Ochreous Precipitates from Smolník Abandoned Mine

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Summary

Metal sulphides of rock origin disrupted by mining activities exposed to oxidation conditions (contact with water and atmospheric oxygen) cause start of processes producing Fe, other metals, sulphates and acidity. The result of oxidizing weathering of iron sulphides is the production of AMD and the consequent formation of ochreous precipitates in drainage systems and in the surroundings of AMD seepage on the surface. Apart from these facts, the genesis of AMD is facilitated by indigenous chemolithotrophic iron and sulphur oxidizing bacteria, especially of genus Acidithiobacillus and Leptospirillum. The long-term monitoring of AMD waters collected at the shaft Pech point at the enduring risk of contamination of particular components of environment in mining area Smolník. Elemental analysis, X-ray diffraction, Mössbauer spectroscopy and scanning electron microscopy of the ochreous precipitates formed in Smolník AMD stream revealed Schwertmannite as the dominant solid phase in the precipitates. The chemical analysis of AMD effluents and the elemental composition of related sediments indicated considerable scavenging potential of the ochreous precipitates towards arsenic, aluminium, lead and other metal species.

Keywords: acid mine drainages, ochreous precipitates, schwertmannite

Introduction

Extremely acidic environments ($pH<3$) occur naturally, though more frequently they are associated with mining and metallurgy activities. [1] After intensive mining for hundreds of years it is possible to observe the negative effect of acid mine drainage effluents in mined areas. Uncontrolled discharges of waste effluents from mostly flooded mines contaminate surface waters and surrounding environment by heavy metals, sulphate and other oxyanions. [2]

Accordingly most research interest has focused on iron- and sulphur oxidizing bacteria. They play essential role in the weathering of sulphide minerals as they accelerate the oxidation of iron and sulphur entities in pyrite and other metal sulphides, leading to mineral dissolution and acid generation. [3] The result of microbial oxidation of Fe- sulphides in oxic zones of acid mine drainages and AMD-impacted sediments is the formation of secondary weathering products, primarily schwertmannite and minerals of the jarosite group. [4]

The precipitation of ferric iron as Fe(III)-hydroxysulfates is pH-dependent, and the chemical composition of AMD–effluents also greatly influences the mineralogical composition of forming precipitates. [4] A pH range of 3.0 to 4.5 and sulphate concentrations in the range of 1000 to 3000 mg/L are optimum for the formation of schwertmannite, while lower pHs at sufficiently high $[SO4]^{2-}$ lead to formation of jarosites. Furthermore, schwertmannite formation does not require the presence of monovalent or divalent cations and removes more ferric iron and less sulphate from the solution phase as compared to jarosite precipitation. [5, 6]

This work points out to the correlation between aqueous geochemistry of AMD and ochreous precipitates. It also presents the results of the analysis of selected physical and chemical parameters of mine drainage and associated stream sediments at the abandoned Smolník deposit (East Slovakia).

Material and methods

Samples of AMD were collected from the sampling site at the shaft Pech quarterly according to the Water Act No. 364/204 Coll. as amended by the Act No. 384/2009 Coll. and related legislative documents. The measurement of tempera-

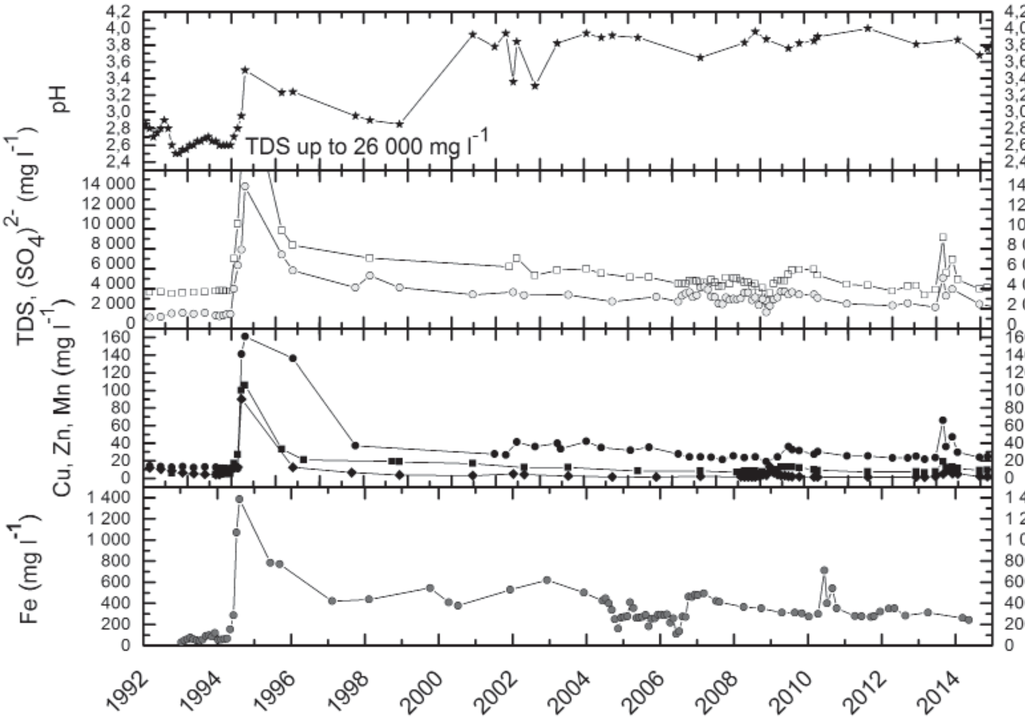

Fig. 1. Chemical analysis of water samples from shaft Pech

Rys. 1. Analiza chemiczna próbek wody pobranej z wału Pech

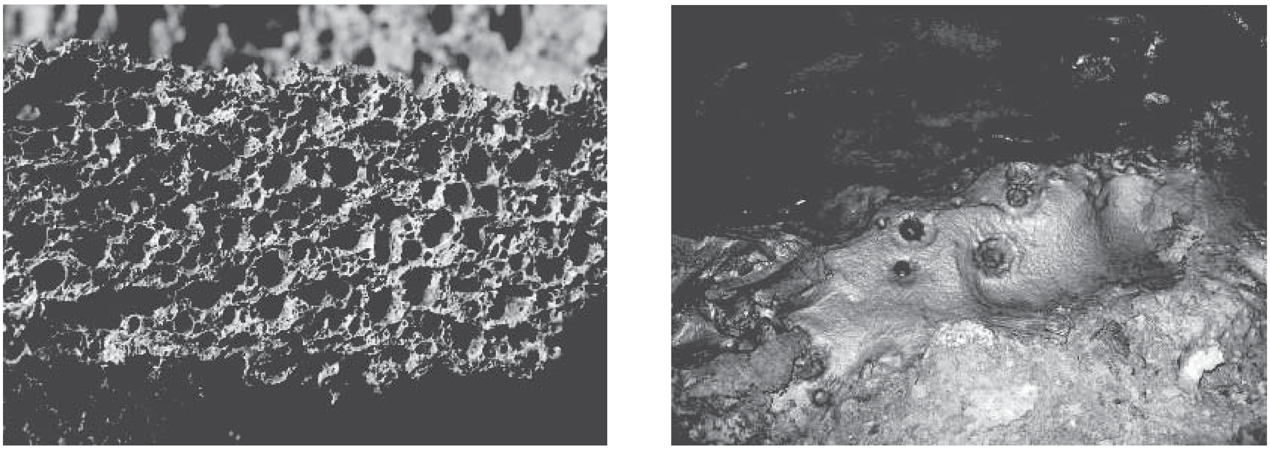

Fig.2a

Fig.2b

Fig. 2. Natural schwertmannit (a) and the colloid phase at the entrance of the mine tunnel covered by ochreous crusts (b)

Rys. 2. Naturalnie występujący schwertmannit (a) i faza koloidalna u wejścia tunelu kopalni pokrytego skorupą ochrową (b)

Tab. 1a. Chemical analysis of ochreous precipitates collected from shaft Pech in Smolník abandoned mine (NSW) and colloid phases (CP-1,2) (major elements)

Tab. 1a. Analiza chemiczna osadów ochrowych zebranych z wału Pech z opuszczonej koplani w Smolniku (NSW) i faz koloidalnych (CP – 1,2) (większe cząsteczki)

Sample	**Fe**	**S**	**Al**	**Ca**	**Mg**	**K**	**Na**
	weight %						
NSW	44.89	5.53	0.38	0.1	0.07	1.13	0.02
CP-1	4.99	0.73	12.1	0.02	0.82	2.9	14.06
CP-2	6.26	1.01	12.72	0.012	0.42	2.72	10.8

ture, pH and redox potential were realised during the sampling using a combined pH electrode and a combined Pt-Ag/AgCl redox electrode. Water samples for the consequent analysis were acidified with concentrated HNO_3. Metals dissolved in AMD were measured with atomic absorption spectrometry (AAS). Total dissolved solids (TDS) were determined gravimetrically and the sulfate concentration by nefelometric method with $BaCl_2$.

The colloid phase sedimentated in the acid mine drainage effluents were collected both near the entrance to the mine tunnel (CP-1) and also in the caxern area with AMD seepage on the surface (CP-2). Ochreous precipitates were collected from the bottom and walls of shaft Pech receiving the majority of waters draining the flooded Smolník mine area. The colloid phase and ochreous precipitates were air dried, homogenized, resolved and than analysed by AAS.

XRD patterns were measured by using a Philips PW 1820 powder diffractometer with CuKα radiation. The JCPDS PDF database was utilized for phase identification. Mössbauer spectra were taken in transmission geometry at temperature T=293 K. A $^{57}Co/Rh$ γ-ray source was used. The velocity scale was calibrated relative to ^{57}Fe in Rh. The Recoil spectral analysis software was used for the quantitative evaluation of the Mössbauer spectra.

Solid precipitates were also examined by scanning electron microscope (SEM, TESCAN MIRA3 FE), equipped with an ion microprobe for energy dispersive analysis of X-rays (EDS, OXFORD).

Results and discussion

Water sample from shaft Pech (Smolník)

The pH of the water sample from shaft Pech after the end of flooding was 3.1 and during the following years it increased to 3.7. It doesn't change either after intense rains. Concentrations of iron, sulphates, some heavy metals and total dissolved solids present in these water samples were figured on Figure 1.

Ochreous precipitates, crusts and colloid phase

On Figure 2 ochreous precipitates floating on the surface of AMD (Figure 2a) and the colloid phase (covered with schwertmannite crusts) sampled in the entrance to the mine tunnel (Figure 2b)

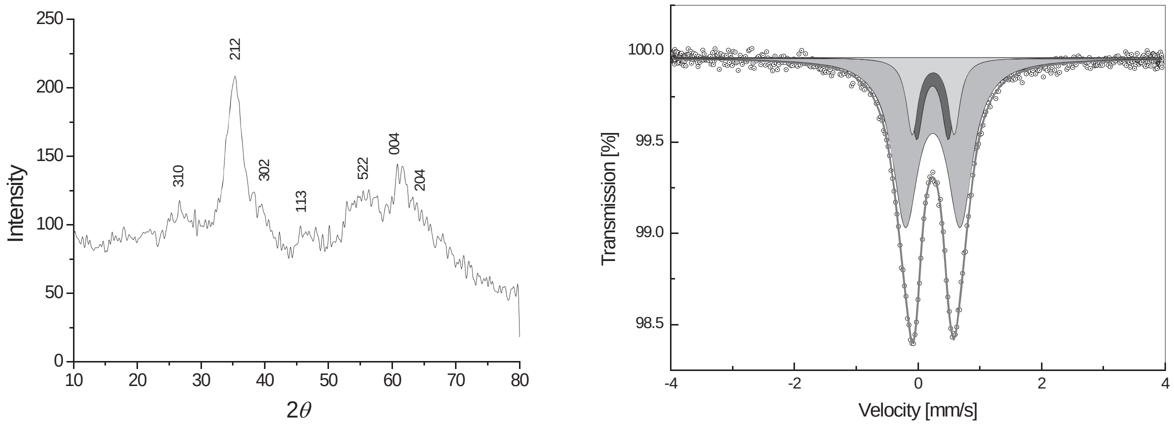

Fig. 3. X-ray diffraction pattern (left) and fitted ^{57}Fe Mössbauer spectrum of natural sample from shaft Pech (right)

Rys. 3. Układ Dyfrakcji rentgenowskiej (po lewej) i dopasowane żelazo ze spektrum Mössbauer'a naturalnej próbki z wału Pech (po prawej)

Tab. 1b. Chemical analysis of ochreous precipitates collected from shaft Pech in Smolník abandoned mine (NSW) and colloid phases (CP-1,2) (heavy metals)

Tab. 1b. Analiza chemiczna osadów ochrowych zebranych z wału Pech w opuszczonej kopalni w Smolniku (NSW) i faz koloidalnych (CP – 1,2) (metale ciężkie)

Sample	As	Cu	Mn	Zn	Ni	Cd	Pb	Cr	Co	Sb
	[ppm]									
NSW	2800	700	210	235	16.3	0.7	1074.5	23.5	--	102
CP-1	87.8	160	435	230	91.9	0.8	15.9	126	289.7	19.5
CP-2	35	100	270	200	217.2	--	12	111	--	8.7

Tab. 2 Mössbauer parameters, isomer shift (IS), quadrupole splitting (QS) and area of natural sample at 293 K

Tab. 2. Parametry Mössbauer'a, przemieszczenie izomeryczne (IS), rozdzielanie kwadrupolu (QS) i obszar naturalnej próbki na 293K

Phase	IS [mm/s]	QS [mm/s]	Area [%]
Doublet 1	0.35	0.89	69
Doublet 2	0.35	0.51	16
Doublet 3	0.36	0.68	15

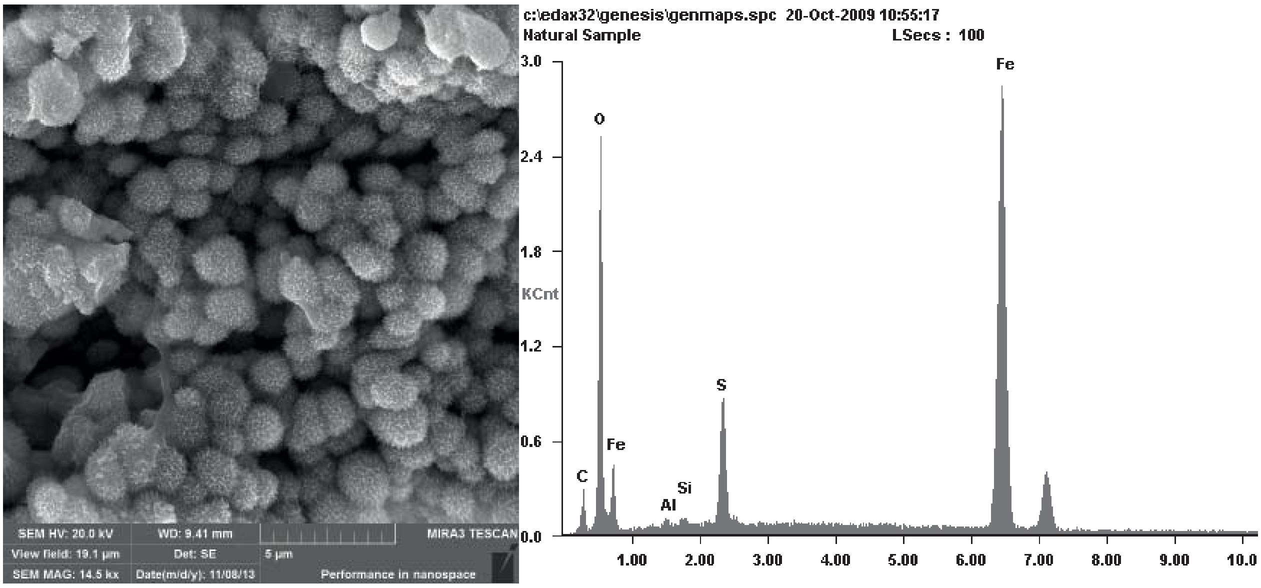

Fig. 4. SEM micrographs (left) and EDX analysis (right) of natural schwertmannite

Rys. 4. Mikrografia SEM (po lewej) oraz analiza EDX (po prawej) naturalnego schwertmannitu

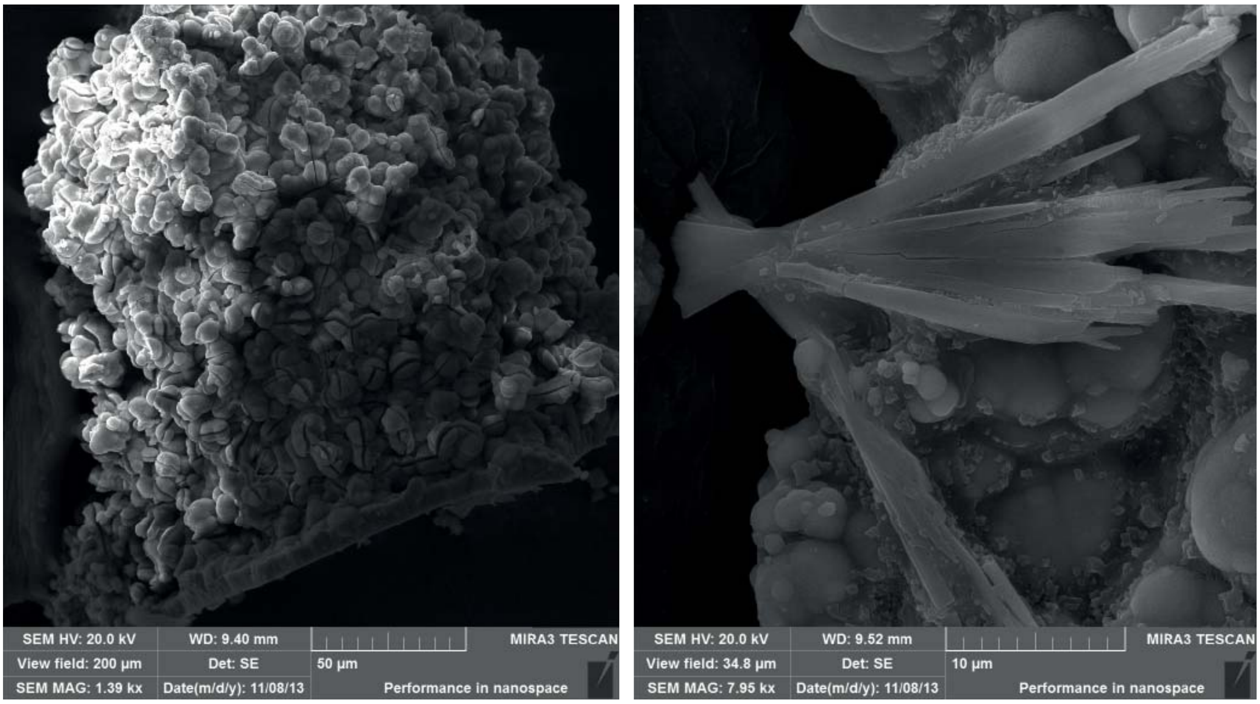

Fig. 5. SEM micrographs of schwertmannite crusts floating on the surface of AMD

Rys. 5. Mikrografia SEM skorupy schwertmannitu unoszącej się na powierzchni AMD are depicted. Their chemical composition is stated in Table 1a, b.

XRD analysis of schwertmannite can be readily distinguished from the associated minerals if specimens are reasonably pure. In the case of mixed assemblage with other minerals it may be difficult because of its poor crystallinity. The powder diffraction pattern of schwertmannite consists of eight broad peaks for d>1.4 Å. [4] The strongest peak for natural sample (Figure 3) occurs at about 2.54 Å (212). Although it can be easily confused with the strongest peak of ferrihydrite, but its symmetrical character confirms the presence of schwertmannite as well as the reflection at 1.64 Å (522), which is significantly displaced from that at 1.72 Å for ferrihydrite. Distinct identification of two following reflections occuring at 2.27 (302) and 1.94 Å (113) is difficult, because the d-spacings characteristic for schwertmannite (2.28 and 1.95 Å) are very close to d-values characteristic for ferrihydrite (2.21 and 1.96 Å). Similar situation occurs also in the case of reflections exhibited at 1.51 (004) and 1.45 Å (204), but in the case of ferrihydrite, the intensity ratios are reversed. Furthermore, in contrast to ferrihydrite, schwertmannite exhibits two more reflections at 3.39 and 4.86 Å, from which the peak at 3.38 Å (310) is detected on the XRD-pattern of natural sample. The above- mentioned d-values responding to reference of schwertmannite [47-1775] were also confirmed by Rietveld LeBail profile matching technique. [2]

The ^{57}Fe Mössbauer spectrum of natural sample measured at room temperature consists of an asymmetric doublet, that was fitted with a combination of three ferric doublets with following Mössbauer parameters (Table 4). An average quadrupole splitting 0.69 mm/s of these doublets is characteristic of schwertmannite [7].

The density of natural schwertmannite in the case of hard fraction (precipitates settled down on the bottom of the concrete pool of shaft Pech) was 2.86 ± 0.02 g/cm^3 and in the case of light fraction (precipitates floating on the surface of AMD in shaft Pech) was 2.8 ± 0.02 g/cm^3. Specific surface area was 4.54 ± 0.06 m^2/g and pore size 0.0079 cm^3/g. SEM and EDX analysis of schwertmannite is depicted in Figure 4. The EDX analysis revealed 69.60% Fe, 5.72% S, 23.83% O, 0.46% Al and 0.39% Si content in this mineral phase. The Fe/S molar ratio was 6.98, which belongs to the range of naturally occured schwertmannites published by Bigham et al. [5]

Figure 5 depicts the SEM micrographs of schwertmannite crusts floating on the surface of AMD in shaft Pech and covering the colloid phase. The EDX analysis of striking crystals growing through schwertmannite crusts revealed 17.9% Ca, 3.6% Mg, 20.9% S, 1.7% Al, 1.5% Fe, 54.0% O and 0.5% Mn, which seemingly presents a cocrystallized form of calcium and magnesium sulphate.

Conclusions

With respect to the continuous increase of the contamination of surface and groundwater, the need of solving the problem of water resources contaminated with acid mine drainage effluents is urgent and is calling for immediate attention. This work deals with the correlation between the chemical composition of AMD, colloid phases forming in AMD surrounds and ochreous precipitates forming in them and their recipients in the presence of indigenous iron-oxidizing bacteria Acidithiobacillus ferrivorans.

Results acquired during this research provide informations about the possibilities to use natural processes leading to formation of ochreous precipitates for attenuation of negative impact of AMD effluents on the environment. Furthermore, the ochreous precipitates seem to be successful scavengers of arsenic and other metal species, respectively they can support their building into the aimed mineral structures with the possibility of their consecutive processing.

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Ochrowe osady z opuszczonej kopalni w Smolniku

Siarczki metalu pochodzące ze skał naruszonych przez prace kopalniane, zostały narażone na warunki oksydacyjne (kontakt z wodą i tlenem atmosferycznym) i zaczęły produkować żelazo, inne metale, siarki i kwasowatość. Wynikiem wietrzenia oksydacyjnego siarczków żelaza jest produkcja AMD i następnie wytrącanie osadów ochrowych w systemach drenażowych i w pobliżu wycieku AMD na powierzchnie. Ponadto, powstanie AMD ułatwia naturalnie występująca bakteria oksydująca żelazo chemilitotroficzne oraz siatkę, szczególnie z rodzaju Acidithiobacillus i Leptospirillum. Długa obserwacja wód AMD w wale kopalnianym Pech wskazuje na utrzymujące się ryzyko poważnego zanieczyszczenia środowiska w okolicy kopalni Smolnik. Analiza cząsteczkowa, dyfrakcja rentgenowska, spektroskopia Mössbauer'a oraz mikroskopowe badanie elektronów osadów ochrowych tworzących się w nurcie wody AMD wykazały Schwertmannit jako dominującą stałą fazę w osadach. Analiza chemiczna odcieków AMD i składu cząsteczkowego powiązanych osadów wykazały znaczny potencjał oczyszczania się kwasów ochrowych z arszeniku, aluminium, ołowiu i innych gatunków metali.

Słowa kluczowe: kwaśny drenaż kopalni, osady ochrowe, schwertmannit