

# WEATHERING OF SULFIDE MINE TAILING IMPOUNDMENT

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**Abstract:** The result of tailing sulfide minerals weathering is release acidity and metal and sulfate removing in inactive mine impoundments in the Smolník and Banská Štiavnica mine areas. Strongly acid oxidic zones have occurred in the water unsaturated parts of tailing, where secondary sulfates (gypsum and jarosite) and iron oxyhydroxides have concentrated. The waters discharging from impoundments are enriched in iron, which precipitates in a form of Fe<sup>3+</sup> oxyhydroxides (ochres) in open drainage channels and reduced the amount of dissolved metals.

**Key words:** pyrite, tailing, secondary minerals, metals.

## Introduction

Some twenty sulfide mine-tailing impoundments were decommissioned in Slovakia during the past fifteen years. Most of them are dry covered but their covers were not modified to match the amounts of sulfides, respective sulfides weathering and oxidation. To document the sulfide weathering processes in the dry tailings it was selected two tailing impoundments in the Banská Štiavnica and Smolník mine areas. Mines and various types of sulfide mine wastes produced acid mine drainage water, which contaminate the surface water and/or the soils in selected mine areas (Lintnerová, 1996, 2000, Lintnerová et al., 1999, Líšková et al., 1999, Šucha et al.1997). The objectives were to monitor the processes of sulfide/pyrite oxidation in tailings and to study the mineralogical and chemical composition of the oxidation products in the impoundment with mineralogical variable tailings, to assess the potential environmental risks of impoundments.

## Tailing impoundments

The Smolník mine tailing impoundment was used between 1954 and 1990 and about 3 mil tons of tailings were disposed. The mine impoundment is located at a valley slope and its dam is 80 m high. The tailings are composed by major chlorite-quartz-mica wall rocks and by quartz-carbonate (dolomite, ankerite, siderite) vein minerals admixture. The pyrite is a dominant sulfide mineral in tailings representing 5-6 %. The contents of chalcopyrite, galena and sphalerite are lower than 0.5 %. Between 1994 and 1996 the Smolník impoundment was covered by about 15 cm thick layer of wood

waste and soil. The impoundment dam has been stabilized and remedied continuously during the whole operation time. Due to acidification of soils the vegetation has been retarded. Large amounts of ochre colored iron precipitated in the drainage channels. Samples of tailings, oxidation products, acid soils and precipitates were collected in 1994 to 2001.

The Banská Štiavnica tailing impoundment (“Seven women”) was operational since 1975 and contains about 2.4 mil tons of tailings. The frontal wall of impoundment is about 40 m high. Pyrite and sphalerite are most abundant sulfide minerals in the tailings. 82 to 97 % of the tailings are made up of quartz and feldspars, while mica, clays and other minerals are less abundant and the carbonates are subordinate. The reclamation of the impoundment surface has been completed recently. The wall rock from the mine dump was graded over the soft tailings surface and covered by waste organic (cellulose) matter. The dry cover is 1 m thick approximately. The impoundment dam wall has been stabilized and covered by thin soil (earth) layer continuously during the operation time. The ochre colored surfaces, acid reaction of soils and increased erosion of the damp soils were found and indicating the sulfide oxidation (Líšková et al. 1999). The samples were taken from the soil (at depths between 0.1 to 0.2 m) in seven sections running across the impoundment dam and from pits, 1.2 to 2.0 m depths. Drainage precipitates were collected in 1998 to 2001.

## **Results**

### ***Smolník***

The oxidized horizons developed 4-5 years after the reclamation of the impoundment. 0.5 to 0.7m thick oxidized - ochre colored zones with “hardpans” developed on the dam site of the impoundment (Tab.1). Greenish-gray laminae and „gray hardpan“ developed in and below ochreous zones in more wet part (the mountainside) of the impoundment. The reduced Fe(II) laminae/hardpans form when Eh values decrease below 200 mV (between +200 and –90 mV). Typically Eh values between 300 and 600 mV occur in the Fe(III) ochreous zones and hardpans. The thickness of oxidized zone varies and reflects the mineralogical composition (pyrite vs. carbonate content), grain size and redistribution of grains (quartz, carbonates vs. chlorite, mica) during the sedimentation and compaction of sludge, but mainly the variation in the water saturation and the depths of capillary refringe zones. In spite of relatively high primary carbonate (ankerite and siderite) content in the Smolník impoundment the dam soils are locally strongly acid (Tab.1). The amount of

extractable Al was increased in such acid soils or tailing horizons. The pH values below 3 suggest the progressive pyrite oxidation and acid leaching and/or dissolution of silicates, but mainly chlorites.

The chemical composition of water discharging from various sides of the Smolník impoundment differs, but the compositional variations in water running from the same sides are relatively small during the year. The water is slightly acid (pH 5,5 to 6,6) and Fe (0,6 to 6 mg/l, respective more than 20 mg/l on the left side of impoundment) and sulfate (300 to 800 mg/l) enriched. The increased amount of Al in the Smolník iron ochres (2443 to 21168 mg/kg, seven samples) documented a tendency of Al to mobilize by the pore water. The content of As in the Smolník ochres is also very high (1174-4693 mg/kg) The oxidation processes remove the As from the pyrite and arsenopyrite. As-anions (e.g.  $\text{AsO}_4^{3-}$ ) and sulfates may be bound to positively charged Fe-oxyhydroxides in acid condition. The cations have been co-precipitated or adsorbed later, in neutral condition (e.g. Cu: 680-4770 mg/kg). Large amounts of Fe precipitate form in the open part of the drainage channels in both impoundments. The precipitate form under nearly neutral conditions and relatively good crystallized goethite has been identified by the X-ray diffraction analyses. The crystalline character of the drainage precipitates was documented by the TEM study. However, less stable/crystalline phases also occur together with goethite in the drainage sediments in both impoundments. Beside the peaks of well crystalline gypsum two wide/diffuse bands of ferrihydrite (0.25 and 0.22 nm gave and) and probably lepidocrocite (0.62 and 0.32 nm) can be distinguished also in the X-ray diffraction profilers.

### **Banská Štiavnica**

In the Banská Štiavnica impoundment dam in the same pit two or three ochreous and/or hardpan horizons can be found at depth (Fig 1). Because of steep slopes the dam benches are locally very intensively eroded and the removed material buries the original surface with oxidic horizon to larger depths. The groundwater level is relatively deep and the tailings are stronger dried and aerated, the sulfide oxidation may be even extensive and reach deeper levels on the impoundment dams. The results of the dam soil monitoring have demonstrated that pH (1.7 to 7) and other parameters ( $\text{SO}_4^{2-}$ , Al, Fe) quickly changes and indicates to what degree the dam benches were eroded and acid hardpans were destroyed. The extractable Al (60 to 200 mg/kg) may

be scavenged by the sulfates and thus its toxicity/availability to plants should be reduced. The water dissolved sulfate concentration in soils (50 to 14 000 mg/kg) represented the „potential acidity“ stored in secondary minerals. The amounts of secondary iron oxyhydroxide and sulfate phases in the studied dam soils and undestroyed hardpans widely vary between 7 to 27 wt% of samples. It has been mentioned, that iron oxyhydroxides are important because can attenuate dissolved metals. The Fe-oxyhydroxides formed under strongly acidic conditions are relative enriched in Al and Mn, however total content of bounded metals (Al, Mn, Pb, Zn, Cu and As) increased in more neutral samples. The relatively high correlation between Zn vs. Pb and Pb vs. Cu (regression coefficients  $r^2 = 0.933$  respective  $0.708$ ) indicate an importance of primary sulfate mineralogy and total content of metals in the tailings. The relation like this has raised when the results of iron precipitate from drainage analyses have been interpreted. Iron precipitates from drainage water are enriched in Pb (751 to 1680 mg/kg) and Zn (3048 to 15750 mg/kg). The contents of Cu, Mn, As and Al are relatively high and documented high attenuation abilities of iron oxides when compare the element concentration in precipitates with relevant element contents in drainage water. Using the Norm of Slovak Republic the selected element (Zn, Cu, Pb and Fe) contents in water have not exceeded the limiting values for surface water pollution. However, the water content of sulfates (300-500 mg/l) exceeds the recommended water upper limit (250 mg/l). It is well-known that the sulfate concentration can increase over 1000 mg/l when iron oxyhydroxides are precipitated in a place of drainage discharge and release of sulfate in neutral condition has been verified by experiments (Blowes and Ptacek 1994, Lintnerová 2001).

### **Conclusion**

Oxidation zones with hardpan like horizon form in the near surface vadose zones of both impoundments. Sulfides, mainly pyrite, are completely dissolved, the acid products (pH 2,8-3,7) accumulate in the oxidized zone with “hardpans” on top of capillary refringe zones at depth between 0.3 to 0.9 m. Fe (II) and Fe(III) sulfate (melanterite, jarosite), low crystalline Fe oxyhydroxide and gypsum are the main secondary minerals of oxidized zone and hardpans. Increasing acidity effectively mobilized potentially toxic metals elements Al, As, Fe, Mn, Cu, Pb, Zn in the oxidized zone.

Secondary mineral formation and its water stability are important factors, which control the mobility of metals and potential pollution of water and soils. Fe-oxyhydroxides, mainly „stable“ goethite effectively scavenge the dissolved metals (Cu, Mn, Zn, Pb, As, Al) under less acid conditions. High contents of mobilized metals and sulfates indicated that the mine impoundments could be potential source of sulfate pollution.

Preliminary investigations of these remedied impoundments with mineralogical variable tailings indicated that relatively low sulfide (pyrite) contents are potential sources of pollution and a possible cause of the reclamation failure. The originally alkaline (pH 12) sludge portions are being leached by rainwater and oxidized by air-oxygen, and acidify the soil to a depth of 0.15-0.25 m (pH range between 2,1 and 4,0) and these processes persisted for about 5 year in the Smolník impoundment.

The type of reclamation, using only wood waste and a thin earth bed, which was applied in the Smolník impoundment practically represents “open system” and cannot prevent the sulfide oxidation. The tailings should be covered (and kept permanently under) by low oxygen diffusion layer to reduce risk of the acid generation. The acidification of impoundment dam tailings increases the risk of the dam erosions. To further investigation is necessary to asses environmental risk of studied impoundment.

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**Tab.1.** The Smolník impoundment: characteristics of pit samples, collected in 1999. pH, Al and Fe were analysed in 1M KCl extract (exchangable form), Ca, SO<sub>4</sub><sup>2-</sup> - water extract. \*mg element in 1kg of tailings, \*\* Fe-oxyhydroxides, \*\*\*sample with primary siderite.

Sample	Depth (m)	PH (KCl)	Al (KCl)	Fe (KCl)	Ca (H <sub>2</sub> O)	SO <sub>4</sub> (H <sub>2</sub> O)	Carbonate	Secondary minerals
			mg/kg*				wt%	
SMO 1	0.02 - 0.08	4.04	71	276	3070	21550	0	Fe - oxide**
SMO 2	0.08 - 0.10	2.79	110	312	780	14850	0	Fe - oxide**, gypsum
SMO 3	0.25 - 0.35	2.32	232	425	3650	13350	0	Fe - oxide**, gypsum
SMO 4	0.40 - 0.50	2.68	29	350	950	8600	0	Fe -oxide, jarosite
SMO 5	0.65 - 0.75	7.95	0.7	4.7	1500	7250	38.4	rozenite (melanterite)***
SMO 6	0.75 - 0.80	7.92	0.6	1.3	1370	5150	24.8	rozenite (melanterite)***
SMO 7	0.80 - 1.00	6.77	0.8	11.9	735	8450	3.8	

**Fig 1:** Sulfide oxidation zone developed on the Banská Štiavnica –dam bench. Sulfide oxidation zone

