THE LINKS BETWEEN THE PHYSICO-CHEMICAL CHARACTER OF DIFFERENT MINING WASTE IN SLOVAKIA AND THEIR ENVIRONMENTAL IMPACTS

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Abstract: Smolník and Banská Štiavnica are two mining areas in Slovakia with very serious impact of mining activities on environment. Massive pyrite oxidation and free sulphuric acid production are the major reason for mine water acidification in Smolník. Fe-ochre precipitates have formed after mixing of acid mine waters and have fixed large quantities of dissolved metals and sulphates. Acid waters at Šobov are typical AMD with low pH (1.2 - 2.5) and dissolved salt concentrations that range between 15 and 50 gL^{-1}. The AMD causes also significant changes in the soil biology and surface vegetation.

Key words: acidification, acid main drainage, impact of mining

Introduction

Elimination of the consequences of mining activities belongs to the most serious environmental problems nowadays. As a result of chemical oxidation and other chemical processes in overflowed mines, on mining waste dump and tailings impoundment, acid mine drainage (AMD) with high metal concentrations and usually with low value of the pH (about 2-3) are formed. AMD create when the sulphides minerals (e.g. pyrite) are oxidised. The first step of this oxidation process is a chemical oxidation, which goes on relatively slowly. But it causes decrease of pH. By low pH values (below 3) microorganism Thiobacillus ferrooxidans start their catalytic activity. These microorganisms obtain energy for their life by changing Fe^{2+} to Fe^{3+}. Furthermore, Fe^{3+} can act as an oxidant of pyrite or it can precipitate as Fe hydroxides.

Their outflow represents serious danger for the environment as they cause pollution of surface and ground waters, soil degradation and changes in vegetation. They can induce chemical decomposition of other minerals, which can be the potential sources of toxic elements.

Šobov

The Šobov mine is situated NE of the city of Banská Štiavnica in Central Slovakia. Šobov is an open mine for exploration of the hydrothermal quartzite used for producing refractory bricks. Deposit is associated with syngenetic and subsequent hydrothermal mineralization rich in clays (mainly illite and pyrophyllite) and pyrite (Uhlík & Šucha, 1997). Clays and pyrite are regarded as waste, and they have been accumulated at the mine site for more than 30 years.

Acidification sources in the region are mine dump and open mine. The main transportation medium of pollution is acid water distributed by the several ways. Among them belongs the water acidified by dissolved sulphates covering the surface of the open mine as well as the ground water acidified by mineralogical and geochemical processes in the mine dump (Tab .1). The mine and waste dumps are located near the top of a hill so AMD migrates down the slope.

Table 1. Chemical analysis of AMD from Šobov 1987-1999 (limit 1 – for surface water SR 242/1993, limit 2 for drinking water STN 75 7111). Concentration of elements in mg/L (Dubíková, 1999, modify by Šottník, 2000).

Element	limit (1)	limit(2)	1987	1993/10	1995/7	1996	1998	1999/9
Al	3	0.2	1145	1060	923	1119	774	850
As	0.5	0.01	-	-	0.67	-	-	-
Cd	0.01	0.003	-	0.9	0.1	0.1	-	-
Co	-	-	-	2.5	-	-	-	-
Cr	0.2	0.05	-	0.3	-	-	-	-
Cu	1	0.5	-	7.9	8.6	7.5	-	4.59
Ca	200	>30	242.6	233	-	-	125	248
Fe	15	0.3	2913	3500	3625	3521	1350	2260
K	-	-	-	0.1	-	-	2	-
Mg	100	10až 30	127	310	-	-	416	-
Mn	0.3	0.1	-	80	71	84	-	51
Na	-	-	-	4.23	-	-	3	-
Pb	0.5	0.01	-	0.02	-	-	-	-
Zn	2	3	-	9	8	10	-	-
SO4	250	250	11472	16540	15986	17890	10000	12876
pH	6 až 7	6.5-8.5	1.8	2	2	2.1	2.3	2.25

Properties of geological structures affect the migration of polluted water. Particularly the horizon of altered tuffs of the Šobov Formations acts as a barrier against vertical circulation of AMD. We assume that the deepest circulation of pollution is at 6 m. We expect the existence of a small depression of the sealing clay-rich horizon under the waste dump. Acid springs were observed at some points along the slope, where sealing horizon almost reaches surface (60-80 cm deep). AMD occasionally flows along the slope over the soil surface. Due to these facts, no vertical soil pH zonation was observed in contaminated areas (Šucha *et al.*, 1997), however lateral zonation is very well developed and can be traced by measuring soil pH. Natural soil pH ranges between 5.5 and 6.5, whereas, the pH of the most acidified soil drops to 2.3 (Šucha *et al.*, 1997). Polluted area represents about 145 000 m^2. Badlands area without any vegetation and humus cover reaches 35 000 m^2.

Acid waters collected from a mine site at Šobov are typical AMD with low pH (1.2 - 2.5) and dissolved salt concentrations that range between 15 and 50 gL^{-1} (Šucha *et al.*, 1997). (Table 1). The major dissolved components are Al, Fe and SO_4^{2-}. The pH values and salt concentrations depend on the quantity of AMD discharged from the waste dump. After heavy rain or snow melt, when the discharged AMD reaches 2-3 L s^{-1}, the pH is higher and the amount of dissolved salts is lower. The lowest pH and the highest salt concentration are observed during dry seasons.

The natural soil at Šobov is classified as a Dystric Cambisol developed on andesite rocks (Holub *et al.*, 1993). Major soil minerals identified by XRD are quartz, alkali and Ca, Na feldspars and phyllosilicates. Since the soil was formed on hydrothermally altered andesitic tuffs its clay content is rather high. The most abundant clay minerals are illite, kaolinite and vermiculite. In most of the samples pyrophyllite was also determined. Rarely the smectite and chlorite were found. Main effect of acid rock drainage on soils in the vicinity of waste dump is formation of secondary sulphate minerals and amorphous or very poorly crystalline matter rich in Fe, Al and Si. Preferential precipitation of gypsum and jarosite consuming K, Ca, Fe and sulphates as well as precipitation of ferrihydrite were clearly documented and they support precipitation models based only on chemical composition of AMD.

The AMD causes also significant changes in the soil biology and surface vegetation. As the soil pH drops, the number of plant species significantly decreases from about 25 to 0 at pH 3 (Holub *et al.*, 1993, Banásová & Šucha, 1998). Significant changes were also observed in microorganism ecology (Holub *et al.*, 1993). Miadoková *et al.* (1998) documented phytotoxicity and genotoxicity caused by AMD from the Šobov site. Further recrystallization of Fe precipitates is probably retarded by the content of Si bound to Fe-rich matter.

Smolník

Smolník is situated in the eastern Slovakia. The Early Palaeozoic volcanic-sedimentary chalcopyrite-pyrite deposit was mined for several centuries. The ore mining was finished in 1990. More than 6 million tons of pyrite ores of various qualities have been abandoned in the mine. Waters from the earth surface penetrated the mine and they were enriched with metals and their pH values decreased. The whole mine complex produce large amounts of AMD, which enters the Smolník stream.

Massive pyrite oxidation and free sulphuric acid production are the main reason for mine water acidification. It appeared, that pyrite oxidation was intensive not only in the upper part with descending water but also in the saturated part of the mine aquifer (Jaško et al., 1996, Lintnerová, 1996). This indicate chemical analyses of waters sampled in 1995 and 1997/1998 (Tab. 2).

The water quality of the Smolník Stream dramatically decreased a short time after the drainage of the Smolník mine works. The marked change in the pH value of the stream water can be observed downstream from the Smolník mine works to confluence of the stream with the Hnilec River (Jaško et al., 1996). The mine water pH values are about 3 to 4 (Tab. 2) and the same pH level was found in the most polluted part of the Smolník Stream. The mine waters also have increased contents of metals and sulphates. The water composition in mine changed relatively slightly under 100 m depth and it shows the highest TDS in the mineshaft 265-m under the surface.

The surface water in the mine vicinity is slight acidic. The Smolník Stream water is neutral in the upper part of the stream (without contamination by mine waters, but contaminated by municipal waste). This nearly neutral water diluted acid mine waters and acidity, concentration of sulphates and metals decreased. Fe-ochre precipitates have formed after mixing with acid mine waters and have fixed large quantities of dissolved metals and sulphates. Jarosite, schwertmannite and goethite have been identified in the ochre deposits. High acidity and sulphate concentration controlled the jarosite and schwertmannite formation.

Tab.2. Chemical composition of acid mine drainage outflowing from Smolnik mine (Jaško et al., 1995, 1998, Šottník 2000).

	1995	1997	8.-10. 1999	5.-9. 2000
PH	3,23	2,9	3.87 - 3.98	3,36
Na	5,55	4,71		
K	0,99	1,02		
Ca	185,76	242,2	208 - 238	214,5
Mg	1078,9	539,7	36.1 - 39.1	399,5
Cl	8,87	10,6		
NO3	2,3	<2,5		
SO4	7407,8	5331	3290 - 3540	3652
HCO3	3,05	-		
TDS	9861,4	7084		6217
Zn	33,38	39,38	13.7 - 16.9	17,75
As	0,004	0,002		
Cd	0,028	0,027		
Cu	12,59	6,73	2.24 - 3.17	5,19
Al	36,38	239	92.1 - 128	133,2
Fe	784,5	409	511 - 580	573
Mn	82,6	66,34	366 - 410	41,83

Conclusions

On the basis of our previous studies we have prepared common project with Join Research Centre in Ispra (Italy): "Study on the links between the physico-chemical character of different mining waste in Slovakia and their environmental impacts using modelling concepts and tools. This project is one part of the project "Environmental impact of toxic mining waste in Pre-accession countries (PECO)".

The main objectives of this study are:

- to analyse toxic emission and their environmental impact generated by the mining activities in the Smolník and Banska Štiavnica minig areas
- to develop an assessment that, using hydrochemical modelling, geographic information systems and remote sensing, makes it possible to use the studies sites as reference areas for environmental impact assessment of mining waste on catchment area scale.

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