Influence of Acid Mine Drainage on Surface Water Quality

M. Bálintová, E. Singovszká, M. Holub, and Š. Demčák

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Abstract Acid mine drainage (AMD) has been a detrimental by-product of sulphidic ores mining for many years. In most cases, this acid comes primarily from oxidation of iron sulphide, which is often found in conjunction with valuable metals. AMD is a worldwide problem, leading to ecological destruction in watersheds and the contamination of human water sources by sulfuric acid and heavy metals, including arsenic, copper and lead.

The Slovak Republic belongs to the countries with long mining tradition, especially in connection with the mining of iron, copper, gold, silver and another polymetallic ores. The abandoned mine Smolnik is one of these mines where AMD is produced.

Acid mine drainage from an abandoned sulphide mine in Smolnik, with the flow rates of 5–10 L s^{-1} and a pH of 3.7–4.1, flows into Smolnik creek and adversely affects the stream's water quality and ecology. High rainfall events increase the flow of Smolnik Creek, which ranges from 0.3 to 2.0 m^3 s^{-1} (monitored 2006–2016).

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Increased flow is associated also with a pH increase and precipitation of metals (Fe, Al, Cu and Zn) and their accumulation in sediment. The dependence of pH on flow in Smolnik Creek was evaluated using regression analysis.

The study also deals with the metal distribution between water and sediment in the Smolnik creek depending on pH and the metal concentrations.

Keywords Acid mine drainage, Heavy metals, pH, Surface water

1 Introduction

Mine waters origin during the exploitation, mainly after closing down the exploitation of mineral deposits running in the contact zones of water and geological environment [1]. Mine waters contaminate the ground and surface waters by a wide range of elements. Besides that, a part of heavy metals accumulates in both the inorganic part of the soil profile and the organic matter, thence inducing major deformations of their macro and microbiological structures. Acid mine drainage negatively affects the plants, animals, fish and aquatic insects (zoobentos) [2]. The pH of mine water is determined by the quality/quantity of present minerals in the deposit. Generally speaking, the mine water from deposits containing mainly acidic (sulphide) minerals produce acid mine water (pH $<$ 6); deposits containing mainly alkaline (carbonate) minerals (also in case of the significant content of sulphide amounts) produce alkaline mine water (pH $\geq$ 6). In the deposits with sulphide content occurs specific type of mine water, called acid mine drainage (AMD) with pH values $<$4.5. Their formation is also determined by the existence of autochthonous chemolithotrophic iron- and sulphur-oxidizing bacteria of the genus *Acidithiobacillus*. AMD transport dissolved substances up to the surface, where oxidation of Fe occurs after their contact with air or surface water, producing the ochre precipitates (mainly goethite, jarosite, schwertmannite and ferrihydrite) [3, 4]. Various technologies have been developed and applied for treatment of AMDs, usually divided to passive and active approaches [5]. In the recent 30 years, the facilities of passive and active treatment of mine drainage waters have shifted from experimental testing in laboratory conditions, through the semipilot and pilot plants, to the implementation in large scale in numerous deposits throughout the world. Many research projects confirmed that AMDs treated by both passive and active systems do not negatively affect the environment.

The selection and application of the approaches depend on geochemical, technological, natural, financial and other factors. The virtue of passive treatment of AMDs resides in the use of naturally occurring chemical, biochemical and biological processes. Examples of passive AMD treatment include natural wetlands, constructed wetlands, anoxic limestone drains, systems gradually increasing the environment alkalinity, lime lagoons, open lime canals and bioremediation [1]. Passive systems produce a major disadvantage – production of large amounts of sludge requiring further treatment (as they are composed of a heterogeneous mixture of various compounds with metal content), or final disposal, which is quite finances consuming approach. Active systems of AMD treatment require a continuous presence of personnel, facilities and monitoring systems based on external energy power; however, they provide selective metals recovery from AMDs [6].

Active systems involve methods of chemical neutralization by addition of neutralization agents ($Ca(OH)_2$, CaO, NaOH, etc.), which induces pH increase and subsequent precipitation of metals in the form of hydroxides [5]. Other active systems for metal removal from AMDs use precipitation of metals in the form of weak soluble sulphides using the precipitation agents (sodium sulphide, ammonium sulphide or hydrogen sulphide) prepared either by chemical means [7] or biologically using the sulphate-reducing bacteria [6]. Active systems also involve aeration, neutralization (with precipitation of metals and sulphates), chemical precipitation of metals and sulphates, membrane processes, ion exchange, adsorption and biological-chemical methods.

Environmental technologies, specifically bioremediation gain the higher level of topicality by a solution of AMD problematic. The ground of the bioremediation is the controlled intensifying of the biogeochemical cycles of metals, routinely running in the natural waters under the influence of microorganisms (MO), which participate on the basis of their fundamental metabolic processes in the solubilization and immobilization of metals in AMD [8, 9]. Bioremediation is the economic and ecological option of conventional physical-chemical processes of metals elimination in waters and sediments. It makes use the genetic diversity and metabolic versatility of MO. Metals immobilization under the MO impression can be the result of biosorption, bioaccumulation, or precipitation [10].

1.1 The Sources of Mine Waters in Slovakia

The main sources of mine waters stem from remnants of mining activities (flooded shafts, dumps and sludge lagoons) representing the old mine loads belonging to the group of environmental loads [11]. The issues of elimination of environmental loads concerning the legislation are encompassed in various strategic documents of the Government of Slovak Republic, such as National Programme of Remediation of Environmental Loads (2010–2015), Regulation No. 153/2010, Act 409/2011 Coll. on Certain Measures Concerning Environmental Load, etc.

Typical examples of old mining loads are abandoned deposits Smolník, Poproč, Čučma, Pezinok, waste storage in Šobov, etc. [11–13]. The main sources of environmental risks in mentioned deposits are water discharges with limit exceeding concentrations of metals and metalloids in comparison with SR Government Regulation 269/2010 Coll [14, 15]. AMD production with the occurrence of genus *Acidithiobacillus* bacteria and limit exceeding concentrations of metals and sulphates is documented in bearings Smolník, Šobov, Pezinok, Slovinky, Rožňava and Rudňany [16]. Discharges of highly mineralized and mild alkaline/alkaline mine water, containing limit exceeding concentrations of metals/metalloids, are located in bearings Poproč, Čučma and Dúbrava [15]. Deposit Smolník belongs to historically most important and richest Cu-Fe ores deposits of Slovakia. Mining was carried out with pauses for several centuries, and the main raw materials were sulphidic pyrite-chalcopyrite ores, from which mainly copper was obtained. Besides classical mining of copper ore, there was also extracted copper by cementation at the site for many centuries.

In view of the spreading rate, pH 3.5–3.9, limit exceeding metal contents (Fe, Zn, Cu, Al and Mn) and sulphates content, as well as presence of genus *Acidithiobacillus* bacteria in acid mine drainage in the effluent from the former shaft Pech (Smolnik), is the object considered to be the most important source of contamination of that site. Based on the results of chemical analysis and flow rate of AMD (cca 10 L/s), it is possible to assume that from the shaft Pech, without spending any costs of mining, leak out 280 t of S, 90 t of Fe, 22 t of Al, 7 t of Mn, 2.5 t of Zn and 370 kg of Cu per year [17]. Given that in the flooded mine remains a large amount of pyrite (approximately 6 miles tonnes) and pyrite is additionally dispersed in the surrounding rock complexes, it is assumed that this process can continue for a very long time [18]. For the purpose of the mentioned AMD remediation, there were studied processes of water dilution, neutralization, application of sorptive/bio-sorptive, precipitating/bio-precipitating and testing pilot project of passive (in situ) treatment system for these mine water [18–20]. The research results have provided a number of positive experiences but also pointed out some negatives. They have contributed to the intention of further research, especially in the field of selective metal removal possibilities [21, 22].

Abandoned deposit Poproč belongs among important, historically mined stibnite ore deposit in Spis Gemer Ore Mountains. The antimony ore mining began probably in seventeenth century. In 1939 there was built flotation plant. Mining finally ended in 1965. After mining and mineral processing, activities remained at the site Poproč piles of mine tailings and ponds with deposited material from the treatment plant, which cause significant pollution of surface water, soils and stream sediments in the river basin Olšava. Another significant source of pollution is especially mine water leaking out from shafts Agnes and Anna. The main contaminants are As and Sb. The highest concentration of As (2,400 μg L^{-1}) was detected in mine water from the shaft Agnes and in seepage water from the tailing pond (1,950 μg L^{-1}). The highest concentration of Sb was detected in water from the shaft Anna, which flows through the heap material (840 μg L^{-1}), in mine water from the shaft Agnes (380 μg L^{-1}) and in seepage water from the tailing pond (400 μg L^{-1}) [23].

Mineralogical, hydrological, pedological and environmental-geological studies of Poproč deposit have been examined especially from the Faculty of Natural Sciences, Comenius University in Bratislava [24]. They obtained results pointing to the possibility of remediation of these mine waters by sorption using Fe0, which was applied in the form of granules, fragments, powder and waste Fe shavings.

Spontaneous self-improvement of the water quality is not feasible; hence it is necessary to monitor the condition of presented mine waters. Simultaneously, the attention should be focused on development of methods for their treatment with the aim to valorise their as potential resources of beneficial metals/metalloids in the form of useful products for practice [10, 25].

2 Influence of AMD on the Smolnik Creek

2.1 Characterization of Study Area

The stratiform deposit Smolnik belongs to the historically best known and richest Cu-Fe ore deposits in Slovakia. In 1990 the mining activity at the locality was stopped. The mine was flooded till 1994. In 1994 an ecological collapse occurred, which caused the death of fish and a negative influence on the environment. The mine system represents a partly opened geochemical system into which rain and surface water drain [26, 27]. More than 6 million tons of pyrite ores of various qualities have been abandoned in this mine. The analysis of water in the deserted mine and in the broader area surrounding this mine was made after the ecological accident in the Smolnik creek in 1995. Waters from the earth surface penetrated the mine, and they were enriched with metals, and their pH values decreased [12]. Acidity is caused mainly by the oxidation of sulphide minerals. The Pech shaft receives the majority of waters draining from the flooded Smolnik mine area and discharges them in the form of acid mine drainage (pH = 3–4, Fe 500–400 mg L^{-1}; Cu 3–1 mg L^{-1}; Zn 13–8 mg L^{-1} and Al 110–70 mg L^{-1}). "This water acidifies and contaminates not only the Smolnik creek water but transports pollution into the Hnilec River catchment" [28].

2.2 Water and Sediment Quality Monitoring in Smolnik Creek

Water and sediment sampling sites are located at 48° south latitude and 20° east longitude (Fig. 1). The first two sampling sites were situated in the upper part of the Smolnik creek not contaminated by acid mine water from the Pech shaft (1, outside Smolnik village; 2, small bridge, crossing to the Pech shaft). Another two sampling localities were located under the shaft (4, 200 m downstream of the Pech shaft; 5, inflow to the Hnilec river). The outflow of AMD from Pech shaft (Smolnik mine) is numbered as 3. Water and sediment samples were collected from the Smolnik creek during the years 2006–2016. GPS coordinates of sampling sites are in Table 1. Samples were collected according to ISO 5667-6-2005 Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams. Samples were collected once a year (15 sediments and water per year), triplicate sampling from each sample sites.

To determine the pH of water samples, a multifunction device, MX 300 X mate pro (METLER TOLLEDO) was used. The concentrations of metals in water samples were determined by ICP-AES (Varian Vista-MPX, Australia). The samples of sediment were air-dried and ground by using a planetary mill and sieved to a fraction of 0.063 mm. The chemical composition of sediments was determined by means of X-ray fluorescence (XRF) method using SPECTRO iQ II (Ametek, Germany). The sediment samples were prepared as pressed tablets with a diameter of 32 mm by

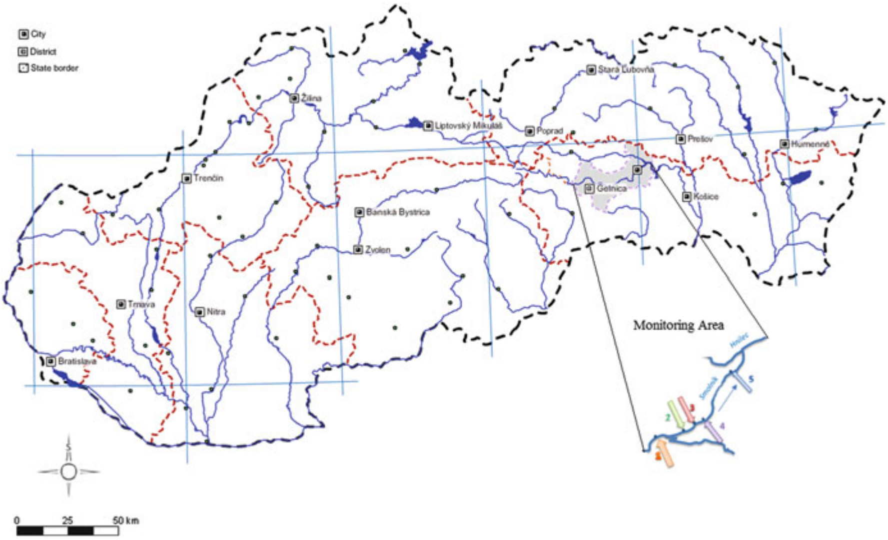


Fig. 1 Location of the Smolnik creek on the map of Slovak Republic and sampling sites No. 1–5 in the study area

Table 1 GPS coordinates of sampling sites

Sample site	GPS coordinates	Description
1	48° 43′ 27.6965658″ N 20° 42′ 59.2164803″ E	Site 1: Uncontaminated part
2	48° 44′ 21.9978463″ N 20° 45′ 37.2264862″ E	Site 2: Uncontaminated part
3	48° 44′ 18.0496747″ N 20° 45′ 44.9512482″ E	Site 3: Source of AMD – shaft Pech
4	48° 44′ 46.1817014″ N 20° 46′ 28.4995937″ E	Site 4: Contaminated part
5	48° 45′ 02.2642765″ N 20° 46′ 39.4108200″ E	Site 5: Contaminated part

mixing 5 g of sediment and 1 g of dilution material (M – HWC) and pressed at a pressure of 0.1 MPa m^{-2}.

For infrared spectroscopy in this study, the spectrum of 4,000–600 cm^{-1} (Alpha FTIR Spectrometer, BRUKER OPTICS) was used.

The crystal structure of sediments was identified with diffractometer Bruker D2 Phaser (Bruker AXS, GmbH, Germany).

Flow data of Smolnik creek were provided by the Slovak Hydro-meteorological Institute (SHI) in Kosice, and the corresponding pH of the surface water was provided by the Slovak Water Management Enterprise (SWME), Kosice. The results were compared to the limit values according to the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. stipulating the requirements for a good water stage achievement. Results of chemical analyses of the sediment were compared with the limited values according to Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields.

3 Monitoring of Water Quality in the Smolnik Creek

The average values of chemical analysis of water samples (samples 1, 2, 4 and 5 in the Smolnik creek as well as AMD from shaft Pech (sample 3) in 2006–2016) are presented in Table 2 and pH of samples in Table 3.

The results in Tables 2 and 3 were compared to limited values in accordance with the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. Stipulating requirements for the quality and qualitative goals of surface water and limit values of indicators of pollution of water wastes and separate waters.

Based on this comparison, we can state that acid mine drainage flowing from the Pech shaft has a permanent adverse effect on the surface water quality in Smolnik creek and produces values exceeding the limits values of the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. Due to increased flows of Smolnik creek in 2011, 2012, 2013 and 2014, pH value of samples No. 1, 2 and 5 (2012, 2013, 2014) was in compliance with limits. From the chemical analysis, given in Table 1, follows, that AMD exceeds each of the evaluated indicators, except Ca, Pb, Mg and As. After AMD dilution with surface water in the Smolnik creek, the concentrations of sulphates, Fe, Mn, Al, Cu and Zn, also exceeded defined limits.

3.1 Study of Sediment Quality in the Smolnik Creek

Results of chemical analyses of the sediments (Table 4) were compared with the limit values according to the Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields. The results showed that rated sediments did not meet the limit values for arsenic and concentrations of lead was also exceeded in two samples.

From the results of chemical analysis of sediments (Table 4), the increase in the concentration of Fe, Cu and Zn in samples S4 and S5 is evident compared to sediment samples S1 and S2. The results are in accordance to literature [29, 30] where iron is precipitated at pH 3.5–4.5, copper at pH 5.5–6.5, Zn at pH 5.5–7.0 and Al at pH 4.5–5.5. The impact of flow on the pH of surface waters in the Smolnik creek was the subject of the next research.

Table 2 Results of chemical analyses of water from Smolnik in 2006–2014

Metals	Unit	Sampling stations					Limits
		1	2	3	4	5	
Ca	mg L^{-1}	9.99 ± 1.34	12.08 ± 2.00	**158.09 ± 19.07**	20.56 ± 5.92	20.03 ± 5.86	**100**
Mg		3.54 ± 0.28	4.74 ± 1.30	**249.64 ± 51.80**	15.90 ± 7.93	23.36 ± 31.76	**200**
Fe		0.12 ± 0.19	0.83 ± 0.88	**322.73 ± 87.58**	**12.74 ± 8.85**	**5.46 ± 5.64**	**2**
Mn		0.01 ± 0.01	0.12 ± 0.11	**25.34 ± 6.27**	**1.17 ± 0.74**	**0.91 ± 0.62**	**0.3**
Al		0.03 ± 0.03	0.15 ± 0.21	**65.11 ± 19.44**	**1.17 ± 1.60**	**0.35 ± 0.72**	**0.2**
Cu	μg L^{-1}	4.09 ± 4.35	12.55 ± 7.45	**1,512.0 ± 736.27**	**96.91 ± 116.09**	**43.00 ± 63.75**	**20**
Zn		4.27 ± 1.35	40.64 ± 42.67	**7,233.5 ± 2,268.8**	**348.82 ± 250.10**	**254.27 ± 213.64**	**100**
As		1.73 ± 1.27	1.36 ± 0.92	**37.36 ± 18.68**	1.55 ± 1.04	1.18 ± 0.60	**20**
Cd		0.30[a]	0.31 ± 0.03	**12.19 ± 8.77**	0.73 ± 0.58	0.41 ± 0.24	**1.5**
Pb		5.00[a]	5.00[a]	**50.18 ± 16.91**	5.27 ± 0.91	5.00[a]	**20**

Within row (for each medium and metal), mean ± standard deviation are significantly different at $p < 0.05$ ($n = 11$)
Within column (Total mean metals within a medium), mean ± standard deviation are significantly different at $p < 0.05$ ($n = 11$)
Bold values are the values that exceed limits according to the Slovak legislative: The Regulation of the Government of the Slovak Republic No. 269/2010 Coll. Stipulating requirements for the quality and qualitative goals of surface water and limit values of indicators of pollution of water wastes and separate waters
[a]Values under detection limits

Table 3 Results of pH of water sampled from Smolnik in 2006–2016

Sample site	pH	Limit
1	6.29 ± 0.77	6–8.5
2	6.44 ± 0.86	
3	4.02 ± 0.13	
4	5.82 ± 1.07	
5	6.06 ± 1.05	

The sediment quality influenced by AMD was evaluated using FTIR and XRD methods. The infrared spectrum of sample S3 confirmed the presence of schwertmannite [31] which is dominated by a broad, OH-stretching band centred at 3,100 cm^{-1} (Fig. 2). Another prominent absorption feature related to H_2O deformation is expressed at 1,634 cm^{-1}. Intense bands at 1,124 and 1,038 cm^{-1} reflect a strong splitting of the $\nu_3(SO_4)$ fundamental due to the formation of a bidentate bridging complex between SO_4 and Fe. This complex may result from the replacement of OH groups by SO_4 at the mineral surface through ligand exchange or by the formation of linkages within the structure during nucleation and subsequent growth of the crystal. Related features due to the presence of structural SO_4 include bands at 981 and 602 cm^{-1} that can be assigned to ν_1 (SO_4) and ν_4 (SO_4), respectively. Vibrations at 753 and 424 cm^{-1} are attributed to Fe-O stretch; however, assignment of the former is tentative because similar bands in the iron oxyhydroxides usually occur at lower frequencies. A broad absorption shoulder in the 800–880 cm^{-1} range is apparent in some specimens and is related to OH deformation (δ(OH)) [32]. These results are in accordance with work [33] where was determined the presence of $Fe_{16}O_{16}(SO_4)_3(OH)_{10}\cdot 10H_2O$ by XRD method in sediment from AMD Smolnik.

FTIR spectra of all homogenized sediment samples (S2 and S4) showed similar features. Based on the concentration of silicon in Table 2 and data from the literature [34] IR spectrum (see Fig. 3), it can be said that the main part of compounds are silicates including quartz (982, 825, 753, 695, 518 cm^{-1}), but hydroxides (3,600–3,650 cm^{-1}; 1,652 cm^{-1}) are present, too. The sample S4 has a bigger portion of hydroxides than sample 2. It is influenced by the metal concentration in surface water influenced by AMD.

The XRD patterns of sediments (S2, S3, S4) are shown together in Fig. 4. The spectra of S2 and S4 sediments are almost identical and contain the phases: Q, quartz SiO_2 (PDF 01 – 075 – 8322): M, muscovite 2M1, ferrian K $Al_{1.65}$ $Fe_{0.35}$ $Mn_{0.02}$ $(Al_{0.7}$ $Si_{3.3}$ $O_{10})$ $(OH)_{1.78}$ $F_{0.22}$ (PDF 01 – 073 – 9857); and C, clinochlore 1MIIb, ferroan $(Mg, Fe)_6$ $(Si, Al)_4O_{10}$ $(OH)_8$ (PDF 00 – 029 – 0701). The most dominant component is quartz with six broad peaks (the strongest line at 26.623° 2Θ).

The spectrum of sediment S3 points to a small part of the crystalline phase. It contains only three weak peaks of clinochlore and one peak of quartz. According to the literature [35], AMD precipitates from shaft Pech contains minerals such as ferrihydrite, goethite, jarosite or schwertmannite. Fresh precipitates are weakly crystallized; formed crystals are very small (tens to hundreds of nm), which is typical for all studied precipitates. Due to their weak crystallinity, it is hard to

Table 4 Results of chemical analyses of sediment from Smolnik in 2006–2014

Elements	Unit	Sampling stations					Limits
		1	2	3	4	5	
$(SO)_4^{2-}$	%	0.03 ± 0.03	0.38 ± 0.28	11.98 ± 3.08	0.74 ± 0.70	0.73 ± 1.47	–
Ca		0.29 ± 0.08	0.21 ± 0.09	0.87 ± 2.61	0.25 ± 0.14	0.22 ± 0.08	
Mg		0.78 ± 0.08	0.73 ± 0.05	0.47 ± 0.40	0.74 ± 0.09	0.68 ± 0.17	
Fe		4.15 ± 0.51	5.05 ± 1.59	34.86 ± 5.49	7.58 ± 3.66	9.40 ± 7.76	
Mn		0.09 ± 0.03	0.05 ± 0.01	0.02 ± 0.03	0.06 ± 0.02	0.06 ± 0.02	
Al		7.39 ± 0.59	6.80 ± 0.38	2.16 ± 1.31	6.49 ± 0.40	6.28 ± 1.25	
Cu	$mg\ kg^{-1}$	131 ± 42	272 ± 103	478 ± 192	378 ± 231	509 ± 154	**1,000**
Zn		149 ± 25	173 ± 48	114 ± 80	189 ± 68	239 ± 47	**2,500**
As		**44 ± 12**	**77 ± 20**	**2,259 ± 812**	**134 ± 75**	**97 ± 25**	**20**
Cd		0.50[a]	0.50[a]	1.10 ± 1.96	0.50[a]	0.50[a]	**10**
Pb		43 ± 10	94 ± 33	**642 ± 837**	160 ± 91	111 ± 42	**750**

Within row (for each medium and metal), mean ± standard deviation are significantly different at $p < 0.05$ ($n = 11$)
Within column (Total mean metals within a medium), mean ± standard deviation are significantly different at $p < 0.05$ ($n = 11$)
Bold values are the values that exceed limits according to the Slovak legislative: The Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields
[a]Values under detection limits

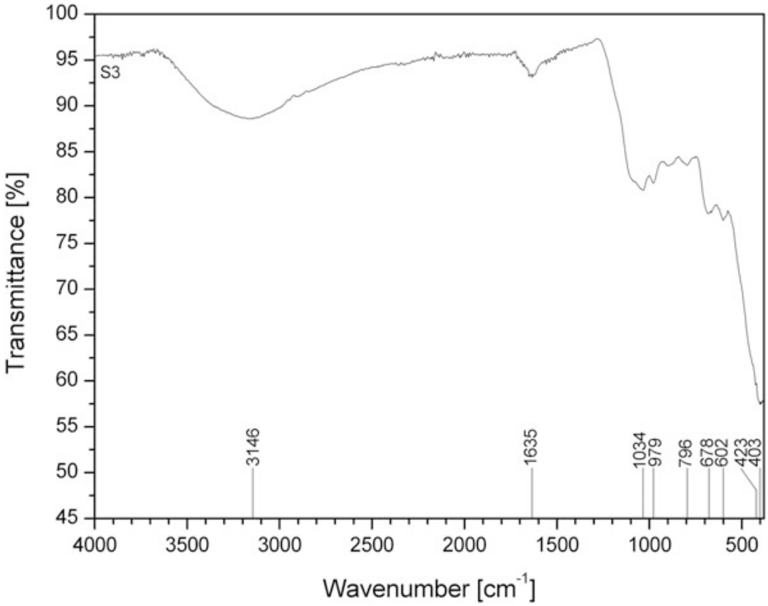


Fig. 2 FTIR spectrum of sediment S3

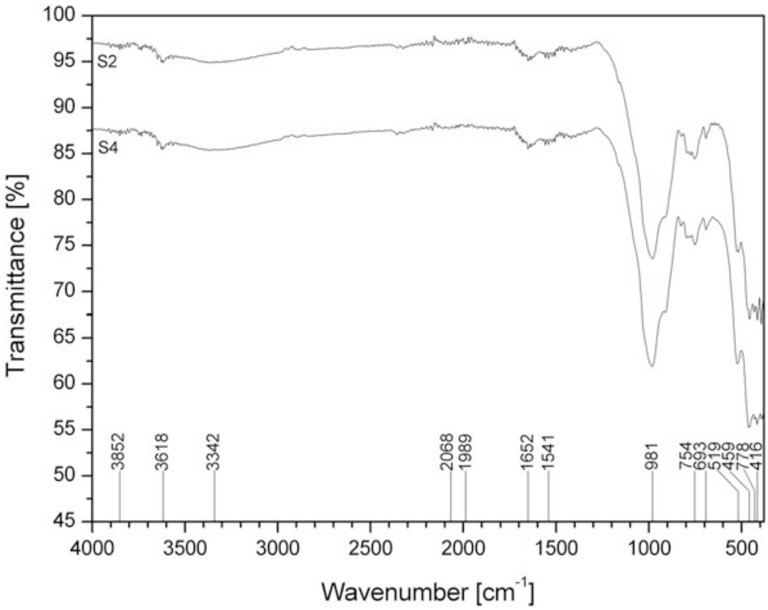


Fig. 3 FTIR spectrum of sediments S2 and S4

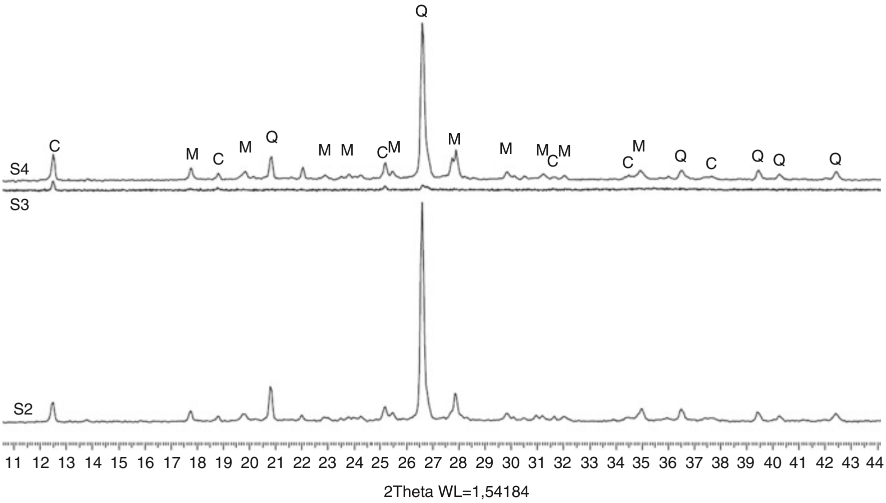


Fig. 4 XRD patterns of sediments S2, S3, S4 (identified compounds: Q, quartz; M, muscovite 2M1, ferrian; C, clinochlore1MIIb, ferroan)

identify only by X-ray diffractometry (XRD) [36], what is evident from XRD pattern of sample S3. Just by a combination of XRD, Mössbauer and infrared spectroscopy, a characterization of their structure is possible.

4 Influence of AMD on pH in Surface Water of the Smolnik Creek

The interdependence between the flow rate and pH in the study area was determined by Gnuplot software and MS Excel [37] (www.gnuplot.info). According to the nature of the data, a logarithmic relation between the values of u (pH) and the flow rate Q, expressed in m^3 s, was considered. This logarithmic relation can be explained by the mixing of creek water and mine drainage, considering process time to be an independent parameter and using the mixing equation:

$$10^{-u_S} Q + 10^{-u_A} Q_A = 10^{-u}(Q + Q_A), \tag{1}$$

in the form

$$u = u_S + \log(Q + Q_A \cdot 10^{u_S - u_A}), \tag{2}$$

where u_S denotes the pH of the water upstream of the pollution source and u_A is the pH of the mine drainage and Q_A the mine drainage flow. The typical values of Q_A can be neglected with respect to Q, and, if the creek flow is relatively small, then Q can be considered to be relatively small with respect to $10^{u\mathrm{S}-u\mathrm{A}}\ Q_{\mathrm{A}}$ as $10^{u\mathrm{S}-u\mathrm{A}} \approx 10^3$. Thus, using the known approximate logarithm relationship:

$$\log(1+\varepsilon) \doteq \varepsilon, \text{for any sufficiently small } \varepsilon, \tag{3}$$

provides the logarithms in the formula (2) with $\varepsilon = Q_{\mathrm{A}}/Q$ and $\varepsilon = 10^{u\mathrm{A}-u\mathrm{S}}Q/Q_{\mathrm{A}}$ in an approximate form:

$$u \doteq u_A - \log Q + \frac{Q_A}{Q} - \frac{Q}{Q_A}10^{u_A-u_S} \tag{4}$$

Then, only one logarithmic function remains. Additionally, the flow Q_{A} is small compared to Q within the given range of water flow, so the term Q_{A}/Q can be neglected. The regression model then consists of linear dependencies on Q and log(Q). Hence, it can be considered in the form:

$$R1 : u = b_1 + a_1 \log Q - c_1 Q \tag{5}$$

This was applied as the principal regression model. It required us to estimate $a_1{}^e$, $b_1{}^e$ and $c_1{}^e$ of unknown parameters a_1, b_1 and c_1 in the numerical analysis by the nonlinear least square method [38]. The computer program Gnuplot (www.gnuplot.info) and, in particular, the command *fit*, which fits a user-defined function to a set of data points, were used.

Given the resulting evaluation and relevance of the model, the calculation was supplemented by statistical analysis [39]. First, a normal distribution of values u with the constant standard deviation σ was assumed. The estimate of the standard deviation S, also calculated by the *fit* command, was calculated by the weighted sum of the squared residuals (WSSR), i.e.:

$$\mathrm{WSSR}_r = \min_{a_r, b_r, c_r} \sum_i \left(u_{ri} - u_{ri}^e\right)^2, \tag{6}$$

where u_{ri}^e was obtained by using a particular regression model R. The *fit* command also provided asymptotic standard errors as a criterion for the qualitative assessment of the *fit* parameter estimates a_r^e, b_r^e and c_r^e.

The average flow rates Q and pH of the AMD from the Pech shaft is presented in Table 5. It can be observed that both flow rate and pH are in a very narrow interval of values. Due to this fact, this data were not further analysed.

Table 5 The average annual values of pH and water flow rates of acid mine drainage from the Pech shaft in 2002–2012

Year	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	Average
Q (L/s)	5.65	6.57	7.3	8.89	7.01	5.25	5.89	6.29	8.24	6.13	4.19	6.49
pH	3.92	3.94	4.01	3.86	3.88	4.11	3.99	3.94	3.81	3.97	3.99	3.95

4.1 Regression Analysis of the Flow Rate and pH of Surface Water in Smolnik Creek

A regression analysis [38, 39] was made in order to find the dependence that pH, denoted as u, had on the flow of water (Q) in Smolnik Creek. For this analysis, 102 values of Smolnik Creek flow rate (SHI) and corresponding pH (SWME) data, collected from 2000 to 2012, were used. For a better interpretation of correlation, extreme flow rates (during the flood in June 2010) exceeding 2 m^3 s were excluded for, as mentioned earlier, Eq. (4) was formulated assuming that the values of Q_A were small with respect to Q. The typical values of Q_A in Table 5 correspond to this assumption.

A nonlinear least squares regression was used to estimate parameters a_1, b_1 and c_1 of Eq. (5). The results obtained by the command fit of the Gnuplot software are shown (Fig. 3). Nevertheless, it seems that the estimates of the parameters (see also the results below for the regression analysis relative to Eq. (8)) do not correspond to the proposed model Eq. (4). The best correspondence is achieved for the parameter b_1, which should correspond to the value $u_A - \log Q_A = 6.138$, using the average values from Table 5. It also reflects the expectation of the pH being a bit less than 7 for higher flow rates of Q. Because the other parameter's estimates are far from the expected values of Eq. (4). Another regression relationship was considered in addition to $R1$ in Eq. (5) to cope with the data obtained and the nature of u distribution. The second chosen model is based on a natural exponential relationship in the form:

$$R2 : u = b_2 - a_2 \exp(-c_2 Q). \tag{7}$$

From this model, the nonlinear least square method determines the estimates a_2^e, b_2^e and c_2^e of the unknown parameters a_2, b_2 and c_2. The results are shown in Fig. 5.

It can be observed that the estimate ${b_2}^e$ in the exponential model is approximately equal to 7 because increasing the flow rate neutralizes the acidic nature of the surface water (pH = 7). The other two parameters reflect the chosen exponential dependency, though there is no way to guess their expected values. In the calculation, we assumed a normal distribution. Such an assumption should confirm 95% of the measured data ranged in the interval $({u_r}^e - 2\sigma, {u_r}^e + 2\sigma)$. This interval is also shown in Fig. 2, where the standard deviation σ is estimated by S or WSSR from Eq. (6). Using the asymptotic error, the parameter estimates obtained from both regression models $R1$ and $R2$, Eqs. (5) and (7), can be written as:

$$\begin{aligned} R1 &: a_1^e = 4.451 \pm 0.618, b_1^e = 7.763 \pm 0.435, c_1^e = 1.088 \pm 0.437, \\ R2 &: a_2^e = 4.256 \pm 0.379, b_2^e = 6.985 \pm 0.178, c_2^e = -2.673 \pm 0.484. \end{aligned} \tag{8}$$

Although the measured data are rather scattered and affected by factors not included in the experiment such as metal precipitation, which lowers the pH [40], the results of the exponential model can be used to predict the values of pH (u), depending on the flow rate Q for a relatively wide range of flow rates. While the

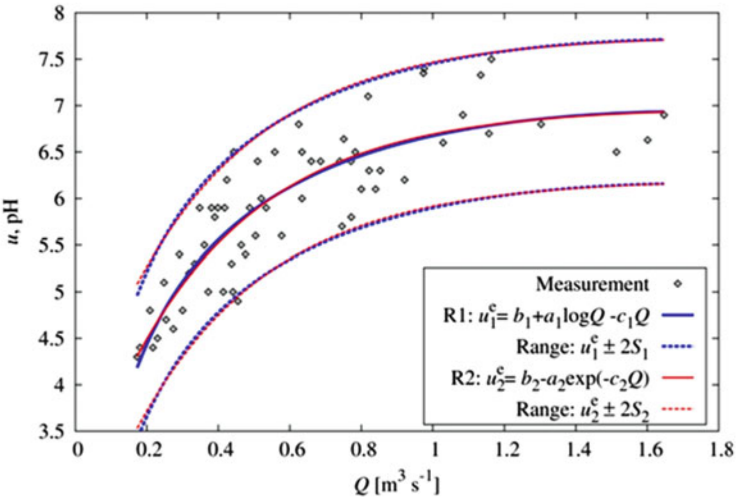


Fig. 5 Dependence of pH and water flow – regression analysis with two models: $R1$ from (Eq. 5) and $R2$ from (Eq. 6)

graphs in Fig. 2 for both proposed regression models are rather coincidental, the asymptotic errors in the parameters are smaller for the exponential model than for the logarithmic one.

5 Study of Metals Distribution Between Water and Sediment in the Smolnik Creek

To study surface water and sediment quality, two sampling localities along the Smolnik creek were chosen (4, approx. 200 m under the shaft Pech; 5, inflow into the Hnilec river). The influence of AMD on surface water and sediment quality and redistribution of the selected metals was studied in the water samples (data from Table 1, sampling stations 4 and 5) and sediments from the Smolnik creek in 2006–2011 (data from Table 4, sampling stations 4 and 5).

Based on laboratory results oriented to the selected metals precipitation from AMD Smolnik [41, 42] and the data from the literature, the redistribution of metals Cu, Fe, Mn, Zn and Al between water sediment in the Smolnik creek was evaluated.

The results of metal concentration decrease in surface water and an increase of metal concentration in sediment were compared with the results of the experimental study focused on pH influence on iron, copper, aluminium, zinc and manganese precipitation from raw AMD from mine Smolnik [21, 41, 42]. It was determined that aluminium is precipitated (98.5%) in the pH range from 4 to 5.5. Precipitation of copper was carried out in accordance with the literature, where copper begins to precipitate at pH $>$ 4 and total precipitation occurs at pH 6 with the efficiency 92.3%.

In spite of iron occurrence in AMD mainly as Fe^{2+}, which precipitates at pH < 8.5, the experimental results confirmed the iron precipitation across studied pH range (4–8) by the progressive oxidation of Fe^{2+} to Fe^{3+} by oxygen from air and its precipitation in the form of $Fe(OH)_3$, which starts at pH 3.5. Zinc is precipitated in the range of pH 5.5–7, and 84% of total Zn was precipitated in this interval.

Precipitation of copper begins at pH > 4 and total precipitation occurs at pH 6. Figure 6 presented dependence of immediate Cu concentration in surface water on its concentration in sediment independence of the pH. As it is seen in Fig. 3, in spite the concentration of Cu in AMD, the decreasing of Cu concentration in surface water with the increasing of pH is connected with its increase in sediment. This is in accordance with literary data and our results [43, 44].

It was determined [41] that iron is in AMD present mainly as Fe^{2+}, which should be precipitated at pH < 8.5 [30, 45, 46]. The reason of the iron precipitation across the range of studied pH may be progressive oxidation of Fe^{2+} to Fe^{3+} in the presence of oxygen and its precipitation in the form of $Fe(OH)_3$, which starts at pH 3.5. From the study of the dependence of Fe concentration in water and sediment resulted, that Fe concentration in sediment varies in the slightest measure in comparison to its concentration in water (Fig. 7).

The interaction among the metals can influence the reaction rate and oxidation state of the metals in the precipitate. For example, manganese will be simultaneously precipitated with iron (II) in water solution at pH 8, only if the concentration of iron in the water is much greater than the manganese content (about four times more). If

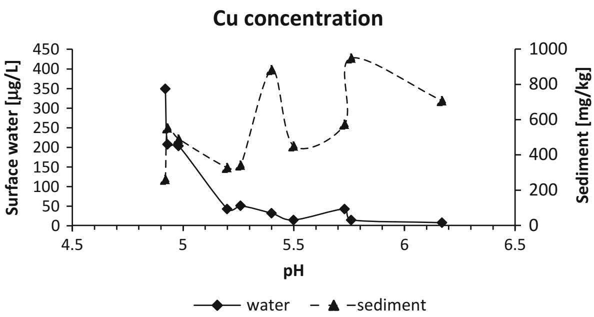


Fig. 6 Influence of pH on Cu concentration in water and sediment in the Smolnik creek

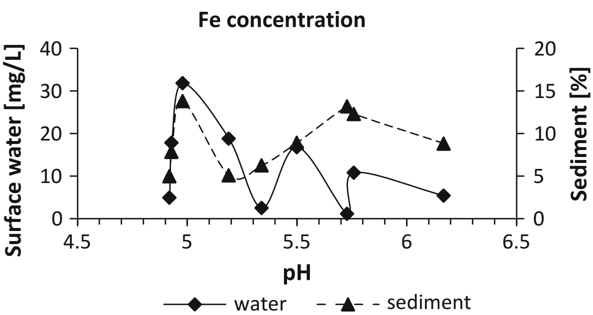


Fig. 7 Influence of pH on Fe concentration in water and sediment in the Smolnik creek

the concentration of iron in AMD is less than four times of the manganese content, then the manganese can be removed from the solution at pH > 9 [47].

The fact that in the presence of a large excess of iron the manganese is precipitated at pH 8 was not confirmed. At pH 8.2 was precipitated only 15.9% of total Mn in AMD. Only at pH 11 was precipitated 93.0% of Mn [42].

In Fig. 8 the dependence of the pH on Mn concentration in water and sediment is presented. As it results from Fig. 3, the variation of Mn concentration in water has minimal influence on its concentration in sediment. The result is in accordance with literature and our research [48, 49].

According to Xinchao et al. [30], Balintova and Kovalikova [45] and Balintova et al. [46], zinc is precipitated in the range of pH 5.5–7. In this interval was precipitated 84% of total Zn [41]. This effect was confirmed by rapid decreasing of Zn concentration in water and its simultaneous increasing in sediment at pH 5.8 (Fig. 9).

Aluminium hydroxide usually precipitates at pH > 5.0 but again dissolves at pH 9.0 [30, 47]. According to Balintova and Petrilakova [42], 98.5% of total aluminium is precipitated from AMD Smolnik in the pH range from 4 to 5.5. The similar tendency can be observed for aluminium, where at the pH > 5.0, the content of Al is decreasing in water and increases in sediment (Fig. 10).

Fig. 8 Influence of pH on Mn concentration in water and sediment in the Smolnik creek

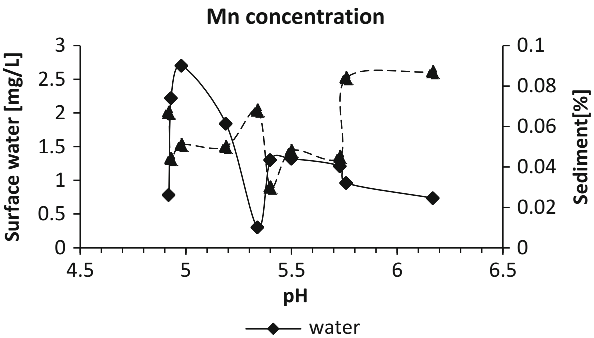


Fig. 9 Influence of pH on Zn concentration in water and sediment in the Smolnik creek

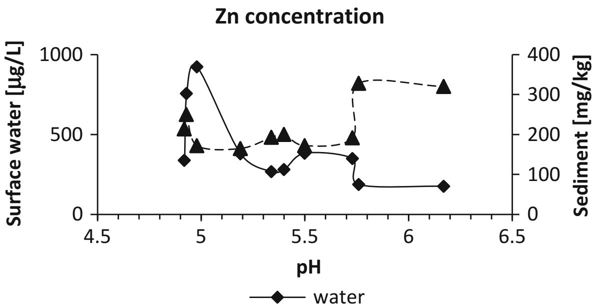
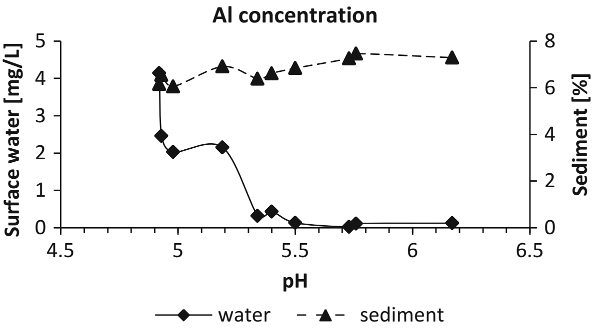


Fig. 10 Influence of pH on Al concentration in water and sediment in the Smolnik creek



6 Conclusions and Recommendations

Smolnik deposit belongs to many localities in Slovakia, where the unfavourable influence of acid mines drainage on the surface water can be observed. Acid mine drainage discharged from abandoned mine Smolnik (shaft Pech) contaminates the downstream from the Smolnik mine works to confluence of the stream with the Hnilec river, because of decreasing pH and heavy metal production. This fact was confirmed by exceeding the limited values of followed physical and chemical parameters in water and sediments in Smolnik creek according to Slovak legislation.

The effect of pH and water flow was studied using regression analysis. The statistical analysis confirmed the significance of the exponential relationship between pH and flow rate. Though both of the models were statistically relevant, the exponential relationship is preferred due to its asymptotic behaviour for increasing flow rate. The obtained numerical results also provide expected values of parameters in the proposed exponential model. The confidence is limited by the scattered character of the experimental data caused by phenomena not considered in the test.

The variability of pH also influences the sediment-water partitioning of heavy metals (e.g. Fe, Cu, Zn, Al, Mn) in Smolnik creek polluted by acid mine drainage, that has been confirmed by presented results. Because AMD generation at the Smolnik locality is not possible to stop and there is no chance of self-improvement of this area, it is necessary to accept this situation, monitor the quality of these waters and develop treatment methods.

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