Qualitative characterization of sediment from the Smolnik creek influenced by acid mine drainage

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Abstract

Acid mine drainage (AMD) is considered as one of the worst environmental problems associated with mining activity. In Slovak Republic there are some localities with existing AMD generation conditions. The most critical values were observed in the abandoned deposit Smolnik. Waters from the earth surface penetrated the mine and they were enriched with metals and their pH values decreased. Acidity is caused mainly by the oxidation of sulphide minerals. The whole mine complex produces large amounts of AMD, discharging from the flooded mine (pH = 3-4, Fe 500-400 mg/l; Cu 3-1 mg/l; Zn 13-8 mg/l and Al 110-70 mg/l), that acidified and contaminated the Smolnik creek. The paper presents comparison of results of qualitative XRF analysis of sediments from the Smolnik creek sampled in uncontaminated part of creek and in the part influenced by AMD. The characterisation of sediments by FTIR and XRD methods are presented, too.

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1. Introduction

Acid mine drainage from abandoned mines poses a long-term threat to the environment and directly impacts it by polluting streams, rivers, waterways drinking water, and groundwater; disrupting wildlife habitat, and destroying the natural landscape. Runoff from mining operations can have negative impacts
on the surrounding aquatic environment including heavy loads of suspended solids, decreased pH levels and increased levels of heavy metals. The Smolnik mine is a historical Cu, Fe, Ag, Au-mining area that was exploited from the 14th century to 1990. The mine-system represents partly opened geochemical system into which rain and surface water drain. The Smolnik mine was definitely closed and flooded from 1990 till 1994. More than 6 million tons of pyrite ores of various qualities have been abandoned in this mine. Acid mine drainage (AMD) is a serious environmental problem resulting from the weathering of sulphide minerals, such as pyrite (FeS$_2$) and its polymorph marcasite ($\alpha$–FeS). It is characterized by a low pH-value and high levels of sulphate and metals [1]. Moses et al. [2] noted that FeS$_2$ is oxidized to Fe(II) sulfate faster at lower pH, but that abiotic oxidation of Fe(II) to Fe(III) is slower at lower pH. Oxidation of Fe(II) to Fe(III) could be biomediated or photo-induced in order to facilitate jarosite formation from FeS$_2$ at low pH. Temple and Delchamps [3] noted early on that aqueous Fe(III) at low pH is a more aggressive oxidant for pyrite than dissolved oxygen. Sulfate is an oxyanion that is commonly found in extremely high concentration near acid mine runoff and is produced as a result of the geochemical cycling of pyrite [4]. Laboratory experiments and field observations have shown that jarosite typically forms at pH values below 3, whereas schwertmannite precipitates preferentially at pH values between 3 and 4, and ferrihydrite is observed at pH 5 and above; goethite has been observed to form throughout the pH range (2.5 to 8) of sulfide oxidation [5].

2. Materials and methods

Water and sediment sampling localities are shown in Figure 1. Two localities were in the upper part of the Smolnik creek without contamination by acid mine waters from shaft Pech (1 – outside the Smolnik village, 2 - small bridge - crossing to the shaft Pech) and another two sampling localities were located under the shaft (4 - 200 m under the shaft Pech, 5 – inflow into the Hnilec river). The outflow of AMD and sediment from shaft Pech (Smolnik mine) has number 3.

![Fig. 1. Location Smolnik creek on the map of the Slovak Republic and sampling localities](image)

The chosen physical and chemical parameters were determined by multifunctional equipment METTLER TOLEDO in situ and chemical analyses of water samples were realized by AAS (SpectrAA-30, Varian), Samples of sediment were taken off from the Smolnik creek at the places showed in Fig. 1.
The sediment was dried, homogenized and sieved below 0.063 mm. Chemical analyses were realized by the XRF and the functional groups were determined using IR method.

The sediment samples were prepared as pressed tablets with diameter of 32 mm by mixing of 5 g of cement and 1 g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m2. The prepared tablets were studied by X-ray fluorescence spectrometry. The chemical composition of sediments was determined by using SPECTRO iQ II (Ametek, Germany). For infra-red spectroscopy in this study, was used spectrum through 4000 cm-1 to 600 cm-1 (Alpha FT-IR Spectrometer, BRUKER OPTICS).

The crystal structure of sediments was identified with diffractometer Bruker D2 Phaser (Bruker AXS, GmbH, Germany) in Bragg-Brentano geometry (configuration Theta-2Theta), using the 1.54060 Å CuKα radiation, Ni Kβ filters and scintillation detector at a voltage of 30 kV and 10 mA current. Scan conditions were identical for all samples, recording times about 5 hours, a step size of 0.05° (2Θ) and step time of 15 s. The XRD patterns were processed using the software Diffrac.EVA v. 2.1. The ICDD PDF database (ICDD PDF – 2 Release 2009) was utilized for the phase identification.

3. Results and discussion

The influence of AMD from shaft Pech (sample 3) on the surface water quality in the Smolnik creek (sample 4 and 5) is presented in Table 1. 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. Based on the results in Table 1 we can state that acid mine drainage flowing from the shaft Pech has an adverse effect on the surface water quality in Smolnik creek and causes exceeding of the limit values according to the Regulation of the Government of the Slovak Republic No. 269/2010 Coll. From chemical analysis, given in Table 1, follows that AMD exceeds each evaluated indicators. After AMD dilution with surface water into the Smolnik creek, the concentrations of Fe, Mn, Al, Cu, Zn are exceeded, too.

Table 1. Results of chemical analyses of water from the Smolnik creek and the shaft Pech

| Sample | pH | Ca [mg/L] | Mg [mg/L] | Fe [mg/L] | Mn [mg/L] | Al [μg/L] | Cu [μg/L] | Zn [μg/L] | As [μg/L] | Cd [μg/L] | Pb [μg/L] |
|--------|----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1      | 6.29 | 12.4 | 3.94 | 0.038 | 0.015 | <0.02 | 3 | 4 | <1 | <0.3 | <5 |
| 2      | 6.17 | 13.8 | 4.36 | 0.351 | 0.065 | 0.09 | 11 | 17 | <1 | <0.3 | <5 |
| 3      | 3.97 | 151 | 265 | 312 | 25.8 | 75.3 | 1700 | 7996 | 6 | 17.8 | 52 |
| 4      | 5.1 | 28.3 | 24.5 | 19.8 | 1.89 | 1.33 | 164 | 655 | <1 | 1.9 | <5 |
| 5      | 5.16 | 28.9 | 22.0 | 11.8 | 1.56 | 0.35 | 120 | 491 | <1 | 1.1 | <5 |
| Limits | 6-8.5 | 200 | 100 | 2 | 0.3 | 0.2 | 20 | 100 | 30 | 5 | 20 |

From the analyses of sediments’ quality in the Smolnik creek (Table 2) oriented towards the influence of AMD on sulfate and heavy metals concentration; and from the comparison of uninfluenced samples by AMD (S1 and S2) and influenced (S4 and S5), it can be stated that the differences are not so evident.
Table 2. The results of chemical analysis of sediments using XRF method

| No. | (SO₄)²⁻ | Ca [%] | Mg [%] | Fe [%] | Mn [%] | Al [%] | Si [%] | Cu [mg/kg] | Zn [mg/kg] | As [mg/kg] | Cd [mg/kg] | Pb [mg/kg] |
|-----|----------|--------|--------|--------|--------|--------|--------|------------|------------|------------|------------|------------|
| S1  | 0.07     | 0.36   | 0.81   | 4.92   | 0.12   | 8.08   | 19.65  | 148        | 197        | <0.5      | 43         |            |
| S2  | 0.12     | 0.32   | 0.79   | 5.83   | 0.08   | 6.77   | 19.51  | 467        | 273        | <0.5      | 147        |            |
| S3  | 10.9     | 0.12   | 0.44   | 33     | 0.02   | 2.37   | 2.54   | 756        | 1975       | <0.5      | 1081       |            |
| S4  | 0.36     | 0.27   | 0.8    | 5.42   | 0.06   | 6.54   | 17.48  | 363        | 191        | <0.5      | 110        |            |
| S5  | 0.32     | 0.32   | 0.79   | 5.73   | 0.07   | 6.71   | 20.54  | 427        | 242        | 93         | <0.5      | 117        |

The infrared spectrum of sample S3 confirmed presence of schwertmannite [6] which is dominated by a broad, OH-stretching band centred at 3100 cm⁻¹ (Fig. 2). Another prominent absorption feature related to H₂O deformation is expressed at 1634 cm⁻¹. Intense bands at 1124, and 1038 cm⁻¹ reflect a strong splitting of the ν₃(SO₄) fundamental due to the formation of a bidentate bridging complex between SO₄ and Fe. This complex may result from the replacement of OH groups by SO₄ 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 SO₄ include bands at 981 and 602 cm⁻¹ that can be assigned to ν₁ (SO₄) and ν₄ (SO₄), 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 to 880 cm⁻¹ range is apparent in some specimens and is related to OH deformation (δ(OH)) [7]. This results are in accordance with work [8] where was determined the presence of Fe₁₆O₁₆(SO₄)₃(OH)₁₀.₁₄H₂O 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 [9] IR spectrum (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 (3600-3650 cm⁻¹; 1652 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.

Fig. 2. FTIR spectrum of sediment S3
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)$_4$O$_{10}$ (OH)$_8$ (PDF 00 – 029 – 0701). The most dominant component is quartz with 6 broad peaks (the strongest line at 26.623° 2Θ).
The spectrum of sediment S3 points to a small part of crystalline phase, it contains only three weak peaks of clinochlore and one peak of quartz. According to the literature [10], AMD precipitates from shaft Pech contain 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 identify only by X-ray diffractometry (XRD) [11], 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. Conclusions

The sediment quality influenced by AMD was evaluated using XRF, FTIR and XRD methods. Presented results confirmed the presence of inorganic compounds, mainly hydroxides, sulfates mainly in a form schwermannite in sediment influenced only AMD from shaft Smolník. The presence of silicates, namely quartz, and iron hydroxysilicates (muscovite and clinochlore) was confirmed in the sediment of the Smolník creek by FTIR method. Presence of sulfates in the sediments from surface water of the Smolník creek was not confirmed. It can be suggested, that sulfates are changed into the soluble form due to dilution of AMD in surface water. It follows from our experiments that acid mine drainage has bigger impact on the surface water quality than on the sediment quality.

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