GEOCHEMICAL CHARACTERISTICS OF ACID MINE DRAINAGE AT THE SMOLNÍK DEPOSIT (SLOVAK REPUBLIC)

Andrea Šlesárová[1], Josef Zeman[2] and Mária Kušnierová[1]
[1] Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 04353 Košice, Slovak Republic
[2] Institute of Geological Sciences, Faculty of Science, Masaryk University in Brno, Kotlářska 2, 61137 Brno, Czech Republic

Abstract
The attenuation of mining activity in the Slovak Republic that started in 1989 led to the extensive closing of deposits using wet conservation, i.e. flooding. Negative effects of AMD can be observed mainly in the localities where sulphide ores and sulphide-containing raw materials used to be mined. The Smolník deposit is one of the historically best-known and richest Cu-Fe ore deposits in the Slovak Republic. The discharging mine waters of pH 3.7 containing high concentrations of sulphates, Fe, Mn, Cu, Zn, Al have a negative effect, mainly on the Smolník stream.
In order to propose an effective and economically acceptable remediation method to prevent the negative influence of AMD on this locality, a regular monitoring of AMD quality was carried out. The article presents the results of monitoring carried out in 1986 – 2006. The geochemical modeling of AMD quality was also realized. It was aimed at the simulation of AMD evolution during its gradual ascent from the depth of 200 m to the surface when reacting with pyrite. On the basis of modelling results it is assumed that the amorphous ferric hydroxide, jarosite and pyrolusite will gradually precipitate.

Introduction
Acid mine drainage (AMD) is considered as one of the worst environmental problems associated with mining activity. Mining activity in the Slovak Republic has a long tradition, especially in connection with the gold, silver, copper, iron and polymetallic ores mining. The gradual attenuation of mining activity that started in 1989 resulted in the extensive closing of deposits by flooding. This led to the creation of favourable conditions for AMD generation. The negative influence of AMD can be observed mainly in the localities where sulphide ores and sulphide-containing raw materials used to be mined, for example in Smolník, Šobov, Hodruša, Pezinok, Rudňany, Rožňava, Slovinky.
The Smolník deposit is a typical example of AMD occurrence and generation. The development of successful remediation method for this locality requires a sufficient database to estimate the long-time evolution of AMD quality. Understanding the causes of changes in the AMD composition is also of great importance. The results of periodical monitoring of AMD quality provide us data to estimate the basic trends in the evolution of AMD quality. The geochemical modelling helps us to understand these processes in detail.
The paper presents the results of AMD quality monitoring in the Smolník locality in 1986 – 2006 and geochemical modelling to describe the influence of atmospheric oxygen on the AMD quality evolution.

Materials and Methods
Water samples for chemical analyses were collected and filtered with 0.45 µm cellulose membrane filters, stored in 1.5 L – polyethylene bottles and acidified down to pH < 2 with concentrated HNO_3. Field parameters such as pH, Eh and temperature of the water samples were measured *in situ*. Cations were analysed by atomic absorption spectrometry. Sulphates were analysed using nephelometric analysis. TDS were analysed by gravimetric analysis.
The Geochemist's Workbench® (Rockware, Inc., Golden, CO, USA) (Bethke, 1996; Bethke, 2004) was used for geochemical modelling. 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.

Site description
The Smolník deposit is one of the best-known and richest Cu – Fe ore deposits in the Slovak Republic. It is situated between the villages of Smolník and Smolnícka Huta, in the valley of the Smolník stream, 11 km south–west of the village Mníšek nad Hnilcom (Fig. 1). Geomorphologically, the locality is situated in the area of Slovenské Rudohorie (West Carpathians) (Jaško et al., 1996). The main minerals of the deposit include pyrite and chalcopyrite. The relief and the surroundings of the former mining plant are marked with 735 years of mining activity (Rojkovič, 2003) that stopped in 1990. The gradual flooding of the deposit area was realized

from December 1990 till May 1994. Mine waters with flow of 5 – 9 L/s drain directly into the Smolník stream and their negative influence is visible all along its course.

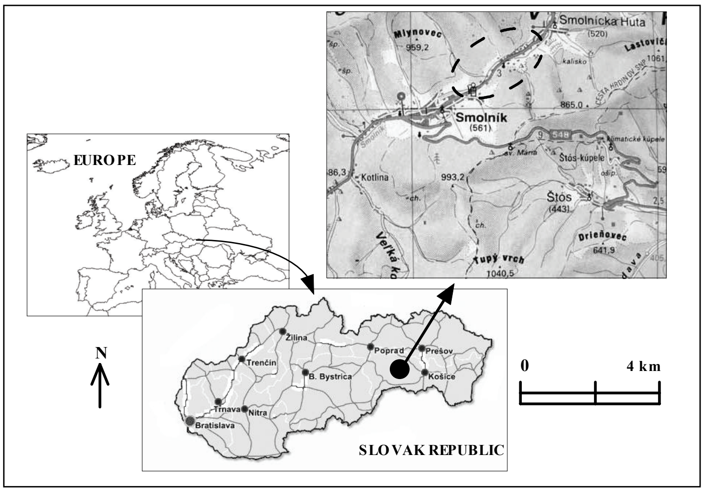

Figure 1. Location map of the Smolník deposit.

Results and Discussion

The basic trends in the AMD quality evolution at the Smolník locality are shown in Figures 2 and 3. The composition of draining mine waters changed suddenly soon after the end of flooding in June 1994. The rapid increase in the concentrations of sulphate, TDS, Fe, Mn, Cu and Zn resulted in an enormous degradation of the environment. The concentrations of Cu, Zn and Mn (Fig. 2) after the rapid increase immediately decreased followed by current linear evolution. The concentrations of sulphates, TDS and Fe (Fig. 3) decreased less markedly compared with the concentration of Cu, Zn and Mn. At the present time a linear evolution of sulphates and TDS concentrations is observed. The repeated increase of Fe concentrations in 2001 – 2002 was followed by linear evolution with moderate increase in 2006. The pH values ranged from 2.5 to 3.2 during and after the deposit flooding. In the last 5 years the pH values range from 3.5 to 4.

The review of the AMD quality evolution trends enable us to state that the situation at the locality has stabilised in the recent years. However, the concentrations of components monitored between 2005 and 2006 (Table 1) indicate the continuing negative effect of AMD.

In addition to their type and geological structure, the similar behaviour of mine waters has been observed recently at various ore or coal deposits all over the world (Geller et al., 1998; Ladwig et al., 1984; Zeman and Kopřiva, 2002; Kopřiva et al., 2004).

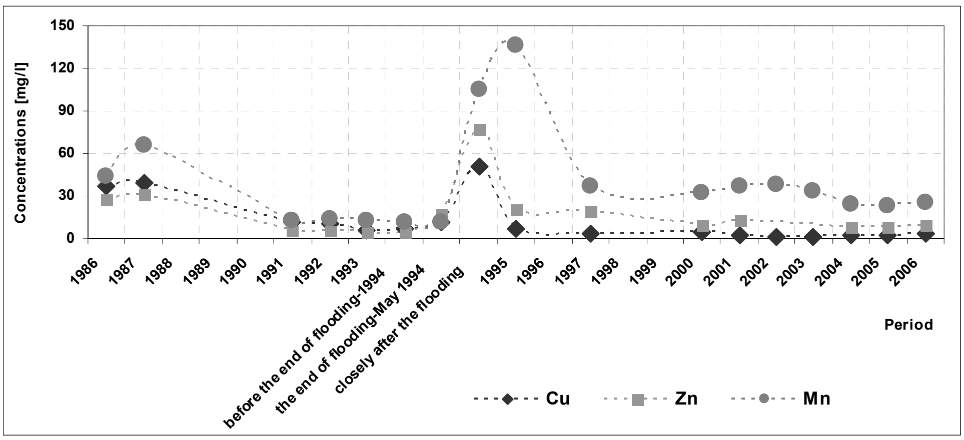

Figure 2. The evolution of Cu, Zn and Mn concentrations at the Smolník locality in 1986 - 2006.

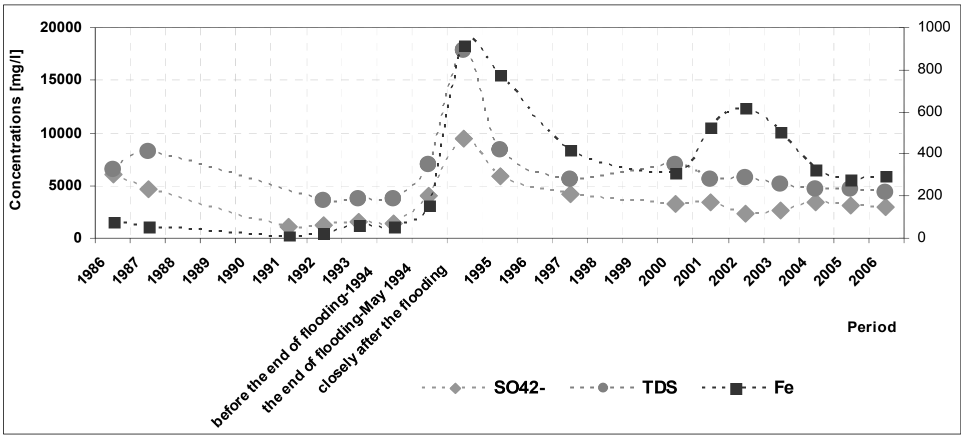

Figure 3. The evolution of SO_4^{2-} and TDS concentrations at the Smolník locality in 1986 - 2006.

Table 1. Average values of selected components in AMD at the Smolník locality in 2005–2006.

Chemical characteristics	pH	ORP	SO_4^{2-}	TDS	Fe_{total}	Mn^{2+}	Cu^{2+}	Zn^{2+}	Al^{3+}
		V	mg/L						
2005	3.8	0.5	3163	4652	282	23.5	2.1	8.0	62.4
2006	3.7	0.5	2965	4311	295	25.9	4.0	8.9	72.9

In addition to *in situ* measurements and laboratory analyses of water samples, the geochemical modelling is one of the effective methods to study the AMD generation and evolution. The geochemical modelling is used more frequently to investigate the geochemical system evolution, e.g. the interaction of AMD with wall rocks, migration of species in the studied systems.

The geochemical modelling was used to describe the atmospheric oxygen influence on the AMD quality evolution during the gradual ascent of AMD from the depth 200 m to the surface. While ascending, AMD reacts with pyrite contained in the wall rocks. As it is impossible to take the mine water samples from the depth, the input data for modelling were taken from the analyses of mine water samples taken from the depth 200 m in 1997 (Table 2) (Jaško et al., 1998). The modelling was carried out using the geochemical modelling software - the Geochemist's Workbench®. The input basis consisted of 1 L of AMD and 10 mg of pyrite.

Table2. Chemical composition of AMD used in geochemical modelling at 14 °C.

Component		Concentrations	Component		Concentrations
T	°C	16	Li^+	mg/L	2.9
pH		3.70	Mn^{2+}	mg/L	352.3
ORP	V	0.095	NH_4^+	mg/L	3.8
TDS	mg/L	42858.2	SO_4^{2-}	mg/L	32680.0
Fe^{2+}	mg/L	4973.0	Cl^-	mg/L	11.5
Fe^{3+}	mg/L	943.9	F^-	mg/L	0.1
Ca^{2+}	mg/L	338.5	HCO_3^-	mg/L	0.1
Mg^{2+}	mg/L	4095.3	NO^{3-}	mg/L	0.0
Na^+	mg/L	12.0	PO_4^{3-}	mg/L	0.2
K^+	mg/L	4.4	$SiO_2(aq)$	mg/L	49.3

The AMD was taken from the depth of 200 m. The AMD has equilibrated with atmospheric oxygen but is no longer in contact with it. Then, 10 mg of pyrite was added to the system to let it react to equilibrium with the fluid. The reaction continued until the $O_2(aq)$ was consumed, dissolving 0.3 mg of pyrite. Consequently, the system from the first step was leading to the contact with atmospheric oxygen. The partial pressure of oxygen was gradually increased to the value of 0.2. During the gradual ascent of the system to the surface; the gradual contact of system with the atmosphere and gradual pyrite dissolution, the decrease of pH from 3.70 to 3.05 and the increase of redox potential (ORP) to 1.0 V is possible to be expected (Fig. 4). It is also possible to expect the gradual precipitation of jarosite–K at pH 3.67, jarosite–Na at pH 3.47, amorphous ferric hydroxide at pH 3.55 and pyrolusite at pH 3.06 (Fig. 5). The presence of precipitated minerals predicted on the basis of geochemical modelling was confirmed with the samples taken at the point of AMD discharge on the surface (Jaško et al., 1996; Lintnerová and Šefčíková, 2002; Lintnerová et al., 2004).

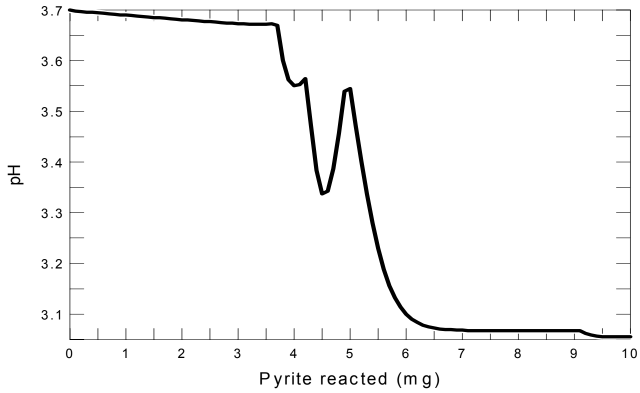

Figure 4. Change in pH in the simulation of AMD quality evolution after AMD reacting with 10 mg of pyrite during its gradual contact with atmospheric oxygen.

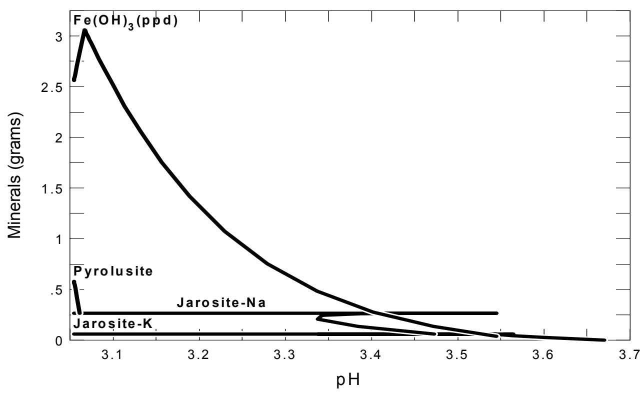

Figure 5. Minerals precipitated in the simulation of AMD quality evolution after AMD reacting with 10 mg of pyrite during its gradual contact with atmospheric oxygen.

Conclusions

The negative results of AMD activity can be observed in many localities of the Slovak Republic. The problem is the most marked at the Smolník deposit. The quality of mine waters at this deposit is very unfavourable for the environment. The current evolution in the AMD quality shows that the situation has stabilised in the last 3 years, but the results of geochemical modelling show that the oxidation of sulphide materials is very intensive. A considerable improvement of the ecological situation cannot be observed. It is expected that the negative effect of AMD on the surrounding environment will continue for tens of years without any visible improvement of the water quality.

The adequate monitoring of AMD quality and the use of modern evaluation methods and modelling tools may facilitate the long-term prediction of AMD quality. Based on the above studies it will be possible to propose the effective method of AMD remediation in the Smolník locality.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-51-027705 and the Slovak Grant Agency for Science VEGA grant No. 2/5148/5.

References

Bethke C.M. (1996). Geochemical reaction modelling. Oxford University Press, USA, 397 pp.
Bethke C.M. (2004). The Geochemist's Workbench®, Version 5.0. A User's Guide, University of Illinois, USA, 377 pp.
Geller W., Klapper H., Salomons W. (1998). Acidic mining lakes: Acid mine drainage, limnology and reclamation. Springer, Heidelberg, 435 pp.
Jaško V. et al. (1996). Smolník - komplexné hydrogeologické a hydrochemické posúdenie ložiska Cu - Fe rúd. Report, Aquipur a.s. Bratislava, 125 pp.
Jaško V. et al. (1998). Smolník - monitoring vývoja kvality vôd ložiska Cu - S rúd. Report, Aquipur a.s. Bratislava, 1998, 52s.
Kopřiva A., Jež J., Zeman J. (2004). Sezónní a dlouhodobé trendy ve vývoji složení důlních vod. Proceeding of the Conference Geochémia 2004, Bratislava, 122-124.
Ladwig K.J., Erickson P.M., Kleinmann R.L.P., Posluszny E.T. (1984). Stratification in water quality in inundated anthracite mines, Eastern Pennsylvania. US Bureau of Mines Report of Investigations RI-8837, US Bureau of Mines, Pittsburgh, 35 pp.
Lintnerová O., Šefčíková B. (2002). Zachytávanie a uvoľňovanie kovov a síranov oxyhydroxidmi železa v sulfidickom banskom odpade. Mineralia Slovaca 34, 219-232.
Lintnerová O., Šottník P., Šoltés S. (2004). Vznik kyslých banských vôd a toxických riečnych sedimentov v okolí opustenej bane Smolník. Proceedings of the Conference Geochémia 2004, 129-131.
Rojkovič I. (2003). Ore deposits in Slovakia. Monograph, University of Comenius, Bratislava, 107 pp.
Zeman J., Kopřiva A. (2002). Geochemický vývoj vod po uzavření a zatopení dolů. Proceedings of the Conference Geochémia 2002, Bratislava, 79-83.