Mineralia Slovaca, Web ISSN 1338-3523, ISSN 0369-2086, https://doi.org/10.56623/ms.2022.54.1.4
54, 1 (2022), 47 – 68, © Authors 2022. CC BY 4.0

Use of analysis of seasonal hydrochemical regime for better understanding of mine water genesis and more accurate estimate of its impact on stream water quality at flooded Rudňany ore mine (North-Gemeric zone, Slovakia)

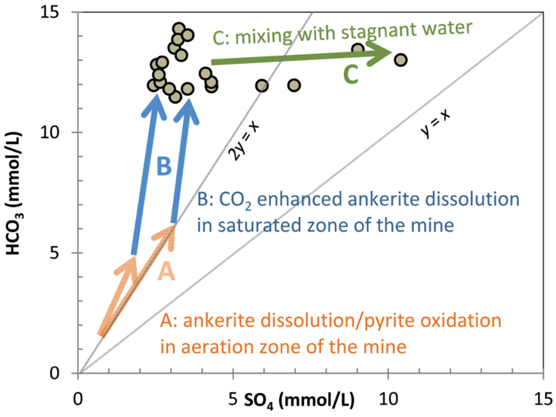
PETER BAJTOŠ

State Geological Institute of Dionýz Štúr, Markušovská cesta 1, SK-052 01 Spišská Nová Ves, Slovak Republic;
peter.bajtos@geology.sk

Abstract: Seasonal hydrochemical regime of water flowing out of the Rochus Fe-Cu mine in the Spiš-Gemer Ore Mts. was monitored by discharge measurements and laboratory analyses of mine water chemical composition. Regression analysis of these data showed a statistically significant dependence of concentration of many important chemical elements on mine water discharge. The obtained data made it possible to better understand the processes of mine water chemical composition genesis, as well as to determine in more detail the degree of its environmental impact. Geochemical calculations and forward geochemical modelling suggest that chemical composition of mine water is formed in three stages. First phase takes place in the aeration zone of the mine, where ankerite dissolution, intensified by pyrite oxidation, dominates. In saturated zone of the mine, ankerite dissolution is probably controlled by CO_2 input in open carbonate system. These two main geochemical processes take place permanently and at the time of low flow conditions they lead to relatively stable composition of water outflowing from mine. In time of higher flow conditions, concentration of SO_4, Mg, Ca, Na and As significantly increases, probably as a consequence of mixing with stagnant water from deeper or hydraulically more isolated parts of the flooded mine. Water flowing out from mine enters the Rudniansky potok creek and contaminates it mainly by manganese. The limit for Mn content in surface water is exceeded here at the time of low flow conditions – usually for 180 days a year. Anomalous concentrations of SO_4, Mg, As and Sb in mine water are sufficiently diluted in stream water were they do not exceed environmental limits.

Key words: mine water, hydrochemical regime, surface water pollution, geochemical modelling, manganese, arsenic contamination

Graphical abstract



Highlights

- Positive dependence of SO_4, Mg, Ca, Na and As concentrations in mine water discharge was revealed by observation of seasonal hydrochemical regime.
- Geochemical calculations and forward modelling based on mine water samples suggest three main phases of the mine water chemical composition formation.
- Water quality of the Rudniansky potok creek is endangered mainly by manganese – its surface water quality limit is usually exceeded for 180 days a year.
- The example clearly demonstrates that detailed knowledge of seasonal hydrochemical regime is necessary for understanding of mine water genesis.

Introduction

As remnants of historical and modern mining, hundreds of abandoned mines occur in the territory of Slovak Republic. Most of them are historic, but many were closed after the transition to a market economy in Slovakia after 1989, when the State declared attenuation in ore mining programme. Among allocated 14 mining-deposit regions, Gemer zone in eastern Slovakia is the largest one and richest in mine occurrences and as many as 656 mine water sources were documented here with total discharge of 663 L/s (Bajtoš, 2016). Of these, up to 535, with total discharge of 456 L/s, are connected to siderite-sulphidic veins hosted by Paleozoic metamorphites. As the chemical composition of these mine waters is very variable, some of them meet the conditions for the use as drinking water sources and some pose an environmental risk, mainly due to their high As, Sb, Mn and SO_4 content. The chemical composition of the largest mine water outflows is generally known, but it is based only on repeated sampling. Therefore, their hydrochemical regime is practically unknown. However, detailed knowledge about the fluctuation in the content of hazardous elements over time is important for the evaluation of mine water sources in terms of possible use but also for assessing the risk of their negative environmental impact. In addition, it is useful for understanding of genesis of mine water chemistry.

The Rudňany mine is one of the largest mines in the Gemer zone, encompassing the Gemeric tectonic unit. Throughout all history of ore mining, but also since 1993, when it was flooded, it negatively affected the quality of the nearby Rudniansky potok creek. The presented study firstly describes the extent of seasonal fluctuations in the risk elements present in this mine water and evaluates its impact on stream water quality. Additionally, the presented interpretation of the acquired knowledge brings a better understanding of geochemical processes taking place in studied flooded mine. These findings can be applied in the study of mine water genesis at other mines, connected to siderite-sulphidic veins hosted by Paleozoic metamorphites, not only in Slovakia.

Study area

The Rudňany ore field is spread over an area of 20 km^2 in the north-eastern part of the Volovské vrchy Mts., in eastern Slovakia. The altitude of this area ranges from 430 to 870 m above sea level. Climate is relatively cold (annual air temperature 3–6 °C) and wet (annual precipitation total 630–800 mm), (Landscape Atlas of SR, 2002). The majority of area is dewatered by the Rudniansky potok creek to the Hornád river. Discharge of the Rudniansky potok creek is observed by Slovak Hydrometeorological Institute (SHMI) on gauge-discharge station No. 8425, situated close to its effluent into the Hornád river (Fig. 1). In the period 2012–2013 the discharge of this stream fluctuated from 0.05 to 5.8 m^3/s, with median of 0.158 m^3/s (Fig. 3). Stream discharge exceeded its average value of 0.351 m^3/s for 26 % of the time.

In the Rudňany ore field there are 7 shafts with 13 main mining levels (Figs. 2, 3) with the deepest level in 120 m below the sea level. All mine workings are interconnected into one large mine. It is excavated in Paleozoic rocks of Gemeric unit, which crop out in the southern part of the Rudňany ore field. To the north, Paleozoic rocks are covered with Mesozoic and Paleogene sediments. For these reasons, mine workings that reach the land surface are concentrated in southern part of area, especially in headwater of the Rudniansky potok creek. Therefore this location represents the main infiltration area of the mine, as it is documented by previous hydrogeological study (Bajtoš, 1999a, b). Here, main ore vein of the ore field – the Droždiak vein – reaches land surface and is accompanied by caving falls.

The Droždiak vein is hosted by metasandstones, phyllites and metamorphosed volcanic rocks (Zlatník Formation, Dobšiná Group of North-Gemeric unit, Late Carboniferous; Grecula, 1982; Vozárová & Vozár, 1988) or by cover conglomerates of Knola Formation, Krompachy Group of North-Gemeric unit, Early Permian). Common feature of these rocks is relatively low hydraulic conductivity ($k = 5.30*10^{-9} - 8.99*10^{-4}$ m/s, geometric mean $1.65*10^{-6}$ m/s) and transmissivity ($T = 2.80*10^{-7} - 1.65*\ 10^{-2}$ m^2/s, geometric mean $3.13*10^{-5}$ m^2/s), decreasing with increasing depth (Bajtoš in Grecula et al., 2011). Under such conditions, shallow groundwater circulation prevails and slightly alkaline water of Ca–Mg–HCO_3 or Ca–Mg–HCO_3–SO_4 chemical types, with low TDS content of 0.1–0.4 g/L is formed. Dissolution of carbonate and aluminosilicate minerals is the main water chemistry forming process. Groundwater recharge occurs mainly in the spring due to snow melting, and also during colder rainy periods with low evapotranspiration. According to long term observation of snow chemical composition in sampling point in Dobšiná, atmospheric water is acid, pH = 5.5 in average (Bodiš et al., 2000), with average concentrations of Cl, SO_4, NO_3 of 1.45, 4.47 and 1.92, respectively.

Ore vein mineralization in the Gemeric region is a product of Permian metamorphic-magmatic and hydrothermal cycle (Radvanec & Gonda, 2019). Ore veins are of the siderite-barite-sulphidic type with developed transversal as well as vertical zonality (Grecula et al., 1995). Their uppermost parts consist of barite, siderite and variable content of sulphide minerals. Siderite proportion gradually increases downwards and it totally prevails in the middle parts of ore veins, while in their lower parts the siderite amount decreases at the expense of quartz and ankerite. Sulphides are represented mainly by tetrahedrite (schwatzite), chalcopyrite and pyrite. The relative contents of chalcopyrite and pyrite increase proportionally with depth. Siderite contains relatively high portion of magnesium and also non-negligible portion of calcium and manganese – the formula $(Ca_{0.01}Fe_{0.82}Mg_{0.13}Mn_{0.04})CO_3$, calculated from 156 siderite samples taken from Droždiak vein (Cambel & Jarkovský, 1985), gives its average stoichiometry. Beside that the average contents of microelements were determined: 13.7 ppm Ti, 13.8 ppm V, 63.4 ppm Ni, 22.2 ppm Co, 6.1 ppm Sc, 15.5 ppm Cr and 78.8 ppm Sr. Those authors also state that other carbonate minerals most represented in ore veins (instead of siderite) are ankerite, Fe-dolomite and Mg-dolomite; minerals of isomorphic series magnesite-siderite often occur and calcite is rarely present. Typical formula for

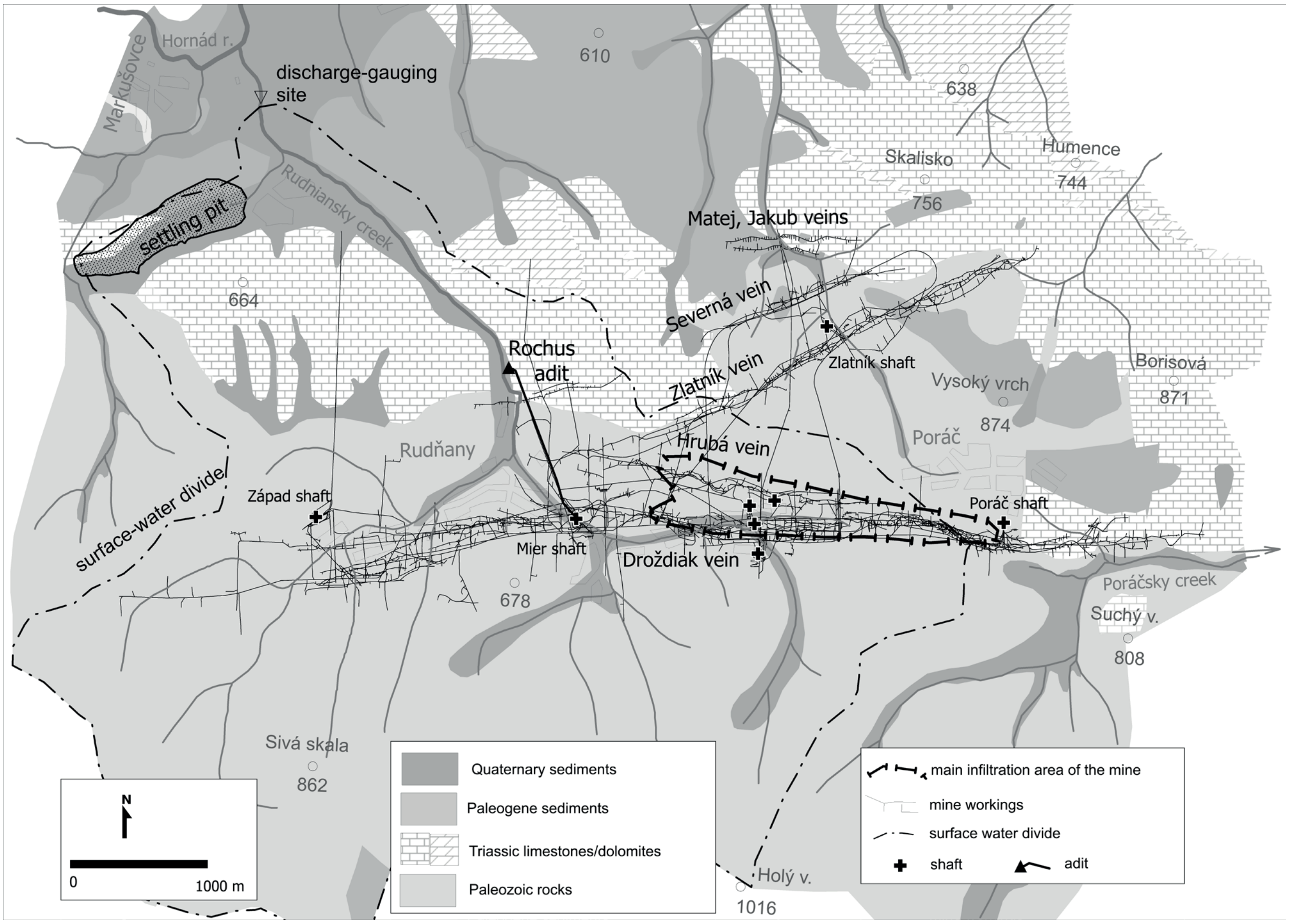


Fig. 1. Geological situation of the Rudňany mine (compiled on the basis of geological map of Mello et al., 2000).

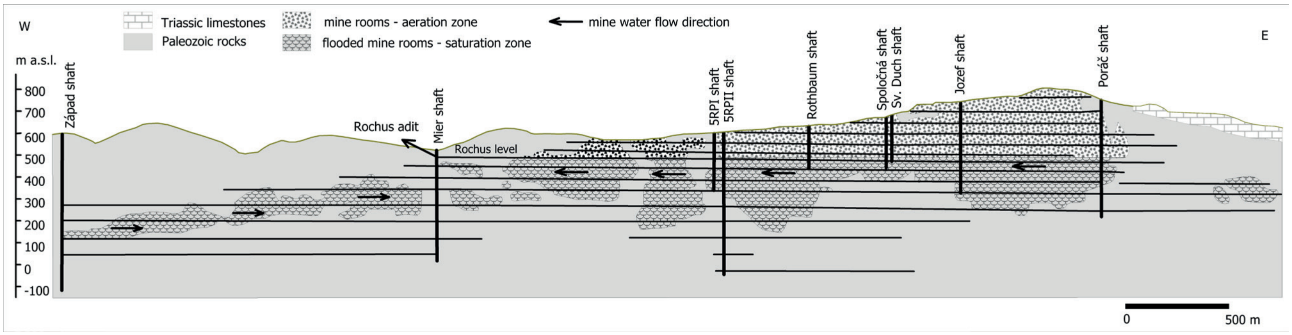


Fig. 2. Longitudinal cross-section through the Drožďiak.

ankerite from Rudňany calculated from 11 samples is $Ca_{1.008}(Fe_{0.372}Mg_{0.574}Mn_{0.046})(CO_3)_2$, for calcite from 3 samples $(Ca_{0.915}Fe_{0.019}Mg_{0.052}Mn_{0.013})CO_3$ and for Fe-dolomite from 10 samples $Ca_{1.033}(Fe_{0.242}Mg_{0.705}Mn_{0.020})(CO_3)_2$.

The Rudňany mine was flooded in 2006. Since then, all water drained by the mine flows out of the Mier shaft and from it flows to the surface through a 1.2 km long Rochus adit by gravity. According to measurements performed 2–6 times a year the mine water discharge fluctuated from 12 to 40 L/s in the period 2007–2011 and it contributed to contamination of the Rudniansky potok creek mainly by high Mn, SO_4, TDS and Sb concentrations (Bajtoš et al., 2012).

Data and methods

Sampling

Mine water samples were collected on the mouth of Rochus gallery in 2012 and 2013. Sampling frequency was irregular (Fig. 4) – aimed on documentation of wide range of climate/discharge conditions. The water samples were filtered with a 0.45 µm Whatman filter using Nalgene vacuum hand-operated pump into PE sample bottles, which were prepared by lab. Water for Fe(II) measurement was sampled into 300 ml glass bottle and fixed with 6 ml of sodium acetate solution and 6 ml of dilute acetic acid. A WTW Multi 340i was used to quantify pH, specific conductance, temperature, dissolved O_2 and Eh (platinum electrode) in sampled water. In time of sampling, the mine water discharge was measured using A.OTT C1 current meter.

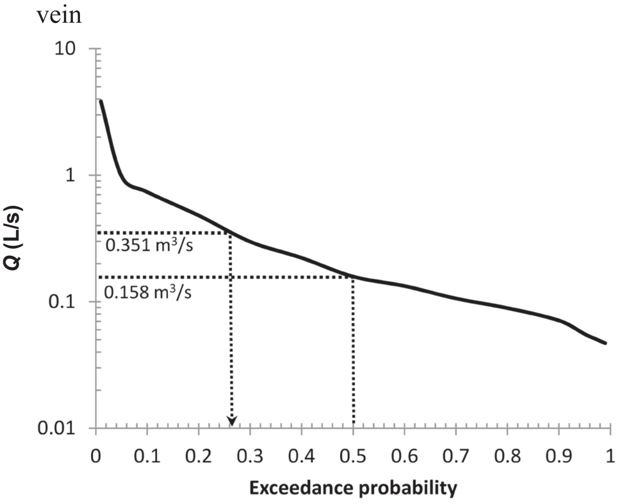


Fig. 3. Flow duration curve of the Rudniansky potok creek recorded in the period 2012–2013 by Slovak Hydrometeorological Institute on gauging station No. 8425 in Markušovce locality.

Chemical analysis

Bicarbonate and carbonate anions were measured using Titroline 7000 alkalinity titrator. Sulphate, chloride, fluoride and nitrate were measured by ion chromatography using DX-120 IC apparatus. Concentrations of Na, K, Al, Ba, Ca, Cu, Fe, Mg, Mn, Ni, SiO_2, Sr, Zn and U were determined by the ICP-OES technique using VARIAN Vista-MPX and CETAC Technologies Ultrasonic Nebulizer. Concentrations of As, Bi, Sb, and Se were measured by atomic absorption spectrometry using SPECTRAA-20 AAS-GH. Atomic absorption spectrometer AMA-254 was used for mercury determination. Using UV-VIS spectrophotometer Hach Lange DR 5000, concentrations of ammonium ion, nitrite and Fe(II) were determined. Mine water samples were delivered to the laboratory within 3 hours of collection. All chemical analyses were performed at the Geoanalytical Laboratories (GAL) of the State Geological Institute of Dionýz Štúr (SGIDS), located in Spišská Nová Ves. GAL is accredited by Slovak National Accreditation Service – regular member of European Cooperation for Accreditation – for chemical and physical-chemical tests of all types of waters and water leachates, as well as for water sampling.

Geochemical calculations and geochemical modelling

The PHREEQC computer program with minteq.v4 database was used for speciation and saturation index (SI) calculations. These types of calculations, referred to as speciation calculation or speciation modelling, requires only a SOLUTION data block for each water analysis (Parkhurst & Appelo, 2013). Speciation calculation distributes total concentrations of element in solution among aqueous species by using an aqueous model – the results are the activities of all of the aqueous species including gas phases (CO_2, O_2). The activities are used for calculating saturation indices for minerals, relative to water. Carbonate minerals, gypsum and Fe and Mn hydroxides are considered to be most relevant for study of water-rock interactions in Rochus mine. The Eh measured in the field were employed to predict the speciation of Sb and As in mine water samples.

Forward geochemical modelling uses hypothesized geochemical reactions to predict water and rock compositions (Plummer, 1992). This approach allows to simulate mineral solubilities, mass transfers, reaction paths, pH and pe by using available solid-aqueous data in aqueous specification models. In this study, forward modelling is applied to simulate the evolution of mine water chemical composition at the Rochus mine. The hypothesis is that ore minerals (carbonates, pyrite) dissolution, precipitation of calcite, goethite, ferrihydrite, manganite and rhodochrosite, and consumption/release of carbon dioxide and oxygen are sufficient to account for the changes in water composition of all the major ions, iron and manganese. Taking into account the complexity of the modelled environment, results of presented simulation should be considered as indicative. The calculation uncertainty is mainly due to the variability of primary carbonate minerals composition combined with the lack of available values of *log K* for these minerals, as well as temporal and spatial variability of CO_2 and O_2 partial pressure in studied environment.

Some ore carbonate minerals present with documented average stoichiometry (Cambel & Jarkovský, 1985) were added to the thermodynamic database (minteq.v4) used for SI calculations and forward modelling. Due to the lack of data on their solubility product (*log K*) in the literature, these data were estimated by linear interpolation between the *log K* values of main end-members of respective solid solutions. *Log K* = –9.87 was estimated for siderite(Ry) $Ca_{0.01}Fe_{0.82}Mg_{0.13}Mn_{0.040}CO_3$, by interpolation between siderite $FeCO_3$ (minteq.v4; *log K* = –10.89) and magnesite

$MgCO_3$ (phreeqc database; *log K* =–7.46). Similarly, *log K* = –8.48 of calcite $Ca_{0.916}Fe_{0.019}Mg_{0.052}Mn_{0.013}CO_3$ was determined from data for calcite (*log K* = –8.475, minteq. v4) and magnesite. *Log K* = –17.31 for ankerite(Ry) $Ca_{1.008}(Fe_{0.372}Mg_{0.574}Mn_{0.046})(CO_3)_2$ and of *log K* = –17.35 for ankerite(f) $Ca_{1.0}(Fe_{0.46}Mg_{0.5}Mn_{0.04})(CO_3)_2$ were determined from data for ordered dolomite (*log K* = –17.09; minteq. v4) and ankerite $Ca(Fe_{0.6}Mg_{0.4})CO_3)_2$ (*log K* = –17.40; Al et al., 2000).

Statistical data treatment

Regression analysis was used to evaluate the direction and strength of relationship between mine water discharge as independent variable and content of observed chemical compounds dissolved in it, by using the software STATISTICA Cz version 10 (StatSoft CZ). The strength of a monotonic (Spearman correlation) relationship between those variables was also evaluated. The interdependence of

Tab. 1

Basic physico-chemical parameters and ion concentrations of mine water samples together with time corresponding mine water discharge Q at the Rudňany mine.

Date	Q [L/s]	T_{H2O} [°C]	EC [mS/m]	pH [–]	E_H [mV]	O_2 [%]	Ba [mg/L]	Fe [mg/L]	Fe^{2+} [mg/L]	Mn [mg/L]	As [µg/L]	Sb [µg/L]	Hg [µg/L]	SO_4 [mg/L]
13. 9. 2011	14.7	11.7	143.9	7.55	511	56	0.03	0.216	< 0.1	1.37	5	8	0.1	244
28. 2. 2012	14.2	9.4	161.0	7.84	421	90	0.028	0.081	< 0.1	1.19	5	6	0.1	299
12. 3. 2012	13.4	10.0	163.1	7.69	389	91	0.03	0.064	< 0.1	1.38	5	4	0.3	313
21. 3. 2012	17.6	10.4	162.9	7.76	395	83	0.036	0.072	< 0.1	1.52	5	5	0.2	310
28. 3. 2012	20.8	10.8	165.0	7.70	446	79	0.035	0.087	< 0.1	1.54	3	3	0.1	323
4. 4. 2012	19.7	10.7	161.5	7.65	396	77	0.03	0.074	< 0.1	1.52	4	9	0.1	320
10. 4. 2012	20.9	9.7	158.4	7.70	435	78	0.033	0.079	< 0.1	1.21	5	8	< 0.1	297
17. 4. 2012	32.6	10.9	148.6	7.54	444	70	0.042	1.11	< 0.1	1.07	4	13	< 0.1	279
26. 4. 2012	31.9	10.8	154.5	7.48	85	74	0.035	0.137	< 0.1	1.35	3	14	< 0.1	271
3. 5. 2012	25.9	11.1	153.4	7.54	490	78	0.038	0.087	< 0.1	1.42	3	26	0.1	263
24. 5. 2012	20.3	11.4	154.9	7.67	500	82	0.03	0.012	< 0.1	1.41	5	6	0.1	261
29. 5. 2012	19.2	11.2	156.1	7.65	450	80	0.039	0.1	< 0.1	1.65	4	3	0.2	265
4. 6. 2012	17.6	11.7	158.5	7.67	350	79	0.039	0.1	< 0.1	1.65	5	4	0.2	271
13. 6. 2012	30.3	11.3	148.7	7.53	343	75	0.039	0.147	–	1.53	6	5	0.2	271
13. 9. 2012	20.4	11.7	159.7	7.72	411	75	0.03	0.099	–	1.37	5	6	< 0.1	340
5. 3. 2013	76.6	11.3	162.6	7.47	294	89	0.057	0.47	< 0.1	1.32	18	7	0.2	414
12. 3. 2013	127.4	11.5	201.2	7.50	238	99	0.028	2.15	–	1.16	18	6	0.2	867
19. 3. 2013	123.0	11.1	199.5	7.51	201	84	0.024	0.804	0.46	0.98	20	9	< 0.1	670
3. 4. 2013	52.1	10.7	147.9	7.53	364	57	0.035	0.33	–	1.36	11	9	0.3	302
9. 4. 2013	59.3	11.3	169.9	7.57	277	51	0.033	0.63	–	1.25	11	8	< 0.1	413
16. 4. 2013	65.0	12.9	254.9	7.60	176	29	0.026	1.41	0.77	0.90	6	21	–	1 000
23. 4. 2013	117.5	11.9	193.2	7.86	199	39	0.028	1.02	0.36	1.00	14	14	< 0.1	570
6. 5. 2013	70.0	11.3	141.6	7.53	481	59	0.032	0.193	< 0.1	1.24	9	9	< 0.1	235
14. 5. 2013	60.1	11.1	141.1	7.67	357	61	0.03	0.199	< 0.1	1.37	7	6	0.2	251
19. 6. 2013	59.4	11.2	143.5	7.27	531	73	0.041	0.161	< 0.1	1.57	6	6	0.1	255
11. 7. 2013	69.8	11.2	144.7	7.27	411	76	0.03	0.08	< 0.1	1.29	8	5	0.1	283
18. 9. 2013	29.8	11.6	165.8	7.46	326	77	0.042	0.166	< 0.1	1.64	8	20	< 0.1	395
3. 10. 2013	26.2	11.4	170.0	7.60	522	74	0.031	0.197	< 0.1	1.22	5	10	< 0.1	431

Tab. 1 (continued)

Date	Na [mg/L]	K [mg/L]	NH_4^+ [mg/L]	Ca [mg/L]	Mg [mg/L]	Sr [mg/L]	Zn [µg/L]	Cu [µg/L]	Ni [µg/L]	Co [µg/L]	Cl [mg/L]	NO_2 [mg/L]	NO_3 [mg/L]	HCO_3 [mg/L]	SiO_2 [mg/L]
13. 9. 2011	11.4	7.65	0.08	85.9	168	1.27	17	5	9	5	11.9	< 0.01	2.08	781	3.72
28. 2. 2012	9.8	6.21	0.09	69.8	156	1.05					15.3	0.01	1.2	824	3.51
12. 3. 2012	11.6	7.56	0.12	77.2	177	1.26	6	< 2	9	4	15.3	< 0.01	1.14	872	4.05
4. 4. 2012	12.4	7.65	0.06	84.8	183	1.42	8	2	6	4	17.2	< 0.01	2.3	805	4.07
24. 5. 2012	12.3	7.75	0.23	77.9	186	1.23	3	< 2	5	3	14.8	< 0.01	2.37	787	3.84
13. 9. 2012	11.7	7.79	0.32	78	171		9	3			14.9	0.01	1.98	856	3.43
5. 3. 2013	16.8	8.68	0.15	98.9	166	1.72	3	4	14	7	15.2	0.02	3.08	726	4.69
12. 3. 2013	59.8	14.1	0.27	116	259						15.7		1.2	819	4.92
19. 3. 2013	44.9	11.00	0.27	98.2	230	2.89	3	< 2	9	5	16.2	0.03	5.19	729	4.31
3. 4. 2013	12.8	6.28	0.57	82.2	146						15.6		6.2	700	3.53
9. 4. 2013	23.9	8.00	0.19	87.3	190						18		5.3	737	3.57
16. 4. 2013	68.7	16.7	0.34	114	280	4.06		2	8	5	18.5	0.02	3.62	793	4.14
23. 4. 2013	37.3	9.28	0.24	93.6	200						17.9		5.8	728	3.78
6. 5. 2013	10.7	5.82	0.29	74.2	144						16.2		5.76	729	3.48
14. 5. 2013	10.5	5.58	0.08	76.2	166	1.04	6	2	8	5	16.4	0.01	5.26	720	2.84
19. 6. 2013	12.7	7.40	0.25	93	172						18.3		6.7	737	4.01
11. 7. 2013	12.3	6.45	0.22	78.7	151	1.16	5	2	10	5	17.1	0.01	5.83	720	3.25
18. 9. 2013	10.6	6.51	0.31	95.5	167						18.2		3.01	759	3.64
3. 10. 2013	11.2	6.92	0.14	101	184	1.49	5	4	10	7	18.6	< 0.01	12.4	756	4.47

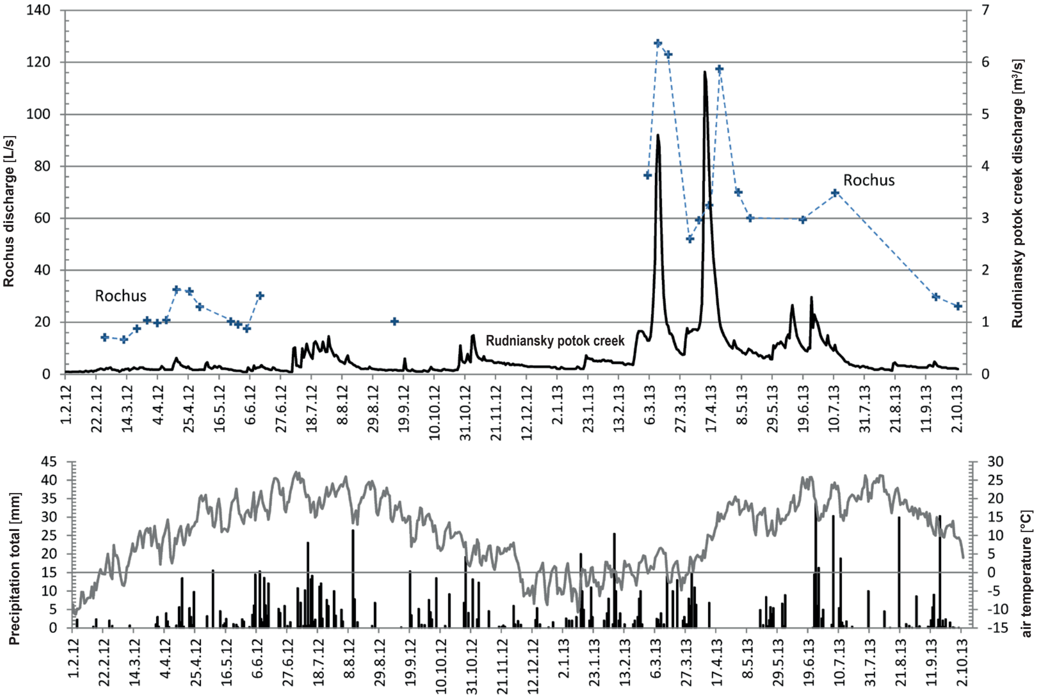


Fig. 4. Sampling frequency represented by discharge values of the Rochus mine water (plus marks) in the background of local climate and runoff regime. The Rudniansky potok creek discharge was measured on discharge-gauging station no. 8 425 in Markušovce village, daily precipitation totals measured at precipitation stations in the Rudňany willage, air temperature measured at climatic station in Rožňava; measurements were performed by SHMI Bratislava.

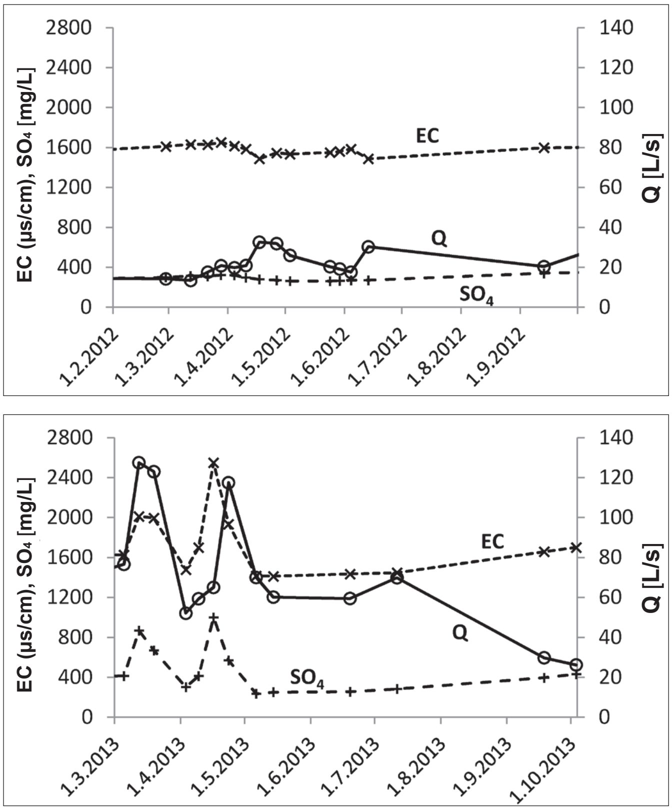


Fig. 5. Temporal changes of mine water discharge Q, EC value and sulphate concentration during sampling periods 2012 and 2013.

chemical compounds and some geochemical indicators is evaluated and presented by regression graphs by using the software MS EXCEL.

Results

Mine water chemistry

Water discharged from the Rochus gallery is slightly alkaline with pH values 7.3–7.9 (Tab. 1). The total dissolved solids (TDS) content in samples ranged from 1.2 to 2.3 g/L. Magnesium (70–75 eq %) is the most dominant cation, followed by calcium (18–30 eq %). Bicarbonate (38–70 eq %) and sulphate (28–60 eq %) are dominant anions. Therefore, samples represent Mg–Ca–HCO_3–SO_4, Mg–HCO_3–SO_4 or Mg–SO_4–HCO_3 type, according to water chemistry classification based on presence of major (> 20 eq %) ions. Sodium (2–9 eq %), potassium (1 eq %) and chloride (1–3 eq %) are secondary major ions. Concentration of nitrogen species is low – ammonium ion and nitrate do not exceed 0.6 mg/L and 12 mg/L, respectively. Among the trace elements, strontium and manganese is present in units of mg/L, iron in tenths of mg/L, antimony, barium in tens of μg/L, arsenic, zinc, cobalt, nickel and copper in units of μg/L and mercury in tens of μg/L. Concentrations of cadmium and beryllium are under detection limits of analytical method used. In situ measured Eh values of 85–531 mV indicate aerobic conditions.

Hydrochemical regime

Hydrochemical regime of Rochus mine water was observed in two periods – 2012 and 2013. Most of samples were collected during the spring and summer months, when the most significant changes in mine water chemical composition are expected.

Spring warming in March 2012 did not bring much increase of runoff (Fig. 4), probably due to low snow and soil water storage. Low runoff increase on April 14–17 was caused by precipitation total of 20 mm and the Rochus mine water yield rose quickly from 20 to 32 L/s. This increase was accompanied by slight decrease in EC from 165 to 149 mS/m, SO_4 from 0.32 to 0.26 g/L (Fig. 5) and pH value decrease from 7.7 to 7.5. Since March 28 to May 3 the gradual increase of Sb content from 3 to 26 μg/L was recorded while As content remained at the level between 3 and 5 μg/L (Fig. 6).

On the other hand, spring warming in 2013 brought two big runoff increases. The first of them was cau-

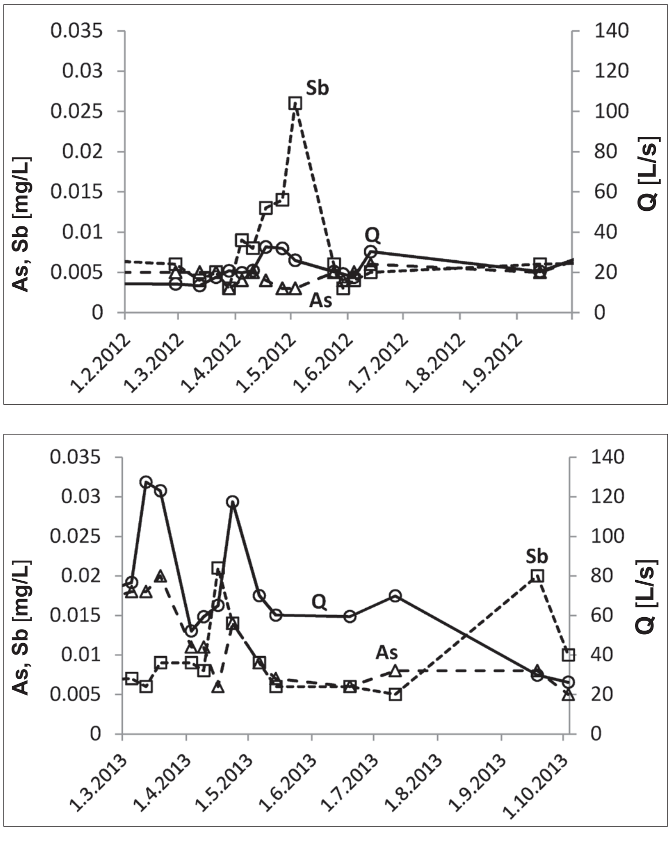
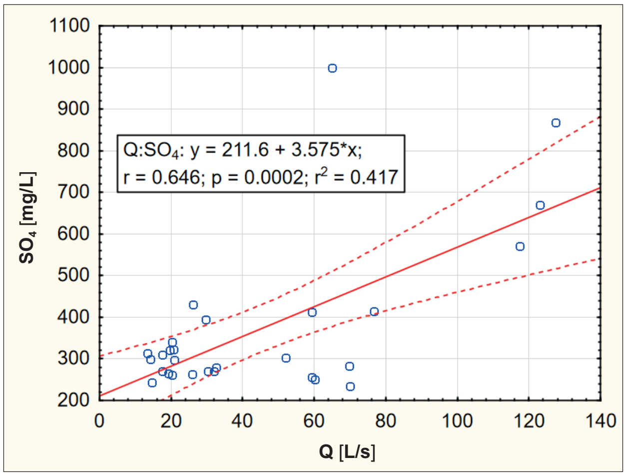


Fig. 6. Temporal changes of mine water discharge *Q* and arsenic and antimony concentration during sampling periods 2012 and 2013.



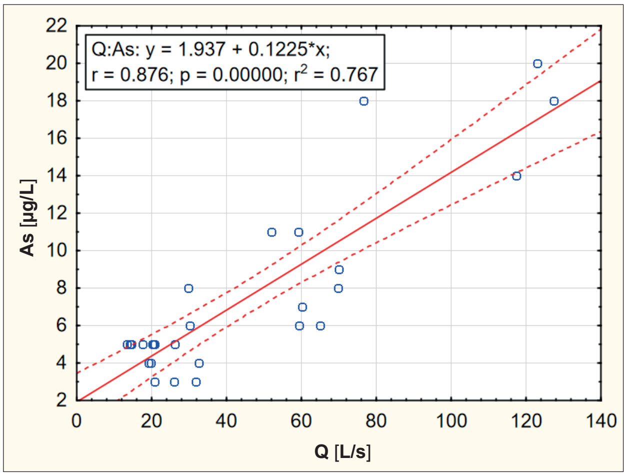


Fig. 7. Dependence of sulphate anion concentration on mine water discharge.
Linear regression line fitted to the data and a 95 % confidence interval for that line.

Fig. 8. Dependence of arsenic concentration on mine water discharge.

Tab. 2

Results of correlation and regression analysis of water chemical composition features and mine water discharge.

Q L/s	n	r – Spearman	r	r^2	t-value	p-value	y-intercept	Slope
pH	28	**–0.554**	–0.280	0.078	–1.485	0.150	7.64	–0.001 1
Eh	26	**–0.431**	**–0.536**	**0.287**	**–3.110**	**0.005**	**455**	**–1.828 0**
EC	28	0.101	**0.471**	**0.222**	2.723	0.011	1 490	3.301 5
O$_2$ mg/L	28	–0.324	–0.226	0.051	–1.181	0.248	7.93	–0.011 2
As	28	**0.719**	**0.876**	**0.767**	**9.242**	**0.000**	1.9	0.122 5
Sb	28	**0.429**	0.121	0.015	0.624	0.538	8.1	0.020 0
Fe	25	**0.616**	**0.594**	**0.353**	**3.546**	**0.002**	**–0.000 7**	**0.007 1**
Mn	28	**–0.507**	**–0.622**	**0.386**	**–4.047**	**0.000 4**	**1.514**	**–0.003 8**
Ba	28	–0.129	–0.193	0.037	–1.002	0.326	0.036	–0.000 04
SO$_4$	28	0.315	**0.646**	**0.417**	**4.314**	**0.000 2**	**212**	**3.575**
Ca	19	**0.498**	**0.539**	**0.290**	**2.638**	**0.017**	**78**	**0.189**
Mg	19	0.207	**0.491**	0.241	2.325	0.033	158	0.479
Na	19	**0.584**	**0.681**	**0.464**	**3.836**	**0.001**	**3.2**	**0.329**
K	19	0.362	**0.506**	**0.256**	**2.418**	0.027	6.2	0.039
NH$_4$	19	0.427	0.295	0.087	1.274	0.220	0.17	0.001
Sr	11	0.445	0.556	0.309	2.005	0.076	1.02	0.015
Cl	19	0.284	0.256	0.065	1.090	0.291	15.7	0.012
NO$_3$	19	0.412	0.174	0.030	0.727	0.477	3.53	0.013
HCO$_3$	20	**–0.604**	**–0.496**	**0.246**	**–2.423**	**0.026**	**807**	**–0.686**
SiO$_2$	19	0.211	0.326	0.106	1.421	0.173	3.61	0.004
Ni	10	0.389	0.393	0.154	1.208	0.261	7.50	0.026 6
Co	10	0.553	0.326	0.106	0.974	0.359	4.45	0.011 3
Zn	10	**–0.648**	–0.515	0.265	–1.698	0.128	9.14	–0.059 4

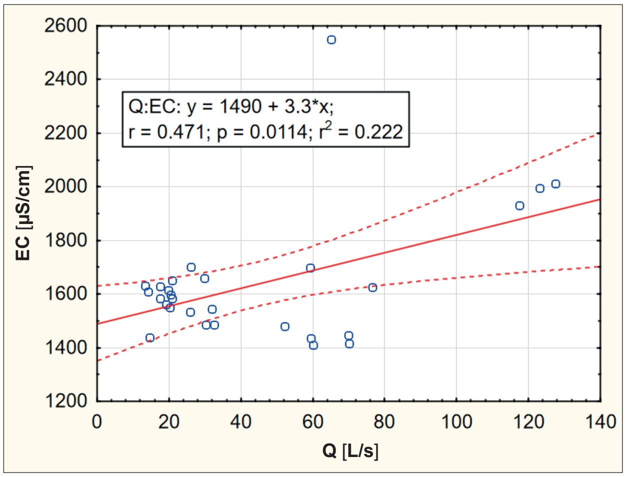


Fig. 9. Dependence of manganese concentration on mine water discharge.

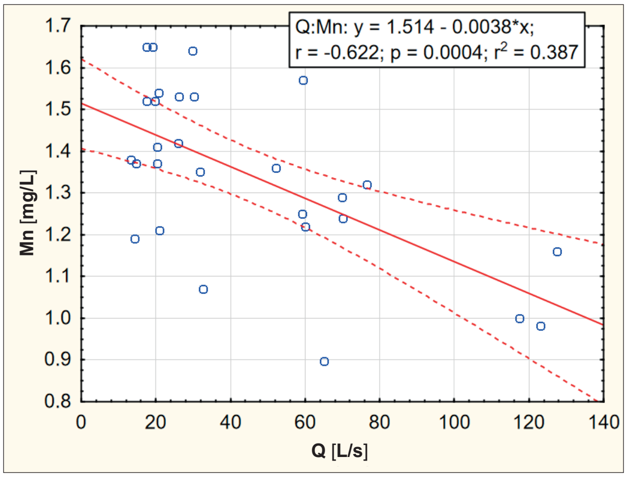


Fig. 10. Dependence of EC(25 °C) on mine water discharge.

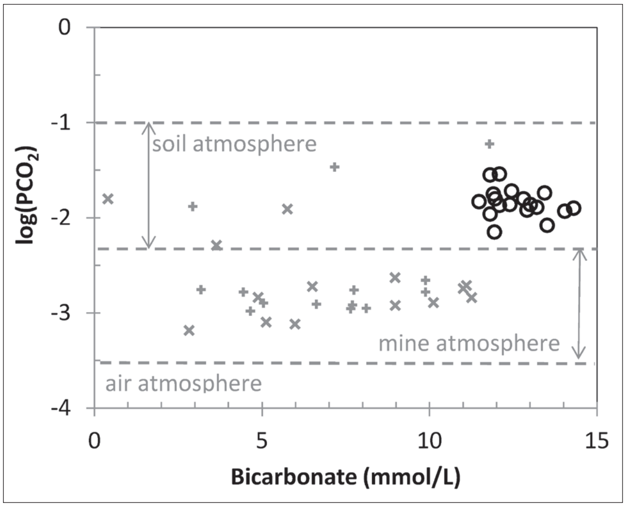


Fig. 11. Computed values of $P(CO_2)$ versus concentration of bicarbonate anion. Empty circles – new samples of mine water from Rochus adit; plus signs – samples of mine water pumped from the mine at the time of its operation 1992–1995, cross marks – seepage samples from mine rooms on the Droždiak vein taken in time of ore extraction, according data from Bajtoš (1993a, b).

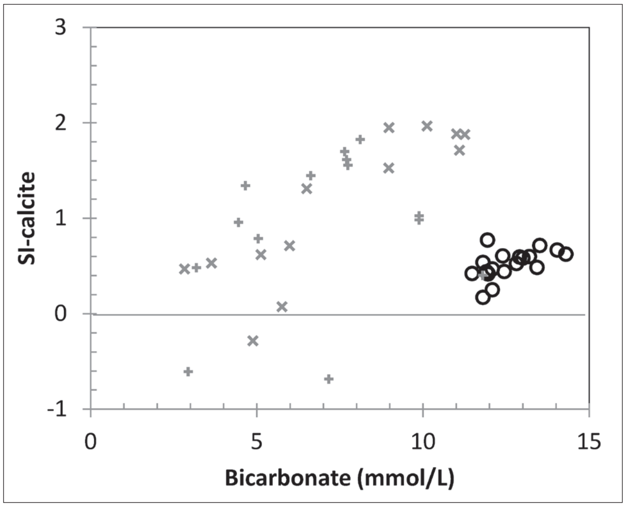


Fig. 12. Computed SI-calcite values versus concentration of bicarbonate anion. Explanations as in Fig. 11.

sed by short terming warming and snow melting in March 7–13, with 4.6 m^3/s peak of the Rudniansky potok creek discharge on March 12. In this time, maximum 128 L/s mine water yield was recorded. During following frosty days runoff dropped almost to its original level, but permanent warming that began on April 9 has brought another rapid increase of the Rudniansky potok creek discharge, with its 5.4 m^3/s peak on April 13. Mine water discharge also increased rapidly in this time, but its peak occurred a few days later – between 16 and 23 April. During these high mine water discharge stages, both EC values, sulphate and arsenic concentrations have significantly increased (Figs. 5, 6). Concentrations of antimony have increased only during second discharge peak, from 8 to 21 µg/L. Increases of EC values, SO_4 and As content reached up to 107 mS/m, 0.7 g/L and 14 µg/L, respectively. The pH value increased slightly during the first discharge peak from 7.5, reaching its maximum of 7.86 in time of the second discharge peak.

The relationship between mine water chemical composition features and mine water discharge

Regression analysis was applied to examine the relationships between mine water chemical composition features (dependent variables) and mine water discharge (independent variable). Its results reveal that many of them have statistically significant relationship (Tab. 2). All the major ions concentrations significantly depend on mine water discharge – most sulphate anion (Fig. 7), with 42 % of its variability explained ($r^2 = 0.42$), followed by calcium ($r^2 = 0.29$), bicarbonate anion ($r^2 = 0.25$) and magnesium ($r^2 = 0.24$). In accordance with EC ($r^2 = 0.22$), sul-

Tab. 3

Saturation indices of mine water samples with respect to selected mineral phases.

	Saturation indices with respect to:							
	siderite	**ankerite(Ry)**	**Fe-dolomite(Ry)**	**calcite**	**monohydrocalcite**	**dolomite**	**nesquehonite**	**rhodochrosite**
	$FeCO_3$	$Ca(Fe_{0.37}Mg_{0.58}Mn_{0.05})(CO_3)_2$	$Ca_{1.03}(Fe_{0.24}Mg_{0.71}Mn_{0.02})(CO_3)_2$	$CaCO_3$	$CaCO_3{*}H_2O$	$CaMg(CO_3)_2$	$MgCO_3{*}3H_2O$	$MnCO_3$
Average	–2.21	0.08	0.23	0.51	–0.85	1.50	–1.74	0.65
Minimum	–5.16	–1.32	–0.94	0.17	–1.19	0.79	–2.10	0.35
Maximum	–0.15	1.28	1.21	0.77	–0.59	2.05	–1.45	0.92

Tab. 4

Saturation indices of mine water samples with respect to selected mineral and gas phases.

	Saturation indices with respect to:							
	manganite	**ferrihydrite**	**goethite**	**K-jarosite**	**gypsum**	**quartz**	$CO_2(g)$	$O_2(g)$
	MnOOH	$Fe(OH)_3$	FeOOH	$KFe_3(SO_4)_2(OH)_6$	$CaSO_4{*}2H_2O$	SiO_2	$\log(P_{CO2})$	$\log(P_{O2})$
Average	–0.98	2.88	5.69	1.63	–1.23	0.00	–1.84	–30.9
Minimum	–4.47	1.69	4.50	–2.55	–1.44	–0.13	–2.15	–43.7
Maximum	1.71	3.76	6.55	5.21	–0.82	0.12	–1.54	–20.0

Tab. 5

Predicted antimony (as % Sb_T), arsenic (as % As_T) and manganese (as % Mn_T) speciation in Rochus mine water based on measured Eh values (milivolts).

	Eh (mV)	$Sb(OH)_6^-$	SbO_2^-	$HAsO_4^{2-}$	$H_2AsO_4^-$	Mn^{2+}	$MnHCO_3^+$	$MnSO_4$
13. 9. 2011	511	99.9	0.1	86.5	13.5	84.8	9.1	6.0
28. 2. 2012	421	99.9	0.1	92.4	7.6	83.9	9.5	6.6
12. 3. 2012	389	99.9	0.1	89.9	10.0	83.1	9.6	7.3
4. 4. 2012	396	99.9	0.1	89.1	10.8	83.7	8.9	7.4
24. 5. 2012	500	99.9	0.1	89.5	10.4	84.8	8.9	6.2
13. 9. 2012	411	99.9	0.1	90.6	9.4	82.4	9.5	8.1
5. 3. 2013	294	99.9	0.1	84.5	15.5	82.4	8.0	9.6
12. 3. 2013	238	99.9	0.1	86.8	13.2	78.1	7.3	14.6
19. 3. 2013	201	99.9	0.1	86.5	13.4	80.4	7.0	12.5
3. 4. 2013	364	99.9	0.1	85.7	14.3	83.9	8.2	7.8
9. 4. 2013	277	99.9	0.1	87.4	12.6	83.1	7.6	9.2
16. 4. 2013	176	99.9	0.1	89.2	10.8	75.5	6.9	17.5
23. 4. 2013	199	99.9	0.1	93.3	6.7	80.8	7.3	11.8
6. 5. 2013	481	99.9	0.1	85.6	14.4	84.8	8.8	6.3
14. 5. 2013	357	99.9	0.1	89.4	10.6	83.4	8.2	8.3
19. 6. 2013	531	99.9	0.1	77.2	22.8	85.3	8.5	6.2
11. 7. 2013	411	99.9	0.1	76.8	23.2	84.1	8.5	7.3
18. 9. 2013	326	99.9	0.1	84.2	15.8	82.4	8.4	9.2
3. 10. 2013	522	99.9	0.1	88.3	11.7	82.2	8.1	9.6

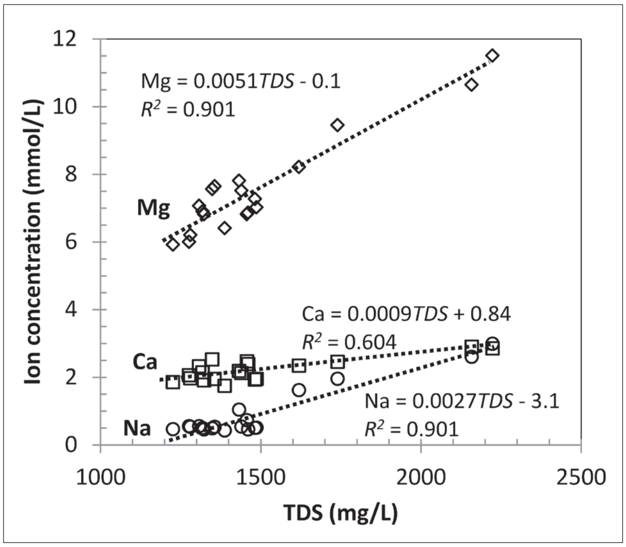


Fig. 13. Concentrations of main cations versus TDS content in mine water samples.

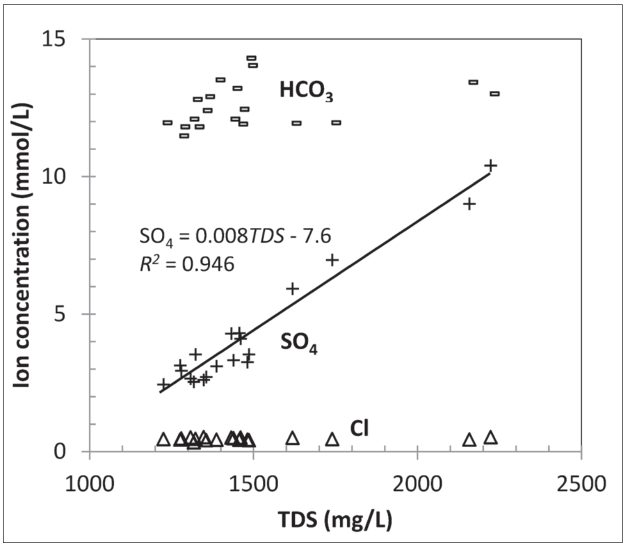


Fig. 14. Concentrations of main anions versus TDS content in mine water samples.

phate, calcium and magnesium are correlated positively. However, bicarbonate anion is negatively correlated with discharge. Statistically significant positive correlation is found also for secondary major ions as sodium and potassium, as well as for minor ions as arsenic (Fig. 8) and iron. On the other hand, manganese is negative correlated (Fig. 9). As *Eh* dependence reveals, mine water tends to reflect less oxidizing conditions in time of higher discharge. According to Spearman coefficient of correlation for pH value, mine water reaction is slightly more acidic during higher discharge stages (Tab. 2).

Geochemical calculation and modelling

Calculated SI values show that almost all samples are undersaturated (some of them are near equilibrium) with respect to the main ore carbonate mineral – siderite. Saturation with respect to other present carbonate ore minerals – ankerite and Fe-dolomite – varies around zero (Tab. 3). All samples are supersaturated with respect to possible secondary ore minerals: dolomite (SI = 0.8–2.1), calcite (SI = 0.2–0.8, Fig. 12) and rhodochrosite (SI = 0.4–0.9). Computed values of log(PCO_2) range from –2.15 to –1.53, suggesting that water composition is formed in open carbonate system, with relatively stable CO_2 partial pressure corresponding to conditions typical for the soil atmosphere (Tab. 4, Fig. 11).

The presented results of speciation calculations relate to most environmentally significant elements. They reveal that SbO_3^- represents almost all mass of total Sb-species in mine water samples (Tab. 5). The $HAsO_4^{2-}$ prevails among As species, making up 77–93 % of total As content. Rest of total As content is represented by $H_2AsO_4^-$. Manganese is almost exclusively represented by Mn^{II} species, with a simple ion Mn^{2+} making up about 80 % of its total Mn^T concentration and its remaining portion consist of complex $[MnHCO_3]^+$ cation and neutral $[MnSO_4]^0$ complex.

Water Quality

Comparing to Slovak drinking water standards (The Decree of the Ministry of Health of the Slovak Republic No. 247/2017), mine water of Rochus gallery exceeds “highest limit value” for antimony and arsenic and “limit value” for water electric conductivity and concentration of manganese, magnesium and sulphate. Limit exceeding for EC, Mn and Mg was documented in all and for SO_4 for almost all samples. From 28 samples taken, Sb content exceeded its limit value 5 μg/L in 21 and As content exceeded its limit value 10 μg/L in 6 samples.

Concerning protection of stream water quality (Regulation of the Slovak Government No. 96/2010 Coll.), mine water of Rochus gallery is risky due to its high Mn, As, Mg, SO_4 and TDS content. Contamination risk by manganese is most significant, as Mn concentration in mine water is permanently 3.0–5.5 times higher than limit for surface water. Recorded SO_4 values mostly slightly – but during high discharge seasons up to 4-times – exceeds limit value of 250 mg/L. Limit value for magnesium is exceeded only rarely, maximally 1.4 times. Arsenic concentration is usually (in 22 cases from 28) lower than limit value, its maximum exceedance is 2-fold. TDS values are 1.3–2.3 times higher than respective limit value of 110 mS/m. Antimony is not included in the list of surface water quality indicators. However, for surface water intended for the abstraction for drinking purposes, Sb limit value is 5 μg/L for the best category A1 (only simple physical water treatment and disinfection needed) and 25 µg/L for categories A2 and A3 (physico-chemical treatment or intensive physico-chemical treatment needed). Only one of the samples taken does not meet the limit for A2 and A3 cathegory.

Discussion

Geochemical background of seasonal variability of mine water chemical composition

Variation of TDS content in the Rochus mine water is given mainly by variation of Mg and SO_4 content, while the Ca content fluctuation is less pronounced (Figs. 13, 14). The HCO_3 content is relatively stable. Also sodium content slightly contributes to TDS variation, being positively correlated with sulphate anion.

As gypsum or anhydrite practically absent in rock environment of Rudňany mine, sulphide minerals can be considered as the main source of sulphate anion in studied mine water. Although tetrahedrite and chalcopyrite are the most abundant sulphide minerals present there, pyrite is the most geochemically significant. Chalcopyrite is known as one of the most resistant sulphides to oxidation (Plumlee, 1999), with an oxidation rate of 1–2 orders of magnitude less than pyrite (Rimstidt et al., 1994). Tetrahedrite is reported as mineral whose leaching reaction proceeds slowly in acidic oxidative (Baláž, 2000) and also alkaline (Awe et al., 2010) conditions. Supposed little geochemical importance of chalcopyrite and tetrahedrite at studied site is also indicated by low Cu content in mine water (Tab. 1), as well as a rare occurrence of cuprite, malachite or azurite in oxidation zone of ore veins (Bernard, 1961). Immobilization of released Sb(V) by adsorption on Fe(hydr)oxides may not be significant here, as sorption maxima of Sb(V) occur at low pH values which extent up to pH 7 and desorption of Sb rapidly increases above pH 7 (Tighe et al., 2005). Many studies presented that sulphide oxidation depends on a wide variety of factors, such as oxygen concentration, the presence of water, ferric ion concentration, acidity, microbial population and temperature (Nordstrom & Southam, 1997; Nordstrom & Alpers, 1999). Pyrite oxidation in water with dissolved oxygen may be written according to equation (1), where ferrous cation, sulphate anion and two protons are released. The overall process taking place in an aerobic environment, including, in addition to pyrite oxidation, also hydrolysis of Fe^{3+} and precipitation of iron hydroxide (eq.1 + eq.2 + eq.3 = eq.4), produces 4 protons per mol of pyrite. When present in the system, ferric iron becomes the primary oxidant of pyrite (Nordstrom et al., 1979; Moses et al., 1987; Ehrlich, 1996 (eq.5).

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad (1)$$

$$Fe^{2+}\ 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O \quad (2)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \quad (3)$$

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+ \quad (4)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (5)$$

Strong positive correlation of Mg to SO_4 content in mine water (Fig. 13) suggests that pyrite oxidation is accompanied with the Mg-rich ore carbonates dissolution. During this process, the acid produced by pyrite oxidation is neutralized and in addition to magnesium, also calcium, iron and manganese are released into solution. Ore carbonates present in the Droždiak vein in Rudňany have a known typical composition (Cambel & Jarkovský, 1985) and dissolve according to the equations 6, 7 and 8 for siderite, ankerite and Fe-dolomite, respectivelly:

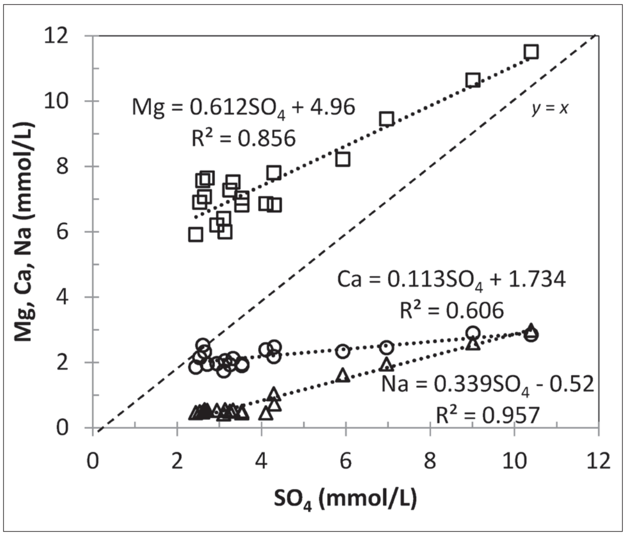


Fig 15. Magnesium, calcium and sodium content versus sulphate concentration in mine water samples.

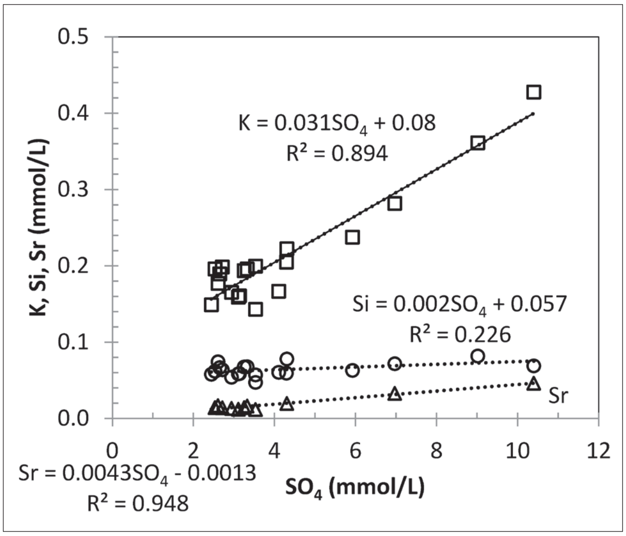


Fig 16. Potassium, silicon and strontium content versus sulphate concentration in mine water samples.

$$(Ca_{0.008}Fe_{0.823}Mg_{0.129}Mn_{0.04})CO_3 + H^+ \rightarrow 0.008\ Ca^{+2} + 0.823\ Fe^{+2} + 0.129\ Mg^{+2} + 0.04\ Mn^{+2} + HCO_3^{-2} \quad (6)$$

$$Ca_{1.008}(Fe_{0.372}Mg_{0.574}Mn_{0.046})(CO_3)_2 + 2\ H^+ \rightarrow 1.008\ Ca^{+2} + 0.372\ Fe^{+2} + 0.574\ Mg^{+2} + 0.046\ Mn^{+2} + 2\ HCO_3^{-2} \quad (7)$$

$$Ca_{1.033}(Fe_{0.242}Mg_{0.705}Mn_{0.02})(CO_3)_2 + 2\ H^+ \rightarrow 1.033\ Ca^{+2} + 0.242\ Fe^{+2} + 0.705\ Mg^{+2} + 0.02\ Mn^{+2} + 2\ HCO_3^{-2} \quad (8)$$

As the positive correlation of Na and K to SO_4 content suggests, also dissolution of alumosilicate minerals (plagioclases, K-feldspars and micas) participates in this process. Sodium content can be derived from the dissolution of NaCl only at its lowest concentration levels (less than 0.6 mmol/L; Fig. 17). Higher sodium concentrations can be explained as plagioclase (Na-Ca feldspar with variable composition) acidic dissolution. Plagioclase andesine, for example, dissolves according to equation (9). Dissolved SiO_2 as co-product of alumosilicate dissolution is not significantly correlated with SO_4 content, probably due to precipitation of quartz as suggested by its stable SI values close to zero (Tab. 4).

$$Na_{0.55}Ca_{0.45}Al_{1.45}Si_{2.55}O_8 + 5.8\ H^+ \rightarrow 0.55\ Na^+ + 0.45\ Ca^{2+}\ 1.45\ Al^{3+} + 2.55\ SiO_2 + 2.9\ H_2O \quad (9)$$

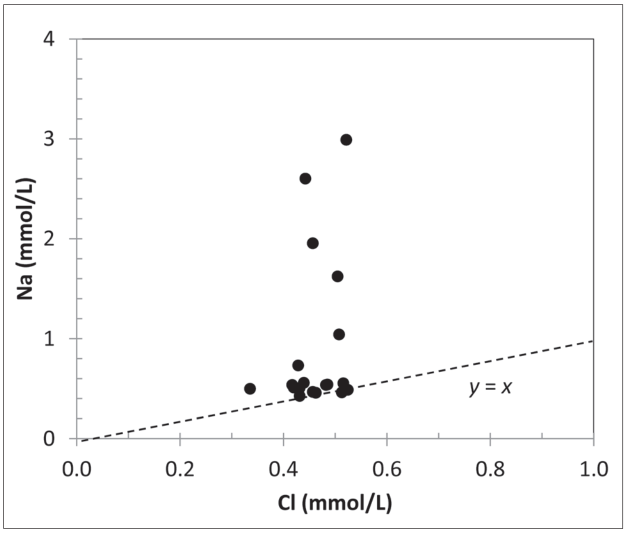


Fig. 17. Sodium versus chloride anion concentrations in mine water.

High content of bicarbonate anion in studied mine water can be considered as a result of ore carbonate dissolution, which can take place in two ways: 1. via sulphuric acid (eq. 1–5) and 2. via carbonic acid (proportional to pCO_2 of underground atmosphere). To determine the relative significance of these processes, it is useful to compare the ratio of relevant ions found in the samples with the ratio derived from governing chemical reactions.

In case the dissolution of carbonates is generated by oxidation of pyrite by oxygen, the ratio of ions HCO_3^-/SO_4^{2-} released to the solution is 1 : 1 if no solid $Fe(OH)_3$ precipitate (equation 1), and 1 : 2 if all Fe(II) released from pyrite precipitate (equation 4). Most of mine water samples from flooded Rudňany mine, when shown on the graph, lie around the trend line 4 $HCO_3 = SO_4$ (Fig. 18). It suggests that dissolution of ore carbonates via sulphuric acid is to a large extent accompanied by their dissolution via carbonic acid.

$P(CO_2)$ values calculated from mine water samples taken from Rochus adit indicate that the conditions of an open carbonate system persist in the zone of water chemistry formation, with relatively stable CO_2 partial pressure of $10^{-2.1}$–$10^{-1.5}$ atm (Fig. 11). Such a level of $P(CO_2)$ value is typical for the soil atmosphere conditions. However, $P(CO_2)$ values, obtained from archival mine water samples, representing a mine atmosphere conditions at the time of mine operation (Fig. 7), indicate transition between air and soil atmosphere. Similar character of mine atmosphere can be expected also in the aeration zone of the current mine, which implies that the mine water acquires its final high and stable bicarbonate content in saturated zone of this mine.

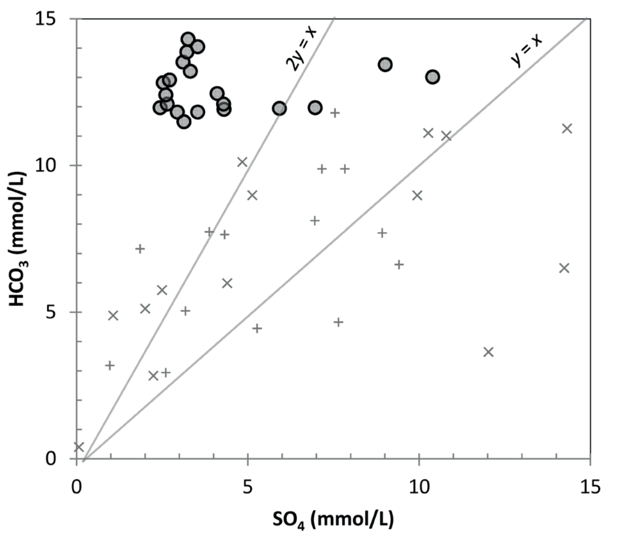


Fig. 18. Scatter plot of bicarbonate and sulphate content in mmol/L.

Forward modelling of mine water chemistry genesis with PHREEQC

For validation of former results and better understanding the evolution of mine water chemical composition at the Rochus mine, a series of simulations has been performed using PHREEQC computer program (Parkhurst & Appelo, 2013). Forward geochemical modelling was used for simulation of the chemical composition of a solution formed on the surface of carbonate minerals occurring

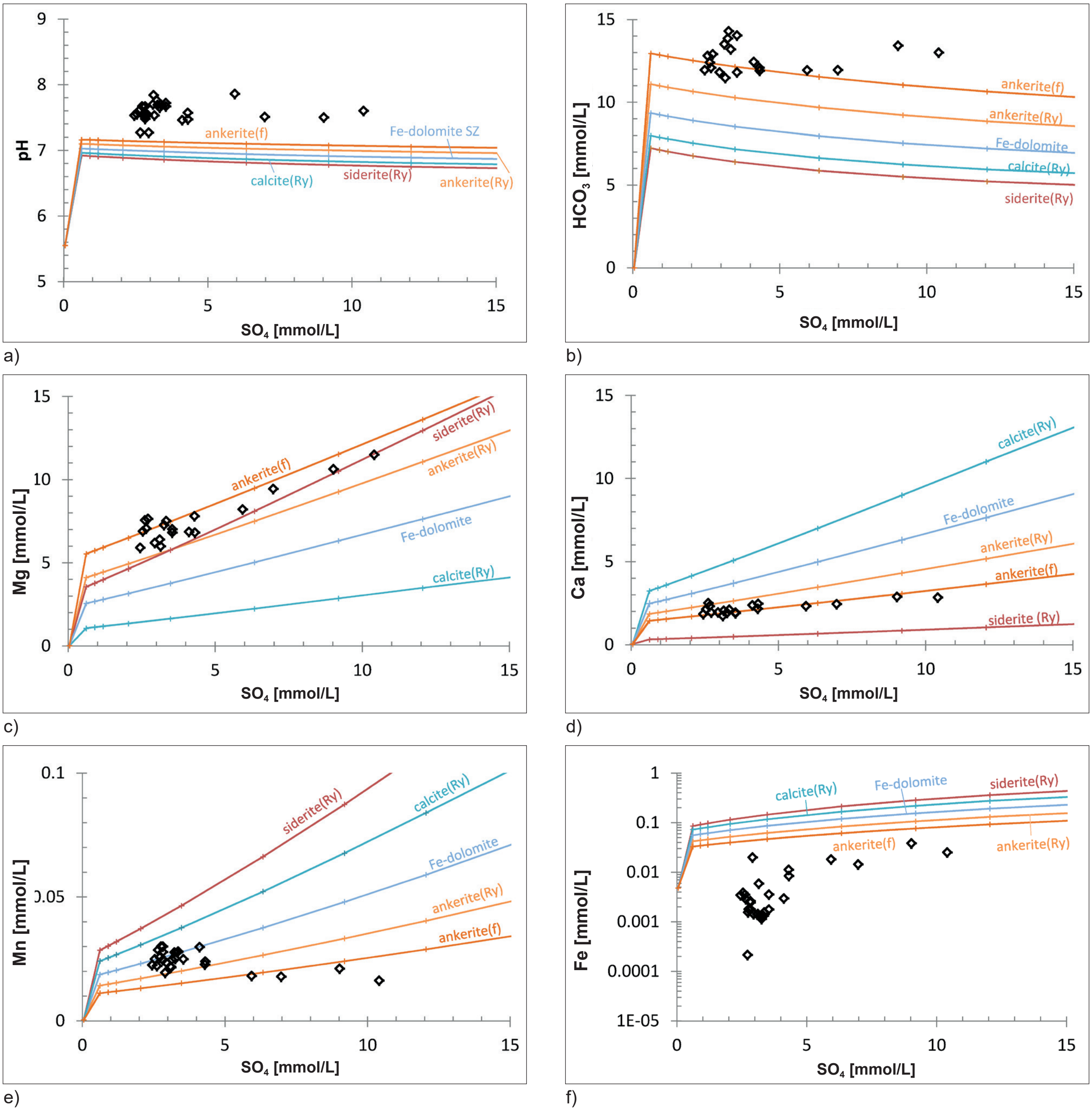
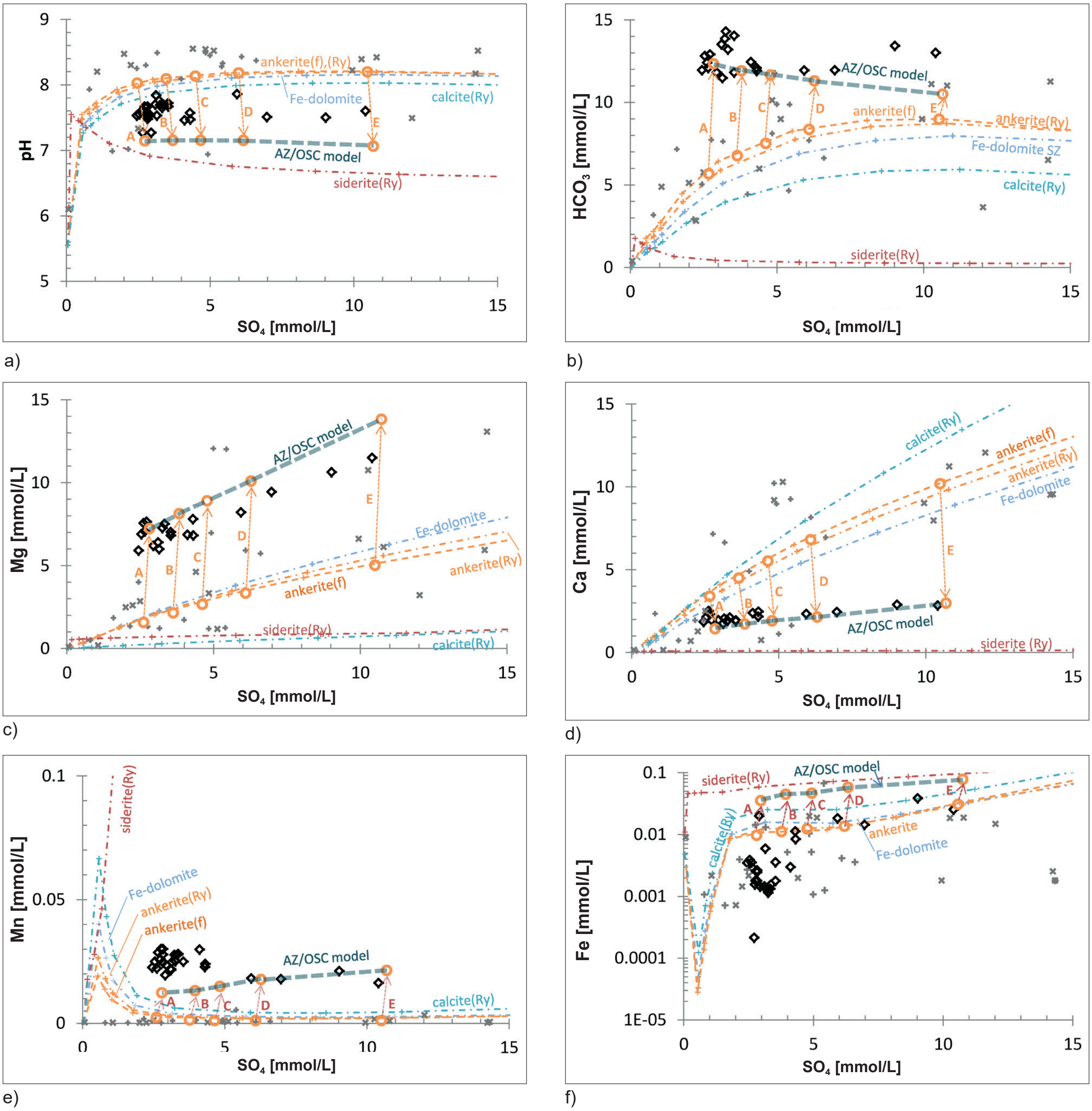


Fig. 19. pH values, bicarbonate, Mg, Ca, Mn and Fe versus sulphate concentrations in mine water samples (points) together with their simulations for variable extent of pyrite oxidation coupled to different ore carbonate minerals dissolution (solid lines), explanation in the text.

in the Droždiak vein, at different intensities of pyrite oxidation, with the possibility of precipitation of various solid phases, under different conditions of CO_2 presence. The simulation results were analysed by comparing them with macro-chemical composition (pH, Mg, Ca, Fe, Mn, SO_4, HCO_3) of mine water samples.

The first series of simulations describes the dissolution of individual ore carbonate minerals via sulphuric acid released under different intensity of pyrite oxidation by oxygen, in open carbonate system (OCS model). In the simulation, oxygen is added irreversibly to atmospheric water in nine amounts (0, 0.5, 1, 2.5, 5, 10, 15, 20, and 30 mmol). Pyrite and one of local ore carbonate minerals [siderite(Ry), ankerite(Ry), Fe-dolomite(Ry) or calcite(Ry)] are allowed to dissolve to equilibrium and carbon dioxide partial pressure (P_{CO2}) is maintained at $10^{-1.4}$ atm (expected partial pressure in “main reaction zone” of mine system). In addition, calcite, siderite, rhodochrosite, nesquehonite, goethite, manganite and gypsum are allowed to precipitate if they become supersaturated.



a)

b)

c)

d)

e)

f)

Fig. 20. pH values, HCO_3, Mg, Ca, Mn and Fe versus sulphate concentrations in mine water samples from the Rochus adit (bold black cross marks), archival samples of pumped mine water (grey plus marks) and water from non-flooded mine rooms on the Droždiak vein (cross marks) together with AZ model (dash dotted line) and AZ/OSC model simulations, for variable extent of pyrite oxidation. Arrows A to E indicate metamorphosis of hypothetical initial solutions, the chemical composition of which is the result of the AZ model, in the saturated zone of the mine (AZ/OSC model). Further explanation is in the text.

Of the model lines constructed from the results of this simulation, the "ankerite(Ry) line" has the best agreement with macro-chemical composition of mine water samples (Fig. 19). As this model slightly underestimates the bicarbonate content (Fig. 19b), the composition of ankerite with a better agreement of the simulation was sought. It was found that the model considering ankerite composition $Ca(_{Fe0.46}Mg_{0.50}Mn_{0.04})(CO_3)_2$ [ankerite(f)] well simulates the concentration Mg, Ca, HCO_3 and Mn. The pH and Fe concentration are simulated less accurately, but best compared to other minerals tested. It follows from the above that among the carbonate minerals present, ankerite can be considered crucial in the formation of the chemical composition of studied mine water.

The second series of simulations describes the dissolution of individual ore carbonate minerals via sulphuric acid released under different intensity of pyrite oxidation by oxygen, in aeration zone of the mine (AZ model). The AZ model is simulated in two steps. In the first of them, oxygen is added irreversibly to atmospheric water in nine amounts (0, 0.5, 1, 2.5, 5, 10, 15, 20, and 30 mmol). Pyrite and one of local ore carbonate minerals are allowed to dissolve to equilibrium. In addition, gypsum, nesquehonite, rhodochrosite, goethite and manganite are allowed to precipitate if they become supersaturated. In the second step, to simulate conditions in aeration zone, P_{CO2} is maintained at $10^{-2.6}$ atm and goethite, manganite and rhodochrosite is allowed to precipitate after reaching supersaturation. Model lines constructed for individual ore carbonate minerals (Fig. 20) show that the dissolution of none of them, or the mixing of the solutions formed by their dissolution (see HCO_3–SO_4 and Mg–SO_4 model lines on Fig. 19b, 19c), does not explain the composition of samples from flooded mine. However, the model lines constructed for the individual ore carbonate minerals are in relatively good agreement with concentrations of SO_4, HCO_3, Mg, Ca, Mn, Fe and pH (Fig. 20) found in mine water samples representing the aeration zone of the mine. These samples were taken from mine workings and from the water pumped from the mine during its operation (Bajtoš, 1999a). This model assumes that Ca-Mg carbonates do not precipitate from solution in significant amounts due to quick movement of water through mine workings, so water is supersaturated with respect to calcite and dolomite.

Hydrogeological conditions of the flooded Rudňany mine determine that mine water chemistry is formed in two main phases. The first phase takes place in aeration zone, where the water gravitationally descends through mine workings and their chemical transformation is described by AZ model. Due to the large spatial variability of the mineralogical composition of ore veins, a diverse chemical composition of individual effluents can be expected. These numerous small tributaries feed the saturation zone, in which they mix during the flow to the Mier shaft. The processes taking place in saturated zone represent the second phase of the mine water chemistry formation. Since oxygen is present in limited amounts below the water table, pyrite oxidation and subsequent acidity production is not intense here and therefore further dissolution of the carbonates can take place only via carbonic acid. Simulations by OCS model showed that high HCO_3 concentrations in the water flowing out of the Mier shaft can be explained by relatively high and stable CO_2 partial pressure of $P(CO_2) = 10^{-1.4}$ atm. However, since previous simulations with this model consider atmospheric water as the initial solution, another/third series of simulations was performed in which the chemical composition of the initial solution is derived from the simulations with AZ model. Five hypothetic initial solutions were defined: A and B solutions correspond to simulated smallest amounts of oxygen consumed by pyrite oxidation, which have been documented at the time of low flow conditions. The C, D and E initial solutions represent middle, higher and highest amounts of oxygen consumed / flow conditions of the mine. Such combination of OCS and AZ model – OCS/AZ model – was used for simulations which assume that ankerite(f) is dominant carbonate mineral considering resulting chemical composition of mine water.

In these models, the relevant initial solution A–E is exposed to $P(CO_2)$ at $10^{-1.4}$ atm, ankerite(f) dissolve and goethite, manganite and rhodochrosite is allowed to precipitate after reaching supersaturation. Graphical connection of endpoints of individual AZ/OCS-A–E simulations on graphs (Fig. 20) creates AZ/OCS model lines representing expected final water chemical composition. The agreement of these model lines with the projection points of water samples from the Rochus adit is very good (taking into account the complexity of modelled environment) for HCO_3, Mg and Ca. The measured pH values are 0.3–0.7 units higher than simulated ones, due to the release of free CO_2 from water during flow through Rochus adit from the Mier shaft to its mouth. Observed Mn concentrations (Fig. 20e) correspond well with those simulated for higher SO_4 levels, for lower ones they are approximately 2 times higher. Detected Fe concentrations (Fig. 20f) are in most cases more than 1 order of magnitude lower than simulated ones, probably due to Fe-ochre precipitation from water during the flow through the Rochus adit. As iron is very redox sensitive element, such a weak agreement was expected in given complex conditions.

The studied process of mine water chemistry formation also includes precipitation of solid / mineral phases. If we consider dissolving ankerite(f) as the only carbonate mineral in saturated zone in AZ model – in the range of measured low flow data corresponding to the consumption of 3.9–6.10 mmol/L of oxygen in the oxidation of pyrite – the amount of 1.2–1.9 mmol of pyrite and 3.3–4.6 mmol of ankerite(f) is dissolved and 2.8–4.9 mmol of goethite precipitate and 0.8–1.6 mmol CO_2 per liter of water is released into underground atmosphere. Subsequent mine water chemistry modification/transformation in saturated zone is predicted by AZ/OCS model. According to AZ/OCS-A simulation, 1 liter of initial solution dissolves 11.2 mmol of ankerite(f), 0.1 mmol of pyrite and 5.4 mmol of $CO_2(g)$, while 13.1 mmol of calcite, 5.2 mmol of siderite and 0.4 mmol of rhodochrosite precipitates. With increasing TDS content in initial solutions (in water entering saturated zone), the amount of dissolved ankerite(f) and precipitated solid phases increases, while amount of CO_2 consumed decreases. The amount of dissolved pyrite is low and stable, as only oxygen brought by advective transport in the initial solution is available.

Most of the evaluated samples (20 of 28) of water discharging through the Rochus adit correspond to low or middle flow conditions, when 20–70 L/s of water flowed out of the mine. The SO_4 content in this group of samples varies from 235 to 340 mg/L (2.44–3.54 mmol/L), which corresponds to simulated conditions when 3.2–5.1 mmol/L (OCS model) or 3.9–6.1 mmol/L (AZ model) of oxygen is consumed in the oxidation of pyrite coupled to ankerite(f) dissolution in aeration zone of the mine. Whereas at water saturated conditions the oxygen concentration is limited to solubility of oxygen in water, or 0.26–0.40 mmol/L at 25–5 °C, such an intensity of oxidation must be forced not only by advective transport of oxygen with atmospheric water, but also by air convection or diffusion.

The presented analysis of hydrochemical data suggests that chemical composition of the flooded Rochus mine water arises in three main phases (Fig. 21). The first (A phase) takes place in aeration zone of the mine, where the oxidation of pyrite by oxygen and the ankerite dissolution dominate. The saturated zone of the mine is probably dominated by the dissolution of ankerite intensified by the supply of deep CO_2 (zone B), which causes an increase and stabilization of HCO_3^- content in the mine water. These two phases of mine water genesis are permanent and during low flow conditions lead to a relatively stable mine water composition. During high flow conditions, mine water of shallow circulation probably mixes with stagnant, higher mineralized water (C phase), which causes an

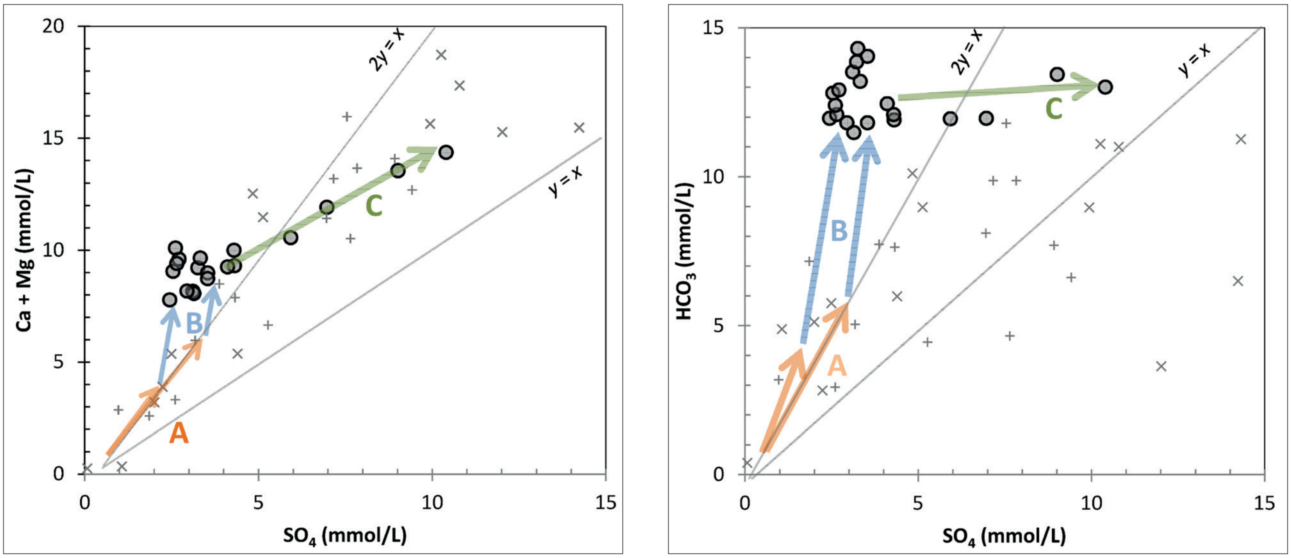


Fig. 21. Concentrations of $Ca^{2+} + Mg^{2+}$ and HCO_3^- versus SO_4^{2-} in mine water outflowing from flooded mine (full circles on the chart) as the result of three-phase (A, B, C) evolution. Archival samples of pumped mine water are represented by grey plus marks and water from non-flooded mine rooms on the Droždiak vein by cross marks. Further explanation is in the text.

Only 8 of the evaluated samples correspond to high flow conditions when the SO_4 content reaches up to 1 g/L (10.4 mmol/L). This would correspond to 17 or 20 mmol/L of oxygen consumed, according to models OCS and AZ/SZ, respectively. However, in such flow conditions, the influence of other factors can also be expected. An increase in concentrations of macro-chemical components during high flow rates may be due to rapid dissolution of soluble salts which have gradually accumulated in aeration zone during precipitation-free periods. However, these salts are also a product of sulphide oxidation. Another possible explanation is the mobilization of more mineralized stagnant water from deeper or less hydraulically connected parts of the mine, where water stratification occurs. Taking into account high and relatively stable bicarbonate content in mine water, the second from these options seem to be more likely.

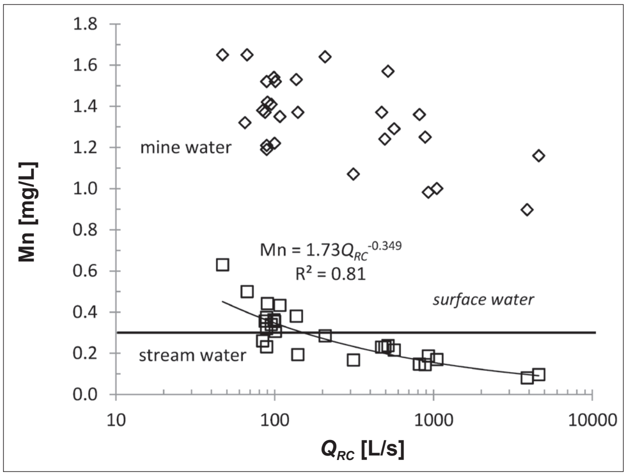


Fig. 22. Manganese concentration in mine water samples (rhombus marks) and calculated manganese concentration in water of the Rudniansky potok creek (square marks) in relation to discharge of this creek (Q_{RC}).

significant increase in SO_4, Mg, Ca content, as well as to less significant increase in content of other compounds.

The performed simulations show that the concentrations of calcium, iron and manganese in mine water are significantly controlled by precipitation of solid phases. In simulations performed in this study, the choice of calcite precipitation showed better match with observations than aragonite precipitation. However, aragonite is reported to occur in the form of crusts and aggregates on walls of mine workings (Cambel & Jarkovský, 1985). Concerning Fe- and Mn-precipitates, limonite, goethite and psilomelane are mentioned (Bernard, 1961). Regarding the iron content, better simulation results were obtained when considering precipitation of goethite than ferrihydrite. As iron is very redox sensitive element, the achieved low agreement of the simulations with observations was expected in given complex conditions. Manganese is less sensitive in this respect, so the agreement of simulations with measurements is much better – provided that rhodochrosite precipitates (manganite MnOOH is not thermodynamically forced to precipitate according to the simulation results).

Environmental issues

Mine water currently flows out from the Rochus adit directly into the stream, without any treatment. According to SHMI observations, discharge of the Rudniansky creek reaches only 50 L/s during periods of lowest flow conditions. Whereas mine and stream discharges fluctuate almost synchronously (Fig. 4), the mine water with minimum discharge of 13.4 L/s makes up approximately 25 % of the stream discharge in such periods. The proportion of mine water in the stream decreases during higher flow conditions, but positive impact of dilution is partially reduced because of the effect of positive correlation of hazardous substances content with mine water discharge (Tab. 5, Figs. 7, 8 and 10). However, this is not the case with manganese, which correlates negatively (Fig. 9). Manganese concentration in the Rudniansky potok creek in a place under the inflow of mine water, calculated using mixing equation, vary between 0.081 and 0.631 mg/L. It negatively correlates with the Rudniansky potok creek discharge (Fig. 22) suggesting that surface water quality limit is usually exceeded at stream discharges below 150 L/s – which usually last 180 days a year. Concentration of sulphate anion drops to 50–110 mg/L after dilution, well below the limit. Also TDS and Mg content are attenuated by dilution effectively.

Manganese is considered less of an environmental hazard than many others metals and evidence from the literature suggests that the acute and chronic toxicity of Mn to many freshwater biota was low in the mg/L range (Harford et al., 2015). However, more recent studies have reported some particularly sensitive species (Peters et al., 2010; Harford et al., 2015). Mine water brings manganese to the Rudniansky potok creek mainly in the form of simple Mn^{2+} cation (Tab. 5) which is considered to be more toxic than complex $[MnSO_4]^0$ and $[MnHCO_3]^+$ species present. The Mn^{2+} portion in total Mn^T concentration is relatively stable over time, but slightly negatively correlates with mine water discharge (Fig. 23).

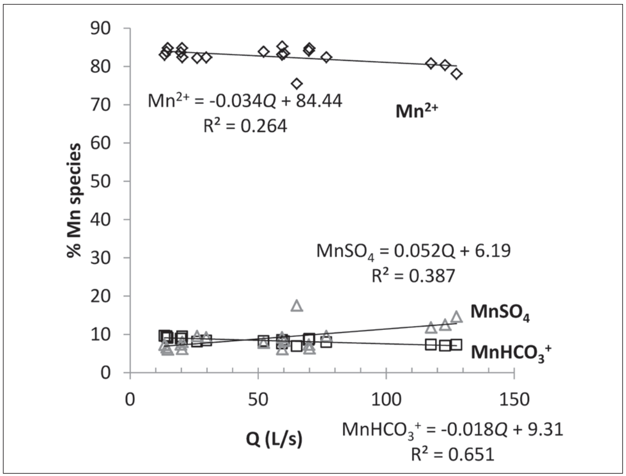


Fig. 23. Distribution of Mn species in mine water samples in relation to mine water discharge.

Arsenic from mine water is diluted in the stream water to concentrations of 2–4 μg/L. Speciation modelling suggests that As occurs in mine water in the form of pentavalent arsenate As(V) species, when major species $HAsO_4^{2-}$ (77–93 % of total content) dominates over $H_2AsO_4^-$ (7–23 %; Tab. 5). The proportion of these components is not subject to hydrologic regime or seasonal variation (Fig. 24). After dilution in stream water highly saturated with oxygen, arsenic remains in oxidation state (V). Arsenates are generally less soluble and toxic comparing to arsenites As(III) (Korte & Fernando, 1991) and therefore pose less environmental risk. If water treatment is required, arsenates can be more readily removed from the water than arsenites.

Antimony is considered a metalloid non-essential for optimal functioning of biological processes in an organism which, at high concentrations, is more toxic than As (Elinder & Friberg, 1979; Reimann & Caritat, 1998). The leaching of Sb from Sb-containing minerals and rocks may therefore have important ecotoxicological implications. Sb(III) is reported to be more toxic than Sb(V), inorganic species are generally more toxic than organic ones (Stemmer, 1976; WHO, 2008; Filella et al., 2009). Antimony concentration 3–26 μg/L in the mine water of Rochus adit decreases after mixing with the water of the stream to 3–11 μg/L. Such a concentration level classifies this mixed water in category A2 in the classification of surface water intended for the abstraction for drinking purposes (Regulation of the Slovak Government No. 96/2010 Coll.). As can be expected from previous studies at Sb-contaminated sites (Johnson et al., 2005; Takaoka et al., 2005; Okkenhaug et al., 2011), antimony occurs in studied mine water almost exclusively in the form of pentavalent oxyanion, $Sb(OH)_6^-$ species (Tab. 5).

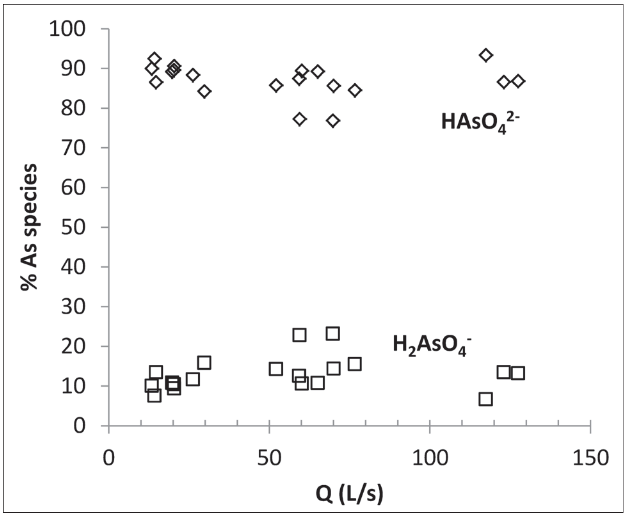


Fig. 24. Distribution of As species in mine water samples in relation to mine water discharge.

Elevated concentrations of Mn, As and Sb caused by the inflow of mine water into the Rudniansky potok creek gradually decrease during its downward flow due to natural processes. The most important factors are dilution by hidden karst groundwater inflows and hydrochemical processes such as precipitation of solid phases and sorption. At the discharge gauging site located 2.7 km below the Rochus adit mouth, contents of Mn 0.10–0.15 mg/L, As 2–11 µg/L and Sb 9–15 µg/L were found by state monitoring of mining impact on the environment (www.geology.sk) in stream water in the years 2012–2013.

Conclusions

Observation of mine water hydrochemical regime at the flooded Rudňany mine (Volovské vrchy Mts, eastern Slovakia) connected to siderite-sulphidic veins hosted by Paleozoic metamorphic rocks revealed positive correlation of the macro-chemical components with mine water discharge. Geochemical calculations and forward modelling based on mine water samples suggest that the mine water chemical composition is formed in three main phases. In the aeration zone of the mine, pyrite oxidation coupled to ankerite dissolution and goethite precipitation in relatively low $P(CO_2)$ conditions is the main geochemical process (A phase in Fig. 21), although most abundant ore minerals are tetrahedrite and chalcopyrite among present sulphides and siderite among carbonates. In saturated zone of the mine (phase B), ankerite dissolution combined with calcite and siderite precipitation in stable, relatively high $P(CO_2)$ conditions (open carbonate system – deep CO_2 supply?) leads to an increase of magnesium, decrease of calcium and stabilization of high hydrocarbonate ion content in water flowing out of the mine. During high flow conditions, mine water of shallow circulation probably mixes with stagnant, higher mineralized water (C phase), which causes an significant short-term increase in SO_4, Mg, Ca content, as well as to less significant increase in content of other compounds.

Concerning protection of stream water quality, studied mine water is risky due to its high Mn, As, Mg, SO_4 and TDS content. Water quality of the Rudniansky potok creek into which the water from the mine flows is endangered mainly by manganese – presented date suggest that its surface water quality limit is usually exceeded for 180 days a year. Concentration of sulphate anions, magnesium and TDS, as well as arsenic and antimony, drops to levels well below the quality limits after dilution.

Studied mine water is not suitable for drinking purposes due to permanently high TDS, Mn, Mg and SO_4 content, as well as the arsenic and antimony contents occasionally do not meet the limits. Possible future utilization of this mine water for drinking will require, in addition to reducing the concentration of above mentioned elements, also filtration of colloidal ferric (oxy)hydroxides.

The above example clearly demonstrates that detailed knowledge of seasonal hydrochemical regime is necessary for understanding the mine water genesis. It is also indispensable for accurate assessment of the impact of mine water on surface water quality, as well as design of water treatment technologies.

Acknowledgement

The results of this study were obtained owing to the project support of the Ministry of Environment of the Slovak Republic, namely the project "Partial monitoring system – Geological factors", what is gratefully acknowledged by the author. Suggestions and comments of reviewers Renáta Fľaková and Peter Malík contributed to quality of primary manuscript.

References

Al, A. A., Martin, Ch. J & Blowes, D. W., 2000: Carbonate-mineral/water interactions in sulfide-rich mine tailings. *Geochim. Cosmochim. Acta, 64, 23, 3933–3948.*

Awe, S. A., Samuelsson, C. & Sandström, A., 2010: Dissolution kinetics of tetrahedrite mineral in alkaline sulphide media. *Hydrometallurgy, 103, 167–175.*

Bajtoš, P., 1993a: The nordern part of the Rudňany ore field, hydrogeological study (in Slovak). *Manuscript. Bratislava, archive SGIDŠ.*

Bajtoš, P., 1993b: Novoveská Huta – Rudňany, mine waters. Hydrogeological survey report (in Slovak). *Manuscript. Bratislava, archive SGIDŠ.*

Bajtoš, P., 1999a: Mine water genesis in the Rudňany ore field (Podmienky tvorby banských vôd Rudnianskeho rudného poľa). *Podzemná voda, 2, 74–80.*

Bajtoš, P., 1999b: Impact of mine working on the hydrogeological conditions of the Rudňany ore field. Proceedings: XXIX. Congress of IAH – Hydrogeology and land use management, Bratislava – Slovakia, 733–738.

Bajtoš, P., Pramuka, S. & Rapant, S., 2012: Partial monitoring system – Geological factors. Subsystem 04: Impact of mining on the environment (in Slovak). *Manuscript. Bratislava, archive SGIDŠ.*

Bajtoš, P., 2016: Mine Waters in the Slovak Part of the Western Carpathians – Distribution, Classification and Related Environmental Issues. *Slovak Geol. Mag., 16, 1, 139–158.*

Bajtoš, P., Záhorová, Ľ., Rapant, S. & Pramuka, S., 2012: Geological monitoring of mining influence on the environment in risk-bearing Slovak areas in years 2007–2011 (in Slovak with English summary). *Miner. Slov., 44, 375–392.*

Baláž, P., 2000: Extractive Metallurgy of Activated Minerals. *Amsterdam, Elsevier.*

Bernard, J. H., 1961: Mineralogie und Geochemie der Siderit – Schwerspatgänge mit Sulfiden in Gebiet von Rudňany (Tschechoslowakei). *Geol. Práce (Bratislava), 58, 1–222.*

Bodiš, D., Lopašovská, M. & Rapant, S., 2000: Chemical composition of snow pack in Slovakia – the results of 25 years monitoring (in Slovak with English summary). *Podzemná voda, VI, 2, 172–173.*

Cambel, B. & Jarkovský, J. (Eds.), 1985: Rudnianske rudné pole – geochemicko-metalogenetická charakteristika (The Rudňany ore field – geochemical-metallogenetic characteristics) (in Slovak with English summary). *Bratislava, Veda.*

Dold, B., 2010: Basic Concepts in Environmental Geochemistry of Sulfidic Mine-Waste Management. In: Sunil Kumar (ed.): Waste Management. *IntechOpen, 1–242.* ISBN 978-953-7619-84-8.

Ehrlich, H. L., 1996: Geomicrobiology. *New York, Dekker, 719 pp.*

Elinder, D. G. & Friberg, L., 1979: Handbook on the Toxicology of Metals (Friberg, L., Nordberg, G. F. & Vouk, V. B. – eds.). *Amsterdam, Elsevier, 283 pp.*

Filella, M., Williams, P. A. & Belzile, N., 2009: Antimony in the environment: knowns and unknowns. *Environ. Chem., 6, 95–105.*

Grecula, P., 1982: Gemerikum – segment riftogénneho bazénu Paleotetýdy (in Slovak with English summary). *Bratislava, Alfa, 1–263.*

Grecula, P., Kobulský, J., Gazdačko, Ľ., Németh, Z., Hraško, Ľ., Novotný, L., Maglay, J., Pramuka, S., Radvanec, M., Kucharič, Ľ., Bajtoš, P. & Záhorová, Ľ., 2011: Vysvetlivky ku geologickej mape Spišsko-gemerského rudohoria 1 : 50 000. *Bratislava, Št. Geol. Úst. D. Štúra, 1–308.*

Grecula, P. (Ed.), Abonyi, A., Abonyiová, M., Antaš, J., Bartalský, B., Bartalský, J., Dianiška, I., Drnzík, E., Ďuďa, R., Gargulák, M., Gazdačko, Ľ., Hudáček, J., Kobulský, J., Lörinz, L., Macko, J., Návesňák, D., Németh, Z., Novotný, L., Radvanec, M., Rojkovič, I., Rozložník, L., Rozložník, O., Varček, C. & Zlocha, J., 1995: Mineral deposits of the Slovak Ore Mountains. Vol. 1. *Bratislava, Geocomplex, 834 pp.*

Harford, A. J., Mooney, T. J., Trenfield, M. A. & van Dam, R. A., 2015: Manganese (Mn) toxicity to tropical freshwater species in low hardness water. *Environ. Toxicol. Chem., 34, 12,* 2856–2863. DOI: /10.1002/etc.3135/.

Johnson, C. A., Moench, H., Wersin, P., Kugler, P. & Wenger, C., 2005: Solubility of antimony and other elements in samples taken from shooting ranges. *J. Environ. Qual., 34, 248–254.*

Korte, N. E. & Fernando, Q., 1991: A review of arsenic (III) in groundwater. *Crit. Rev. Environ. Contr., 21, 1–39.*

Landscape Atlas of the Slovak Republic, 2002: 1st ed. *Bratislava, Ministry Environ Slovak Rep. – Banská Bystrica, Slovak Environ. Agency, 344 pp.*

Moses, C. O., Nordstrom, D. K., Herman, J. S. & Mills, A. L., 1987: Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochim. Cosmochim. Acta, 51, 1561–1571.*

Mello, J., Filo, I., Havrila, J., Ivanička, J., Madarás, J., Németh, Z., Polák, M., Pristaš, J., Vozár, J., Koša, E. & Jacko, S., 2000: Geological map of the Slovenský raj – Galmus Mts. and Hornád Depression at a scale of 1 : 50 000. *Bratislava, Ministry Environ. Slovak Rep. – St. Geol. Inst. D. Štúr.*

Nordstrom, D. K., Jenne, E. A. & Ball, J. V., 1979: Redox equilibria of iron in acid mine waters. In: Jenne, E. A. (ed.): Chemical modeling in aqueous systems. *Amer. Chem. Soc., Symp. Washington, D.C., 93, 51–79.*

Nordstrom, D. K. & Alpers, C. N., 1999: Geochemistry of acid mine waters. In: Plumlee, G. S. & Logsdon, M. J. (Eds.): The Environmental Geochemistry of Mineral Deposits. *Rev. Econ. Geol., 6A, Soc. Econ. Geol., 133–160.*

Nordstrom, D. K. & Southam, G., 1997: Geomicrobiology of sulphide mineral oxidation. In: Banfield, J. F. & Nealson, K. H. (Eds.): Geomicrobiology: Interactions between Microbes and Minerals. *Rev. Miner., 35, 361–390.*

Okkenhaug, G., Zhu, Y.-G., Luo, L., Lei, M., Li, X. & Mulder, J., 2011: Distribution, speciation and availability of antimony (Sb) in plants from an active Sb mining area. *Environ. Pollution, 159, 2427–2434.*

Parkhurst, D. L. & Appelo, C. A. J., 2013: Description of input and examples for PHREEQC version 3 – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *U.S. Geol. Surv. Techn. Methods, 6, A43, 497 p.* (available only at http://pubs.usgs.gov/tm/06/a43/).

Peters, A., Crane, M., Maycock, D., Merrington, G., Simpson, P., Sorokin, N. & Atkinson, C., 2010: Proposed EQS for Water Framework Directive Annex VIII substances: manganese (total dissolved). *Bristol, United Kingdom, Environ. Agency.*

Plumlee, G. S., 1999: The environmental geology of mineral deposits. In: Plumlee, G. S. & Logsdon, M. J. (Eds.): Rew. Econ. Geol. The environmental geochemistry of ore deposits. Part A: *Processes, Techniques Health Iss., 6A, 71–116.*

Plummer, L. N., 1992: Geochemical Modeling of Water-Rock Interaction: Past, Present, Future. In: Kharaka, Y. K. & Maest, A. S. (Eds.): *Water-Rock Interation, 1, Balkema, Rotterdam, Brookfield, 858 pp.*

Radvanec, M. & Gonda, S., 2019: Genetic model of Permian hydrothermal mineralisation in Gemeric unit (W. Carpathians) from the deep-seated zone of anatectic melting to volcanic-exhalative SedEx mineralisation on the surface. *Miner. Slov., 52, 109–156.*

Regulation of the Slovak Government No. 96/2010 Coll. laying down requirements for achieving good water status.

Reimann, C. & de Caritat, P., 1998: Chemical elements in the environment – Factsheets for the Geochemist and Environmental Scientist. *Berlin – Heidelberg, Springer.*

Rimstidt, J. D., Chermak, J. A. & Gagen, P. M., 1994: Rates of reaction of galena, sphalerite, chalcopyrite and arsenopyrite with Fe(III) in acidic solutions. In: Alpers, C. N. & Blowes, D. W. (Eds.): Environmental geochemistry of Sulfide Oxidation. ACS Symposium Series. *Washington, DC, 550, 2–13.*

Stemmer, K. L., 1976: Pharmacology and toxicology of heavy metals: antimony. *Pharm. Ther., A, 1, 157–160.*

Takaoka, M., Fukutani, S., Yamamoto, T., Horiuchi, M., Satta, N., Takeda, N., Oshita, K., Yoneda, M., Morisawa, S. & Tanaka, T., 2005. Determination of chemical form of antimony in contaminated soil around a smelter using X-ray absorption fine structure. *Analyt. Sci., 21, 769–773.*

The Decree of the Ministry of Health of the Slovak Republic No. 247/2017 on requirements for drinking water quality, drinking water quality control, monitoring and management risk of drinking water supply).

Tighe, M., Lockwood, P. & Wilson, S., 2005: Adsorption of antimony(V) by floodplain soils, amorphous iron(III) hydroxide and humic acid. *J. Environ. Monit., 7, 1177–1185.*

Vozárová, A. & Vozár, J., 1988: Late Paleozoic in the West Carpathians. *Bratislava, Geol. Úst. D. Štúra, 314 pp.*

WHO World Health Organisation, 2008: Guidelines for Drinking-water Quality. 3rd ed. incorporating the 1st and 2nd addenda. 1, *Recommendations, 668 pp.*

Využitie analýzy sezónneho hydrochemického režimu vody v zatopenej rudnej bani Rudňany na lepšie pochopenie jej genézy a presnejší odhad jej vplyvu na kvalitu vody v povrchovom toku

Na Slovensku sa nachádzajú stovky opustených hlbinných baní, ktoré sú pozostatkom historickej, ale aj nedávnej ťažby nerastov. Spomedzi 14 vyčlenených banskoložiskových oblastí je najväčšie gemerské pásmo so Spišsko-gemerským rudohorím. Bol v ňom zdokumentovaný výskyt 656 zdrojov banskej vody so sumárnou výdatnosťou 663 L/s (Bajtoš, 2016). Až 535 z nich s celkovou výdatnosťou 456 L/s sa sprístupnilo na ťažbu sideritovo-sulfidických žíl vyvinutých v metamorfovaných horninách paleozoika gemerika. Keďže chemické zloženie týchto zdrojov banskej vody je pomerne variabilné, niektoré z nich môžu slúžiť ako zdroje pitnej vody. Mnohé však predstavujú environmentálne riziko, a to najmä pre anomálny obsah As, Sb, Mn a SO_4. Poznatky o chemickom zložení týchto zdrojov sú zatiaľ založené len na opakovaných laboratórnych analýzach, takže ich hydrochemický režim je zdokumentovaný len čiastočne. Poznanie rozsahu kolísania rizikových prvkov v čase je dôležité pri hodnotení z hľadiska praktického využitia aj pri hodnotení ich environmentálneho rizika. Navyše, môže významne prispieť k pochopeniu geochemických procesov prebiehajúcich v banskom kolektore, ktorých výsledkom je chemické zloženie vody vytekajúcej z bane. Preto sa v rokoch 2012 a 2013 sledoval hydrochemický režim banskej vody zatopenej bane Rochus v Rudňanoch, jednej z najväčších baní v Spišsko-gemerskom rudohorí. Monitoring bol zameraný na dokumentáciu intenzity sezónnych zmien chemického zloženia banskej vody vytekajúcej do Rudnianskeho potoka. Interpretácia získaných údajov smerovala k prevereniu závislosti zmien koncentrácie zložiek rozpustených v banskej vode od jej meniacej sa výdatnosti, identifikácii geochemických procesov prebiehajúcich v banskom kolektore a hodnoteniu miery ovplyvnenia kvality vody Rudnianskeho potoka banskou vodou.

Regresná analýza vzťahu medzi koncentráciou prvkov rozpustených v banskej vode (nezávislé premenné) a jej výdatnosťou (závislá premenná) ukázala, že koncentrácia hlavných iónov Mg, Ca, SO_4 a vedľajších iónov Na, K a As štatisticky významne rastie s rastúcou výdatnosťou (tab. 2, obr. 7, 8). Obsah HCO_3 a Mn (obr. 9) s rastúcou výdatnosťou mierne klesá. Z hľadiska požiadaviek na pitnú vodu najvyššiu medznú hodnotu vo väčšine vzoriek presahuje obsah Sb a vo viacerých vzorkách obsah As. Medznú hodnotu presahujú hodnoty EC a obsah Mn, Mg a SO_4.

Geochemické výpočty a úvahy naznačujú, že pri tvorbe chemického zloženia banskej vody sa uplatňuje rozpúšťanie prítomných rudných karbonátov ako ankerit a siderit (rovnice 1 – 8, obr. 15 a 16) a rozpúšťanie alumosilkátov (rovnica 9), intenzifikované oxidáciou pyritu, ale aj oxidom uhličitým v otvorenom karbonátovom systéme (obr. 11 a 18). Simulácie vývoja chemického zloženia banskej vody tieto predpoklady potvrdzujú, pričom identifikujú ankerit ako geochemicky dominantný rudný karbonát (obr. 19, 20). Výsledkom geochemickej analýzy je predkladaný trojfázový model tvorby chemického zloženia banskej vody vytekajúcej z bane Rochus. Prvá fáza prebieha v nenasýtenej zóne bane, pričom najvýznamnejšími procesmi sú rozpúšťanie ankeritu a oxidácia pyritu. Druhá fáza prebieha v nasýtenej zóne bane, pričom dominuje rozpúšťanie ankeritu, ktoré je pravdepodobne intenzifikované prínosom hlbinného CO_2. Uvedené dva procesy prebiehajú permanentne počas nižších vodných stavov a vedú k relatívne stabilnému chemickému zloženiu banskej vody. V období vyšších vodných stavov významne narastá koncentrácia SO_4, Mg, Ca, ale aj Na a As, pravdepodobne ako dôsledok primiešania vyššie mineralizovanej vody stagnujúcej v hlbších alebo hydraulicky viac izolovaných častiach zatopenej bane.

Banská voda vyteká z bane do miestneho Rudnianskeho potoka a negatívne ovplyvňuje jeho kvalitu hlavne prínosom mangánu. Jeho obsah v toku prevyšuje environmentálny limit v obdobiach, keď je prietok toku nižší ako 150 L/s. Zvyčajne to trvá 180 dní v roku. Anomálny obsah SO_4, Mg, As a Sb v banskej vode je po jej vstupe do potoka dostatočne zriedený a neprekračuje environmentálne limity.

Doručené / Received: 2. 6. 2022
Prijaté na publikovanie / Accepted: 21. 6. 2022