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Environmental characteristics of the mining area affected by sulphide minerals and acidification (Banská Štiavnica, Slovakia)

Introduction

The presence of sulphides in heaps and tailing ponds connected with the oxidation and subsequent acidification represents risk for the environment. Iron sulphates and H_2SO_4 are formed during reaction of the sulphides, air, and water. Fe^{2+} may be consequently oxidized and produce more acids. Bacteria have an important role in this process that significantly accelerates the oxidation (Ledin, Pedersen, 1996). The oxidation of the sulphides is a natural process, although naturally taking place much slower in geological time periods (Akcil, Koldas, 2006; Moreno, Neretnieks, 2006; Lottermoser, 2007; Jennings et al., 2008). Acidification removes mould, Ca, and Mg from the soils, mobilizes metals, and reduces the sorption capacity of the upper horizon causing its gradual destruction. Water entering the mining areas can enhance the oxidation process and pose a significant risk of acid mine water (AMD) formation. The metals released from AMD both to the surface water and groundwater are dangerous, particularly because of bioaccumulation, through which they are further spread into the food chain (Salomons, 1995; Thornton, 1996; Bell et al., 2001; Marqués et al., 2001; Šottník, 2005). Some of the mining waste pond sites may seem harmless, without producing AMD and become a source of contamination in few years or decades after the termination of mining operations and revegetation (Younger, Wolkersdorfer, 2004).

The aim of this study was to examine the environmental characteristics of the mining area affected by sulphide minerals and acidification (Banská Štiavnica, Slovakia).

Study area, materials and methods

Banská Štiavnica is situated in the southern part of Central Slovakia and belongs to the Protected Landscape Area Štiavnické Vrchy Mts. In the past, Banská Štiavnica belonged to the most important Ag- and Pb- Zn- deposits of Europe. Areas of interest in this study are the tailing pond Sedem Žien and nearby hydroquartzite quarry Šobov. The deposit is situated in Neovolcanic rocks (diorite, andesite, rhyolite, and younger basalts). The dominant vein minerals are quartz, carbonates, sphalerite, galena, pyrite, chalcopyrite, hematite, gold, argentite, and stephanite (Koděra, 1963).

The tailing pond was intentionally built according to the project of the mining company Banský projekt Košice (Križáni, Andráš, 2008). The pond is 44 m deep with the volume of 2.5 million cubic meters (Masarovičová et al., 2007). The area of the tailing pond is approx. 22 ha, and the dam of the pond consists of mine waste rocks and local soils. The pond is filled with mud from the flotation treatment plant of galena-sphalerite ore (Masarovičová et al., 2007). The tailing pond was in operation from 1963 until 1994. During the reclamation, the plain of the pond was covered with 2–3



Fig. 1. Localisation of the sampling points. S1 – 3: soil samples; R1 – 3: rock samples; W1 – 3: water samples (Maps source: Google earth)

meters of waste rocks coming from galena-sphalerite mine and partially of waste from the Šobov quarry on which was spread a layer of dam soils (Masarovičová et al., 2007).

Sampling sites for soil material were as follows: sample 1 S1 – soil forming the second terrace of the pond's dam; S2 – soil from the fourth terrace of the pond's dam; and, S3 – soil from the surface of the top plane of the tailings pond. Rock samples were selected as follows: R1 – the rock material from the lower part of the Šobov quarry; R2 – rock material from the upper parts of the Šobov quarry; and, R3 – Pb-Zn ore. The analysed soils were sampled from the upper layer (20 cm) of the soil. At the sampling points of the water, pH, conductivity (Eh), dissolved oxygen and total dissolved solids of the samples were measured.

The Šobov quarry is situated in the southwest direction from the pond. The deposit is formed by secondary quartz with dispersed pyrite. The tailing pond, Sedem Žien, and the Šobov quarry fulfil the technical and legislative requirements for categorisation in the group of permanent environmental burdens (Masarovičová et al., 2007; SAZP.sk, 2015).

Three sampling sites for each type of sample are presented in figure 1. The following water sampling sites were selected: water sample 1 (W1) – red coloured drainage percolating Sedem Žien tailing pond; water sample 2 (W2) – transparent drainage percolating tailing pond; and water sample 3 (W3) – accumulated drainage from hydroquartzite quarry Šobov.

The mineralogical composition of the pulverised soils and rocks samples was determined by X-ray diffraction analysis (XRD) using a Philips X'Pert Pro Multipurpose X-ray Diffractometer, and the mineral morphology of the samples was studied by scanning electron microscope FEI XL 30.

The concentrations of macro elements (Ca, Mg, Na, K) and metals (Fe, Al, Pb, Zn, Mn, Co, Cr, Ni, Cu) were measured in rock, soil, and water samples. The soils and rocks samples were moistened with 5 ml of HF to dissolve the silicates and with 1.5 mL of HClO₄ to oxidize of the organic matter. The resulting compound was dried for 2 days at 150°C to dry salts. After the addition of 3.75 mL of 37% HCl and 1.25 mL of 69% HNO₃ the samples were evaporated for 1 hour and mixed with distilled water. Analyses of metals and macro elements were realised by atomic absorption spectrometry using a Fast Sequential Atomic Adsorption Spectrometer Varian AA240 FS.

The measurement of anions in the water was carried out with use of ion chromatography. Measuring F⁻, Cl⁻ and sulphates (SO₄)²⁻ was performed by a Dionex ICS-1000 Ion Chromatography System.

The rinse pH (soil reaction) was measured in a suspension of 5 g soil sample in 25 ml of distilled water. A similar procedure was chosen for the determination of paste pH, which was measured in a suspension of 5 g soil in 25 ml of 1 M KCl after 1 hour of mixing in a magnetic stirrer.

Determination of isotopes of selected elements (carbon, oxygen, deuterium, sulphur, nitrogen) is crucial in identifying the origin of the elements. $\delta^{13}\text{C}$ represents the ratio between carbon isotopes $^{13}\text{C}/^{12}\text{C}$, $\delta^{18}\text{O}$ represents the ratio between $^{18}\text{O}/^{16}\text{O}$, $\delta^{34}\text{S}$ is $^{34}\text{S}/^{32}\text{S}$ ratio, and δD is the ratio of deuterium to light hydrogen $^2\text{H}/^1\text{H}$ (Mook, 2001; ŠGÚDŠ, 2012). Isotope measurements of sulphur ($\delta^{34}\text{S}$) were carried out in all samples. The measurement of deuterium isotopes (δD or $\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) was made in water samples, and carbon isotopes ($\delta^{13}\text{C}$) measurements were made in rock and soil samples. In order to measure the isotopes of sulphur and carbon, solid samples were weighted in tin capsules and mixed with a catalyst of vanadium pentoxide (V_2O_5). For the sulphur isotopes measurements, precipitation of barium sulphate (BaSO_4) from the water samples was needed. The pH value of the samples was adapted to a value of 1 by the application of HCl. After adding 4 g of NaCl, the samples were boiled for 5 min, and consequently BaCl_2 was added to the solution until a sufficient amount of BaSO_4 was precipitated. Water samples measured for deuterium and oxide isotopes were filtered before analysis through a $0.2\ \mu\text{m}$ membrane. Deuterium and oxygen were measured by a laser absorption spectroscope Laser Water Isotope Analyser OA-ICOS DLT-100 from Los Gatos Research, and isotopes C and N were measured by a mass spectrometry analyser Flash HT Plus Elemental Analyser connected to the instrument Delta V Advantage Isotope Ratio Mass spectrometer from Thermo Scientific. Isotopes are reported using the conventional δ notation relative to Canyon Diablo Troilite (V-CDT) for ^{34}S , Vienna Standard Mean Ocean Water (V-SMOW) for D and ^{18}O , and Vienna Pee Dee Belemnite (VPDB) for ^{13}C (Đurza, 2007).

Tab. 1. Quantitative representation of the minerals in studied rock samples

Sample	ang	anh	ank	ant	cal	clc	ccp	fsp	gn	ms	po	py	qtz	toz	sp
R1				+			+				++		++++		+
R2		+		*				+		++		++	+++	++	
R3	+		+		+	+	+		+++		++	+++	+++		++++

Explanatory notes: from + mild representation, to ++++ dominant representation, * traces of the mineral; ang – anglesite, anh – anhydrite, ank – ankerite, cal – calcite, clc – clinocllore, ccp – chalcocopyrite, fsp – feldspar, gn – galena, ms – muscovite, po – pyrrhotite, py – pyrite, qtz – quartz, toz – topaz, sp – sphalerite

Soil samples were analysed for the availability of metals and macro elements by single chemical extraction adapted from Tipping et al. (2003). The extraction of soil samples with grain size $\leq 2\ \text{mm}$ was performed with $0.43\ \text{M}\ \text{HNO}_3$. Triplicates of each soil at a ratio of 2 g air dried soil to 20 ml of extractant were mixed by end-over-end shaking for 2 hours and filtered through a $0.2\ \mu\text{m}$ membrane. Samples were then analysed using AAS Varian AA240 FS equipment.

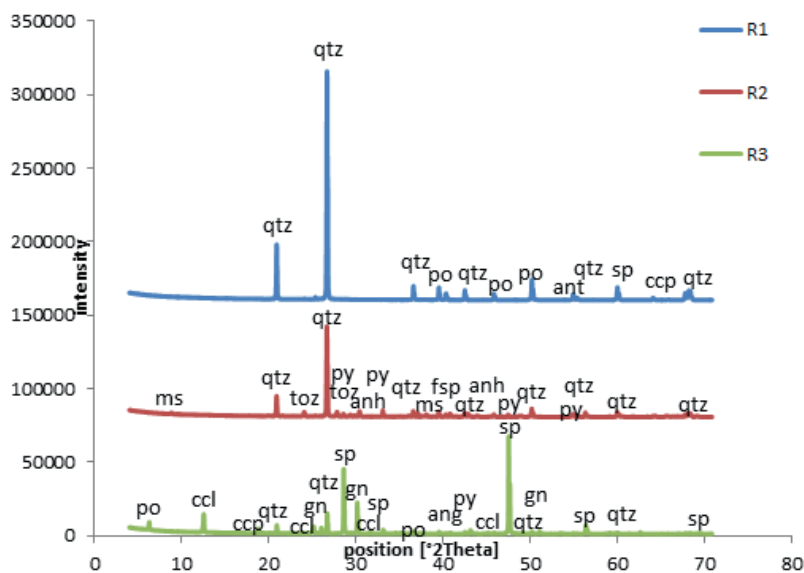


Fig. 2. The mineralogical composition of rock samples determined by XRD; Explanatory notes: ang – anglesite, anh – anhydrite, ank – ankerite, cal – calcite, clc – clinocllore, ccp – chalcopyrite, fsp – feldspar, gn – galena, ms – muscovite, po – pyrrhotite, py – pyrite, qtz – quartz, toz – topaz, sp – sphalerite

Results

Mineralogical characteristics of the rock samples

XRD and SEM analyses of the rock samples' mineralogical compositions showed that silica with sulphide minerals predominate in the samples. Sample R3 represents sphalerite-galena ore. XRD analysis confirmed the presence of the following sulphide minerals in the next samples: R1 – pyrrhotite, chalcopyrite, and sphalerite; in R2 – pyrite; and, in R3 – pyrite, pyrrhotite, chalcopyrite, galena, and sphalerite (Fig. 2; Tab. 1). SEM analysis enabled us to distinguish the following in sample R1: quartz – SiO₂, fine-grained pyrite – FeS₂ in the quartz matrix, galena – PbS, sphalerite – ZnS, anatase – TiO₂ and zircon – ZrSiO₄ (Appendix 1 – Fig. I). SEM analysis identified the following in sample R2: quartz, anatase, topaz, anhydrite, and pyrite (FeS₂; Appendix 1 – Fig. II). In rock sample R3 the following were identified: quartz, ankerite, clinocllore, dolomite, pyrite, galena, sphalerite, and chalcopyrite (Appendix 1 – Fig. III).

Mineralogical characteristics of the soil samples

XRD analysis of soil samples confirmed the presence of the following minerals: quartz, albite, biotite, calcite, clinocllore, illite, ilmenite, jarosite, kaolinite, muscovite, and orthoclas (Fig. 3; Tab. 2).

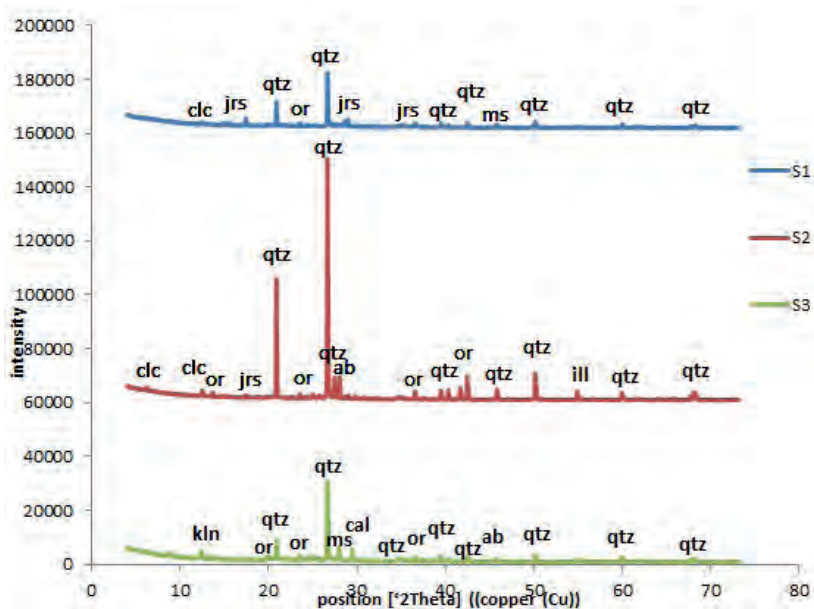


Fig. 3. The mineralogical composition of soil samples determined by XRD. Explanatory notes: ab – albite, bt – biotite, cal – calcite, clc – clinocllore, ill – illite, ilm – ilmenite, jrs – jarosite, kln – kaolinite, ms – muscovite, or – orthoclase, qtz – quartz

Tab. 2. Quantitative representation of the minerals in studied soil samples

Sample	ab	bt	cal	clc	ill	ilm	jrs	kln	ms	or	qtz
S1		++		+			++		+	++	+++
S2	+			+	++		+		+	++	+++
S3	++		+	+		+		+	++	++	+++

Explanatory notes: from + mild representation, to ++++ dominant representation, * traces of the mineral; Abbreviation of minerals as in figure 3

Tab. 3. AAS analysis of rock and soil samples

Sample	CaO	MgO	Na ₂ O	K ₂ O	Al ₂ O ₃	Fe ₂ O ₃	Mn	Pb	Co	Cr	Cu	Ni	Zn
	[mg.kg ⁻¹]												
R1	0.23	0.13	0.08	0.35	1.61	4.67	0.04	82.48	4.96	531	9.71	173	137
R2	0.27	0.10	0.12	4.65	22.47	75.82	0.01	<D.L.	14.85	315	19.34	78.19	34.74
R3	2.97	42.57	0.12	0.24	52.52	108	13.58	95594	43.03	173	2834	45.37	218767
S1	2.2	6.82	4.72	38.66	102	14.12	0.22	1584	<D.L.	83.06	233	10.67	383
S2	2.48	6.83	2.62	45.44	81.56	29.3	1.18	787	<D.L.	98.1	233	8.21	549
S3	21.21	9.46	6.08	25.06	127	42.87	1.48	797	8.36	120	93.99	18.48	862

SEM analysis identified the following minerals in the soil samples: sample S1 – quartz, muscovite, jarosite, biotite, and cerium phosphate (Appendix 1 – Fig. IV); sample S2 – quartz, biotite, mica, chlorite, orthoclase, anglesite, and iron oxide (Ap-

pendix 1 – Fig. V); sample S3 – muscovite, quartz, illite, plumbojarosite, apatite, and ilmenite (Appendix 1 – Fig. VI).

Heavy metals contamination

The chemical analysis of the samples indicates that the investigated area is contaminated by heavy metals, which correspond to the metals occurring in rocks and ores from the study area (Tab. 3). The quartzite samples (R1 and R2) contain an increased amount of Fe_2O_3 due to the presence of pyrite in the samples. Sample R3 represents Pb-Zn ore. Samples contain a high amount of Fe_2O_3 (108 g.kg^{-1}), which influences the course of oxidation. Soils from the 2nd and 4th terrace of the pond dam (S1 and S2) show a strongly acidic soil reaction (Tab. 4).

Tab. 4. Rinse and paste pH

Sample	$\text{pH}_{\text{H}_2\text{O}}$	pH_{KCl}
S1	2.28	2.07
S2	3.25	2.81
S3	7.26	6.95

Water samples contain high concentrations of metals. The red coloured tailing drainage water (W1) contains a large amount of Fe, Mn, and Zn, and the second drainage water percolating the tailing pond (W2) contains high concentrations of Pb ($3773 \mu\text{g.L}^{-1}$). W3 (from Šobov quarry) is rich in Fe (311 mg.L^{-1}) and Al (157 mg.L^{-1}) (Tab. 5). Sample W3 is the only sample among analysed drainages that were highly acidic (pH 2.17), and it had the highest values of conductivity and total dissolved solids (Tab. 6). High concentrations of sulphates ($966\text{-}2599 \text{ mg.L}^{-1}$, Tab. 7) were found in water samples.

Tab. 5. AAS analysis of water samples

Sample	Ca	Mg	Na	K	Al	Fe	Mn	Pb	Co	Cr	Cu	Ni	Zn
	[mg.L^{-1}]								[$\mu\text{g.L}^{-1}$]				
W1	297	59.11	16.01	34.85	0.30	9.63	4.37	73	<D.L.	<D.L.	140	<D.L.	1720
W2	461	64.82	14.32	49.3	0.48	0.75	0	3773	<D.L.	0.3	160	<D.L.	400
W3	79.54	98.35	2.57	2.26	157	311	10.74	126	270	170	890	160	1690

Tab. 6. pH, electroconductivity, dissolved oxygen and total dissolved solids values measured at the sampling points

Sample	pH	EC [$\mu\text{S/cm}$]	DO [mg.kg^{-1}]	TDS [mg.kg^{-1}]
W1	7.60	2093	6.26	1049
W2	8.81	2870	10.22	1434
W3	2.17	6457	6.20	3226

Explanatory notes: EC – electroconductivity. DO – dissolved oxygen. TDS – total dissolved solids

Tab. 7. IC analysis of anions in water samples

Sample	F ⁻	Cl ⁻	(SO ₄) ²⁻
	[mg.L ⁻¹]		
W1	1.08	52.76	966
W2	1.54	39.79	1666
W3	1.56	52.92	2599

Percentages of macro- and microelements in soils are shown in table 8.

Tab. 8. Percentages of available elements in soils

Sample	pH	CaO	MgO	Na ₂ O	K ₂ O	Al ₂ O ₃	Fe ₂ O ₃	Mn	Pb	Co	Cr	Cu	Ni	Zn
		[%]												
S1	2.28	13.11	5.38	0.3	0.11	0.69	39.27	11.3	2.37	-	1.93	27.23	5.19	57.34
S2	3.25	10.75	1.19	0.11	0.04	0.63	2.74	6.02	2.31	-	1.83	9.11	8.58	8.29
S3	7.26	99.89	9.92	0.22	1.17	2.17	4.82	52.74	56.85	55.55	3.22	33.69	11.09	75.06

The isotopic composition of the drainage water samples shows the meteoric origin of the waters. δD values fluctuate in the range from -42.73 to -74.78‰, and values $\delta^{18}O$ vary from -6.11 to -10.17‰. The sulphur isotope composition $\delta^{34}S$ in samples W1, W2, and W3 is 3.37, 4.6 and -2.19, while the isotopic compositions of sulphur in the solid samples vary from $\delta^{34}S$ -1.48 to 4.48‰. Isotopes ^{13}C (-4.25 to -27.73‰) represent isotopic composition characteristic for carbonates (probably of biogenic origin) (Tab. 9–10; Fig. 4).

Tab 9. δD , $\delta^{18}O$ and $\delta^{34}S$ isotopes in water samples

Sample	δD (‰vs. V-SMOW)	$\delta^{18}O$ (‰vs. V-SMOW)	$\delta^{34}S$ (‰vs.V-CDT)
W1	-74.40	-10.17	4.60
W2	-74.78	-10.35	3.37
W3	-42.73	-6.10	-2.19

Tab. 10. ^{34}S and ^{13}C isotopes in soil and rock samples

Sample	$\delta^{34}S$ (‰ vs. V-CDT)	$\delta^{13}C$ (‰ vs. VPDB)
R1	<D.L.	-27.73
R2	-1.48	-25.07
R3	4.48	-4.25
S1	1.37	-25.53
S2	-0.62	-24.54
S3	4.15	-24.65

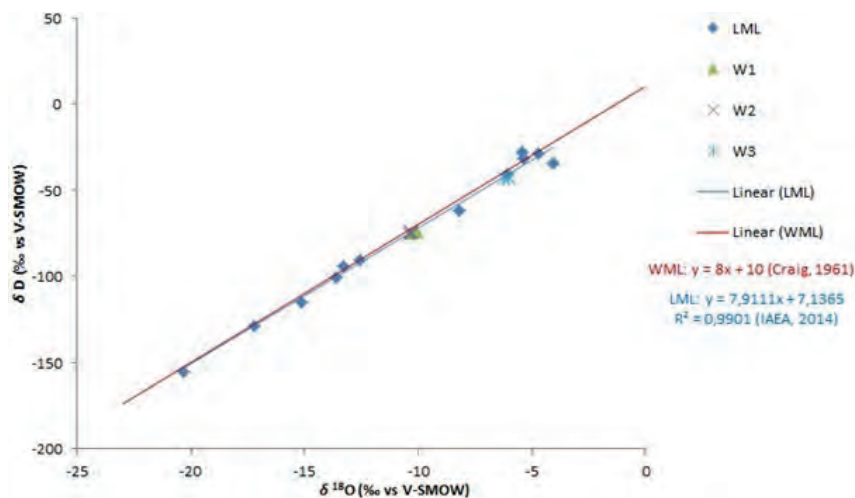


Fig. 4. Overlap of WML – world meteoric water line and LML – local meteoric water line, with values measured for water samples

Discussion

The study confirmed the significant effect of the mining activity on the observed area. This phenomenon is conditioned by the geological structure of the area, including the mining activity, which facilitated the weathering of rocks and the subsequent release of hazardous elements into the environment. The soils of the tailing's dam show very acidic reactions, while the soil from the pond surface has a neutral reaction, which is probably due to application of a limestone layer during reclamation. Low pH is a cause of the depletion of Ca and Mg in soil samples S1 and S2.

Mobility of the metals is affected by many aspects. Factors that can affect the activity of metals and other elements are, e.g., the pH and Eh of the soil, moisture, temperature, soil type, the content of metals in the soil and their binding, the content of humus components in soil, the presence of clay minerals, cation exchange capacity, or the presence of Ca and Mg (Čurlík et al., 2015). Tipping et al. (2003) assumed that HNO_3 extraction is one of the methods providing the best measures of geochemical active metals. The high Ca and Mg contents are typical for alkaline soil reactions, and, on the contrary, the absence of these cations usually indicates acid soil reactions. The Ca/Mg ratio in the sorption complex significantly affects the rate of the entering of heavy metals into plants. In soil Samples S1 and S2, the Ca/Mg ratio is <1 (Tab. 3), which is characteristic for the presence of acidic rocks (McCarten, 1992), whereas S3 sample shows $\text{Ca/Mg} = 2.24$ caused by landfill of CaCO_3 . Extraction of the Ca from the soils was higher than the extraction of Mg. Calcium is usually characterized by a higher level of availability than magnesium (Čurlík et al., 2015). Despite the neutral pH, soil

sample S3 showed the highest percentage of availability for all analysed metals, except Fe. The pH dependence on the level of the extractability of metals from soils can be seen when comparing samples S1 and S2, where the metals of S1 with pH 2.82 were more accessible than the metals in sample S2 with pH 3.25.

All investigated soils exceeded Pb, Zn, Cu, and Cr content limits for agricultural land under the *Act No. 220 Coll. on the conservation ...* (2004).

Although the drainage waters percolating the tailing pond Sedem Žien have different appearances, they have similar composition and comparable pH. Differences were observed in concentrations of Fe, Zn, and Pb and sulphates. The most significant difference between water samples is higher Fe concentration in sample W1 in comparison to sample W2, causing the red coloration. The drainage water from Šobov quarry (W3) has a low pH value (2.17) and high Al, Fe, and sulphates content. Iron concentrations in water samples W1 (9.63 mg.l⁻¹) and W3 (311 mg.l⁻¹) highly exceed the limit concentrations of Fe (4.0 mg.l⁻¹) for water resulting from the extraction of ores by Government Regulation 269/2010 Coll., which stipulates criteria for achieving good water balance (Tab. 3). Water sample W2 is characterised by high Pb content (> 0.5 mg.L⁻¹, which is current Slovak limit concentration for waters resulting from the extraction of the ores Government Regulation 269/2010 Coll.). Differences in pH values between water percolating the tailing and quarry may be caused by more rapid weathering of disulphides than monosulphides, which could explain a slower oxidation of galena – PbS and sphalerite – ZnS in the tailing pond in comparison to pyrite – FeS₂ dispersed in the quartz. Another reason for the differences in pH may be the presence of acidophilic sulphide-oxidizing bacteria (*Acidithiobacillus ferrooxidans* (Temple & Colmer) Kelly & Wood), which was previously found in the drainage water from Šobov quarry (Šlauková, Bella, 2006; Bella et al., 2010). The limiting factor for the oxidation is the transformation of Fe²⁺ to Fe³⁺, which is very slow in abiotic conditions with pH above 5 (Šottník, 2005).

Interpretation of the geochemistry of stable isotopes (D, O, C, N, S) is complicated because of the fact that the minerals created by different processes may have the same isotopic composition and minerals created by same process; however, under different conditions, they may have significantly different isotopic compositions. Therefore, waters which percolate rocks and soils affected by the composition of ore minerals reflect all of the mentioned aspects. Variations in the isotopic composition of the natural material are the result of isotope exchange reactions and kinetic isotope effects (Hladíková, 1988; Rollinson, 1988).

Sulphur in natural materials can have various sources, and its isotopic composition may reflect different processes that material overcame. In the tailing pond Sedem Žien, the main sources of sulphur are hydrothermal sulphides of mined polymetallic (Pb-Zn) ore and dispersed pyrite from the nearby Šobov quarry.

It is known that $\delta^{34}\text{S}$ values in the surrounding of Banská Štiavnica are relatively homogeneous, and close to zero. Such values indicate the sulphur origin from sedimentary rocks (Sakai et al., 1982; Chaussidon et al., 1989). The negative $\delta^{34}\text{S}$ value in sample W3 (-2.19) is typical for the sulphur originating from the sulphides (Newman et al., 1991). The isotopic composition of sulphur in the solid samples ($\delta^{34}\text{S}$ -1.48 to 4.48‰) mainly reflects the isotopic balance of the sulphides of the main Pb-Zn hydrothermal mineralization in the ore field of Banská Štiavnica as well as the isotopic characteristics of sulphur in pyrite dispersed in the hydroquartzite mined in the vicinity of the tailing pond.

The homogeneity of the composition indicates a magmatic origin of ores and a meteoric origin of the waters (Kantor, 1979; Burian et al., 1985). $\delta^{34}\text{S}$ values of drainage waters of the tailings pond correspond to the range of values for sulphur originating in Central Europe from atmospheric precipitation (+3‰ to 5‰; Newman et al., 1991). Regarding the oxidation of sulphides, many studies on the effects of the isotopic composition have been done. The results of studies of the effects of oxidation in the presence of phototrophic bacteria diverge, but the oxidation in the presence of chemotrophic bacteria shows clearer results. Kaplan-Rittenberg (1964) demonstrated the effect of oxidation in the presence of bacteria *Thiobacillus concretivorus*, as did Kelly & Harrison, when changes reached the range of -18‰ (ŠGÚDŠ, 2010).

Isotopes ^{18}O compose, in comparison with ^{16}O , just a small part of oxygen, and their ratio helps to provide information about origins of the waters (Hoefs, 1987). The dependence between $\delta^{18}\text{O}$ and δD ‰ values in the water indicates formation in the conditions of isotopic equilibrium. The isotopic composition of the δD values in the drainage water (δD 42.73 to -74.78‰) and of $\delta^{18}\text{O}$ (-6.11 to -10.17‰) corresponds, according to Taylor (1974), Sheppard (1981), and Rollinson (1988), to meteoric water.

Conclusion

The studied area is contaminated by heavy metals (mainly by Fe, Pb, Zn, and Cu) and acidified. From the mineralogical point of view, the rock material is rich in quartz and sulphide minerals, which has an important influence on the chemical composition of soils and waters. The isotope study proved the meteoric origin of the waters, and sulphide origin of the sulphur in the waters.

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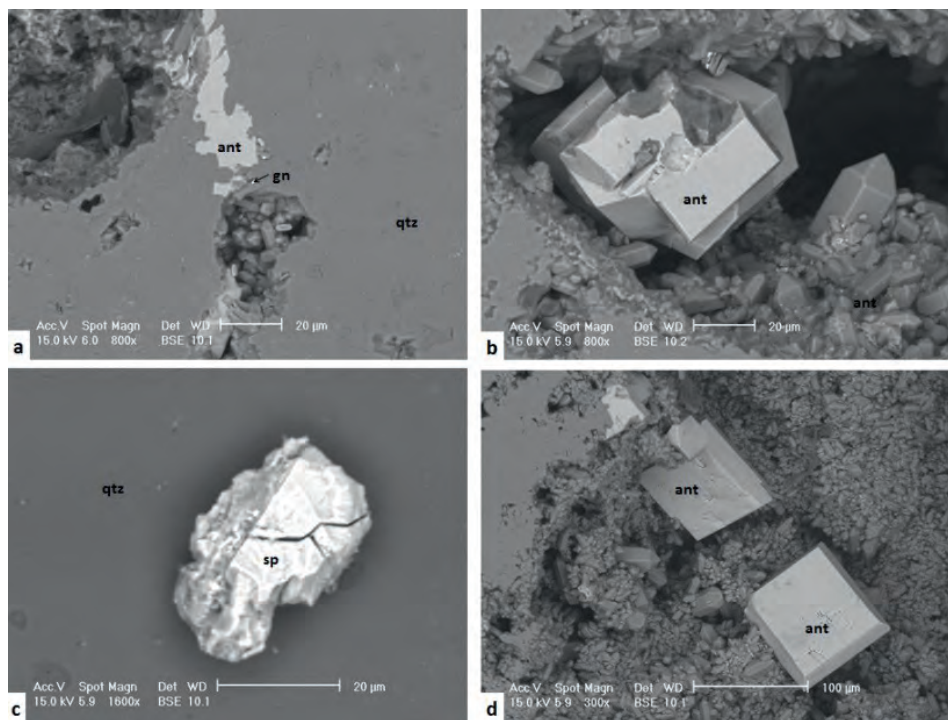


Fig. I. Scanning electron micrographs showing mineral phases of the sample R1; a: qtz – quartz (SiO_2) and ant – anatase (TiO_2) phases with finely dispersed gn – galena (PbS); b: crystals of anatase; c: sp – sphalerite (ZnS) surrounded by quartz; d: other formations of anatase

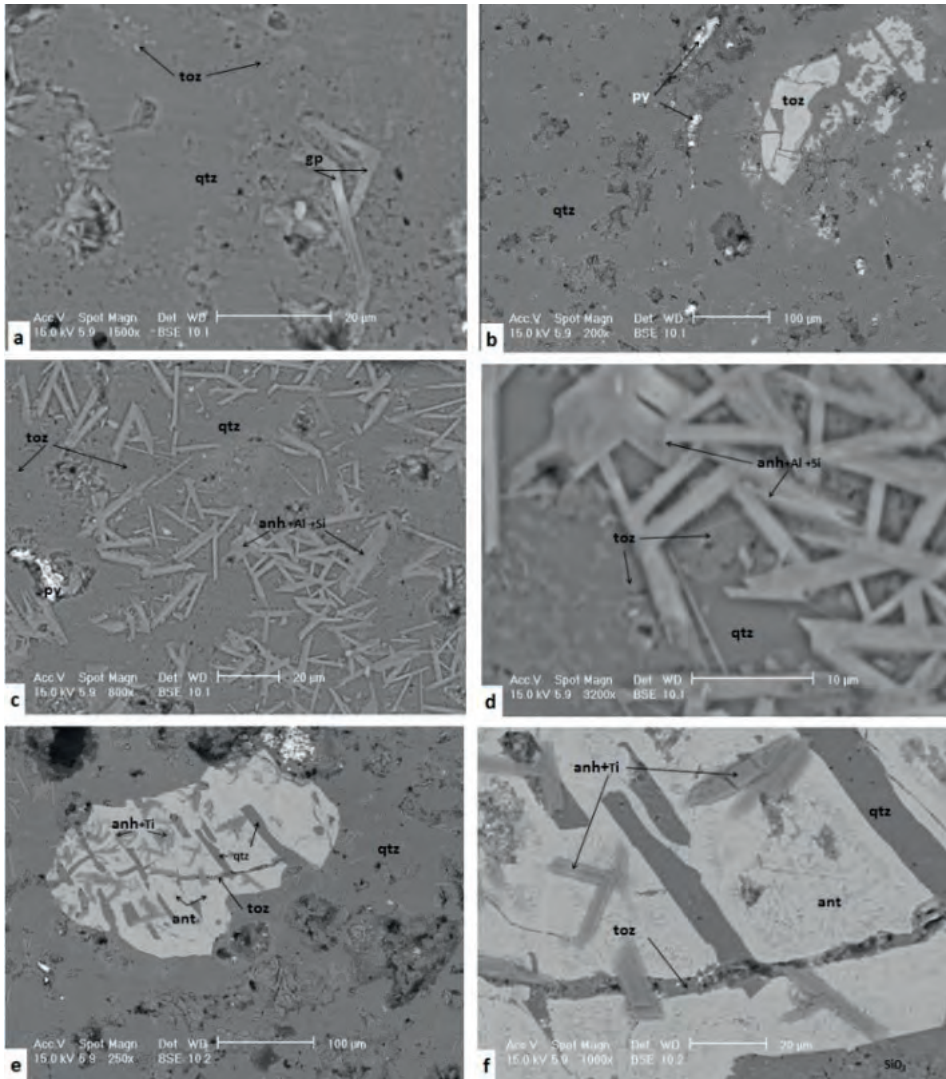


Fig. II. Scanning electron micrographs of sample R2; a, d: qtz – quartz matrix with dispersed toz – topaz and anh – anhydride needles; b, c : inclusions of py – pyrite in the quartz, ant – anatase and anhydride with Si and Al impurities; e, f: penetration of the quartz, topaz, anatase and anhydride

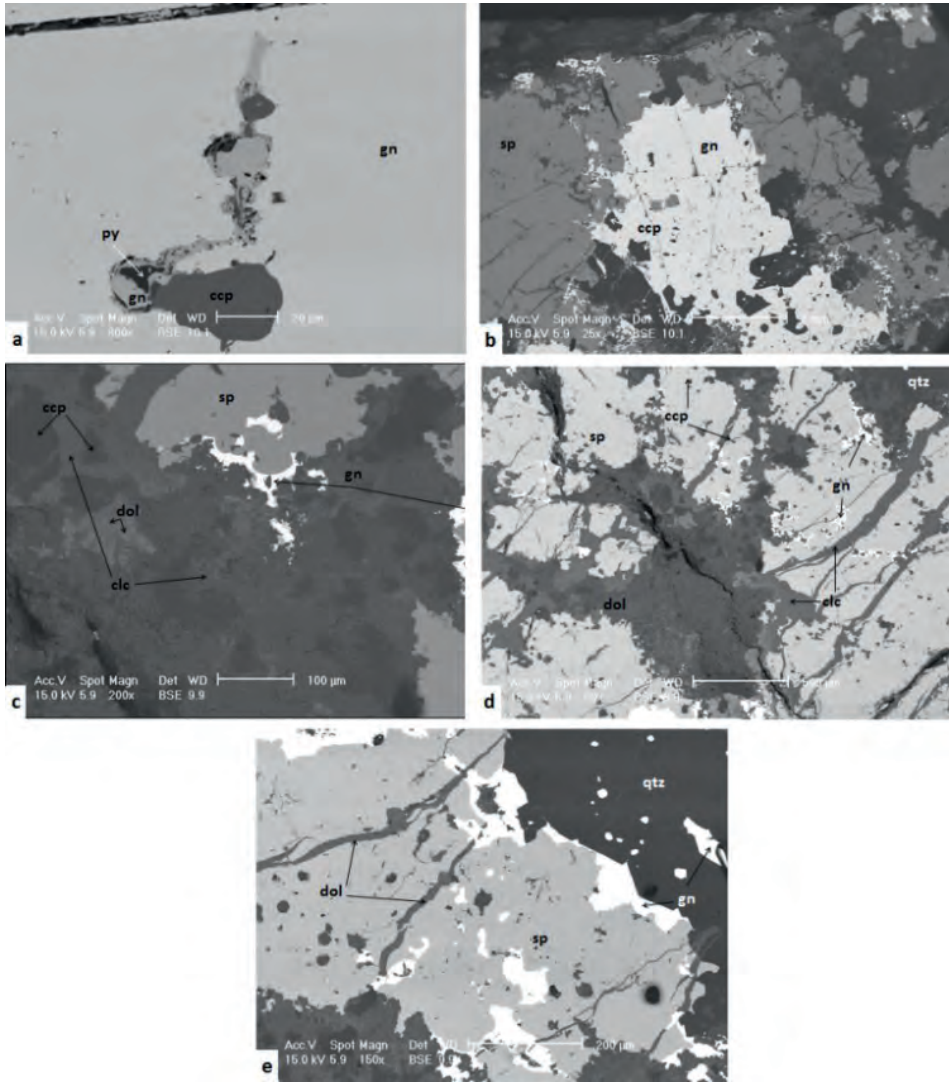


Fig. III. Scanning electron micrographs of sample R3; a: py – pyrite and ccp – chalcopyrite inclusions surrounded by gn – galena; b: chalcopyrite, galena and sp – sphalerite; c: galena, sphalerite and chalcopyrite inclusions among clc – clinocllore and dol – dolomite; d: small inclusions of galena and chalcopyrite in the in the sphalerite matrix; e: sphalerite and galena surrounded by qtz – quartz and intersected by dolomite veins.

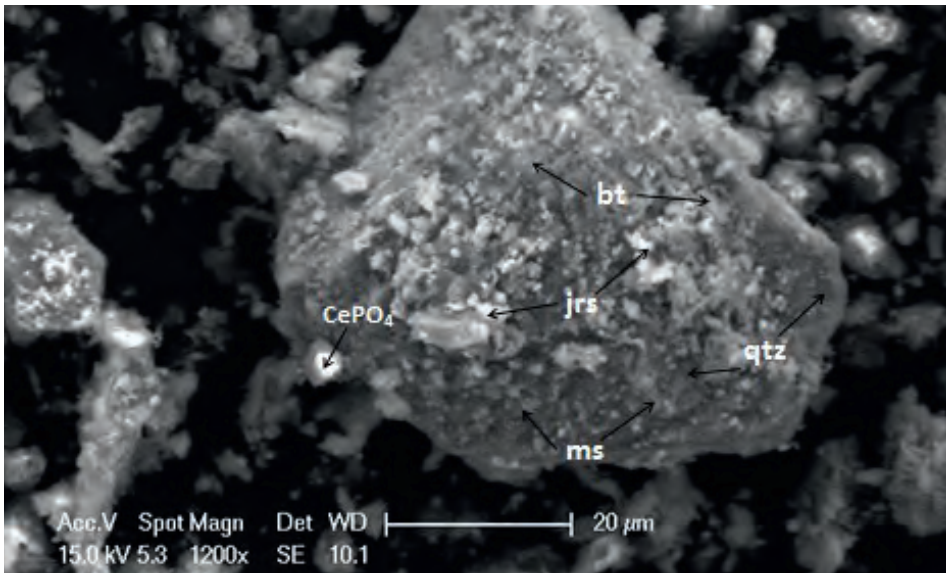


Fig. IV. Scanning electron micrographs of the sample S1; bt – biotite; qtz – quartz; ms – muscovite; jrs – jarosite; cerium phosphate

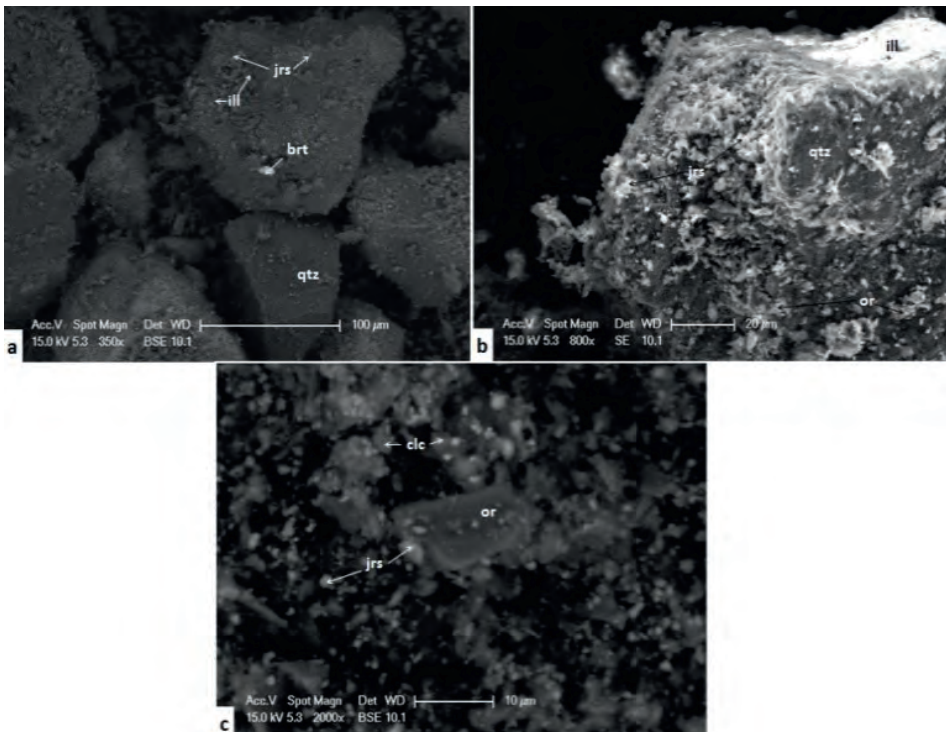


Fig. V. Scanning electron micrographs of the sample S2; a: brt – barite, qtz – quartz, jrs – jarosite, ill – illite; b: , qtz – quartz, jrs – jarosite, ill – illite; c: jrs – jarosite, or – orthoclase, clc – clinocllore

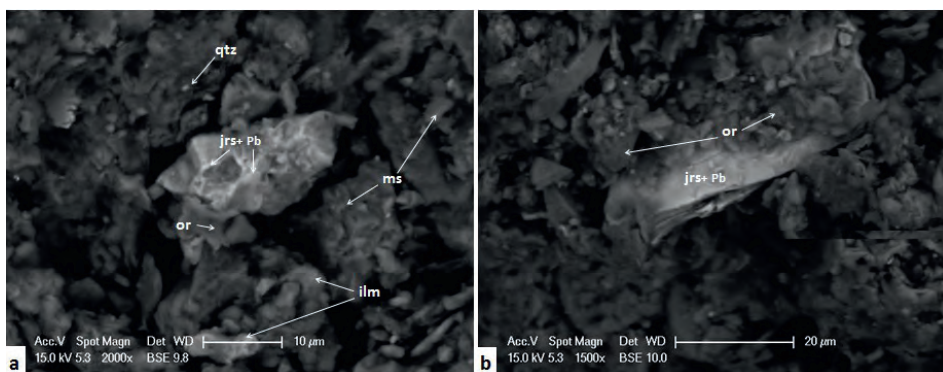


Fig. VI. Scanning electron micrographs of the sample S3; qtz – quartz, ms – muscovite, jrs+Pb – jarosite with Pb impurities, ilm – ilmenite, or-orthoclase

Abstract

The area of Sedem Žien tailing pond and the nearby Šobov hydroquartzite quarry affected by mining activity were investigated by geochemical and mineralogical methods to determine the contaminating chemical compounds and study their availability. Degradation of the hydrothermal base mineralisation (galena, sphalerite, pyrite, pyrrhotite, and chalcopyrite) and of fine-grained pyrite oxidation, which forms impregnations in hydroquartzite, produce Acid Mine Drainage (AMD). The area is acidified and the components (soil, rock, water) are contaminated mainly by Pb, Zn, and Fe. The tailing pond dam forming soils have an acidic pH of 2.28–3.25, whereas the soil on the tailing pond surface is close neutral (pH 7.26). The leaching availability of the metals from the soil is up to 75%. The AMD from the hydroquartzite quarry is, in comparison with those percolating the tailing pond sediments, very acidic (pH 2.71) and contains high concentration of metals (Fe 311 mg.L⁻¹, Zn 1690 µg.L⁻¹, Cu 890 µg.L⁻¹, Pb 126 µg.L⁻¹).

Key words: heavy metals, contamination, acidification, availability

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Charakterystyka środowiskowa obszaru górniczego skażonego minerałami siarczkowymi i zakwaszającymi (Banská Štiavnica, Słowacja)

Streszczenie

Za pomocą metod geochemicznych i mineralogicznych, zbadano obszar osadnika Sedem Žien i pobliskiego kamieniołomu hydro-kwarcytu Šobov, dotkniętych działalnością górniczą, w celu określenia związków chemicznych zanieczyszczających te tereny i zbadania ich dostępności. Degradacja hydrotermalna oparta na mineralizacji (galena, sfaleryt, piryt, pirotyn i chalkopiryt) i utlenianiu drobnoziarnistego pirytu, której formy impregnują hydro-kwarcyt, produkuje kwaśne odcieki z kopalń (AMD). Obszar jest zakwaszony, a składniki lokalne (gleba, skała, woda) są zanieczyszczone, głównie przez Pb, Zn i Fe. Zanieczyszczenia zapory osadnika tworzą gleby kwaśne (pH 2,28 - 3,25), natomiast zanieczyszczona gleba na powierzchni osadnika jest zbliżona do odczynu obojętnego (pH 7,26). Dostępność ługowania metali z gleby wynosi tu aż do 75%. AMD z kamieniołomu hydro-kwarcytu, jest porównywalna z tymi przenikającymi, bardzo kwaśnymi (pH 2,71), zanieczyszczeniami sedymentacyjnymi osadnika i zawiera wysokie stężenia metali (Fe 311 mg.L⁻¹, Zn 1690 µg.L⁻¹, Cu 890 µg.L⁻¹, Pb 126 µg.L⁻¹).

Słowa kluczowe: metale ciężkie, zanieczyszczenia, zakwaszenie, dostępność

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