Original paper The role of jarosite minerals in the attenuation of metals and arsenic in mine drainage system (example from the Pekelská Adit, Czech Republic)

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Mineralogy of stream sediments and acid mine drainage water chemistry were investigated in the Pekelská Adit in Czech Republic. Bulk solid phase composition was determined using total decomposition, X-ray powder diffraction, electron microprobe, X-ray photoelectron spectroscopy, and Mössbauer spectroscopy. Water chemistry at the principal branch is acid (pH < 3.0) with high concentration of dissolved iron and sulfate, but it is close to neutral in the second stream branch and becomes more acidic only after the confluence of both branches. Minerals of alunite group including K-jarosite, plumbojarosite, and hydronium jarosite were identified in the stream sediments of acid branch by combination of complementary instrumental methods. In the acid branch, sediments comprise high contents of As (up to 8,021 ppm) and Pb (up to 4,131 ppm), but contents of Zn are much lower. In contrast, in the neutral branch, there is high content of Zn in sediments (up to 11,667 ppm) linked to goethite, but contents of As and Pb are several orders of magnitude lower. Results confirm that minerals of alunite group can be very efficient in trapping of dissolved contaminants and play crucial role in the natural attenuation of dissolved metals and metalloids in mine drainage waters.

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1. Introduction

Acid mine drainage (AMD) and its discharge into rivers and lakes results in decreasing pH and raise of concentrations of dissolved sulfate, iron and other metals and metalloids such as arsenic. The principal minerals responsible for the formation of AMD are sulfidic minerals such as pyrite and pyrrhotite. When there are neutralization minerals like calcite and dolomite present in gangue rocks and/or mining wastes, only neutral mine drainage (NMD) with close to neutral pH and much lower concentrations of dissolved metals and metalloids develop (Blowes et al. 2003).

Jarosite $[KFe_3(SO_4)_2(OH)_6]$ is a typical AMD mineral of the alunite group which precipitates in low pH and high sulfate conditions. Bulk precipitation typically follows the reaction

 $K^{+}+Fe^{3+}+2SO_{4}^{2-}+6H_{2}O=KFe_{3}(SO_{4})_{2}(OH)_{6}+6H^{+}$

In this case, one mole of precipitated jarosite produces 6 moles of acidity. This means precipitation of jarosite can keep low pH values or pH may even decrease downstream (Sracek et al. 2018). Jarosite and other ferric phases could incorporate high amounts of dissolved contaminants like Cu, Zn, As, and Ni (Kocourková et al. 2011; Sracek et al. 2011, 2018; Sarmiento et al. 2012) by coprecipitation and/or adsorption of high-surface area of precipitated phases. On the other hand, precipitated jarosite is metastable and, depending on pH, it can be transformed later to more stable phases such as goethite (Fukushi et al. 2003; Baleeiro et al. 2018). Study of jarosite transformation indicated first order kinetics and incongruent process with the formation of secondary goethite on the surface of jarosite (Smith et al. 2006). Adsorption of sulfate may play an important role in the formation of secondary ferric phases after jarosite dissolution (Elwood Madden 2012). Also, there can be temporal changes of mineralogical assemblages in the AMD streams caused by changes in water chemistry (Kumpulainen et al. 2007; Burton et al. 2021; Schoepfer and Burton 2021).

Incorporation of contaminants into precipitated jarosite can be highly selective as demonstrated, e.g., at AMD site in Selebi Phikwe, northeast Botswana, where much more Cu than Ni is incorporated into jarosite, in spite of much higher dissolved Ni concentration (Sracek et al. 2018). In open systems with continuous flushing, arsenic incorporation into jarosite results in increasing jarosite dissolution rates (Kendall et al. 2013).

Our study site Pekelská Adit is located at the central part of Bohemian Massif (Českomoravská vrchovina Highlands) in Czech Republic (Fig. 1). We studied mineralogy and aqueous solution chemistry in acid (AMD) and neutral mine drainage (NMD) branches of the underground adits. Objectives of the study were to (1) compare mineralogical assemblages in arsenic-rich systems affected by dynamic neutralization and fast precipitation of secondary phases within these AMD and NMD branches with domination of jarosite–goethite formation, and (2) evaluate how the understanding of such complex geochemical system could lead to a prediction of metal mobility in analogous environments.



2. Site history and geology

The Pekelská Adit is located about 1.1 km NW from Stříbrné Hory close to Havlíčkův Brod town (SE of Prague) in the Českomoravská vrchovina Highlands (Fig. 1). The beginning of exploration is not known exactly, but it is assumed to start in 16th century and potentially even earlier in the Medieval Period. The adit is mentioned for the first time in documents from late 18th century and several times in 19th century, but it is already described as abandoned. There was limited exploitation during the World War II followed by modern geological exploration in 1949–1954 when several new adits were constructed.

The adit has two levels: the lower level, currently completely flooded and accessible from the upper mostly dry level (Fig.1). Accessible adit length is 527 m. In the proximity of the adit there are several pits after surface exploitation in total length of about 90 m probably in the same mineralized zone of NW–SE and W–E direction

exploited in the adit (Dobeš and Malý 2001).

The Pekelská Adit is one of several tens of mining works exploiting from the Medieval polymetallic mineralization in the Havlíčkův Brod Ore District. There is Lower Permian vein mineralization of the Kutná Hora type (Bernard and Žák 1992) labeled as k-pol type of mineralization (Bernard and Žák 1992). The adit was built in strongly high-grade metamorphic rocks of the Moldanubian Zone with dominant biotite and sillimanite-biotite paragneisses, which are generally strongly affected by migmatization. At some spots, granite porphyries and at lower flooded level and also weakly metamorphosed conglomerates were found (Kempný 1954). Mineralization was exploited in the past and only relatively minor mineralized veins 3-8 cm thick are still present in the adit. Principal minerals in the veins are quartz and pyrite forming aggregates or crystals up to 1 cm in size.

Fig. 1a – Site location, **b** – map of Pekelská Adit with location of sampling points.

There is a common occurrence of sphalerite, with variable contents of Fe (from 7.7 to 11.8 wt. %) and indium. Other minerals such as galena, and arsenopyrite, are abundant whereas marcasite, chalcopyrite, cassiterite, stannite (Cu₂FeSnS₄), and pyrargyrite (Ag₂SbS₂) are minor. The host rocks are affected by hydrothermal alterations manifested as intense pyritization and silicification, together with less pronounced conversion of feldspars to sheet silicates (probably illite) and biotite to chlorite. Secondary minerals identified in the past within Pekelská Adit included ferrihydrite FeO(OH)·nH₂O, schwertmannite $\text{Fe}_{8}\text{O}_{8}(\text{OH})_{6}(\text{SO}_{4})\cdot\text{nH}_{2}\text{O}$, jarosite $\text{KFe}^{3+}_{3}(\text{SO}_{4})_{2}(\text{OH})_{6}$, malachite $Cu_2CO_3(OH)_2$, allophanes $Al_2O_3 \cdot (SiO_2)_{13,2} \cdot (2.5-3)$ H₂O, and in small amounts, cerussite PbCO₃, anglesite PbSO₄, and smithsonite ZnCO₂ (Pokorný and Vrabka 1952; Dobeš and Malý 2001).

The average annual temperature at study site is $7 \,^{\circ}$ C, average annual precipitation is about 700 mm. Most precipitation occurs in early spring, when discharge of mine water in the upper adit is at its maximum.

3. Material and Methods

3.1. Sampling of sediment and water

Sampling points were in the AMD branch (S1, S2), in the NMD branch (S3) and in the stream after confluence of both branches (S4, S5). Samples of sediment were taken with a plastic spoon from the upper part of sediment profile (~1 cm). There was no sediment at point S5 (outflow from the adit). Wet solid samples were packed in PE bags, stored in cooler, and transported to the laboratory where they were stored at 4 °C until analyzed. Samples of water were taken at the same sites as sediment samples. Field parameters T, pH, Eh, and EC were measured on site. The field Eh values were corrected with respect to hydrogen electrode (Appelo and Postma 2005). Samples were filtered using 0.45 μ m filter, and stored in PET bottles. For cation analyses were samples acidified by ultrapure HCl to pH about 2.0.

3.2. Bulk composition of solid samples

The samples for analyses of the bulk chemical composition were homogenized and pulverized. The H_2O content was measured by drying at 110 °C ($-H_2O$) and employing the Penfield's method ($+H_2O$). Total sulfur content was measured by titration in a Na₂CO₃+ZnO mixture. Afterwards, the sample was leached with distilled water, filtered and the SO₃ was determined by gravimetry using the leaching in HCl (1:5 ratio). Inorganic carbon (C_{inorg}) was determined by boiling the sample in H_3PO_4 and adsorbing the produced CO₂ on askarite (Fresenius

method). Gravimetric determination was used for SiO₂ measurement: 1 g of the sample was melted in 10 g of Na₂CO₂, washed repeatedly with HCl and air-dried. For the rest of the wet chemical analysis, fresh samples were dissolved in the mixture of HF and HClO₄. The produced solutions were analyzed photometrically using the Helios δ instrument for contents of TiO₂ (with H₂O₂), Fe_2O_3 -bulk (with sulphosalycic acid) and P_2O_5 (as a phosphorus-vanadium-molybdenum complex). Contents of Al₂O₂ and CaO were determined using titration in low acidic and strongly alkaline environments, respectively, with complexone III. Analysis of Mn, Mg, K, Na, Ba, As, Pb, Cu, Zn, Cd and Ag was performed using the atomic absorption spectroscopy (AAS) Solaar instrument by Unicam (Weiss et al. 1983). The FeO/Fe₂O₂(bulk) ratio was determined by dissolution in a mixture of HF+ H_2SO_4 by titration with K_2CrO_4 .

3.3. X-ray powder diffraction

The powder X-ray diffraction analyses were performed using PANalytical X'pert PRO instrument (CoK α radiation at 40 kV/40 mA) equipped with X'Celerator detector and diffracted beam anti-scatter slits. Samples were placed on zero-background Si slides, pressed to obtain a sample thickness around 0.5 mm, and scanned at a near constant radiation volume in the 2 θ range of 5–105° in steps of 0.017° for 4 s per step. The data were processed using HighScore Plus (Malvern Panalytical).

3.4. X-ray photoelectron spectroscopy

In order to determine the oxidation state of As and S in selected sample (S2), the X-ray photoelectron spectroscopy (XPS) measurement has been performed on the Nexsa G2 XPS system (Thermo Fisher Scientific) with a monochromatic Al-Ka source and photon energy of 1486.7 eV. Sample in powder form was mounted to a sample holder using the double-sided tape (SCOTCH). All the spectra were measured in the vacuum of 1.6×10^{-9} mBar and at the room temperature of 20 °C. The analyzed area on the sample was a spot of 100 µm in diameter. The survey spectrum was measured with a pass energy of 150.00 eV and a step of 1.0 eV, while for the highresolution spectra, a pass energy of 50.00 eV and a step of 0.1 eV were used. Charge compensation was used for all measurements. The spectra were evaluated with the Avantage 6.5.1 (Thermo Fisher Scientific) software.

3.5. ⁵⁷Fe Mössbauer spectroscopy

The ⁵⁷Fe Mössbauer spectra of representative sediment samples were collected in a constant acceleration mode

with a 57 Co(Rh) source of 1.85 Gbq at room temperature using MS2007 instrument. The spectra were fitted by Lorentzian functions using the CONFIT2000 software (Zak and Jiraskova 2006). The effects of non-ideal absorber thickness and variable recoil-free fractions for iron atoms in non-equivalent structural sites of different phases were expected to be within experimental error (hyperfine parameters $\pm 0.02 \text{ mm} \cdot \text{s}^{-1}$, relative spectral area $\pm 2 \%$).

3.6. Electron microprobe analyses

Electron microprobe analyses (EMPA) including imaging in the back-scattered electron (BSE) mode were performed using the Cameca SX-100 instrument. The measurements were carried out using a wavelengthdispersive mode under the following conditions: accelerating voltage 15 kV, beam current 5 nA; beam diameter of 1 or 4 μ m. Natural and synthetic standards were: As, Cu – lammerite, Na – albite, Mg - Mg₂SiO₄, Si, Ca - wollastonite, P – fluorapatite, Fe – andradite, Zn – gahnite, K – orthoclase, F – topaz, Mn – spessartine, S – SrSO₄, Pb – vanadinite, Al – andalusite, Ba – barite, Cd – Cd. The raw data were corrected using the PAP correction (Pouchou and Pichoir 1985). The alunite supergroup minerals formulae were calculated on the basis of the B position sum = 3 atoms.

3.7. Water chemistry analyses

Concentrations of principal cations, Al, Fe, and Mn in mine drainage water were analysed by inductivelycoupled plasma optical-emission spectroscopy (ICP-OES, iCAP 6500 radial, Thermo Scientific, Germany). Trace metals were determined by quadrupole-based inductivelycoupled plasma mass-spectrometry (ICP QMS, X Series 2, Thermo Scientific, Germany). The quality of the analyses was checked using reference materials SRM 2711 (NIST, USA, Montana Soil, moderately elevated trace element concentrations) and SRM 2709 (NIST, USA, San Joaquin Soil). The precision of the measurements was < 5% RSD. The concentrations of the major anions $(SO_4^{2-}, PO_4^{3-}, PO_4^{3-})$ NO₂, F⁻, Cl⁻) in water were determined using ionic chromatography (ICS 2000, Dionex, USA). When applicable, the alkalinity was determined by titration to a pH endpoint of 4.5 with 0.05 mol·l⁻¹ HCl, using a Schott Titroline Easy (Schott, Germany) automatic titrator.

3.8. Geochemical modeling

Speciation modeling was performed with software Package Geochemist's Workbench (Bethke and Yeakel 2016) using database minteq.dat. The Eh-pH diagram was constructed using the same software.

4. Results

4.1. Character of stream sediments

4.1.1. Bulk composition of solid samples

Solid samples from the Pekelská Adit seepage stream have a character of yellow (S1) to brown-reddish (S2-S4) ochres comprising fine-grained mud with clasts of surrounding rocks and contain up to 671,900 ppm (S4) of iron (Tab. 1). The Fe³⁺ content increases gradually from S1 (222,000 ppm) at the seepage face to the highest content at S4 (671,900 ppm) after confluence of both branches. On the other hand, Fe²⁺ was detected only in acid branch up to 7,000 ppm. The opposite trend is generally observed for lead, arsenic as well as for sulfur contents. Lead content decreases from 4,131 ppm (S1) to 619 ppm (S4), As and S content decreases from 8,021



Fig. 2 – X-ray diffraction of studied samples (Q – quartz, M – muscovite, K – kaolinite, C – clinochlore, H – hedenbergite).

ppm and 55,503 ppm (S1) to 4,442 ppm and 25,867 ppm (S4), respectively. An exception is the sample S3 on the NMD branch where contents of both elements in the sediment are relatively low (557 ppm As and

Tab. 1 Total contents of main elements in stream sediments (values in ppm).

Sample	Fe^{3+}	Fe^{2+}	Pb	S _{tot}	As	Zn	Cd	Cu	Ag
S1	222,000	5,900	4,131	55,503	8,021	432	4	159	94
S2	474,600	7,000	3,466	35,459	5,208	328	2	93	69
S3	444,600	0	1,442	6,985	572	11,667	115	16	52
S4	671,900	0	641	25,867	4,520	741	2	95	54

6,985 ppm S). Significant content of Zn up to 11,667 ppm and higher content of Cd were found only in the NMD branch (S3). Contents of Cu and Ag are relatively low and more significant only in the acid branch (Tab. 1).

4.1.2. Speciation of iron in the solids

The XRD analysis of all solid samples identified various ferric oxyhydroxides with detrital minerals (quartz, muscovite, kaolinite, clinochlore, and hedenbergite) (Fig. 2). In samples from the acid branch (S1 and S2), ferric minerals are represented mostly by jarosite (only jarosite was identified in sample S1, jarosite in a mixture with goethite was identified in sample S2), whereas samples from neutral branch contain only poorly crystalline goethite. There is no indication of schwertmannite and other phases typical for AMD. This mineralogical composition from S1 to S4 samples clearly reflects the gradual evolution of pH conditions at sampling sites. The absence of well crystalline oxides or oxyhydroxides suggests the



Fig. 3 - Mössbauer spectroscopy of stream solid samples from AMD (S1 and S2) and NMD (S3 and S4) branch.

fresh character of the sediment without any significant re-crystallization of the precipitates.

The ⁵⁷Fe Mössbauer spectroscopy (Fig. 3) is in a good accordance with wet chemical analyses (Tab. 1) demonstrating the dominance of iron atoms in oxidation state 3+, except for the acid branch (S1, S2) where small amount of iron atoms occurs also in oxidation state 2+ (up to 4 % in sample S1). Spectra of the samples S1 and S2 were mostly fitted with two overlapping narrow doublets with hyperfine parameters typical for Fe³⁺ (isomer shift 0.38 and 0.39 mm·s⁻¹ and quadrupole splitting 0.74/0.53 and 1.23/1.09 mm·s⁻¹for S1 and S2, respectively) indicating that the corresponding Fe-bearing phases are in a superparamagnetic state (typical feature

SO₄ **S**1 plumbojarosite S2 Fe>Al beudantite corkite kintoreite segnitite PO_4 AsO₄ plumbophilipsbornite gummite hidalgoite hinsdalite Al>Fe osarizawaite SO_4

of nanocrystalline ferric hydroxides/sulfates; Filip et al. 2007). In agreement with XRD, we can ascribe the doublets with higher quadrupole splitting to jarosite (i.e., 65 % of iron atoms in form of jarosite in sample S1, and 34 % of iron atoms in form of jarosite in sample S2 based on subspectrum area; Fig. 3) and the remaining spectral component is assigned to goethite (31 and 65 % iron atoms in samples S1 and S2, respectively). The absence of detectable goethite in the XRD pattern of sample S1 (Fig. 2) could be explained by its low content in combination with its nanocrystalline character (i.e., it is in doublet form in all Mössbauer spectra, instead of sextet, which is typical for well-crystalline goethite). The Mössbauer spectra of the samples S3 and S4 were fitted only by

one doublet component (isomer shifts 0.38 mm·s⁻¹ for both samples, quadrupole splitting 0.69 and 0.60 mm·s⁻¹ for samples S3 and S4, respectively; Fig. 3) indicating that all iron atoms in Fe-bearing phases are in the oxidation state Fe³⁺ and in paramagnetic/superparamagnetic state. It is in full accordance with the XRD analysis (Fig. 2) where goethite was detected as the only Fe-bearing phase.

4.1.3. Chemical composition of the key minerals

The EMPA revealed differences in chemical composition among the identified phases in the solid samples. Sample S1 is dominated by alunite supergroup minerals (Bayliss et al. 2010), see Fig. 4 and BSE in Fig. 5a, b, when K-H₂O⁺, respectively K-Pb-H₂O⁺ members are also present (Fig. 6). Composition of the Pb-bearing minerals can be expressed in terms of the following end members: plumbojarosite $PbFe_6(SO_4)_4(OH)_{12}$, beudantite $PbFe_{2}(AsO_{4})(SO_{4})$ $(OH)_6$, and plumbogummite

Fig. 4 – Composition of minerals from Pekelská Adit within the Pb-dominant part of alunite supergroup. The nomenclature and boundaries are those of the CNMMN-approved system (Scott 1987) and updated (Bayliss et al. 2010).

	plumbojarosite	beudantite	hinsdalite	corkite/hinsdalite	plumbogummite	hydronium jarosite
As ₂ O ₅	3.41	14.16	5.29	3.89	3.80	0.82
P_2O_5	1.35	0.85	10.02	8.03	12.54	0.27
SiO ₂	0.42	0.25	0.12	0.55	0.16	0.40
Fe ₂ O ₃	38.45	24.87	13.85	20.22	8.02	47.06
Al ₂ O ₃	2.26	6.78	14.96	13.68	17.99	0.17
MgO	0.00	0.00	0.00	0.02	0.03	0.02
CaO	0.03	0.00	0.00	0.04	0.00	0.03
CuO	0.26	0.18	0.14	0.40	0.22	0.00
ZnO	0.45	1.32	0.20	0.00	0.31	0.00
MnO	0.02	0.16	0.14	0.07	0.03	0.05
PbO	21.04	32.12	35.15	32.01	38.50	2.41
CdO	0.01	0.05	0.00	0.00	0.00	0.02
SO3	21.20	11.52	7.27	10.59	6.31	27.59
K ₂ O	1.38	0.04	0.47	1.25	0.12	3.74
Na ₂ O	0.06	0.08	0.00	0.00	0.00	0.36
F	0.00	0.30	0.35	0.09	0.45	0.11
Total	90.34	92.67	87.95	90.82	88.47	83.02

Tab. 2 Selected members of alunite supergroup phases from Pekelská adit, EDX data, sample S1, contents in wt%.

PbAl₃(PO₄)₂(OH)₅*H₂O /hinsdalite PbAl₃(PO₄) (SO₄) (OH)₆ (Fig. 4). Relatively pure hydronium jarosite $H_3O^+Fe_3(SO_4)(OH)_6$, as well as intermediate members of the jarosite-and alunite solid solution were also found (see Tab. 2).

In contrast, only plumbojarosite was identified in sample S2. Part of the solid Fe phase forms a poorly crystalline goethite (see Fig. 5 c, d). Analyses of goethite (Tab. 3) show elevated contents of SO₃ and As₂O₅. Although goethite does not typically contain S and As, in this case it may indicate an adsorption on nanocrystalline goethite particles with expected large surface area. On the other hand, partial substitution of As a S into goethite structure could not be ruled out. No phases other than goethite and jarosite were detected in the sample S2. As expected for such strongly oxidizing environment, XPS spectra collected from sample S2 (Fig. 7) shows that the majority of As is in the As(V) form. Part of As identified in the reduced state As(III) may rather indicate local reduction of As(V) under X-rays beam (Viltres et al. 2020). All of the sulfur in sample S2 occurs as S(VI) (Fig. 7), consistent with the presence in jarosite structure. However, based on the acquired XPS data, it is not possible distinguish S in jarosite from S absorbed on goethite or on other phase(s). The detected sulfur in goethite analyses (Tab. 3) is therefore expected to be adsorbed on goethite surface also in the form of S(VI) (Fig. 7).

Tab. 3 The most common composition of goethite in Pekelská Adit.

sample			S2				S3						
analysis no.	29	30	31	32	34	35	36	2	37	38	39	40	41
As ₂ O ₅	0.64	0.06	0.78	1.66	0.04	0.15	0.04	0.10	0.00	0.02	0.32	0.36	0.37
P_2O_5	0.45	0.43	0.57	0.40	0.04	0.02	0.13	0.01	0.09	0.05	0.02	0.07	0.70
SiO ₂	0.84	2.17	3.17	1.01	10.78	9.20	13.28	4.54	1.62	1.63	3.00	2.57	1.83
Fe ₂ O ₃	79.01	76.90	78.07	79.05	76.37	74.99	68.58	18.39	77.07	76.95	77.02	79.71	80.50
Al ₂ O ₃	0.14	0.37	1.46	0.08	0.65	1.50	3.13	3.20	0.43	0.52	0.78	0.32	0.47
MgO	0.02	0.13	0.04	b.d.	0.05	b.d.	0.03	0.02	b.d.	0.05	b.d.	0.02	0.05
CaO	0.09	0.05	0.03	0.05	0.22	0.15	0.31	0.33	0.03	b.d.	0.02	0.01	0.01
CuO	0.08	b.d.	b.d.	0.07	0.04	0.10	0.02	0.00	b.d.	b.d.	0.22	b.d.	b.d.
ZnO	b.d.	0.26	0.22	0.33	0.24	0.97	0.23	0.19	b.d.	0.32	0.05	0.15	0.11
MnO	0.23	b.d.	b.d.	b.d.	b.d.	2.92	0.03	3.42	0.04	b.d.	0.24	b.d.	0.05
PbO	b.d.	b.d.	b.d.	b.d.	b.d.	0.24	0.04	0.50	0.00	b.d.	b.d.	0.03	0.00
BaO	b.d.	0.37	b.d.	b.d.	b.d.	0.06	0.25	0.00	0.04	0.02	b.d.	b.d.	0.12
CdO	b.d.	b.d.	b.d.	0.07	0.05	0.09	b.d.	0.00	0.09	b.d.	b.d.	b.d.	b.d.
SO3	5.55	4.64	4.77	5.93	2.54	0.49	2.74	0.16	9.70	11.06	10.61	6.37	3.32
K ₂ O	0.03	0.03	0.18	0.03	b.d.	0.03	b.d.	0.04	0.01	0.02	b.d.	0.02	b.d.
Na ₂ O	b.d.	0.01	0.02	0.03	b.d.	0.04	0.01	0.07	b.d.	0.07	b.d.	0.02	b.d.
F	b.d.	b.d.	b.d.	b.d.	0.05	b.d.	b.d.	0.24	0.01	b.d.	b.d.	b.d.	b.d.
Total	87.08	85.41	89.30	88.70	91.05	90.97	88.82	31.21	89.13	90.70	92.27	89.64	87.52



Value/	ъЦ	Eh	EC	Na	K	Ca	Mg	SO ₄	Cl	Fe	Zn	As	Cu	Cd	Pb
sample	рп	mV	mS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	μg/l	μg/1	μg/l	μg/1
S1	2.83	830	2.36	4.1	0.14	34.7	21.3	823	6.9	191	87.7	4,215	1,750	928	27.6
S2	3.25	770	1.55	8.4	1.8	61	30.2	475	12.8	55.5	35.2	331	369	266	18.5
S3	5.89	470	0.34	11.1	2.2	22.1	11.5	106	16.7	1.9	0.97	7.5	2.55	4.8	1.9
S4	4.20	640	0.40	11.2	2.5	27.3	13.2	142	16.6	2.5	2.9	18	21.9	19.3	6.6
S5	3.96	576	0.42	11.2	2.7	29.4	13.3	141	17.4	1.6	3.51	10.2	35.8	26.2	9.3

Tab. 4 Field parameters and water chemistry, concentrations are in mg/L.



Fig. 6 K–Pb– H_3O^+ ternary diagram of jarosite (Fe>Al) from Pekelská Adit, sampling point 1.

Sample S3 on the NMD branch is partly formed by a Fe–Si–SO₄-bearing phase (Fig. 5e, f). The chemical composition of this phase is relatively constant (65–75 wt. % of Fe₂O₃, 7.5–13.3 wt. % SiO₂, and up to 3.15 wt. % SO₃), but only goethite was detected by powder XRD.

Sample S4 after confluence of both branches is predominantly formed by moderately crystalline goethite with adsorbed SiO_2 and SO_3 (see Tab. 3) which often forms (similarly like in S2 and S3) "ooidal" or "concentric" spherical nodules (see Fig. 5g).

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4.1.4. Water chemistry

Concentration of main elements and field parameters for water samples are listed in Tab. 4. Sample S1 located on the AMD branch (Fig. 1) is water seeping and dripping from fractures in the adit wall. It has pH as low as 2.83, Eh value of 830 mV, sulfate concentration of 823 mg/L and iron concentration of 191 mg/l. Respective concentrations of Zn, As, Cu, and Cd are 87.7 mg/l, 4.21 mg/L, 1.75 mg/l, and 0.93 mg/l

Sample S2 further downstream in the AMD branch (Fig. 1) has pH 3.25, Eh is 770 mV, sulfate concentration is 475 mg/l and iron concentration is 55.5 mg/l. Concentrations of Zn, As, Cu, and Cd decrease to 35.2 mg/l, 0.331 mg/L, 0.37 mg/l, and 0.266 mg/l, respectively.

Sample S3, located on the neutral mine drainage (NMD) branch (Fig. 1), has pH 5.89, Eh is 470 mV, sulfate concentration 106 mg/l, and iron concentration 1.9 mg/l. This is the only sample with carbonate alkalinity of 18.3 mg/l as HCO_3 due to its pH>4.5. As expected, respective concentrations of Zn, As, Cu, and Cd are much lower, 0.97 mg/l, 0.007 mg/l, 0.003 mg/l, and 0.004 mg/l.

Sample S4 after the confluence of both branches (Fig. 1) has pH 4.2, Eh is 640 mV, sulfate concentration is 142 mg/l and iron concentration 2.5 mg/l. Concentrations of Zn, As, Cu, and Cd are 2.9 mg/l, 0.018 mg/l, 0.022 mg/L, and 0.019 mg/l respectively.

Finally, sample S5 at the discharge of the adit water (Fig. 1) has pH of 3.96 and Eh of 576 mV, sulfate concentration is 141 mg/l, and iron concentration is 1.68 mg/l. Respective concentrations of Zn, As, Cu, and Cd are 3.51 mg/l, 0.01 mg/l, 0.036 mg/l, and 0.027 mg/l

Concentrations of other potential contaminants are low (i.e., close to detection limit of used analytical techniques), e.g., Pb concentration is in the range from 1.9 to $27.5 \mu g/l$.

4.1.5. Speciation modeling

Selected results of speciation modeling as saturation indices are presented in Tab. 5. All studied water samples are undersaturated with respect to gypsum. Samples S1, S2, and S4 are supersaturated with respect to jarosite, but samples S3 on the NMD branch and S5 (adit outflow) are undersaturated. All samples are supersaturated with

Fig. 5 – Electron microscopy images in BSE mode used for microprobe analyses; $\mathbf{a} - S1$ sample – the brightest rim consists of plumbogummite and beudantite, grey zone is mixture of jarosite with quartz, on Qz grain; $\mathbf{b} - S1$ sample – bright rim composed by mixture of jarosite and micas around the quartz grain, the white parts formed by plumbojarosite-beudantite; $\mathbf{c} - S2$ sample – goethite precipitates and detritic material; $\mathbf{d} - \text{plumbojarosite}$ intergrowing quartz and mica clasts in S2; $\mathbf{e} - \text{precipitated goethite in S3}$ sample, darker part consists of highly hydrated collomorphic Fe₂O₃ phase (see Tab. 3, anal. 2/1), bright part is formed by crystalline goethite with aprox. 10 % of SiO₂; $\mathbf{f} - \text{more}$ compact goethite in S3; (g, h) two main forms of goethite in S4 sample.



Fig. 7 High-resolution XPS spectra collected from representative sample S2: a – As 3d spectrum; b – S 2p spectrum.

respect to goethite, but samples S1 and S5 are undersaturated with respect to ferrihydrite.

Sample S3 in the NMD branch is an exception because it is supersaturated with respect to gibbsite. This is the only sample which has carbonate alkalinity, but its respective SI values for carbonate minerals (not shown in table) calcite, dolomite, and otavite (CdCO₃) are negative: -3.20, -6.59, and -2.11. High log P_{CO2} value of -1.77indicates neutralization by carbonate minerals with slow CO₃ degassing.

Besides jarosite and in some cases ferric oxyhydroxides the samples in the NMD branch and after the confluence are undersaturated with respect to all Zn, As, Cu, and Cd minerals.

5. Discussion

There are two drainage branches in the Pekelská Adit: acidic and neutral. The source of acidity is weathering of sulfide minerals, mainly pyrite, arsenopyrite, galena, and sphalerite. The neutral system is affected only by weak sphalerite mineralization. In the acid branch, iron remains dissolved in water (Tab. 4). Due to the absence of carbonates, there is no neutralization and precipitation of Ca sulfates such as gypsum.

Ferric sulfates and oxyhydroxides are efficient scavengers of metals and metalloids such as Pb, Cu, Ag, Cd, and As. At and near the seepage wall, there is the oxidation of ferrous iron to ferric iron and subsequent precipitation of alunite group minerals [expressed as $KFe_3(SO_4)_2(OH)_6$].

The Eh-pH diagram (Fig. 8), constructed for average dissolved K⁺, Fe³⁺, and SO_4^{2-} activities in the AMD branch, illustrates the position of most points in the AMD branch and after the confluence of both branches is in the jarosite field, but sample S4 and sample S5 are the boundary with aged ferrihydrite field, suggesting that K-jarosite becomes unstable with increasing distance from the source of acid seepage. The position of point in the NMD branch (Sample 3) is in the aged ferrihydrite field, which can be later transformed to goethite (Langmuir 1997). The aged ferrihydrite rather corresponds to the transition between ferrihydrite and goethite during the aging of ochres. Goethite was suppressed in the construction of the diagram because K-jarosite field would disappear completely. Also, the K_{sp} value for K-jarosite was based on the most accepted data of Baron and Palmer (1996), implemented in used database minteq.tdat.

In the acidic branch, the minerals of the alunite group predominate. Although microprobe data indicate the presence of several members of the alunite supergroup, only jarosite was confirmed by the combination of powder X-

Tab. 5 Selected results of speciation modeling, SI - saturation index.

Sample/SI	$PbSO_4$	Chalcanthite	Ferrihydrite	Goethite	Gibbsite	Gypsum	K-jarosite	Manganite	Scorodite	$CdSO_4$
S1	-2.14	-4.86	-0.29	3.60	-4.69	-1.39	4.28	-6.50	-0.90	-8.50
S2	-2.32	-5.53	0.28	4.12	-3.93	-1.15	4.05	-5.89	-1.42	-9.10
S3	-3.57	-7.96	2.07	5.85	0.10	-1.91	-0.02	-3.38	-4.39	-11.29
S4	-2.89	-6.97	0.27	4.07	-2.34	-1.72	0.47	-5.55	-4.01	-10.50
S5	-2.80	-6.77	-1.38	2.45	-2.81	-1.72	-4.11	-7.40	-5.67	-10.36

ray diffraction and ⁵⁷Fe Mössbauer spectroscopy. As the distance from the source of acidity increases, the proportion of goethite in the newly formed precipitate increases. In the acid branch, there is an interesting variety in the composition of minerals from the alunite supergroup, which decreases with distance from the AMD source. This behavior indicates the typical behavior of members of this group and their stability in a strongly acidic environment. They comprise high sediment contents of As (up to 8,021 ppm) and Pb (up to 4,131 ppm) (Tab. 1). In the acidic branch, all potentially toxic elements such as Pb, As, Cd, and Cu are incorporated into the newly formed sulfates or are adsorbed onto the goethite surface (compare bulk content and water chemistry - Tabs 1 and 4). Some ferrous iron may be oxidized before discharge from the seepage face, and there is formation of ferric iron colloids that may settle further downstream. No presence of poorly crystalline ferrihydrite in sediments was observed, perhaps due to its fast transformation to more crystalline phases like goethite (Langmuir 1997; Fukushi et al. 2003; Kumpulainen et al. 2007).

There also are significant contents of Zn and Cd in stream sediments the NMD branch (up to 11,667 ppm, Tab. 1), which are caused by weathering of sphalerite present in small amounts in the surrounding rocks, with

limited content of pyrite and other sulfides. Some chemical analyses of goethite (Tab. 3) correspond more to schwertmannite. According to XRD it is almost pure goethite, but some schwertmannite (overlapping the goethite peaks) cannot be ruled out. However, this mineral generally precipitates in waters with much higher sulfate concentrations (see e.g., Schoepfer and Burton 2021). It is therefore probably goethite with a large amount of adsorbed sulfur, or it may be a mixture with nanocrystalline schwertmannite, which cannot be confirmed by XRD or Mössbauer spectroscopy.

Partitioning coefficients (PC) calculated as the *in-situ* ratio between solid phase content (mg/kg) and water concentration (mg/L) for selected con-

Fig. 8 The Eh-pH diagram for average activities of dissolved species in the Pekelská Adit. Goethite, hematite, lepidocrocite, and magnetite were suppressed (see text).

Tab. 6 Partitioning coefficient (L/kg) for Pb, As, and Zn.

Sample/contaminant	S1	S2	S3	S4
Pb	149.6	187.4	758.9	97.1
As	19.03	15.7	76.3	25
Zn	4.93	9.32	12.03	255.7

taminants (Tab. 6) include several processes, such as implementation of contaminants into the structure of a precipitated minerals, e.g., Pb into plumbojarosite, coprecipitation, and adsorption. The calculation is also complicated by relatively stable contaminant contents in sediment and possible fast temporal changes of dissolved contaminant concentrations in water. In acid branch (samples S1 and S2) values of PC for Pb are an order of magnitude higher than for As and even more for Zn. This is consistent with precipitation of Pb in plumbojarosite and formation of bidentate complexes for As postulated by Gräfe et al. (2008). Sample S3 on the neutral branch composed mostly of goethite has very high value for Zn, but also high values for Pb, and As in a good agreement with their adsorption behavior (Appelo and Postma 2005).

The importance of the investigation of stream sediments from the Pekelská Adit lies mainly in the understanding of the nature of iron sulfates and oxyhydroxides



precipitated from mine drainage. The mineralogical data are in good agreement with results of geochemical modelling. Namely, supersaturation is reached with respect to jarosite, goethite, and in some samples with respect to ferrihydrite which is the precursor of later formation of goethite.

Stability of precipitated phases incorporating dissolved contaminants is an important issue of concern because transformation of jarosite to goethite during aging has been reported by several researchers (Fukushi et al. 2003; Baleeiro et al. 2018). Leaching experiments with jarosite in water were able to release As species bound to jarosite relatively easily (Kocourková et al. 2011). Thus, stability of alunite group phases hosting contaminants should be studied in detail in future.

6. Conclusions

Investigation of stream sediment and acid mine drainage water chemistry in the Pekelská Adit in Czech Republic revealed important role of alunite supergroup minerals, especially jarosites, in attenuation of dissolved metals and metalloids. Water chemistry at principal branch (AMD) is acid (pH < 3.0) with high concentration of dissolved iron and sulfate, but it is close to neutral in second stream branch (NMD), and becomes more acidic again after the confluence of both branches. Minerals of alunite supergroup were identified in stream sediments by several mineralogical methods. In the acid branch, sediments comprise high contents of As (up to 8,021 ppm) and Pb (up to 4,131 ppm), but contents of Zn are much lower. In contrast, there is a high content of Zn (up to 11,667 ppm) in the neutral branch, but contents of As and Pb are several orders of magnitude lower. Results indicate that minerals of the alunite supergroup can be very efficient in trapping of dissolved contaminants. However, their long-term stability remains questionable and should be assessed.

The main ferric phases identified in the stream sediments were minerals of alunite supergroup (plumbojarosite, plumbogummite, beudantite, hydronium jarosite) and goethite, which incorporate Pb, As, Cd and Cu. The Mössbauer spectroscopy confirmed 3⁺ oxidation state of ferric precipitates with a character of ferric hydroxides/ sulfates. No ferrihydrite or schwertmannite, nor Ca sulfates were detected.

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