

Mineralogical and Environmental Evaluation of the Settling Ponds at the Deposit Dúbrava in Nízke Tatry Mts.

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Abstract: In this study, a complex mineralogical and environmental evaluation of the settling pond material has been performed and processes, that occur in these wastes, have been modeled. The settling pond material consist predominantly of the granularity fraction over 50 microns, having a neutral to weak alkaline pH. Gangue minerals largely prevail over sulphide ore minerals. The evaluation of natural barriers against the dispersion of toxic elements, from the settling ponds into water-bearing horizons, has determined that this role is pursued by Fe-oxyhydroxides created in the wastes due to oxidation of Fe-bearing minerals. Also, the importance of carbonates as a natural neutralization component of the wastes was confirmed. Experimental leaching of the waste materials in various conditions (temperature, pH, humic acids) showed sudden pH changes, induced by the presence of carbonates, extensive decomposition of stibnite (the influence of temperature and pH is minimal), the slow ability to leach out Fe and As from pyrite and the arsenopyrite, and minimum influence of humic acids on the amount of leached elements.

Keywords: stibnite, experimental leaching, Nízke Tatry Mts., settling pond, oxidation

Introduction

The Dúbrava deposit, located in the Ďumbier part of the Nízke Tatry Mts used to belong to the largest stibnite deposit in Central Europe. In 1992, after the mine become inactive, it was necessary to deal with the problem of the solid waste, laid down at the settling pond. This could be a source of toxic materials that might pollute the geological environment and the surface and subsurface waters. At the Dúbrava deposit, the possible contamination is of special concern because this area is protected as part of the Nízke Tatry National Park (NAPANT).

A dileterious effect of the mining on the environment has already been observed. Stolečnan (1984) and Stuchliková (1991) studied the influence of the waste on the quality of groundwater. Letko (1992), Arvensis et al. (1994), and Arvensis (1988) examined details of the character of the flotation waste accumulated in the settling ponds and its influence on the environment.

At other Slovak localities similar problems were studied by several additional authors (Šucha et al. 1998). Šucha et al. (1997) and Lišková et al. (1999) studied the acidification around Banská Štiavnica (Štiavnické Vrchy Mts.). Trtíková (1997, 1999) examined the oxidation of sulphides in the wastes after mining activities in the area of Malé Karpaty Mts. Šotník and Rojkovič (1998) studied the weathering of mining and technological wastes in the district of Slovinky and Rudňany. Lintnerová (1996) studied the mineralogy of Fe-ochres originating in acid mining waters at the Smolník deposit.

A complex mineralogical evaluation of a solid flotation waste, the understanding of processes occurring during weathering of the settling ppond material, a study of the mechanism of toxic elements migration into the environment and the modeling of processes occurring at the settling pponds are the main aims of this study.

Geological Characteristic, Mineralisation and Setting Pits at the Dúbrava Deposit

The Dúbrava mining district is located on the northern slopes of the western part of the Nízke Tatry Mts., in the central zone of the Ďumbier anticlinorium. The deposit is underlain by Ďumbier crystalline basement. North of it Mesozoic cover occurs, predominantly formed by dolomites. The crystalline basement is represented by a huge complex of granitoides and extensively metamorphosed crystalline schists. The petrographic research of the surrounding rocks determined the presence of highly prevailing granitoid rocks, less common aplites and pegmatites, gneisses, migmatites, dioritic rocks and basanites (Michálek and Chovan, 1998).

At the Dúbrava deposit quartz-sulphide veins are the prevailing form of ore occurrences, which originated by the filling of fissures. Disseminated and stockwork ores are more rare, and are present mainly near veins in fault zones. Over a length of 5 km Sb ore mineralisation has the character of extensive stockwork in granitoides and migmatites of the Ďumbier crystalline basement. Ore mineralisation is related to the mylonite zones, which

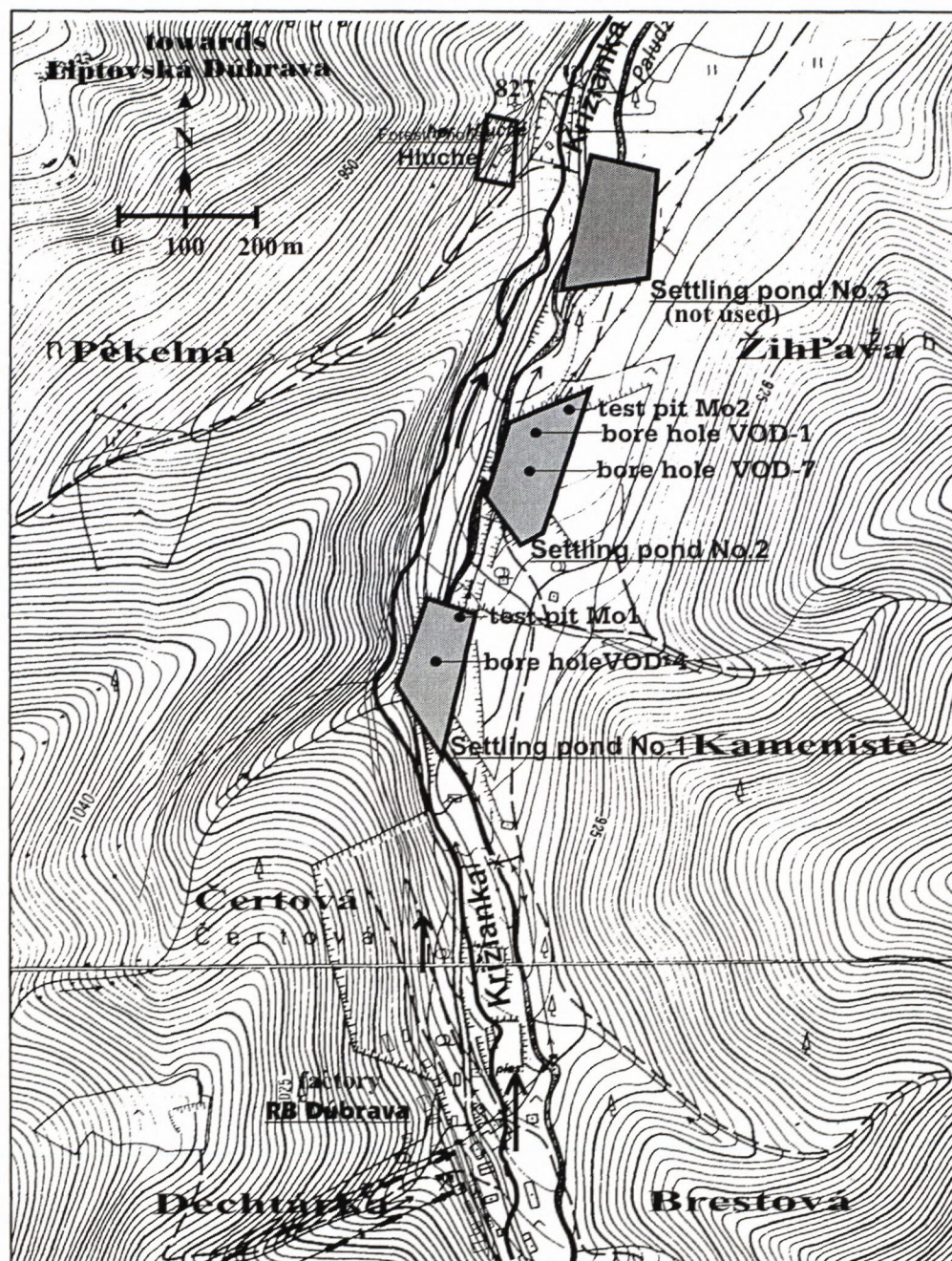


Figure 1: Map of the vicinity of the stibnite Dúbrava deposit with marked locations of sample sites at the settling ponds no. 1 and no. 2.

have discrete veins and veinlets of variable thickness, quality and systematically changing (Michálek and Chovan, 1998).

Due to hydrothermal processed nearly all rocks in the area of the deposit are altered. According to the intensity, the alteration process near quartz-sulphide veins is possible to divide into 3 zones (from the weakest to the strongest): 1.-chloritisation, 2.- muskovitisation, 3.-illitisation and carbonatisation. In the mylonite zones, reactivated during the Alpine orogeny, mainly the presence of illite and traces of smectite and kaolinite were detected by RTG-diffraction analyze (Orvošová et al., 1998).

At the Dúbrava deposit the following minerals were identified (Michálek and Chovan, 1998):

main: stibnite, pyrite,

associated: scheelite, molybdenite, bismuthinite, tetradyomite, marcasite, pyrrhotite, Ni-sulphide (?), argentite, gold, arseno-

pyrite, sphalerite, zinkenite, plagioclase, robinsonite, heteromorphite, semseyite, jamesonite (?), boulangierite, galena, antimony, senarmontite, tetradrite, bourbonite, chalcostibite, „horobetsuite“, Bi-Pb-Sb sulphosalts, hematite, magnetite, rutile,

vein: quartz, Fe-dolomite, baryte, strontianite, calcite, aragonite, siderite, monazite, illite, kaolinite, montmorillonite, smectite,

secondary: romeite, stibioconite, valentinite, bindheimite, cervantite, Sb-ochres, malachite, limonite

For the ore processing three settling ponds were necessary to establish at the deposit (Fig. 1), that are located at the right side of the stream Križianka (Arvensis et al., 1994; Arvensis, 1998): The settling pond no. 1 is situated uppermost in the Križianka valley (875 - 885 m above sea level), just below former factory Rudné bane Dúbrava, at the area of 24 000 m². The settling pond no. 2 is located

below the settling pond no. 1 in the height 855 - 875 m above sea level and covers an area of 27 500 m². It is estimated (according to the archives of Rudné bane Dúbrava), that during 1947-1989 1 223 216 tons of flotation slimes were deposited at the settling ponds no. 1 and 2. In 1992, during the restoration works both settling ponds were covered by a layer of a loamy material. Settling pond no. 3 is the youngest one; it was prepared for the mining predominantly of low grade disseminated ores in 1989. It is situated below the settling pond no. 2. Because of the end of mining activity this area has not been used. The settling pond material contains wastes after flotation treatment of Sb-ores - flotation slimes, that have similar grain size to a loamy sand (Letko, 1992). The character of the flotation waste at the settling ponds is given by mechanical properties of the processed ore material (Arvensis et al., 1994; Arvensis, 1998). The waste components distributed to the settling pond contained increased concentrations of some heavy elements, mainly Sb, As, Cd, Mn and Fe. However, the resulting concentrations in surface and groundwaters (after their mixing with the waste water) did not exceed the indicators of the allowed degree of pollution (Letko, 1992). Analyses of solid phases in the wastes, deposited at the settling pond and in the surrounding of the settling pond, proved the presence of several elements in extremely high concentrations, while the highest concentrations (over 1000 mg.kg⁻¹) were reached by Sb, Sr, Mn and B (Letko, 1992). Before their restoration the settling ponds were free of vegetation and they had apparently a decreased evaporation and surface discharge. The percolation of meteoric waters (pH 4.3 - 4.5) from the settling ponds is nearly over 70 000 m³. The leaching of the settling pond material proved the Sb-content in the leaching solution 1.0 to 32 mg.l⁻¹ while HSbO₂ was the prevailing form of Sb in the leaching solution. According to the norm for drinking water in the EU countries (Sb = 0.001 ppm) the leaching solution from the settling ponds should be diluted at least 100 to 3000 times (Arvensis et al., 1994; Arvensis, 1998). According to the results of the modeling of the transport of the residual Sb from the settling ponds into a solution Jorgensen and Pedersen (1992) in Arvensis et al. (1994) suppose that after 700 - 900 years the Sb-concentration in the leaching solution from the settling pond will be 2-3 mg.l⁻¹.

In the year 1992 the company Geologický prieskum Spišská Nová Ves (GP SNV) bored three drill holes at the settling ponds no. 1 and no. 2, that aimed to determine the sediment composition and hydrogeological and hydro-geochemical relationships in the body of the settling ponds. In the water from the drill holes six microelements had the highest composition: Sb, Ba, Pb, Cu, Zn and As. In the water from the drill hole VOD-1 at the settling pond no. 2 only three of the elements were present, Sb, Ba, Cu, and in the drill hole VOD-7 Pb was present as well (Arvensis et al., 1994; Arvensis, 1998).

Methods

A grain size analysis was performed using the following methods of the settling pond material placed in a

graduated cylinder filled by distilled water using a 0.1M solution of sodium hexametaphosphate and 15 % solution of HCl. The following fractions were obtained: <2, 2-20, 20-50 and >50 micrometers. In the granulometrically separated fraction <2 micrometers we analysed the sorption capacity of clay minerals using the saturation by the vapour.

First, the samples for the measurements were dried at 60°C. After desiccation, from each sample 10g portions were weighted; to the one 25 ml of distilled water was added, and to the other 25 ml of a 1M solution of HCl. The acidity (pH) was measured by the instrument IONOMETER-M931.

All samples from the settling pond material, selected for microscopic observation, weighed exactly 1 kg. They contained a substantial proportion of fine fraction, which was removed by mud discharging and by classic panning. The samples treated by panning were dried and then the ferromagnetic fraction was removed by a permanent magnet. Later, the scheelite content was determined by an ultraviolet light. The separation into the light and heavy fractions was the next phase of sample treatment, for which CHBr₃ has been used, a liquid with a maximum density of 2.88 g/cm³. The heavy fraction was further split into diamagnetic and paramagnetic fractions using an electromagnetic separator. All separated fractions were weighted out on an analytical scale in order to determine their percentage proportions in the initial 1 kg of the original settling pond sample.

Microscopic observations of quantitative and qualitative appearance of minerals and effects, related to their destruction in various fractions, were performed under a binocular microscope and in the reflected, polarised, light on a Jenapol microscope. We used the method of number of grains in a given area for semiquantitative evaluation, while this evaluation was recalculated to 100%. In every separated sample 800 grains were evaluated. RTG-powdery diffraction analysis was performed on the instrument Philips 1710 in the laboratory of the Geological Institute SAV Bratislava, the scanning electron microscopy (SEM) was performed at the instrument JEOL-840 in CLEOM PriFUK and the optical emission spectroscopy was performed on the spectrograph PGS-2 at the Geological Institute PriFUK Bratislava.

From the samples of flotation waste taken from the settling pond no. 2 we prepared leaching solutions using the method of Mehr and Jackson (1960), that is based on dissolution of Fe-oxyhydroxides using the C₆H₅O₇Na₃·2H₂O regulator and Na₂S₂O₄ and, according to the determined content of toxic elements, which these oxides have captured. In the obtained leaching solutions we determined the amounts of Fe, Zn, Cu, As and Sb using the atomic absorptive spectroscopy with flame atomisation at the instrument Perkin-Elmer 1100 in the laboratory of the Geological Institute of the PriFUK.

The simulation of the processes that occur in the mining wastes under laboratory conditions was included in this study. We used three different types of samples shown on table 1.

Table 1: Description of samples used for the simulation of processes occurring in the mining wastes in laboratory conditions.

Sample	Number and amount of samples	Characteristics of the origin of samples
1.a, 1.b, 1.c, 1.d	4 samples (100 g each)	Vein stibnite broken in fraction < 0.8 mm
2.a, 2.b, 2.c, 2.d, 2.e, 2.f	6 samples (500 g each)	Original settling pond material
3.a, 3.b, 3.c, 3.d, 3.e, 3.f	6 samples (500 g each)	Original settling pond material enriched in 1 g of vein antimonite broken in fraction < 0.8 mm

To these samples, after their emplacement into graduated flasks, were added a solution of distilled water with a pH adjusted to 3.2 using HCl and to 7.4 using NaOH and then they were placed into environments with temperatures at +5°C, +30°C and 20°C, respectively. Into 6 samples we added 1 g of humic acids each, in order to evaluate the ability of these organic matters to sorb toxic elements brought into the solution during the oxidation of sulphide minerals. The exact parameters of the experimental leaching conditions of various samples is shown on table 2. During the whole progress of the experiment we measured the pH using the instrument Elteca 110 and we observed the changes occurring at the surface of the material in the graduated flasks.

Table 2: The analysed As, Sb and Fe concentrations in the leaching solutions from the samples of vein stibnite and of settling pond material with characteristics of the leaching conditions for individual samples.

Designation and characteristics of samples	As [µg/l]	Sb [mg/l]	Fe [mg/l]
1.a (pH 3.21, +5°C)	-	21.36	-
1.b (pH 3.21, +30°C)	-	30.64	-
1.c (pH 7.43, +5°C)	-	31.72	-
1.d (pH 7.43, +30°C)	-	30.24	-
2.a (pH 3.21, +5°C)	5.46	2.92	<0.05
2.b (pH 3.21, +30°C)	10.52	3.28	<0.05
2.c (pH 7.43, +5°C)	4.36	3.36	<0.05
2.d (pH 7.43, +30°C)	10.4	4.04	<0.05
2.e (pH 3.21, +20°C, HA)	5.76	3	<0.05
2.f (pH 7.43, +20°C, HA)	11.88	3.2	<0.05
3.a (pH 3.21, +5°C)	10	6.48	<0.05
3.b (pH 3.21, +30°C)	12.44	4.84	0.07
3.c (pH 7.43, +5°C)	7.36	6.68	<0.05
3.d (pH 7.43, +30°C)	14.2	4.2	<0.05
3.e (pH 3.21, +20°C, HA)	13.2	4.76	<0.05
3.f (pH 7.43, +20°C, HA)	15.48	5.24	<0.05

HA – humic acids

After two months of leaching of stibnite samples and samples of settling pond material we frequently partially evaluated the obtained leaching solutions by analysing the amount of Sb, As and Fe, in solution using atomic absorptive spectroscopy on the Perkin-Elmer 1000 instrument in the laboratory of Geological Institute of the PriFUK.

Results

Sediments of the Settling Ponds

Samples from test the pits MO1 (settling pond no. 1) and MO2 (settling pond no. 2) were used for the study of sediments from the settling ponds. The test pit MO1 was 290 cm deep and the test pit MO2 310 cm deep. Altogether 44 samples were taken. The test pits were dug during the field work in 1997. Also, we used the samples from drill holes VOD-1, VOD-4 and VOD-7 (depth interval 0.2 m - 3.5 m) that were drilled at the settling ponds no. 1 and no. 2 by GP SNV in 1992 (Arvensis et al., 1994; Arvensis, 1998) and samples taken from the outlet of the drainage system of the settling pond no. 2.

The pH values of the flotation wastes, analysed in the samples from the settling ponds MO1 and MO2, are 7.9 - 8.1. These values prove, that pH of the wastes is neutral to weakly alkaline, without determination of any substantial changes in relationship to the depth or to the place of sampling at the settling ponds.

Minerals of the Settling Ponds Identified by Optical Methods and by RTG-powdery Diffraction Analysis

Using the mud discharges and panning of all the settling pond material samples (1 kg per sample), by the separation in heavy liquid (CHBr₃) into light and heavy fractions, by the exact determination of weight and the calculation of qualified estimate of mineral proportions of heavy and light fractions in the total volume of the settling ponds it was determined that the light fraction forms about 99.9 % of the total amount of the settling pond material. This fraction is formed by a greater proportion of the sandy fraction and by a smaller proportion of the fine-grained clayey material (about 20 - 40 %), that was removed during mud discharging. Quartz and feldspars are the main gangue minerals that are present in the light fraction, identified by optical methods, as well as by RTG-powder diffraction analysis. Only illite was identified by the RTG-diffraction analysis of the samples of granulometrically separated clayey fraction of <2 micrometers.

The heavy fraction of the settling pond material, which represents about 0.1 % of the total is formed of gangue and ore minerals. The main gangue minerals of the heavy fraction are carbonates. They occur as either a form of hydromorphic grains of a white colour probably calcite, or as a form of hypidiomorphic and allotriomorphic grains of a creamy colour, that are affected by partial oxidation,

probably the Fe dolomite, ankerite, (determined by RTG-diffraction analysis of the heavy fraction).

Using a qualified estimate we calculated that carbonates form nearly half (about 45 %) of the total proportion of the heavy fraction from the settling pond material. Using the optical methods and RTG-diffraction analysis some other gangue minerals present in the heavy fraction were identified: abundant apatite, less common biotite and zircon and accessory chlorite, muscovite (white mica), epidote, garnet, amphibole and titanite. In nearly all of the samples anthropogenous material was identified in accessory amounts.

Ore minerals form about 30 % of the total amount of the heavy fraction from the settling pond material. Pyrite (about 17 %), arsenopyrite (about 6 %) and stibnite (about 1 %) are the main ore minerals, identified using optical methods and RTG-powder diffraction analysis. In addition the heavy fraction has sparse rutile and accessory Sb-sulphosalts, Fe-oxyhydroxides, Sb-ochres, marcasite, sphalerite, ilmenite and hematite.

Using the optical methods, we focused on the study of qualitative and semiquantitative proportions of minerals at the settling ponds and at the evaluation of the differences in the intensity of the sulphide minerals oxidation in the samples from the test pits MO1 and MO2 and in the samples from the drill holes VOD-1, VOD-4 and VOD-7. Qualitative and semiquantitative proportions of minerals from the both types of samples was nearly identical. Smaller differences in the quantitative proportions and in the intensity of the oxidation were determined on pyrite, arsenopyrite and stibnite, as described below. The comparison of semiquantitative proportion of minerals is shown in figure 2.

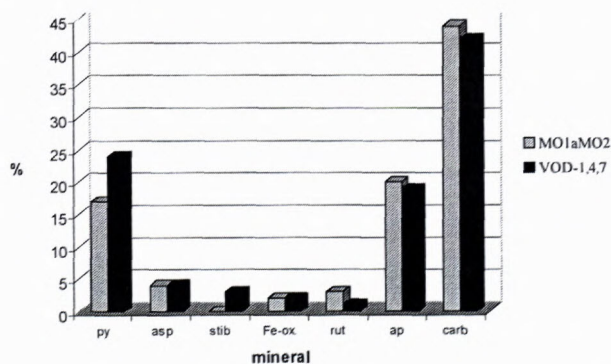


Figure 2: Comparison of the semiquantitative proportions of some heavy fraction minerals from the settling ponds of the Dúbrava deposit in samples from the test pits MO1 and MO2 and in the samples from drill holes VOD-1, 4 and 7, determined by optical observations.

Pyrite - is the dominant ore mineral in all samples.

At the settling pond two generations of pyrite are present: a) pyrite (I.) - hypidiomorphic to allotriomorphic grains in size from 20mm to 2 mm. All grains show traces of mechanical treatment and marginal oxidation. During the study of pyrite in reflected light we determined that, besides the corrosion of margins predominantly in the larger grains, the overprinting of pyrite by secondary

minerals occurs on small cleavages. However, the degree of oxidation of individual pyrite grains varies and weakly oxidised grains prevail, representing their initial stage of destruction. During the observation of the surface of the separated grains using the scanning electron microscopy (SEM), the crusts of secondary minerals are clearly seen, probably represented by Fe-oxyhydroxides. The oxidation processes did not much changed the original morphology of the grains.

In the samples from the drill holes VOD-1, VOD-4 and VOD-7 pyrite grains of the fractions smaller than 0.2 mm prevail, but the intensity of their oxidation is less distinct and many non-oxidised grains prevail.

b) pyrite (II.) - forms very tiny (the size of grains is less than 10 mm), idiomorphic and hypidiomorphic crystals included in quartz. The oxidation of pyrite (II.) was not observed and the grains are unfractured.

Arsenopyrite - is an abundant ore mineral. It occurs in the form of idiomorphic to hypidiomorphic crystals, that are partially fractured by mechanical treatment. Rarely, it appears in the form of hypidiomorphic grains in quartz. The oxidation of arsenopyrite grains from the test pits MO1 and MO2 is clearly visible in reflected light, as well as by SEM. It affects mainly the margins of grains. On some of the grains reddish coating and crusts of oxidation products about 10 mm thick are present. These coatings and crusts are not continuously evolved, but they are limited to definite flakes that are separated from the grains at some places. An apparent destruction of the centres of the arsenopyrite grains was not observed however, at places with fissures after mechanical treatment, thin veinlets of secondary minerals, proceeding inside the crystals, are visible. Arsenopyrite crystals from the samples from the drill holes VOD-1, VOD-4 and VOD-7 show almost no oxidation alterations and their internal structure is not affected, excluding the rare fissures caused by the mechanical treatment.

Stibnite - is the ore mineral, which showed the largest differences in quantitative proportions, as well as in the oxidation intensity, between the samples from the test pits MO1 and MO2 and the samples from the drill holes VOD-1, VOD-4 and VOD-7. Stibnite in samples from the test pits MO1 and MO2 is less abundant. Stibnite occurs in the form of allotriomorphic, oval aggregates with tracks after mechanical treatment. We discovered an important fact, that in individual samples stibnite occurs in the large form of grains only (over 0.2 mm), while its appearance in the under-sized fraction (less than 0.2 mm) is negligible. The destruction is most visible on these aggregates, proceeding from the margins inside their central part. The grains include several tiny veinlets, fissures and cavities, but they are not filled by any products of oxidation. This supports the assumption that in stibnite grains the destruction occurs by sequential decomposition (dissolution). Rarely, aggregates of stibnite, including allotriomorphic quartz grains, are present.

In samples from the drill holes VOD-1, VOD-4 and VOD-7 stibnite is an abundant mineral. Hypidiomorphic and allotriomorphic aggregates occur in intermediate-sized, as well as in under-sized fractions, where they

prevail. The grains are locally fractured, mechanically treated and they are not affected by substantial oxidation.

Toxic Elements in Effluxes from the Settling Pond no. 2

The presence and content of toxic elements in the effluxes from the settling pond no. 2 were determined by analysing the leaching solutions from the sample of flotation waste on the outflow of the drainage system (sample no. 1). Due to comparison also sample from the flotation waste from depth 150 cm from this settling pond was analysed, too (sample no. 2). The amounts the Zn, Cu, As and Sb were determined, which were captured on Fe-oxyhydroxides (FeOOH). Fe, which was liberated by dissolution of these Fe-oxyhydroxides in leaching solutions, was determined, too (table 3).

Table 3: The concentrations of toxic elements in the samples of settling pond material no.1 and no. 2 determined by atomic absorptive spectroscopy

	Fe (g/kg)	Zn (g/kg)	Cu (g/kg)	As (g/kg)	Sb (g/kg)
Sample No.1	12.83	0.032	0.0019	0.004	1.221
Sample No.2	2.685	0.01275	0.00535	0.00285	0.31575

The Fe contents were recalculated for the amount of Fe-oxyhydroxides and we ascertained that in the sample no.1 20.39 g/kg and in sample no.2 4.27 kg of Fe-oxyhydroxides are present. Consequently, the relatively large differences in toxic element contents between the samples no.1 and no.2 are related to the amount of Fe-oxyhydroxides and to the general character of these samples. The sample no.1 was taken from the surface drainage of the settling pond, therefore it was in considerable amount exposed to the climatic effects and to the subsequent oxidation of Fe-sulphides, more than sample no. 2. As shown in table 3, the contents of analysed elements (Zn, Cu, As), excluding the Sb-content (where it was calculated that 1 kg of Fe-oxyhydroxides at the settling ponds would be able to capture up to 60 g of Sb), are rather low in sample no.1. These values suggest that at the settling pond at given conditions a slow oxidation of sulphide minerals is in progress.

Oxidation of Sulphide Minerals from the Settling Ponds of the Deposit Dúbrava under Laboratory Conditions

During two months of observation of the experiment progress an distinct change in pH of the leaching solution was determined in the first week. This change was predominantly related to the samples poured by the solution with a pH of 3.21. Here the pH prevalingly reached the value of 7–8. In the samples receiving the solution with pH 7.43 such a significant changes of pH values were not determined.

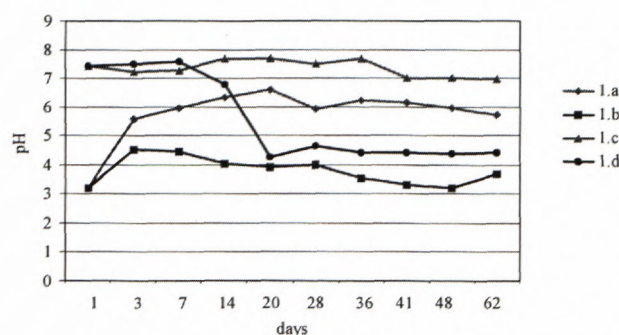


Figure 3: Diagram of pH change of experimentally leached samples of stibnite 1.a-1.d.

At the graphic illustration of the changes in pH values in the samples 1.a -1.d (leached stibnite), (Fig. 3) two different trends of evolution are possible to infer, depending predominantly on the temperature of the environment. The pH value of the sample 1.d, receiving the leaching solution with a pH of 7.43 at the temperature 30°C, progressively decreased to the value 4.4 and the pH value of the sample 1.a, receiving the solution with a pH of 3.21 at the temperature +5°C, increased to the value 6.6.

In the samples 2.a - 2.f (leached settling pond material) and 3.a - 3.f (leached settling pond material enriched in stibnite) (Figs. 4 and 5) an immediate change in pH occurred in all samples receiving the acid solution towards neutral to weak alkaline pH. This pH did not change substantially during the whole time of the experiment. The pH value in the samples receiving alkaline solution slightly increased to 8. Neither temperature, the pH of the leaching solutions, nor the humic acids affected the pH evolution, but probably it was influenced by the mineral composition of the settling pond material.

The next change that was determined during the progress of the experiment, was the origin of the grey spots in the samples of the leached settling pond material, enriched in stibnite (3.a-3.f). In the samples not enriched in stibnite (2.a-2.f) these changes either did not occur or they occurred only rarely. Based on more detailed observations, it was discovered that we are dealing with the process of oxidation and the destruction of stibnite grains in the settling pond material respectively.

The results of atomic absorptive spectroscopy analyses of these leaching solutions are shown on table 2. The determined As-contents are very low, but some dependence of the amount of leached As on the environment, in which the sample was leached (temperature, pH), was possible to observe. As shown on table 2, the highest amounts of As are present in the samples of the settling pond material, emplaced at the temperature +20°C and +30°C. Neither pH nor humic acids substantially influenced the amount of leached As.

Using the analysis of the leaching solutions, a relatively high antimony content was determined in all samples (table 2). The highest amount of Sb was leached

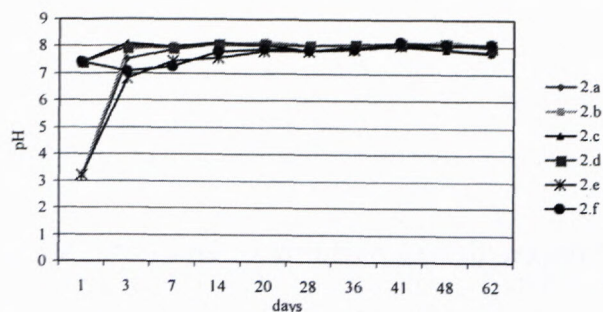


Figure 4: Diagram of pH change of experimentally leached samples of settling pond material 2.a-2.f.

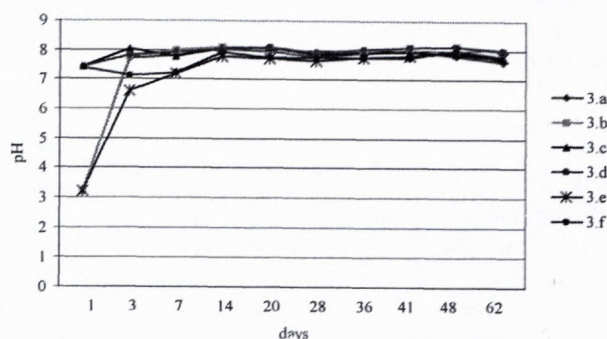


Figure 5: Diagram of pH change of experimentally leached samples of settling pond material enriched by stibnite 3.a-3.f.

from samples of vein stibnite. We did not observe any dependence of the amount of leached Sb on the temperature, pH and humic acids. However, some differences were detected among individual samples of settling pond material, as in all samples 3.a-3.f, enriched in stibnite, higher Sb contents were analysed than in the samples 2.a-2.f, not enriched in stibnite. Consequently, the Sb content in the leaching solution depends on the amount of stibnite, that was present in the leached material.

Discussion

The results of granulometric analysis, used for describing the settling pond material, are in agreement with the results of previous studies, but with some minor differences, that are related predominantly to the proportions of the aleurite and psammite components in this material. While Arvensis et al. (1994) describes these wastes as psammite to aleurite sands of a creamy colour with brownish tint and with predominance of the aleurite component, our results determined the predominance of the psammite component, with its concentration in all analysed samples to 60 - 90 %, while the proportion of the aleurite component was maximum 40 %. Using the grain size analysis we also determined the presence of the pelite (clayey) fraction, with the concentration in samples reaching a maximum of 1 %. However, such amounts can not be generalised for the total grain-size composition of the deposited wastes, if considering the different character

of the material distributed to the settling ponds and the location of the test pits, from which the samples were taken. By the RTG-diffraction analyse of the pelite fraction only illite was unambiguously identified, but its presence was further determined by RTG-diffraction analysis of the samples not granulometrically separated. The presumed presence of other clayey minerals, described by Orvošová et al. (1998) from the underground workings - kaolinite and mainly smectite, was not detected either by using the saturation of the clayey material or by the ethyleneglycol method. However, their presence at the primary occurrences was only rare.

The total quantitative and semiquantitative proportions of minerals could be characterised by a significant predominance of gangue minerals over ore minerals, which form an accessory component of the wastes. Especially the carbonate content (the neutralisation potential of the settling ponds), determined by a qualified estimate, is nearly two times larger than the pyrite and arsenopyrite content. Quartz, plagioclases, K-feldspars, carbonates (Fe-dolomite, calcite) and apatite are the main gangue minerals of the settling ponds. Biotite, muscovite, chlorite, zircon, rutile, garnet, amphibole, epidote and titanite were identified as minor or accessory minerals. The presence of these minerals is in agreement with their average content in the rocks of the Dúbrava deposit. Pyrite, arsenopyrite and stibnite are the primary ore minerals. In accessory amounts unidentified Sb-sulphosalts, Fe-oxyhydroxides, Sb-ochres, marcasite, ilmenite, hematite and sphalerite were detected.

By comparison of the samples from the test pits MO1 and MO2 from 1997 with the samples from the drill holes VOD 1, 4 and 7 from the year 1992 it was determined that the quantitative and qualitative proportions of the minerals of the light and heavy fraction in both types of samples were nearly identical. Pyrite and arsenopyrite had some small differences in the intensity of their oxidation, because in the samples from the test pits MO1 and MO2 weakly oxidised grains of pyrite and arsenopyrite prevail. However, any other significant oxidation alterations were not observed and we suppose that today they are not being oxidised in larger quantity, inasmuch as the carbonates present in the settling ponds hamper the oxidation processes of these sulphides. A neutral to weakly acid character of the deposited wastes is also supported by the results of the pH measurements - the obtained values are 7-8.

Larger differences in the quantitative proportions and in the intensity of the oxidation in both types of samples were detected in one of the sulphide components of the settling pond material - in stibnite. While in the samples from the drill holes VOD-1, 4 and 7 stibnite was present in larger quantities to 5 % without any oxidation alterations that is also supported by the results of Arvensis et al. (1994). The stibnite contents in the samples from the test pits MO1 and MO2 mostly reached accessory amounts only. Stibnite in these samples was much strongly oxidised and fractured, but without the presence of secondary minerals that were not determined in any sample.

The assessment of the increased Sb-content (1221 mg/kg) in the sample taken below the outlet of the drainage system that was absorbed by Fe-oxyhydroxides confirms the assumption, that stibnite is neutral to weakly alkaline pH of the wastes, in the environment without the access of oxygen from the air, it decomposes into unidentified Sb-compounds that penetrate into the settling pond waters and migrate. Fe-oxyhydroxides present in this sample in the amount of 20.39 g/kg (2.04%) replace the absenting clay minerals (smectite) and at the settling ponds they play the role of a natural sorption barrier. These secondary minerals of Fe are generally important due to their ability to transport and capture various elements, that change their composition in the waters (Trtíková, 1997). We calculated, that 1 kg of Fe-oxyhydroxides at the settling ponds of the deposit Dúbrava would be able to capture up to 60 g of Sb.

Based on the results of the microscopic study and on the analysed amounts of Sb, Cu, Zn and As in the sample taken below the outlet of the drainage system, we suppose that at the settling ponds a very quick oxidation of stibnite, its decomposition and subsequent migration of Sb into the environment occurs in the first years of depositing of the wastes at the settling ponds. At the present time, the detected low concentrations of Cu, Zn and As prove the slow oxidation of the sulphide minerals, in which these elements are present, and their small influence on the toxic pollution of the vicinity of the settling ponds.

Two months of experimental observations of the oxidation processes, occurring in the settling pond material and in the samples of leached vein stibnite, gave us valuable results, that could be theoretically applied to the real processes occurring at the settling ponds.

At first it was thought that the relatively high Sb-content in the leaching solutions during the short period of leaching suggested a quick decomposition of stibnite in the aqueous environment without access of oxygen from the air. Using this information it is possible to explain the decreasing Sb-contents in waters from the drill holes VOD-1, 4 and 7 during the two years of monitoring (1992-94), described by Arvensis et al. (1994) and Arvensis (1998). Similarly, we can explain the small amount of stibnite in samples from our test pits MO1 and MO2 from 1997.

The process of leaching and the Sb-content in the leaching solutions in various samples was not affected either by the temperature or by the pH of the environment. Based on this information we inferred that Sb belongs to those elements (Cu, Ni, Cr, Pb), for which according to Letko (1992), no sound relationship have been observed between the solubility and the pH value. Jorgensen and Pedersen (1992) in Arvensis et al. (1994) experimentally proved a very little influence change of the pH of the environment on the ability to leach out Sb.

The determined low Fe and As concentrations prove the show ability to leach out these elements from the settling pond minerals. The result is in agreement with the determination of the relatively low oxidation of pyrite and

arsenopyrite, using the optical observation as well as with the results of analyses of the leaching solutions from the sample taken below the outlet of the drainage system of the settling pond no. 2. The finding of the dependence of the amount of leached As on the temperature, that illustrates the higher concentrations of this element occur in warmer environments, is also a very interesting result.

The experimental modelling of the leaching of elements from the settling pond material was followed also by the presence of humic acids, one of the substantial components of the natural organic matters. These matters, together with fulvous acids, belong to the group of specific natural organic matters that are of relatively high molecular nature, typically with high sorption abilities. They have a dominant position in the processes of interaction with chemical elements, together with other mineral components in soils, waters, sediments (oxides and hydrous Fe and Mn oxides, clay minerals, natural carbonates).

We can evaluate the interaction of chemical elements with components of natural systems from several points of view. The relationship between the form of the binding of a chemical element and its mobility represents one of the views. Today, great interest is devoted to the problems of migration of chemical elements, predominantly toxic metals, in ecosystems. However, data from the literature are still inconsistent, due to the very complicated nature of the related problems. We will mention only some of the complex studies: Alloway et al. (1992), Cibulka et al. (1991). Babčan and Ševc (1994, 1996, 1997) studied the experimental modelling of the relations among Ag, Be, Cd, Hg, Pb, Zn and organic matters at various pH conditions.

In summary, the bindings among the chemical elements and the components of the natural systems are influenced by many factors (pH values, concentrations of organic matters, their structure etc.). The binding of chemical elements for instance with organic matters in natural systems should not be regarded as stable inasmuch as we are dealing with heterogeneous and very dynamic systems. As the result of various biogenetic and abiogenetic processes, several changes in the bindings of chemical elements occur. In the model experiments, the comparison of the results liberation of Sb and As from the settling pond material and from stibnite showed that in the systems with humic acids no binding of these chemical elements on humic acids occur.

Conclusions

Mineralogical and environmental evaluation of the settling pond material using the experimental modelling of the processes occurring in the flotation waste enabled us to find out that today, from the viewpoint of the influence on the environment, the settling ponds are not dangerous for the following reasons:

1. The settling ponds at the Dúbrava deposit are relatively young and they contain a sufficient amount of carbonates that neutralise the environment at the settling

ponds and in this way they decrease the intensity of the oxidation processes and the migration of As, Fe and other elements.

2. At the settling ponds relatively quick decomposition of stibnite and consequently the depletion of Sb-content at the flotation waste occur. Sb, in the form of unspecified compounds, goes into the water solution at the settling ponds and migrates.

3. A part of the Sb-compounds that originated during the oxidation of stibnite without any marked dependence on the pH of the environment is captured by Fe oxyhydroxides at the settling ponds and they do not migrate in substantial amounts into the vicinity of the settling ponds.

The oxidation of stibnite at the settling ponds is relatively quick, but in the flotation sediments still a relatively large amount of pyrite and arsenopyrite remain. Their extensive oxidation, related to the liberation of As and Fe into the surrounded environment of the settling ponds, depends on the neutralisation potential of carbonates, on the amount of infiltrating water and on its properties (pH, temperature).

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