Effluent water quality and the ochre deposit characteristics of the abandoned Smolník mine, East Slovakia

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This paper presents the results of a 20-year survey of selected physical and chemical parameters of mine drainage and associated stream sediments at the abandoned Smolník deposit (East Slovakia). The Smolník mine was in operation intermittently from the 14th century for Au, Ag, Cu, Fe and pyrite (FeS2). In 1990 - 1994 the mine was finally closed and flooded. In 1997 a remediation effort was initiated in an attempt to improve the quality of acid mine drainage (AMD) from the mine site. Monitoring of the AMD water parameters has continued since 2000 in quarterly intervals. Considering the concentration of dissolved constituents and the flow rate of the AMD, the abandoned Smolník deposit brings about continuous loading of more than 500 kg of dissolved metals per day to the adjacent Smolník stream.

The ochreous precipitates formed from AMD stream were characterized by elemental analysis, X-ray diffraction and scanning electron microscopy. Schwertmannite was the dominant solid phase in the precipitates. The chemical analysis of AMD and the elemental composition of related sediments indicated selective scavenging potential of the precipitates for arsenic and other metal species.

Key words: *Acid mine drainage, water quality, monitoring, sediments, schwertmannite, iron, sulfate precipitation*

Introduction

Extensive mining activities in the region of the Spišsko-gemerské Rudohorie (Ore Mountains Mts.) in Slovakia have left a legacy of numerous old, closed mines after the mining industry started to decline in the 1990s. The closed and abandoned sites are mostly mine workings, waste-rock piles, tailing impoundments, and waste dumps. As a consequence of intensive mining for hundreds of years, adverse environmental effects of acid mine drainage (AMD) are now apparent in mine areas such as Pezinok (Andráš et al., 2004); Šobov (Šottník and Šucha, 2001); Smolník, Hodruša, Rožňava (Mária Baňa), Slovinky, Rudňany and others (Jaško et al., 1996, 1998; Kupka, 2004; Lintnerová et al., 2004; Lintnerová et al., 2009; Šlesárová, 2007). Uncontrolled discharges of waste effluents from abandoned (mostly flooded) mines contaminate surface waters and surrounding environment with heavy metals, sulfates and other oxyanions.

AMD is a serious environmental problem in many countries. AMD occur predominantly in sulfide deposits and originates from the weathering of sulfide bearing rocks. Chemolithotrophic, iron- and sulfur-oxidizing bacteria play an essential role in the weathering of sulfide minerals as they accelerate the oxidation of Fe and S entities in pyrite and other metal sulfides, leading to mineral dissolution and acid generation (Singer and Stumm, 1970; Nordstrom, 1982). Iron and sulfate are the major species in the AMD and their mobility in these natural systems is controlled by their co-precipitation in the form of iron(III) (oxy)hydroxides and hydroxysulfates (Bigham and Nordstrom, 2000). When exposed to air, ferrous iron in these systems is readily oxidized to ferric iron that hydrolyzes and precipitates in a variety of poorly soluble iron minerals. Among these, schwertmannite is perhaps the most frequently formed solid phase in acid mine streams (Eqn 1) (Bigham et al, 1996a).

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(OH)_6SO_4 + 22H^+ \tag{1}$$

Schwertmannite is a poorly crystalline, metastable mineral that transforms spontaneously to goethite, releasing structural sulfate and producing protons (Eqn 2) (Bigham et al, 1996b).

$$Fe_8O_8(OH)_6SO_4 + H_2O \rightarrow 8FeOOH + 2H^+ + SO_4^{2-} \tag{2}$$
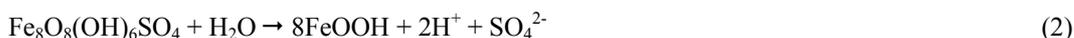
At pH < 2 the transformation of schwertmannite is directed towards jarosite (Eqn 3).

$$Fe_8O_8(OH)_6SO_4 + SO_4^{2-} + K^+ + 16H^+ \rightarrow KFe_3(SO_4)_2(OH)_6 + 5Fe^{3+} + 8H_2O \tag{3}$$

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The transformation of schwertmannite to goethite or jarosite proceeds via the solution phase; i.e., it involves the dissolution of schwertmannite as indicated in the reversal of reaction 1. These interconversions of iron minerals modify the mobility and environmental impact of adsorbed and co-precipitated elements (Cornell and Schwertmann, 2003).

Sediments impacted by AMD receive substantial loads of iron, sulfur and other elements as they co-precipitate with or adsorb onto these secondary mineral phases. Fe(III)-hydroxysulfates from acid mine drainage have been shown to contain arsenic, chromium and a variety of rare earth elements (Schroth et al., 2005; Acero et al., 2006).

This work presents a summary of the results of monitoring the AMD and sediment composition in the Smolník mine area. The Smolník deposit was in operation intermittently from the 14th century for Au, Ag, Cu, Fe and pyrite (Jaško et al, 1996). In 1990 - 1994 the mine was closed and flooded. In 1997 a remediation effort was initiated in order to minimize the production of AMD. This involved diversion of the surface (rain) water upstream the site to decrease the amount of water entering the mine area. The quality of the water draining the site was improved by the addition of alkaline chemicals such as limestone (Jaško et al, 1998). Despite the treatment technologies the AMD still contains appreciable amounts of dissolved metals that exceed the discharge limits pursuant to the Resolution of the Government of the Slovak Republic No. 296/2005. According to the chemical composition and the flow data, a daily loading of total dissolved metals from the flooded mine is approx. 500 kg. The abandoned Smolník sulfide deposit was involved in the list of the most endangered 'hot spot's' sites according to the Inventory of Old Burdens developed by the Ministry of Environment of the Slovak Republic (Palúchová et al, 2008).

Material and methods

Water quality monitoring and evaluation

Multiple samples that provided seasonal variation in water quality were collected from the sampling site at the shaft Pech. This shaft receives the majority of waters draining the flooded Smolník mine area. The water samples were collected, preserved, stored and analyzed according to the Water Act No. 364/204 Coll. as amended by the act No. 384/2009 Coll. and related legislative documents.

The flow rate, temperature, dissolved oxygen, pH, and redox potential (Eh) were measured in the field at the time of water sampling. These measurements were conducted using field-calibrated instruments. Samples for analysis of dissolved metals were acidified with concentrated HNO_3 and transported to the laboratory.

Concentrations of dissolved metals were measured with atomic absorption spectrometry (AAS Spectra AA-30, Varian Scientific Instruments, Mulgrave, Vic., Australia). Iron speciation was determined by the o-phenanthroline colorimetric method (Herrera et al. 1989). Sulfate concentration was determined by the nephelometric method using $BaCl_2$ (Vogel, 1961). Total dissolved solids (TDS) were determined gravimetrically. The pH, Eh, temperature and conductivity were determined by potentiometric and conductometric methods, respectively, using a temperature compensated combined pH electrode, combined Pt-Ag/AgCl redox electrode and conductivity cell.

Analysis of the sediments

Ochreous precipitates were collected from the bottom sediments and walls of the channel that drains the AMD effluent from the shaft Pech into the Smolník stream. The precipitates were washed with distilled water and air dried at 22 ± 2 °C. Dried samples were homogenized in agate mortar and stored in desiccators before analysis.

The chemical composition of solid samples was determined by AAS after digestion with concentrated HNO_3 and HCl (1:1) in a microwave digester.

The X-ray diffraction (XRD) patterns were measured using a Philips PW 1820 powder diffractometer with CuKα radiation. XRD patterns were fitted and analyzed by the Rietveld (profile matching) procedure using the FullProf software package (Rodríguez-Carvajal, 2001).

Solid air dried samples were examined under a model JSM-6400 a scanning electron microscope (SEM) (JEOL Ltd., Tokyo), equipped with an ion microprobe for energy dispersive analysis of X-rays.

Geochemical modeling

The Geochemist's Workbench® (Rockware, Inc., Golden, CO) (Bethke 1996, 2004) was used for geochemical modeling. It is a set of interactive software tools for solving problems in aqueous geochemistry, including those encountered in environmental protection and remediation, petroleum industry and economic geology.

Results and discussion

Monitoring of the AMD effluent from the shaft Pech.

After the closure of the Smolník deposit in 1990, the mine was flooded from December 1990 to May 1994. Changes in the quality of the AMD from 1991 to the present time from the shaft Pech are shown in Fig. 1. After a rapid increase of concentrations of dissolved constituents soon after the end of flooding in June 1994, the concentrations gradually decreased during the subsequent three years. This decrease was connected with the remediation measures. Since 1997, a stable trend of water quality change has been observed. However, the concentrations of individual components are still high and exceed the discharge limits.

In 2010 an intensive rainfall brought about a dramatic increase of concentrations of dissolved components. Owing to anomalous weather conditions in the second quarter of 2010, a substantially larger quantity of water infiltrated the mined area, elevated the level of groundwater and flushed out transiently retained dissolved weathering products of sulfide minerals.

The primary pollutants in the Smolník AMD are iron, sulfate, manganese, aluminum, copper, zinc and arsenic. In the normal regime the flow rate of the mine water reaches 10 l s^{-1} with a pH of 3.9 and an average temperature of 14 °C. Sulfate and ferrous iron, which are the products of pyrite leaching, are the dominant ions in the fresh AMD effluent. The predominance of ferrous iron results from the different kinetics of oxygen-independent sulfide oxidation by Fe^{3+}, and a slower, oxygen-dependent Fe^{2+} reoxidation under oxygen limited conditions in the remaining ore body. In addition, ferric iron is highly insoluble above pH 2.5. Sulfate and ferrous iron are transported in the AMD as dissolved species. When exposed to air, Fe^{2+} can easily be oxidized to Fe^{3+} by chemolithotrophic, acidophilic, iron-oxidizing bacteria that are abundant and indigenous in AMD sites (Kupka, 2001). Hydrated ferric iron hydrolyze and readily precipitate with sulfate in the form of Fe(III)-hydroxysulfates. Aluminum and oxyanions such as arsenate are usually associated with iron precipitates through sorption or solid solution.
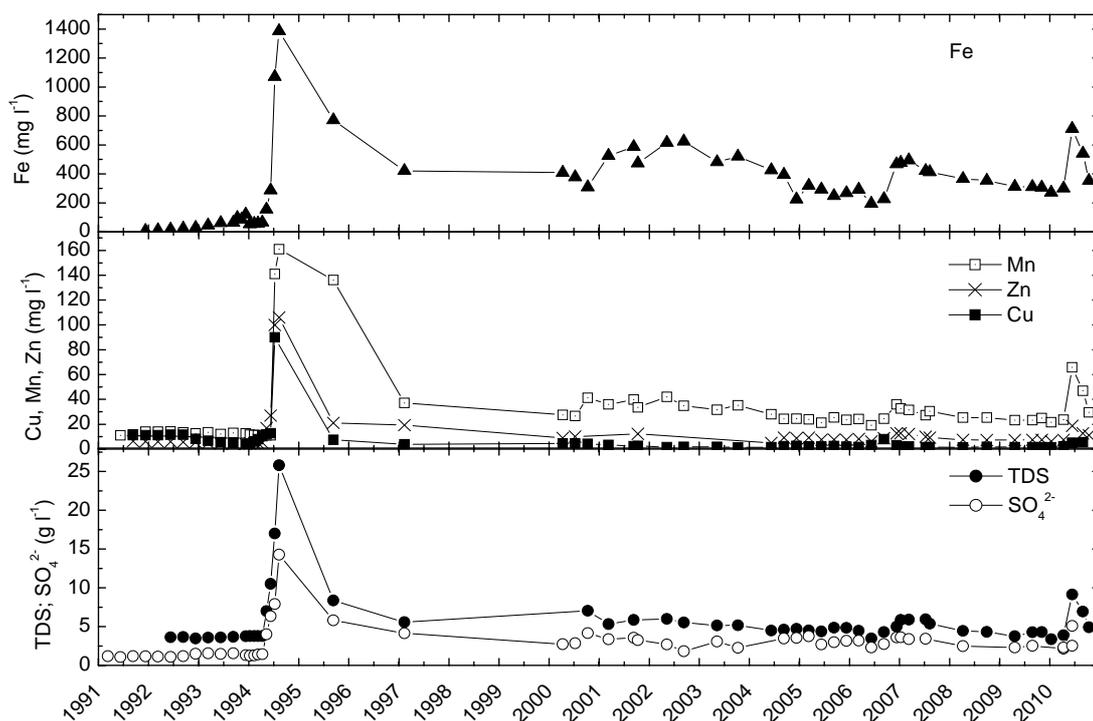
Fig. 1. Changes in the water chemistry at the shaft Pech from 1991 to 2010. Graphs are compilation of author's observations with some data from other sources (Jaško et al., 1996; Jaško et al., 1998; Lintnerová et al., 1999; Šottník et al., 2002).

Geochemical modeling

Geochemical modeling was used to assess the stability of the AMD system and the stability fields of the precipitated minerals (Fig. 2). Under oxidizing conditions, the predominant Fe^{2+} ions in the solution occur mostly as sulfate complexes [FeSO$_4$]^0 and [FeSO$_4$]$^+$. In the range of pH 2.3 to 5.0 iron is stabilized in the form of K-jarosite, and above pH 5.0 it forms amorphous Fe(III)-hydroxide. Thus jarosite and

amorphous Fe(III)-hydroxide control the solubility of iron. High concentrations of sulfates have a significant impact on the stability of this AMD system. The complexing ions Cl^- and F^- have minor impact on the stability of iron in this AMD system.

The thermodynamic database of the Geochemist's Workbench® (version 5.0.6) does not contain thermodynamic constants for schwertmannite. Therefore, the stability field of schwertmannite was approximately delineated in the Eh-pH diagram of the studied AMD system according to the literature data (Schmiermund, 2008) to show its boundaries to the other precipitated compounds.
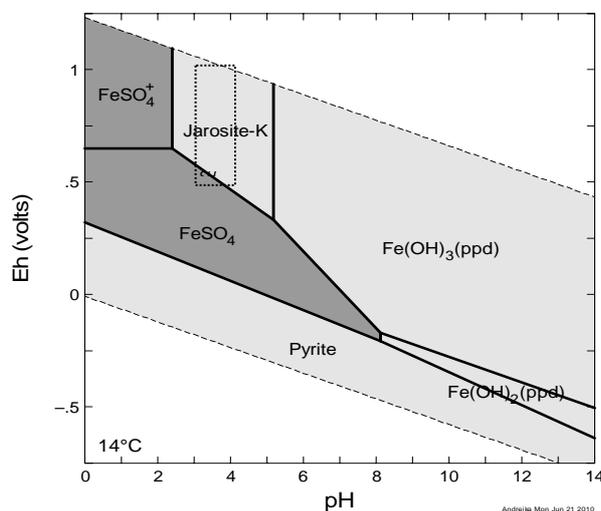
Fig. 2. Eh-pH diagram of the Smolnik AMD system at the shaft Pech (SH = schwertmannite).

Precipitates sampled from the Smolník AMD are shown in Fig. 3. The pH~ 3.9, temperature ~14 ºC and chemical parameters of the water, from which the precipitates are formed, remained relatively stable without significant seasonal variations over a long time periods (Fig. 1). Precipitates occurred in fragile spongy-like formations, which usually occurred on the walls or at the bottom of the draining channel. These formations gradually grew and formed large (>50 cm) blocks of aggregates. Precipitates could be easily removed and dispersed in the water. Large precipitate layers are ultimately broken off by the water movement and transported downstream.

During this study several precipitates were sampled. The specimens were washed in distilled water and dried at 22±2°C. Elemental composition of iron precipitate is summarized in Table 1.

Tab. 1. Chemical analysis of the precipitates formed from AMD (shaft Pech) in Smolník abandoned mine.

Fe	S	Al	Ca	Mg	Na	K	As	Cu	Zn	Mn	Pb
[%]	[%]	[%]	[%]	[%]	[%]	[ppm]	[%]	[ppm]	[ppm]	[ppm]	[ppm]
44.89	5.53	0.38	0.1	0.07	0.02	47.5	0.28	112.5	72.5	35	16.8

The Smolník precipitate sample contained 44.89 % Fe and 5.53 % S, yielding a molar Fe/S ratio of 4.7. This value is within the range of naturally occurring schwertmannites (Bigham et al., 1994). Schwertmannite (ideal formula $Fe_8O_8(OH)_6(SO_4)$) has a molar Fe/S ratio of 8. Variable sulfate content observed in samples of natural schwertmannite is due to a positive charge and high surface area of the mineral, causing sorption of excess sulfate. This results in a higher sulfur content in the analysis (Bigham et al., 1994; Murad et al., 1994; Bigham et al., 1996a).

The presence of minute admixtures of the goethite and of the alunite groups of minerals in the precipitate is likely. The occurrence of arsenic (0.4 wt %) in the sediment suggests strong scavenging by fresh AMD precipitates because the concentration of As in the stream water was relatively low (30 μg.l^{-1}) (Tab. 3).

SEM examination of the precipitate from the shaft Pech (Fig. 1) showed schwertmannite as small, single, quasi-spherical particles of almost identical shape and size as well as aggregates with different sizes. The small spherical particles seemed to be cemented together, forming larger aggregates. The characteristic pin-cushion morphology of schwertmannite described by Bigham et al. (1994) was not discernible in Fig. 1, but this characteristic is not always detectable (Bigham and Nordstrom, 2000). The morphology described here is similar to the one reported by Kawano and Tomita (2001) and Jönsson et al. (2005).

Fig. 3. A sample of ochreous precipitate formed at the AMD discharge from the shaft Pech in the Smolnik abandoned mine.
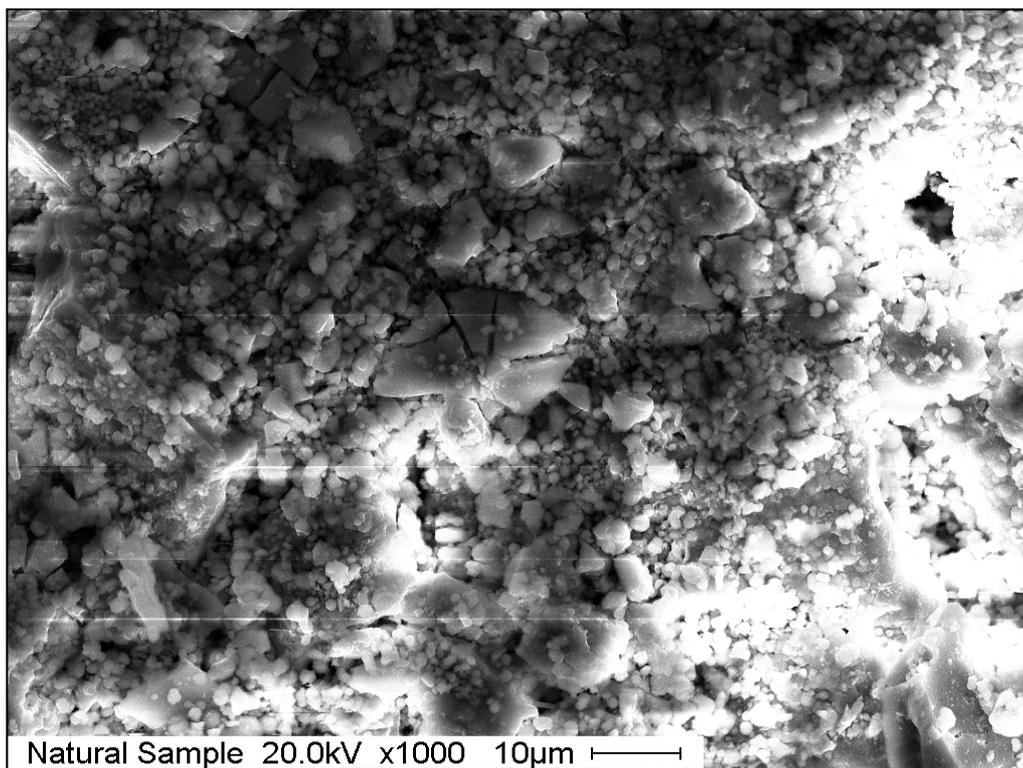
Fig. 4. An SEM micrograph of the Smolník precipitate sample containing schwertmannite as the dominant mineral phase.
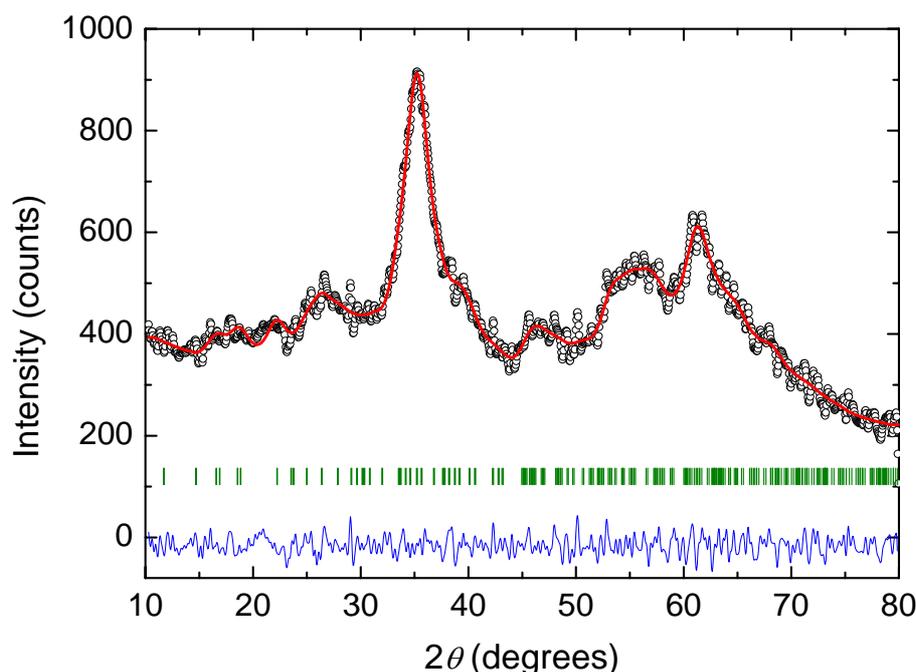
Fig. 5. XRD Rietveld plot of the Smolník precipitate. The measured intensities are indicated by open symbols, overlayed with a calculated line. The positions of all possible Bragg reflections are noted with the vertical marks in the middle. The bottom curve shows the difference between the observed and calculated intensities.

The XRD analysis of the Smolník precipitate gave the characteristic schwertmannite pattern with 8 broad peaks and a relatively high background. The observed pattern of the peak positions, intensity and half width was determined by fitting. This XRD pattern is very similar to that of reference schwertmannite (Bigham, 1994). The refined parameters were consequently determined by the crystal structure refinement procedure using the Rietveld LeBail (profile matching) technique. The observed and refined values of corresponding d_{hkl} are given in the Tab. 3.

Tab. 3. Comparison of observed, calculated and reported XRD peak values for schwertmannite.

Hkl	d_{obs} [Å]	d_{calc} [Å]	d_{calc} [Å] [47-1775]*
210	5.01	4.78	4.86
310	3.43	3.38	3.39
212	2.53	2.55	2.55
302	-	2.30	2.28
412	1.93	1.97	1.95
522	1.66	1.66	1.66
004	1.50	1.51	1.51
204/542	-	1.45	1.46

* JCPDS-PDF, 2004 card number

The refined values of tetragonal cell parameters a = b and c are 10.68(3) Å and 6.02(3) Å, respectively.

The geochemical characteristics of the environment of the Smolník mine site are typical of the other known occurrences of schwertmannite. This mineral usually forms as a result of the rapid oxidation of Fe^{2+} in acid, sulfate rich effluents produced by the decomposition of primary sulfides. Schwertmannite is the most common iron precipitate formed in AMD. The pH range of 3.0 to 4.5 and sulfate concentrations in the range of 1000 to 3000 mg l^{-1} are optimum for schwertmannite formation (Bigham et al., 1996a). Jarosites are good indicators of strongly acidic environments, whereas schwertmannite and goethite (α-FeOOH) are products of pyrite weathering in weakly acidic or neutral environments, respectively (Bigham et al., 1996b). The chemical composition of the mine water from Smolník deposit at the time of sediment sample collection is shown in Tab. 4. The parameters of Pech AMD fit well the geochemical conditions which are conducive to iron precipitation as schwertmannite. Schwertmannite formation is achieved at low levels of potassium and other monovalent cations, which would otherwise facilitate the formation of jarosites. The concentrations

of potassium and sodium (Tab. 4) are insufficient to initiate jarosite formation as dominant phase in fresh AMD precipitates (Gramp et al., 2008).

Tab. 4. Physico-chemical parameters of AMD water from the shaft Pech (April, 2009).

Fe	Al	Ca	Mg	Na	K	As	Cu	Zn	Mn	Pb
[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[µg/l]	[mg/l]	[mg/l]	[mg/l]	[µg/l]
365.6	57.5	115.3	334.4	4.8	3.1	30	1.56	7.3	23.3	20

SO_4	TDS	pH	Redox	O_2	Conduct.	Temp.	Fe^{2+}	Fe^{3+}		
[mg/l]	[mg/l]		[mV]	[%]	[µS/cm]	[°C]	[mg/l]	[mg/l]		
2320.0	3763.5	3.91	375	<10	2490	14.1	366.8	0.03		

Conclusions

The abandoned Smolník sulfide ore deposit is still the source of acid, metal laden effluents that continue to contaminate adjacent streams and sediments. Attenuation of the negative effect of old mine burdens requires long-term and cost-effective technologies that minimize the generation of AMDs. Conventional processes for the treatment of AMDs involve neutralization with alkaline chemicals such as limestone, lime, sodium hydroxide, sodium carbonate or magnesia. Sulfate complexes with calcium form gypsum ($CaSO_4 \cdot 2H_2O$), which precipitates from the solution. This process produces waste sludge containing gypsum and metal hydroxides. The sludge is highly contaminated with heavy metals and must be dewatered and disposed of in landfill (Lyew et al., 1994).

The precipitation of secondary iron minerals from AMD impacts the mobility of iron and sulfate in these systems. The formation of Fe(III)-hydroxysulfates normally takes place at very low pH values which exclude the requirement of neutralizing agent addition, thus minimizing the remediation costs. Iron–oxidizing bacteria facilitate the step of ferrous iron oxidation followed by co-precipitation of sulfate and ferric iron. Freshly precipitated iron minerals can function as sinks for heavy metals and oxyanions.

The design of AMD water treatment technologies should prevent metal transport in both soluble and suspended form in surface waters (Lintnerová et al., 2006). The step that promotes the formation of ferric iron precipitates requires immediate separation of ferric sludge produced in order to ensure retention of the contaminant nearby the source of its origin. The systematic removal of iron precipitates is inevitable because of possible paragenetic transformations between different iron minerals. These interconversions modify the mobility and environmental impact of adsorbed and co-precipitated elements (Cornell and Schwertmann, 2003). Acidophilic iron reducing bacteria that survive in AMD environments cause reductive dissolution of ferric iron minerals in AMD sediments, which promotes mobilization and downstream transportation of iron, sulfate and associated elements (Bridge and Johnson, 2000; Coupland, and Johnson, 2008).

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