IMPACT OF MINING POLLUTION ON WATER QUALITY IN THE SMOLNÍK STREAM (EASTERN SLOVAKIA).

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Abstract
More that 6 mil. tons of pyrit ores of various qualities have been abondoned in the Smolník mine. Copper have been obtained from water outflowing from mines at Smolník, which were rich in metals for many centuries. The mines were adapted to produce as much AMD as possible. These mines were overflood after interruption of mining in 1990. Waters from earth surface penetrate the mine spaces. During the penetration waters are enriched with metals and their pH value are decreased.
Massive pyrit oxidation and free sulphuric acid production are the major reason for mine water acidification. The mine water pH values are about 3 to 4 and the same level was found in the most polluted part of the Smolník stream. The marked change in the pH value of stream water can be observed downstream from the Smolník mine works to confluence of the stream with the Hnilec river.

Introduction
Smolník is situated in the southeastern Slovakia. The Early Palaeozoic volcanic-sedimentary chalcopyrite-pyrite deposit was mined for several centuries. The ore mining was finished in 1990. More than 6 mil. tons of pyrite ores of various qualities have been abandoned in th mine. Copper have been obtained from the water outflowing from mines at Smolnik, which were rich in metals for many centuries. The mines were adapted to produce as much AMD as possible. These mines were overflood after interruption of mining. Waters from the earth surface penetrate the mines spaces. During the penetration waters are enriched with metals and their pH values are decreased. So, the whole mine complex acts as a bioreactor producing large amounts of AMD, which enters the Smolník stream. In the Tab.1. you can see contents of certain elements found in water from mining spaces.

		feb. 98	may 99	aug. 99	april 00	june 02	aug. 02	oct. 02
cond.	mS/cm	4,15	5,07	3,07	2,9	4,56	3,25	3,34
pH		3,04	3,47	4,03	4,06	3,27	3,92	3,97
TDS	mg/l	5582	4893	3884	3716	59990	4290	5258
Na	mg/l	2,78	3,46	3,53	3,74	6,58	4,63	5,29
K	mg/l	1,45	1,16	1,46	1,97	2,7	2,69	3,57
Li	mg/l	0,37		0,38	0,39			
NH4	mg/l	0,18						
Ca	mg/l	181,7	183	191	179	215	125	186
Mg	mg/l	527,6	374	242	260	385	246	336
Cl	mg/l	2,7	2,7	<2,0	3,6	16,8	10,3	14,4
SO4	mg/l	4144	3600	2900	2730	4085	3125	3478
Fe (II+)	mg/l	426,2				551	246	441
Fe (tot.)	mg/l	434,1	572	427	408	659	434	528
Mn	mg/l	37,09	44,1	31,3	27,6	38,5	32,6	34,8

Al	mg/l	151,1	112	87	102	92,5	70,2	84,7
Cu	mg/l	3,92	2,78	2,63	4,53	1,47	2,12	1,97
Zn	mg/l	19,75	15,09	11,3	8,95	10,3	6,85	9,02
Hg	μg/l	<0,2			0,1	0,1	0,1	<0,1
As	μg/l	99	65	10	13	380	29	49
Pb	μg/l	51		221	80	99	70	99
Cd	μg/l	13		8	13	10,3	9,6	11,1
Cr (tot.)	μg/l	9			<2	<2	5	8
V	μg/l	16	14	10	14	<4	<4	11
Ag	μg/l	5				<1	<1	4
Sr	μg/l	190						
Ni	μg/l		160	133	159	3	232	247

Tab.1. Chemical analyses of acid mine water outflowing from mining spaces.

Massive pyrite oxidation and free sulphuric acid production are the major reason for mine water acidification. The water quality of Smolník stream dramatically decreased a short time after the drainage of the Smolnik mine works.
The acid mine water is penetrating throught and flowing into the stream. The marked change in the pH value of the stream water can be observed downstream from the Smolník mine works to confluence of the strem with the Hnilec river. The mine water pH value are about 3 to 4 and the same level was found in the most polluted part of the Smolník stream. The mine waters also have a high level of metals and sulphates. The highest TDS have the waters sampled in the mineshaft 265-m under the surface. The water composition changed relatively slightly under 100m dept in the inundated mine.
The map (Fig.1.) shows monitoring net of Slovak hydrometeorological institute. The graphs illustrate the situation of the strem Smolník and river Hnilec during years 1987-2000. The significant changes of water quality after flooding of mine in Smolník in 1995 can bee seen there. We can observed changes in concentration of metals and pH value up tu monitoring point, which is situated where the river Hnilec flows into the water reservoir Ružín.

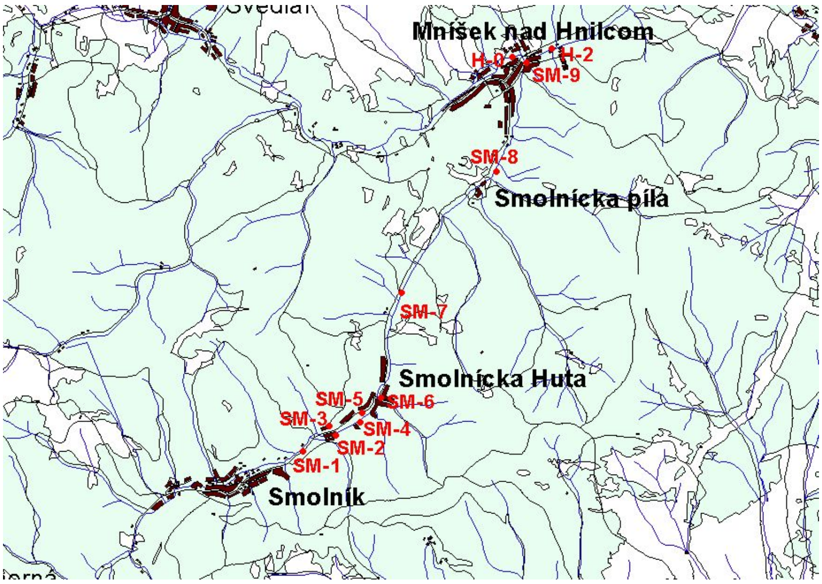


Fig.1. Monitoring net in Smolník stream and Hnilec river

Results and Discusion

Acid mine water outflowing from „new drainage“ of mining spaces (sample SM-2) is the most important sours of contamination in the Smolník stream area (Tab.2.). The stream water below the zone where AMD and stream water mix together (SM-4) has lower pH value and higher metal content (Fe 10-100x, Al 5-30x, Mn 20-60x, Cu 5-80x, Zn 10-70x; depending on climatic conditions) that befor mixing (SM-1). The process of precipitation of different mineral phases can be observed in the mixing zone. It is caused by the increase of pH.

(mg/l)	VI.02	VIII.02	X.02	IV.03
Al	92,5	70,2	84,7	90,7
Fe (tot.)	659	434	528	582
Mn	38,5	32,6	34,8	36,8
SO4	4085	3125	3478	3550
Zn	10,3	6,85	9,02	12,04
As	0,38	0,029	0,049	0,052
Co	0,914	0,662	0,813	0,483
Ni	0,238	0,232	0,247	0,147
Cu	1,47	2,12	1,97	2,037
TDS	5990	4290	5228	5040
pH	4,08	3,92	3,97	4,12

Tab.2. Chemical analyses of acid mine water outflowing from mining spaces (SM-2).

Oxyhydroxides of Fe and Al are carried as water suspension by the stream and deposited on the bottom. This phenomenon leadsto the decrease of metal content in water and thus to its increase in precipitates, stream sediments and soil in and along the stream Smolník.
The concentration of contaminants in ochres is many times higher (Al 20-90x, Cu 40-170x, Fe 600-1300x, Pb 2000-4000x, As 5700-6000x) in comparison with their concentration in water. Different situation in concemtration of SO_4^{2-} and TDS was found. Tailing impoundment (SM-TI) – the another important source of contamination – adds high content of salts to the water (Tab.3.). The concentration of SO_4^{2-} and TDS increases as far as the monitoring point SM-6 that represented water quality below the second mixing zone (water from tailing impoundment + stream water).

(mg/l)	VI.02	VIII.02	X.02	IV.03
Al	<0,03	0,2	0,05	<0,03
Fe (tot.)	**49,8**	1,55	2,63	5,85
Mn	**13,2**	1,16	2,49	4,04
SO4	**1470**	106	198	306
Zn	0,198	0,031	0,044	0,05
As	0,484	0,014	0,036	0,043
Co	0,069	0,007	0,012	0,016
Ni	0,061	0,02	0,023	0,025
Cu	0,006	0,015	0,007	0,006
TDS	**2170**	228	392	498
pH	6,28	6,62	6,35	6,69

Tab.3. Chemical analyses of water outflowing from tailing impoundment (SM-TI).

When the water in strearam is low (as in April 2003) the influence of water from tailing impoundment on the water quality in stream is considerable (Fig.2). Up to the point SM-6 concentration of Cu, Zn anf Fe rise as well.

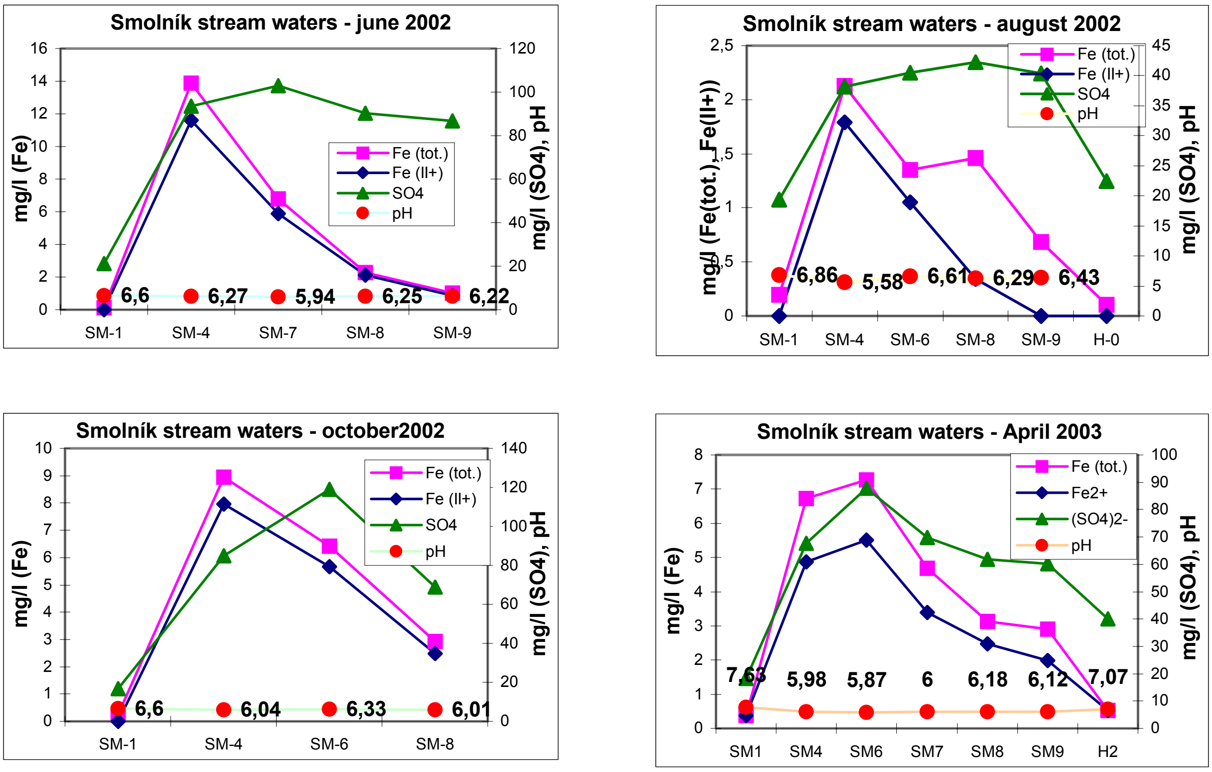
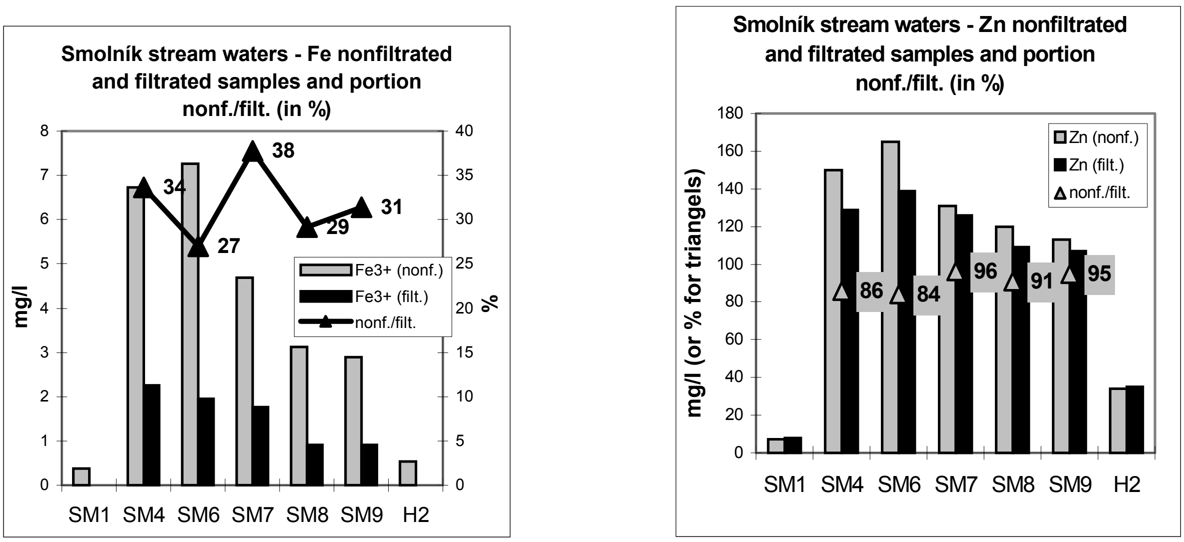


Fig.2. Content of Fe(tot.), Fe^{2+}, SO_4^{2-} and pH value during the monitoring period.

We analysed 2 samples from one monitoring point – „unfiltrated“ water (only through paper filter) and filtrated with 0,45 □m filter – to determine the amount of contamination in water suspension. It was proved that significant quantity of contamination is transported just in water suspension (<0.45 μm), which is demonstrated on the example of Fe, Zn and Mn concentrations. Aproximately 30% of Fe, 90% of Zn and 95% of Mn are transported just in water suspension (Fig.3.). Similar result can be expected in the case of SO_4^{2-} due to their strong positiv correlation with Mn.



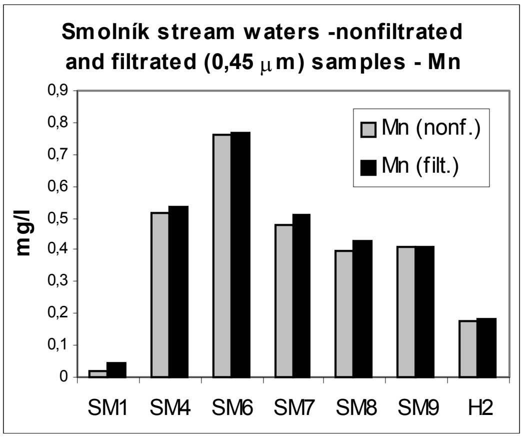


Fig.3. Concentration of Fe, Zn and Mn in filtrated and nonfiltratet samples.

The concentration of contaminants in strem is lower than after the flooding of mine in 1995. However, all the sources of contamination are stable enough and release contaminants to the wate permanently. The following remediation measures have been taken there – artificial stream bed to stop penetration of stream water to the mining spaces, channels around the dumps to stop flow of surface waters through the dumps and recultivation of sulphitic concentrate dump. Laboratory experiments, bench scale and pilot scale of anaerobic wetland for remediation of AMD from mining spaces have been carried out there in 1999.

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