1. water-soluble fraction: characterizes the proportion of the element soluble in the aqueous phase in the form of inorganic salts;
2. ion-exchangeable and carbonate fraction: the fraction of the element adsorbed by inorganic salts and bound to carbonates, released into the environment when the pH changes from neutral to acidic;
3. reducible fraction; element bound to Fe and Mn oxides, from which it is released into the aquatic environment when Eh conditions change;
4. organic-sulphide fraction: element bound to organic matter and sulphides, released as a result of oxidation and subsequent degradation of organic matter and decomposition of sulphides under changing physicochemical conditions;
5. residual fraction called insoluble residue, encompasses the elements in form of no real risk for organisms present in given environment.

The most mobile fractions are fractions 1 and 2, i.e. the fractions present in the soil solution and in the soil sorption complex respectively.

3.3.1 Ochre precipitates formed in a 50 L container

To understand the physicochemical processes of metal fixation, mobility and transport the sequential extraction analysis of ochre sample was provided.

Based on the results of the sequential extraction analysis of the ochre sample (Fe-HB-Š), it can be concluded that both As and Sb are strongly bound and its amount in the mobile fractions (1) and (2) is almost zero. 98.82 % of arsenic is represented in the residual fraction (5), which means that they are bound to insoluble tertiary mineral phases. In fraction (4), As is present in the amount of 0.88 % where As is

bound to organic matter and sulfides and 0.15 % of As is present in the reducible fraction (3). In the case of Fe, 81.98 % is also present in the residual fraction (5), 12.08 % in the reducible fraction (3) and 5.93 % in the organic-sulfide fraction (4). In the case of Mn, up to 52.26 % is bound to the mobile ion-exchangeable and carbonate fraction (2), the residue is represented most in the reducible (3), successively in the residual (5) and least in the organic-sulfidic fraction (4), Tab. 4, Fig. 9. This behaviour of elements correlate with the leaching test results, where the highest Mn mobility was observed after the TCLP test and SBET bioavailability test. The highest abundance in the ion-exchangeable and carbonate fractions (2), means that the element is readily released into the environment when the pH changes from neutral to acidic. These results from the sequential extraction analysis of ochre precipitate indicate, the tight binding of As to Fe oxyhydroxides, where it can bind to various complexes with Fe in $FeAsO_4^-$, $FeOHAs$, etc. (Pitter, 1999).

The oxidation of primary minerals in mining areas often results in the formation of coatings or fringes on these minerals called tertiary minerals, which also affects the mobility of several elements. The resulting

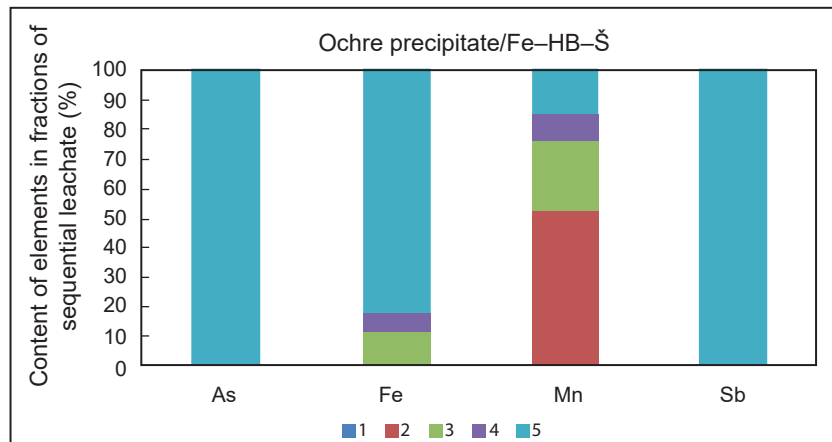


Fig. 9. Amount of extracted element in each extraction step in the ochre precipitate Fe-HB-Š.

Tab. 4

Results of sequential extraction analyses of elements in the ochre precipitate Fe-HB-Š and their amount in individual fractions (%)

Sample	Fraction	As _{TOT} [mg/kg]	As [mg/kg]	As %	Fe _{TOT} [mg/kg]	Fe [mg/kg]	Fe %	Mn _{TOT} [mg/kg]	Mn [mg/kg]	Mn %	Sb _{TOT} [mg/kg]	Sb [mg/kg]	Sb %
Fe-HB-Š	1	24 257	12.1	0.05	399.326	27.3	0.01	2 953	1.94	0.07	41	< 3	0.00
	2		23.2	0.10		16.40	0.00		1 543	52.3		< 3	0.00
	3		37.1	0.15		48 237	12.1		713	24.2		< 3	0.00
	4		214	0.88		23 679	5.93		271	9.18		< 3	0.00
	5		23.971	98.8		327 366	82.0		424	14.3		41	100

coatings may contain elevated concentrations of some elements, e.g. arsenic, iron or antimony. These elevated concentrations of elements in coatings may result from the incorporation of these elements originally present in solution into the coatings during their formation (Majzlan et al., 2011; Hiller et al., 2012). Tertiary precipitates also include gypsum coatings, or the most commonly occurring hydrated iron (or manganese, zinc, and aluminum) sulfates, which can also influence element mobility (Jambor, 1994). Grains of tertiary minerals can be formed by complete replacement of ore or by precipitation from solutions found in mine waste or tailings (Majzlan et al., 2011; Hiller et al., 2012).

3.3.2 Ochre precipitates subjected to leaching tests

The results of the sequential extraction analysis of the ochre precipitate performed after leaching tests is shown in Fig. 10. As was present in the residual insoluble fraction (5) with abundance above 99 % after all leaching tests. The amount of As in the organic-sulfide fraction (4) for each method were as follows: 0.28 % after SBET, 0.46 % after TCLP and 0.66 % after SPLP method. In the reducible fraction (3), 0.12 % As appear for all methods, where it is bound to Fe and Mn oxides, from which it can be released into the aquatic environment when Eh conditions change. A small concentration of As is also present in mobile fractions 1 and 2 (from 0.06–0.15 %), Tab. 5. Fe is also predominantly represented in the last insoluble fraction (5) above 80 % for all leaching methods, then in the reducible fraction (3) and the remainder in the organic-sulphidic fraction (4), Fig. 9. In the case of Mn, the highest proportion of the mobile form 44.01 % is found in the ion-exchangeable and carbonate fractions (2) after SPLP test. For the SBET and TCLP methods, Mn was found in the mobile phases in fraction (2) but also in the water-soluble fraction (1), and the proportion of Mn in the reducible fraction (3) decreased

significantly and increased in the residual fraction (5), Fig. 10. The lowest Mn mobility was in the case of the SPLP test with simulated acid rain pH 4.2, which corresponds with the leaching test results. Increasing the acidity of the

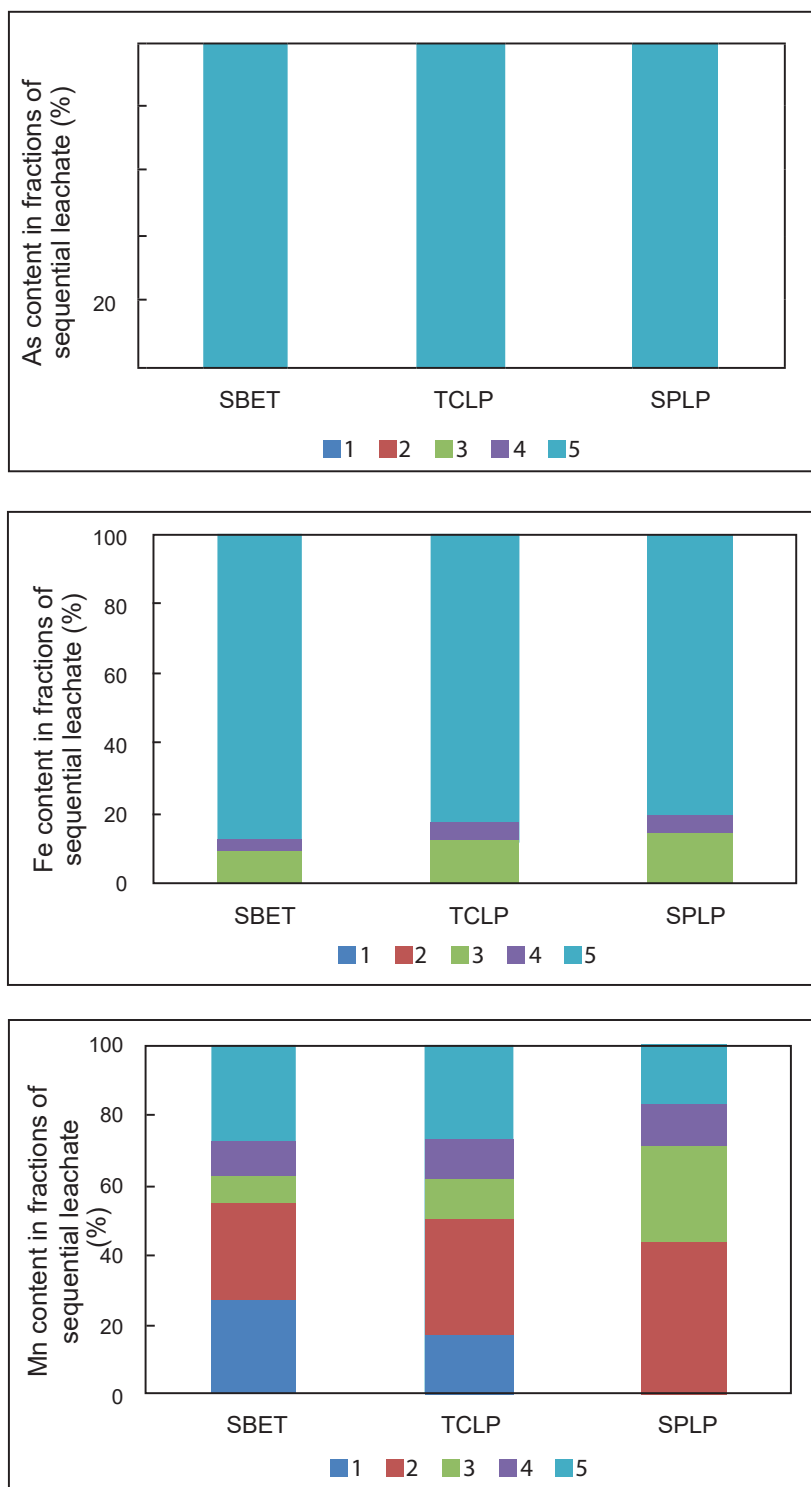


Fig. 10. Amount of extracted element in each extraction step in the ochre precipitate Fe-HB-Š after leaching tests.

Tab. 5

Results of sequential extraction analyses of elements in the ochre precipitate Fe-HB-Š using different leaching methods

Elements		As		Fe		Mn		Sb	
Fe-HB-Š	Fraction	[mg/kg]	%	[mg/kg]	%	[mg/kg]	%	[mg/kg]	%
Ci		36 693		530 948		1 314			
SBET	1	55.0	0.15	1 252	0.24	355	27.0	< 3	0.00
	2	43.0	0.12	1 539	0.29	369	28.1	< 3	0.00
	3	45.0	0.12	46 115	8.69	91.64	6.97	< 3	0.00
	4	102	0.28	20 623	3.88	128	9.72	< 3	0.00
	5	36.448	99.3	461 420	86.9	370	28.2	46.0	100
Ci		26 111		430 725		1 589		55	
TCLP	1	16.0	0.06	68.0	0.02	264	16.6	< 3	0.00
	2	19.0	0.07	477	0.11	527	33.2	< 3	0.00
	3	36.0	0.14	53 190	12.35	184	11.6	< 3	0.00
	4	119	0.46	20 736	4.81	185	11.6	< 3	0.00
	5	25 921	99.3	356 254	82.7	429	27.0	55.0	100
Ci		25 418		424 896		3 081		42	
SPLP	1	16.0	0.06	55.5	0.01	1.74	0.06	< 3	0.00
	2	21.0	0.08	75.4	0.02	1 356	44.0	< 3	0.00
	3	31.0	0.12	57 680.8	13.6	831	27.0	< 3	0.00
	4	167	0.66	24 803	5.84	361	11.7	< 3	0.00
	5	25 183	99.08	342 281	80.56	531	17.2	42.0	100

Explanatory notes:

Ci – input concentrations of elements in the sample mg/kg

% – percentage of elements in each fraction

leaching solution increased the amount of Mn in the mobile fraction, which seems to be related to the binding of Mn in the form of oxides, from which it is readily released into the aqueous environment when the pH and Eh conditions are changed. Mn becomes soluble at low pH and probably binds to tertiary mineral phases in the residual fraction (5). The elemental amounts and concentration (%) in each fraction are given in Tab. 5.

4 Conclusion

The aim of this study was to study the mobility of potentially toxic elements (As, Sb, Fe and Mn) and to determine their content in the bioavailable and unavailable fractions in the resulting ochre precipitates (Fe precipitates from a 50 L container from previous in situ field experiments) using leaching tests (SBET, TCLP, SPLP) and sequential extraction analysis. The bioavailability of iron was relatively high, 621 mg/L in the leachate,

but this represents a mobility of 6.72 % from the input Fe concentration (input 471 000 mg/kg Fe). For As, the mobility was 1.03 % (input 56 945 mg/kg). After TCLP tests (pH = 2.8) simulating conditions of 100 years of leaching in a landfill and SPLP test (pH = 4.2) simulating conditions of waste exposed to 100 years of acid rain, the mobility of Fe and As was minimal, below 0.1 %. Mn was the most mobile element with removed amount above 90 % after the bioavailability and TCLP tests.

The regulatory TCLP limit (5 mg/L) for As in the leachate was not exceeded, indicating that the waste is unable to leach sufficient amounts of the contaminant. Arsenic is probably incorporated directly into the internal structure of the Fe precipitate (formed by hydrated iron oxides) and is bounded to it in internal complexes. It is generally assumed that the porous nature of iron (oxy) hydroxides leads to adsorption of As(V) on internal iron complexation sites.

Even after leaching tests, a sample of ochre precipitate was subjected to a five-step sequential extraction analysis to determine the content of potentially toxic elements in the bioavailable and unavailable fractions. The results from the SEA for Mn correlated with the results from the leaching tests, where the highest Mn mobility was observed after SBET and TCLP tests. Mn was the most mobile element represented predominantly in the (2) ion-exchangeable and carbonate fractions, progressively less in the (5) residual, (3) reducible, and (4) organic-sulfide fractions. In the case of Fe, As and Sb, they were predominantly represented in the residual fraction – non biologically available (5) after all leaching tests. In summary, except of Mn, As and Sb are bounded to tertiary insoluble minerals.

Acknowledgements

The information used in this paper was obtained within the framework of the Operational Programme Quality Environment Programme *Ensuring the monitoring of environmental burdens in Slovakia – Part 2*, which is co-financed by the European Union / Cohesion Fund (application code: NFP310010AXF2). This material is a contribution to the EuroGeoSurveys HORIZON-CSA Geological Service for Europe project. Authors are grateful to reviewers of primary manuscript.

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Legislative standards

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- US EPA 1312: Hazardous Waste Test Methods / SW-846. <https://www.epa.gov/hw-sw846/sw-846-compendium>

Charakteristika okrových precipitátov obsahujúcich arzén z banskej vody a štúdium ich stability pomocou lúhovacích testov a sekvenčnej extrakčnej analýzy

Štôlna Hauser je najhlbšie položené horizontálne úvodné banské dielo v celej rudnej oblasti Zlatej Idky. Zo štôlne vyteká neutrálna až slabo alkalická banská voda s priemerným pH 7,3 a vysokým obsahom arzenu (360 $\mu\text{g/l}$). Vysoký obsah arzenu významne koreluje s obsahom dvojmocného železa. To nám umožňuje predpokladať, že táto vysoko toxická mikrozložka chemického zloženia pochádza z primárneho prostredia formovania chemického zloženia banskej vody – z hĺbky horninového masívu (prítomnosť arzenopyritu v zlatoidčianskom žilnom systéme) (Bačová, 2006). Ide o zdroj kontaminácie, ktorý je permanentný (výtoky zo štôlní, drenážne vody a výluhy banských hald) a bude dlhodobo dotovať povrchovú vodu potokov rizikovými prvkami (Cicmanová a Baláž, 2007). Výtok banskej vody vytvára pod zavaleným ústím štôlne jazierko bez odtoku. Banská voda pravdepodobne vsakuje do sedimentov kvartéru v údolí Idy.

Kritickým parametrom mobility kovov, a teda aj ich bioprístupnosti, je pH. Rozpúšťanie karbonátov a silikátov je dôležitým typom reakcií, ktoré formujú pH vôd. Z hľadiska mocnosti arzenu prítomného vo vodách sa zistilo, že vystupuje len v menej toxickej forme päťmocných iónov. Poukazuje to na výrazné uplatnenie oxidačných podmienok vodného prostredia – pravdepodobne v záverečnej fáze výstupu banskej vody (Cicmanová a Baláž, 2007).

Okrové fázy sa vyrazajú priamo z banskej vody (alebo úniku z odkaliska). Sú charakteristické pre banské lokality, výtoky zo štôlní a ich okolie v dôsledku oxidácie rozpustného Fe^{2+} na nerozpustné fázy Fe^{3+} . Ide o hydratované oxidy železa (HFO), ktoré môžu zahŕňať niekoľko minerálov, ako napríklad ferihydrit, akaganéit, feroxyhyt, goethit, lepidokrokit a limonit. Sú slabo kryštalické, veľmi pórovité, majú veľký povrch a vďaka tomu sú vynikajúcimi sorbentmi rôznych potenciálne toxických prvkov. Sorpčné vlastnosti hydroxidov železa (HFO) závisia od pH okolitej vody, chemického zloženia vody a pomeru rozpustených stopových kovov k množstvu hydratovaných oxidov železa (Dzombak et al., 1987; Davis a Kent, 1990; Stumm, 1992).

Predchádzajúca štúdia bola zameraná na zníženie koncentrácie As z vytekajúcej banskej vody v dynamických/prietočných podmienkach (Bekényiová et al., 2023). Terénne pokusy in situ pozostávali z navrhnutého systému kontinuálneho pretekania banskej vody tak, že priamo v teréne sa osadili dve 50 l nádoby, cez ktoré nepretržite samospádom pretekala banská voda. Vytekajúca banská voda pretekala cez obe nádoby: odkalovaciu (osadená vyššie)

a filtračnú (osadená nižšie), v ktorej boli do vrstiev uložené rôzne frakcie prírodných sorbentov. V odkalovacej nádobe sa počas celého trvania experimentu in situ (4 mesiace) prirodzene tvorili okrové zrazeniny viažuce významnú časť arzenu. V priebehu experimentu sme v 50 l odkalovacej nádobe postupne pozorovali tvorbu a vznik veľkého množstva prirodzene sa vytvárajúcich Fe zrazenín. Pozorovaná jemná vláknitá štruktúra na niektorých miestach súvisí s prítomnosťou železitých baktérií, ktoré zohrávajú významnú rolu v mobilite prvkov. Na základe výsledkov rtg. analýzy možno uvažovať o prevažne amorfnej fáze železitých oxyhydroxidov s malým podielom kryštalického ferihydritu. EDX analýza hrdzavočervených precipitátov z banskej vody zachytených na filtri potvrdila prítomnosť železa v množstve 52 hmot. % aj arzenu 13,2 hmot. % . Z pozorovaného spektra skenovacej elektrónovej mikroskopie boli zreteľne viditeľné duté rúrky, ktoré vzhľadom pravdepodobne zodpovedajú Fe oxidujúcej baktérii *Leptothrix ochracea*. Ide o známu baktériu, ktorá sa v okroch vyskytuje vo vyššom počte, s pravdepodobným významným vplyvom na rýchlosť kryštalizácie hydratovaných oxidov železa a adsorpciu iónov kovov/metaloidov. Železité baktérie rodu *Leptothrix* tvoria schránky s vyžrázaným železom a oxidujú dvojmocné železo na trojmocný hydroxid železa. To, že môžu adaptívne využívať kovy (alebo iné zlúčeniny) ako akceptory elektrónov, im umožňuje žiť v meniacich sa podmienkach, napr. v prechodnej zóne medzi aeróbnym a anaeróbnym prostredím, a prispôbiť sa meniacej sa dostupnosti kyslíka.

Cieľom tejto štúdie bolo aj posúdiť mobilitu potenciálne toxických prvkov a stanoviť obsah potenciálne toxických prvkov v biologicky dostupných a nedostupných frakciách vo vzniknutých okrových zrazeninách (Fe precipitáty z 50 l nádoby z predchádzajúcich terénnych experimentov in situ) pomocou lúhovacích testov (SBET, TCLP, SPLP) a sekvenčnej extrakčnej analýzy. Zistená bioprístupnosť železa pomocou metódy SBET bola relatívne vysoká, vo výluhu 621 mg/l, čo ale pri vstupnej hodnote koncentrácie Fe (vstup 471 000 mg/kg Fe) predstavuje mobilitu 6,72 %. V prípade As bola mobilita 1,03 % (vstup 56 945 mg/kg). Po teste TCLP (pH = 2,8), ktorý simuluje podmienky 100-ročného lúhovania odpadu na skládke, a teste SPLP (pH = 4,2) simulujúcom podmienky odpadu vystaveného 100 rokov kyslým dažďom bola mobilita Fe a As minimálna, nižšia ako 0,1 %. Najmobilnejším prvkom bol jednoznačne Mn so zastúpením vo výluhu vyše 90 % po použitej metóde bioprístupnosti SBET a teste TCLP.

Aj napriek pravidelnej závlaha plodín kontaminovanou banskou vodou v susediacej záhrade boli hraničné hodnoty arzénu stanovené len vo vzorke zemiakov. Tento fakt svedčí o nízkej mobilite arzénu.

Regulačný limit TCLP (5 mg/l) As vo výluhu nebol prekročený. To značí, že odpad nedokáže vylúhovať dostatočné množstvo kontaminujúcej látky. Arzén je pravdepodobne zabudovaný priamo do vnútornej štruktúry Fe precipitátu (tvoreného hydratovanými oxidmi železa) a je s ním viazaný do vnútorných komplexov. Vo všeobecnosti sa predpokladá, že porézna povaha (oxy)-hydroxidov železa vedie k adsorpcii As(V) na vnútorných miestach komplexácie železa. Vzorka vzniknutého Fe precipitátu aj po lúhovacích testoch bola podrobená päťstupňovej sekvenčnej extrakčnej analýze s cieľom stanoviť obsah potenciálne toxických prvkov v biologicky dostupných a nedostupných frakciách. Výsledky zo SEA v prípade **Mn** korelujú s výsledkami lúhovacích testov, kde sa najvyššia mobilita Mn prejavila po metóde SBET a TCLP. Mn bol najviac mobilným prvkom zastúpeným prevažne vo (1) vodorozpustnej a (2) v ionovymeniteľnej

a karbonátovej frakcii, postupne menej v reziduálnej (5), redukovateľnej (3) a najmenej v organicko-sulfidickej frakcii (4) po týchto testoch. Po lúhovaní metódou SPLP s pH 4,2 došlo k prestúpeniu Mn v prospech (2) ionovymeniteľnej a karbonátovej frakcie, úbytku v (5) reziduálnej frakcii a navýšeniu v (3) redukovateľnej frakcii. **Fe, As a Sb** boli vo všetkých vzorkách po všetkých lúhovacích testoch zastúpené prevažne v (5) reziduálnej, teda nemobilnej frakcii. Súhrnne možno konštatovať, že tieto prvky, okrem mangánu, sú viazané na terciárne, ťažko rozpustné minerály.

Tam, kde v okolí výtokov banskej vody dochádza k intenzívnej sedimentácii okra, je potrebné posúdiť, či nie je vhodné tento sediment preventívne odstraňovať a ukladať ho na miesto, kde nespôsobí kontamináciu pôdy a vodných tokov.

Doručené / Received: 21. 11. 2023
Priaté na publikovanie / Accepted: 21. 12. 2023