PERCOLATION MODELING OF THE DUMP AND SETTLING PIT SEDIMENTS AT THE BANSKÁ ŠTIAVNICA ORE-FIELD (WESTERN CARPATHIANS, SLOVAKIA)

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Abstract: The article correlates the results of informative investigation of bio-availability of selected elements in the surrounding of Banská Štiavnica using the method of five-staged sequential analyses of technogenous, creek and bottom land sediments. It also presents the correlation of laboratory modeling of hydroquartzite and sand samples (from the tailings dam) of percolation and static maceration of heavy minerals by acid metal-rich sulphate water. Results are documented in tables, plots and diagrams. The sequential analyses showed that from the selected elements a high portion of Mn, Cu, Zn, Pb, and Cd elements is presented in bio-available forms and low portion of bio-available As, Sb and Hg in bondings. Chemical changes in technogenous sediments attended by microorganisms modify also the mineral composition of sediments of mining dumps and settling pits. Bio-oxidation processes product both inorganic and organic acids that are decomposing quartz and aluminosilicate minerals. Aluminosilicates are formed primary at interest of quartz from clay minerals.

Keywords: dump, settling pit, sediments, sulphide minerals, leaching, *Acidithiobacillus* bacteria

1. INTRODUCTION

Percolation of mechanically disintegrated rocks deposited at the surface of mining dumps and settling pits by rain water accelerate the geochemical processes. Their dynamic and intensity is limited by volume, mineral composition and grain size of dump material. In the area of Banská Štiavnica dumps the oxidation and biological-oxidation processes (in the presence of autochthonous microorganisms like fungi, yeasts, algae, bacteria) exceed over reduction processes after certain time period. Rain water infiltrated within dumps metamorphoses to acid metal-rich sulphate water (Michalková et al., 2008; Welwardt et al., 2006). If this water migrates to surface water body through permeable soil horizons at the impermeable ground it acidifies and

saturates them by toxic metals (Križáni et al. 1994). Life conditions are deteriorated for soil microorganisms and plants in such contaminated soil. In some cases, the desolate unstocked areas originate. There, wind and water erosion removes the mortified soil very fast till in the relief of micro-watershed the deep cutted erosion striae originate. It is only the system of geochemical processes caused by mechanical disintegration and displacement of rocks due to human activity. Man also enters into the geochemical cycle in the improvement processes of mined ores (Križáni & Andráš 2006). He utilizes the density differences of utility and waste minerals for their separation by gravitation methods or chemical influences the mineral surface wetness because of their separation by flotation (Križáni et al., 2007). The original mineral composition of waste products changes in compacting processes in order to obtain concentrates by fluxing agents and heat energy. Their storage causes the origination of dumps filled with rock pieces with ore addition, fine-milled waste minerals with addition of suppressed and lost ore minerals, metal artefacts and flotation reagents. Atmosphere is polluted with dust from the settling pits, aerosols from smelters. Aerosols affect directly breathing apparatus of flora and fauna and solid matter contaminates soil by toxic metals. Outlined and other influences of antrophic modified geochemical processes interferes all country components (Križáni & Jeleň 2002).

2. STUDIED OBJECTS AND EXPERIMENTAL METHODS

The samples from dumps of different age, smelter slag dump, sediments of settling pits and active bottom land sediments of the Štiavnica creek were studied (Fig. 1).

2.1 Dumps

The dump of the New shaft files the valley between spot heights Šobov and Glanzenberg (650 – 710 m above see level) with inclination to east, south – east. The dump is among the biggest in its extent (more than 10 hectare) in the studied area. The extensive mining of polymetallic ores and intensive exploration in 1974 – 1992 caused the covering of the dump in the area of the older Gábor adit and the Upper lagune of Michal adit was buried. Material composition is the most different from all dumps and different at all levels. Hydroquartzite is present as well (Oružinský 1989).

The Šobov quarry and its dump is situated north and east of the New shaft, 1.5 km north – east from the historical center of Banská Štiavnica. The crest part of quarry and dump intersects river-basin of Hron and Ipeľ. The area of quarry and dump is affected by mining activity at veins Bieber and Špitaler. Mined hydroquartzite is utilized as raw material in production of acid fireproof building material and filtration mixture for water treatment. The Šobov dump activity has begun in 1956. It contains uncovering soils, non-conditional hydroquartzite rocks impregnated with pyrite from angles of quarry breaks containing 2 – 20 wt. % of sulphides with dominant pyrite portion. Dump ground creates clay leaching at the propylitized pyroxene andesite and sedimentary filling of intra-volcanic cannon pot (the formation of Red Well). Veins of hydroquartzite moved out solifluxionally direct into mantle rock of slope under the dump (Oružinský 1989).

The dump of the Terézia shaft is situated cca 500 m from the lake Klinger at the east slope of the spot height 938.8 Tanád, at the south border of surface mining points of the Terézia vein exit. Shaft opening is within vein filling. The dump is wooded, situated from the shaft opening in north-east. The cuttings of vein filling with mineralization are largely presented at the dump crest.

2. 2 Settling pits

Settling pits is among the youngest depositions of the fine-grained technogenous sediments. The beginning of their creation is between the 18th and 19th century when the mineral and compacting processes of concentrates was gradually centralized. First settling pits were originated by filling of older hydrotechnical works. The representative of this group of settling pit is Suchý tajch, situated among the west border of Štefultovo and the south border of the Štiavnica mines. Processing plants in Windšachta and Piarg (the present Štiavnické Bane village) produced waste pulp after the gravitation treatment of precious metals – polymetalic ores. It flowed into the settling pit in water mixed with communal sewage. Sediments contain notable portion of organic material. The area of settling pit is covered with cca 1 m thick "reclamation" layer of waste material from the near dump. Local road leads across the north border of settling pit; river basin of the Štiavnica creek determines west and south borders. The area of settling pit is watered and anoxic under the reclamation layer. Heavy metals are enriched on autigenous, amorphous, framboidal Fe sulphides and aggregate grains formatted by idiomorphic anglesite laminae, bonded by crystal high-purity-gold (Križáni & Andráš 2006).

The area of crashed Lintich tajch, situated right from the road between Banská Štiavnica - Svätý Anton was used for the flotation waste deposition from the processing plant near the František shaft in 1964 – 1974. The area of the Lintich tajch settling pit and wider surroundings were devastated by immissions from the near Central Smelter. Settling pit contains 580 thousands cubic meters of fine-grained flotation waste product which was used for the experimental afforestation (Valovič 1981). Since 1987 the sand has been mined from the dam for building purposes. The efflorescence of disulphate salts with gypsum addition has been created at the walls of exploitable pits during dry seasons (Križáni & Jeleň 2002; Križáni & Andráš 2006). Exploitable pits have been filled with building and communal waste. The toe of dam air side was burdened with smelter slag in 1995 – 1997. The slag was displaced from the excavation pit for the water treatment plant at the Štiavnica creek, situated east from the Central Smelter area.

Flotation refinement of polymetalic ores was displaced with the processing plant near the New shaft from 1975 to 1994. Settling pit of this treatment plant is situated among Banská Štiavnica and Banská Belá, called Sedem Žien settling pit. It is the only one settling pit constructed according to the project of Banský Projekt Company. It contains cca 3 million cubic meters of sediments. Settling pit reconstruction was finished in 1995 – 1997. Settling pit was covered with 2 – 3 m of waste rock which came from the crest level of the New shaft dump and partly with waste from the Šobov quarry. This layer was covered with 5 – 10 cm of soil from the retentive basin dam and its bottom sediments.
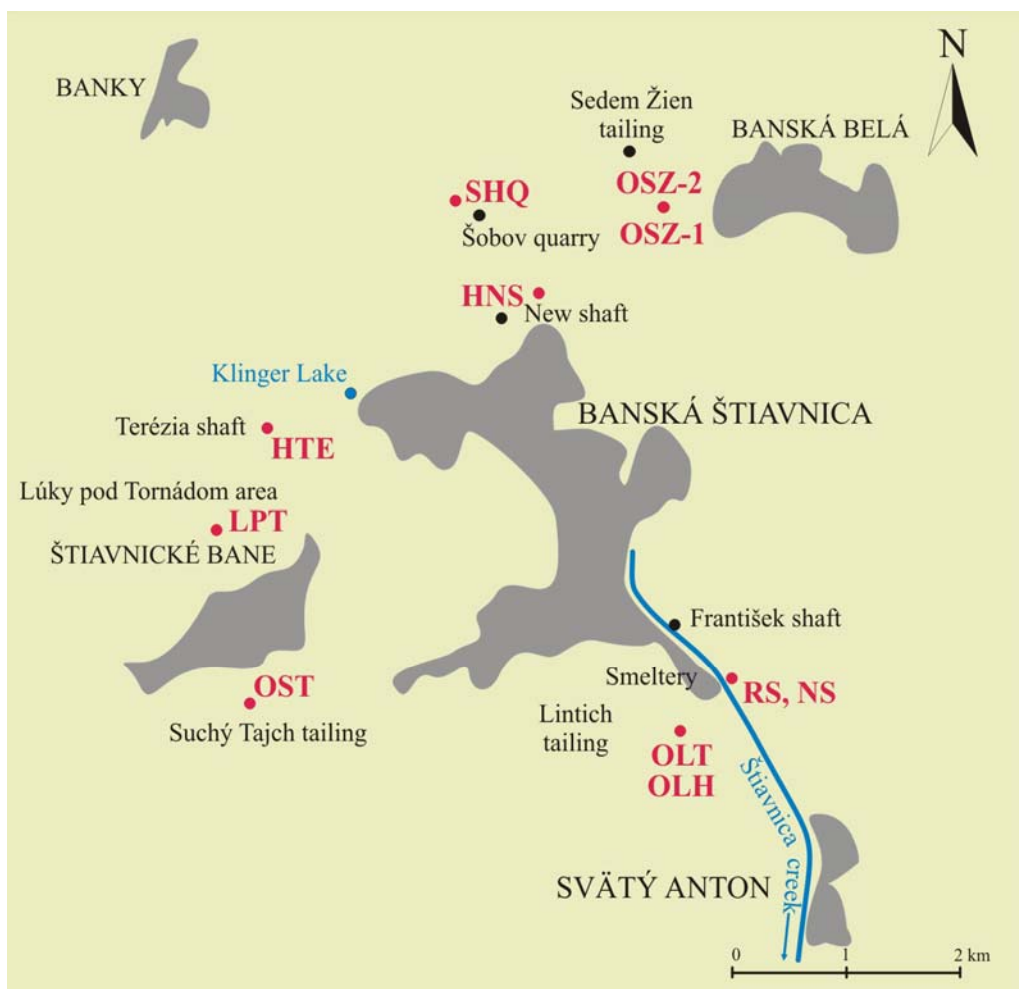
Figure 1. Schematic map showing the investigated objects and localization of samples (SHQ, OSZ-1, OSZ-2, HNS, THE, LPT, OST, OLT, RS+NS) in the surrounding of Banská Štiavnica.

2.3 Experimental

The determination of overall contents of heavy metals and toxic elements in technogenous sediments do not have sufficient cancellation value for examination of their influence on biotic land components because the determination does not make provision for their bioavailability. The bioavailability is possible to determine by analysis of sequential extracts. It is realized by three to six-staged sequential extractions. The five-staged sequential extraction was developed and established in Slovakia (Mackových et al. 2000). Informative study of bioavailability of the selected elements was made by five-staged sequential extraction from the special sampled and treated samples (Fig. 1):

HNS – ore cuts from the bottom level of the New shaft dump,

HTE – ore cuts from the Terézia shaft dump,

OLT – slag fragments from the dump under the Lintich tailings dam,

OSZ-1 – sample from the front of borrow pit in west border of the dam crest of the Sedem Žien settling pit,

OSZ-2 - sample from the front of borrow pit above waste rock of the dam bottom of the Sedem Žien settling pit,

OLT - sample from the front of borrow excavated in the interface zone of facies beach and lagun of the Lintich settling pit.

OLH - sample from the wall of exploitation pit in the Lintich tailings dam,

OST - sample from the front of borrow excavated in west border of the Suchý tajch settling pit,

RS – active sediment from the river basin of the Štiavnica creek in the front of north border of the Svätý Anton village,

NS – bottom land sediment from the probe in undercut-slope bank of the Štiavnica creek in the front of north border of the Svätý Anton village (Fig. 1).

The weight of the samples was 1 – 2 kg. Samples were first dried at the laboratory temperature, crushed and sieved with 0.125 mm sieve. Undersize grain class was treated to the grain size 0.09 mm by non-abrasion homogenization in the agate dish. The total contents of Al_2O_3, Fe_2O_3, FeO, MnO, CO_2, SO_3, $S_{tot.}$, Cu, Zn, Pb, Cd, Bi, Ag, Sb, As, and Hg were stated first. On the base of the results, the samples for the five-staged sequential extraction were determined to find out the bioavailability of Mn, Cu, Pb, Cd, Bi, Ag, Sb, As, and Hg. For evaluation of extractable element portions, 1 g of sample was used. The sequential extraction proceeded as follows:

- Water-soluble fraction (1) was extracted in 50 ml of distilled water in the hermetically closed polyethylene container within 16 hours. Skimmed solution was analyzed and solid residue was used for the extraction in the next step.
- Ion-replaceable and carbonate fraction (2) was extracted in 40 ml solution of 0.11 mol of acetic acid.
- The residue was given into the extraction phase of reducible fraction (4) in 40 ml solution of 0.1 mol of hydroxylamine hydrochloride solution.
- The extraction of organic-sulphide fraction (4) followed from the residue of previous steps. After water evaporation, 10 ml of H_2O_2 was added to solid phase, followed with heating up to temperature 85 °C within 60 minutes. In this step, the volume of suspension was reduced to about 3 ml, consequently 10 ml of H_2O_2 was added and the heating continued until total solution evaporation. After the quantitative sample displacement into the centrifuge with 50 ml solution of 1 mol of ammonium acetate ($C_2H_3O_2NH_4$) the extraction continued within 16 hours. Skimmed solution was analyzed and solid residue was quantitative displaced into the platinum dish. The evaporated water and the dish of known weight with the result of evaporation was weight out again.
- The residual fraction (5) was obtained by total decomposition of the solid residue after the extraction of fractions 1 – 4. 10 ml of concentrate hydroflouride acid and 1 ml of concentrate perchlorate acid was added first. After stirring around, the evaporation at the sand-bath with white fume followed. Then 10 ml of concentrate hydroflouride acid was added and evaporation into dryness followed. The result of

evaporation was sprinkled with 1 ml of concentrate perchlorate acid and 5 ml of hypoboric acid saturate solution was added. The evaporation into dryness followed to evaporate the residues of chlorides. 5 ml of nitric acid was added to the result of evaporation; the solution was digested within 20 minutes. After the temperature reduction the solution was spilled into 50 ml polyethylene bottle and was used for determination of remaining contents of elements besides Hg.

- Hg was determined by TMA method from the solid sample residue after the extraction of fractions 1 – 3.

During the gradual extraction of fractions 1 – 4, the mixture of solid phase and extraction reagent was maintained in suspension at the laboratory shaker within 16 hours. The solutions of individual fractions were separated from the insoluble solid phase by centrifugation at rotation speed 4000 within 20 minutes. The solutions of individual fractions were preserved in the polyethylene containers at the temperature 4°C and were used for the determination of extractable portions of observed elements using ICP and AAS analyses. The results were adjusted to dry state. The accuracy of determination was verified with the reference material CRM – 601.

Element contents extracted by regents 1 – 4 are bioavailable. Applied reagents imitate natural processes of release of elements from the primary bonds into the solutions and their recombination to secondary minerals.

Soňa Cicmanová and Karol Marsina from the Geological Institute of Dionýz Štúr – Regional Centre in Spišská Nová Ves were involved in the process of sampling, treatment, analyzing, and evaluation of results of the sequential analysis. The samples were treated and analyzed at the Geo-analytical Laboratories of the Geological Institute of Dionýz Štúr – Regional Centre in Spišská Nová Ves.

2.3.1 Percolation modeling of the dump and settling pit sediments

The model experiment was aimed at the imitation of natural leaching of heavy metals by comparative technique. It was realized with the following samples:

- SHQ – average sample of hydroquartzite from Šobov prepared from bore powder for bench blasting at the bottom level of the Šobov quarry.
- SZH – sample prepared from the gains from the forehead of borrow pit (vertical interval 0.2 – 2 m) in the section profile in the west part of dam air side. The distance among samples was 50 m.

The laboratory preparation of samples consisted in their drying, skimming, fraction sieving with 1 mm sieve and distribution of undersize classes for 10 parts; 25 g for each part. 3 extraction liquid media were used: 1. distilled H_2O (pH 6.7); 2. solution consisted of 10 ml of concentrate H_2SO_4 + 10 ml of concentrate HNO_3 + 43.5 g of $NaHCO_3$ in 250 ml of distilled water (pH 4.5); 3 real rain water (pH 4.5).

25 g of sediment was washed during the first ά-phase of leaching intermittently by gradual quantization of 250 ml of above listed extraction reagents within 7 days. The break followed for 7 days intended for hard drying, capillary action of residual solutions and crystallization of salts. Consequently the percolation continued at the same regime (β-phase) by new ration of the extraction reagent. Each sample was divided to three parts of weight 25 g. These parts were individually washed by 250 ml

of mentioned liquid media (sets I – III). Extracts were retained into the polyethylene containers. Solid residues from each set were associated and analyzed by AAS method for the following metals: Fe, Mn, Cu, Zn, Pb, Cd and Ag as associated sample (in the laboratories of the Geological Institute of SAS in Banská Bystrica).

2.3.2 Static experiment of acid mine drainage influence from the Šobov locality on sulphide minerals

The aim of experiment was the verification of acid mine drainage (AMD) influence from the Šobov locality inoculated by *Acidithiobacillus* bacteria on the selected sulphide minerals obtained from the sediments of the Sedem Žien tailings dam. The sample of heavy fraction was macerated within 18 months at the static regime in the following solutions: 1. distilled H_2O diluted HNO_3 (1_{H2O}: 3_{HNO3}); 2. AMD from the Šobov locality. The results of experiment were studied by mean of scanning microscope and EDAX analyzer and compared consequently.

3. RESULTS

3.1 Bioavailability of selected elements

The contents of oxides and selected elements in the samples are listed in table 1. The ore from both waste rock dumps differs mainly in content of Fe_2O_3 and S, Mn, Cu, As, Sb, Bi sulphides. Those differences probably reflect the ore origin from different depth levels of ore body or different ages. The smelter slag has glassy character, originally was stored at the alluvial bottom land of the Štiavnica creek. The deposition lasted till the beginning of the 20th Century. Its main component is Fe in the form of Fe_2O_3 which is almost in balance with FeO. Among all analyzed samples the slag has the highest Zn content and the lowest Cd content. Efflorescence of the disulphate salts are macroscopically observed in the cracks of slag fragments. In the group of observed elements the OLH sample has the highest Zn and Cd content. The OST sample has the highest Ag and As content. Quaternary sediments from the Štiavnica stream significantly differ in Zn and Pb content.

Specified contents of selected elements in sequential extracts by mediums listed in the methodology are mentioned in table 2. The portions of element bioavailability in the fractions are adjusted percentage and displayed in the form of cumulative histograms (Fig. 2). Fractions 1 – 4 are bioavailable. Portions of bioavailable elements and insoluble residue are distinguished by different lineation. Individual fractions are distinguished by different column width. Fraction 5 (the widest column) represents insoluble residue transposed into the solution by total decomposition through mineral acids at heat. As and Sb fall to this fraction within 76 – 97 % in almost all samples. Only in the RS sample As content is in residual fraction near to 50 %.

Portions of water-soluble fraction (1) are in all investigated elements the smallest in all analyzed samples. Zn has the most water-soluble portion in bottom land sediment of the Štiavnica creek (NS sample). Over 3 % of water-soluble portion of Sb

is in the samples HNS and RS. Ion-replaceable fraction (2) has the highest Mn and Cd portions (from 68 to 83 %) in the samples NS, THE and OSZ-2. Bioavailable portions of As and Sb (1 – 4) are less than 25 % in all analyzed samples with total As bioavailable portion of 51 %. The sample of smelter slag OLT has As and Sb bioavailable portion of 30 %.

Table 1. Contents of the main oxides and of the selected elements in samples
used for sequence analyse

Unit	Com-po-nents	Samples									
		HNS	HTE	OLT	OSZ-1	OSZ-2	OLL	OLH	OST	RS	NS
wt. %	Al_2O_3	7.58	2.71	3.85	7.30	7.65	7.16	6.61	12.4	12.4	11.1
	Fe_2O_3	16.68	2.82	49.26	5.90	5.26	4.57	5.91	5.56	6.13	8.17
	FeO	2.46	1.30	40.56	1.02	2.02	1.98	1.95	0.29	3.29	1.96
	S $_{sulf.}$	12.00	1.74	2.61	2.34	1.77	1.10	2.04	0.10	1.00	0.03
	SO_3	0.24	0.11	0.17	0.28	0.03	0.07	0.19	0.15	0.22	0.33
	CO_2	1.51	1.85	<0.01	1.18	2.51	2.98	2.87	0.74	3.00	0.01
	Mn	0.20	1.43	0.69	0.79	0.64	0.99	1.17	1.63	0.16	0.29
mg.kg^{-1}	Cu	20 220	1140	2422	326	1151	388	1742	178	339	450
	Zn	23 398	22 750	71 125	3338	6138	3563	7138	1548	4100	855
	Pb	23 190	15 080	27 600	1341	2220	1280	1875	842	1403	3135
	Cd	120.9	140.8	1.0	19.8	37.5	19.1	41.8	8.8	25.6	2.6
	Ag	51.8	47.5	26.5	4.3	4.8	3.0	8.0	98.0	9.8	18.0
	As	62.5	7.4	31.5	33.2	19.8	17.9	28.2	78.8	34.7	54.5
	Sb	13.8	33.3	425.0	18.2	12.0	11.4	12.7	20.0	10.9	17.8
	Bi	66.6	0.9	0.6	1.1	0.3	0.2	0.4	0.4	2.0	3.3
	Hg	0.41	0.22	0.14	0.12	0.10	0.07	0.12	0.71	2.76	1.22

Table 2. Contents of the elements in sequence extracts (fractions); mg.l^{-1}

Fraction	Element	Sample							
		HNS	HTE	OLT	OSZ-2	OLH	OST	RS	NS
1	Mn	20	101	49	6	18	43	108	56
	Cu	5	1	12	<1	<1	<1	<1	5
	Zn	16	28	1398	2	4	4	16	45
	Pb	33	56	240	4	3	3	4	13
	Cd	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	As	<0.1	<0.1	0.3	<0.1	<0.1	0.4	0.9	0.1
	Sb	0.5	<0.1	1.3	<0.1	<0.1	<0.1	0.6	<0.01
	Hg	0.008	0.002	0.003	0.002	<0.001	0.004	0.002	0.005

Table 2. (continuation) Contents of the elements in sequence extracts (fractions); mg.l^{-1}

Fraction	Element	Sample							
		HNS	HTE	OLT	OSZ-2	OLH	OST	RS	NS
2	Mn	868	13789	403	4192	6826	3557	601	245
	Cu	227	75	<1	98	136	28	2	79
	Zn	2484	3479	3189	1544	2204	443	1316	160
	Pb	4470	7135	4586	943	900	2	99	439
	Cd	14.4	19.5	<0.5	10.9	13.9	3.1	0.7	1.5
	As	0.1	0.1	0.8	<0.1	<0.1	<0.1	3.6	<0.1
	Sb	0.6	0.2	14.9	<0.1	<0.1	<0.1	<0.1	<0.1
	Hg	0.001	0.002	0.002	<0.001	0.003	0.004	0.006	0.006
3	Mn	675	1833	1029	1192	2054	13190	309	1610
	Cu	761	101	1	63	81	80	1030	134
	Zn	2518	2860	6610	784	595	589	1225	300
	Pb	8630	6328	4240	816	616	735	959	1564
	Cd	13.7	17.5	<0.5	4.0	3.0	4.6	17.3	0.7
	As	4.5	0.6	6.6	1.4	2	9.6	12	6.2
	Sb	0.9	0.9	11.4	0.3	0.3	0.8	0.5	1.1
	Hg	<0.001	0.001	<0.001	0.001	0.001	0.005	0.003	0.005
4	Mn	72	230	126	171	299	265	59	92
	Cu	11260	740	1941	753	1134	28	171	58
	Zn	8660	12590	39470	2678	3088	157	401	121
	Pb	2476	1047	2535	190	77	24	136	94
	Cd	41.9	76.2	1.2	14.8	16.0	0.6	2.3	<0.5
	As	2.4	0.8	2.0	2.0	3.5	0.9	5.0	0.3
	Sb	<0.1	<0.1	11.4	<0.1	<0.1	0.1	0.1	<0.1
	Hg	0.163	0.042	0.104	0.063	0.074	0.454	1.030	0.904
Σ_{4}^{1}	Mn	1636	15953	1607	5561	9197	17055	1077	2003
	Cu	12253	917	1954	914	1351	136	1203	276
	Zn	13678	18957	50667	5008	5891	1193	2958	626
	Pb	15609	14569	11601	1953	1596	764	1198	2110
	Cd	70.0	113.2	1.2	29.7	32.9	8.3	26.6	2.2
	As	7.0	1.4	9.7	3.4	5.5	10.9	20.5	6.6
	Sb	2.0	1.1	39.0	0.3	0.3	0.8	1.2	1.1
	Hg	0.172	0.047	0.109	0.066	0.078	0.467	1.041	0.920
5	Mn	261	428	3872	765	2149	294	356	439
	Cu	1617	97	346	98	162	38	41	141
	Zn	3264	1818	25730	598	612	171	550	234
	Pb	1730	246	10000	42	57	25	112	566
	Cd	17.8	12.6	<0.5	3.9	3.8	0.6	3.6	<0.5
	As	48.3	16.6	33.0	37.7	56.3	71.6	20.6	66.0
	Sb	12.6	29.7	348.0	10.2	10.5	17.3	11.8	16.1
	Hg	0.238	0.173	0.031	0.034	0.042	0.243	1.72	0.3

The extreme high portion (75 – 91 %) bounded in the reducible fraction (3) were discovered in Mn in the sample OST, Cu in the samples OST and RS, Pb in the samples OST and RS, Cd in the sample RS. The highest portion of Hg (40 – 75 %) is bounded in organic – sulphide fraction (4) in all samples besides THE. Cd appears to the samples HNS, THE, OSZ2 and OLH within 45 – 60 %. In the OLT sample 100 % of Cd is bounded in sulphide fraction. Zn has the similar ranges of abundance in the samples HNS and OLH (Fig. 2a, b); and Cu in the same samples as well.

3.2 Laboratory experiments

The portion of clayey-powdered grain class in the HSQ sample fluctuated around 7 volume percentages and in the SZH sample around 5 volume percentages. In the light fraction of both samples quartz was the main mineral; feldspar and carbonates occurred rarely. The heavy fraction formed the mixture of heavy metal sulphides, Fe and Ti oxides and zircon. The differences among average contents of main oxides (Tab. 3) and selected heavy metals (Tab. 4) in the compared samples show higher abundance in the sediments of settling pit than in hydroquartzite.

Table 3. Content of the main oxides [$_{wt}$ %] in samples SHQ and SZH

Sample	Component										
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
SHQ	92.32	0.44	0.97	3.26	0.26	0.02	0.04	0.11	0.05	0.08	0.12
SZH	71.68	0.31	7.72	2.36	2.20	1.03	1.14	2.28	2.22	3.79	0.10

Table 4. Content of the selected heavy metals [mg.kg^{-1}] in samples SHQ and SZH

Sample	Element				
	Cu	Zn	Pb	Ag	Cd
SHQ	25	52	64	8.27	0.10
SZH	478	3 632	1 138	5.50	18.40

Heavy metal contents in the leachates of both compared substratum by 3 liquid media (1 – distilled water; 2 - solution consisted of 10 ml of concentrate H_2SO_4 + 10 ml of concentrate HNO_3 + 43.5 g of $NaHCO_3$ in 250 ml of distilled water (pH 4.5); 3 - real rain water) are listed in table 5 and 6. Percentage abundance was stated to display the portions of extracted elements by media (Fig. 3).

The portions of observed elements extracted by real rain water from Šobov hydroquartzite (SHQ) show more or less gaussian like ordered toward Zn (Fig 3 SHQ 1-3 ά). The leached element content increases from Fe to Cu and decrease from Pb to Ag. The element contents decrease in range Pb – Cd – Ag both in distilled water as well as in imitated rain water. This holds for leaching in ά-phase, whereas the leaching in β-phase is the described trend markedly altered. The most Fe passed to solution 2 in the leaching β-phase, whereas Pb and Ag were extracted by distilled water and Cd by 100 % real rain water in β-phase. Zn was 90 % extracted by distilled water in β-phase.
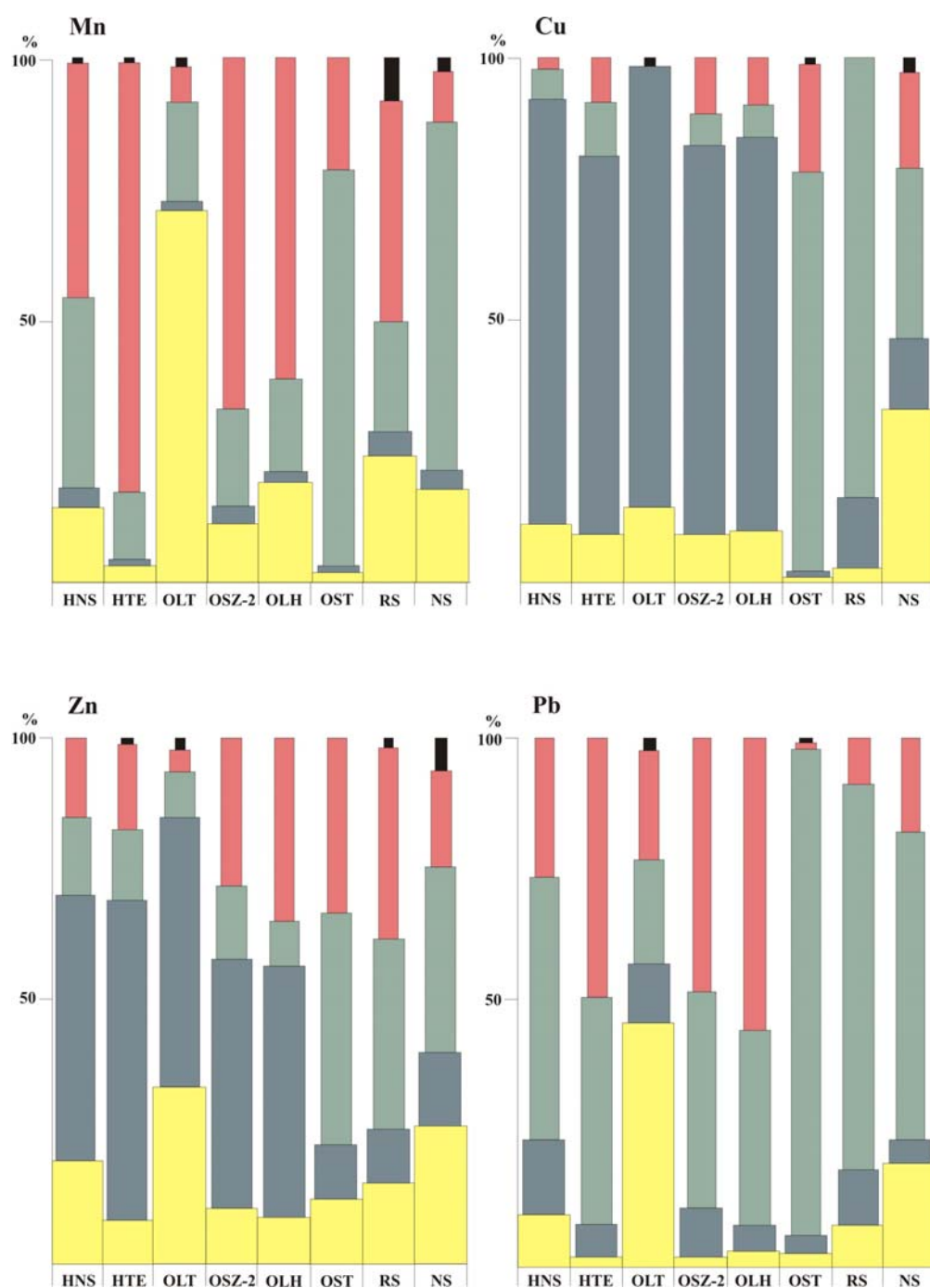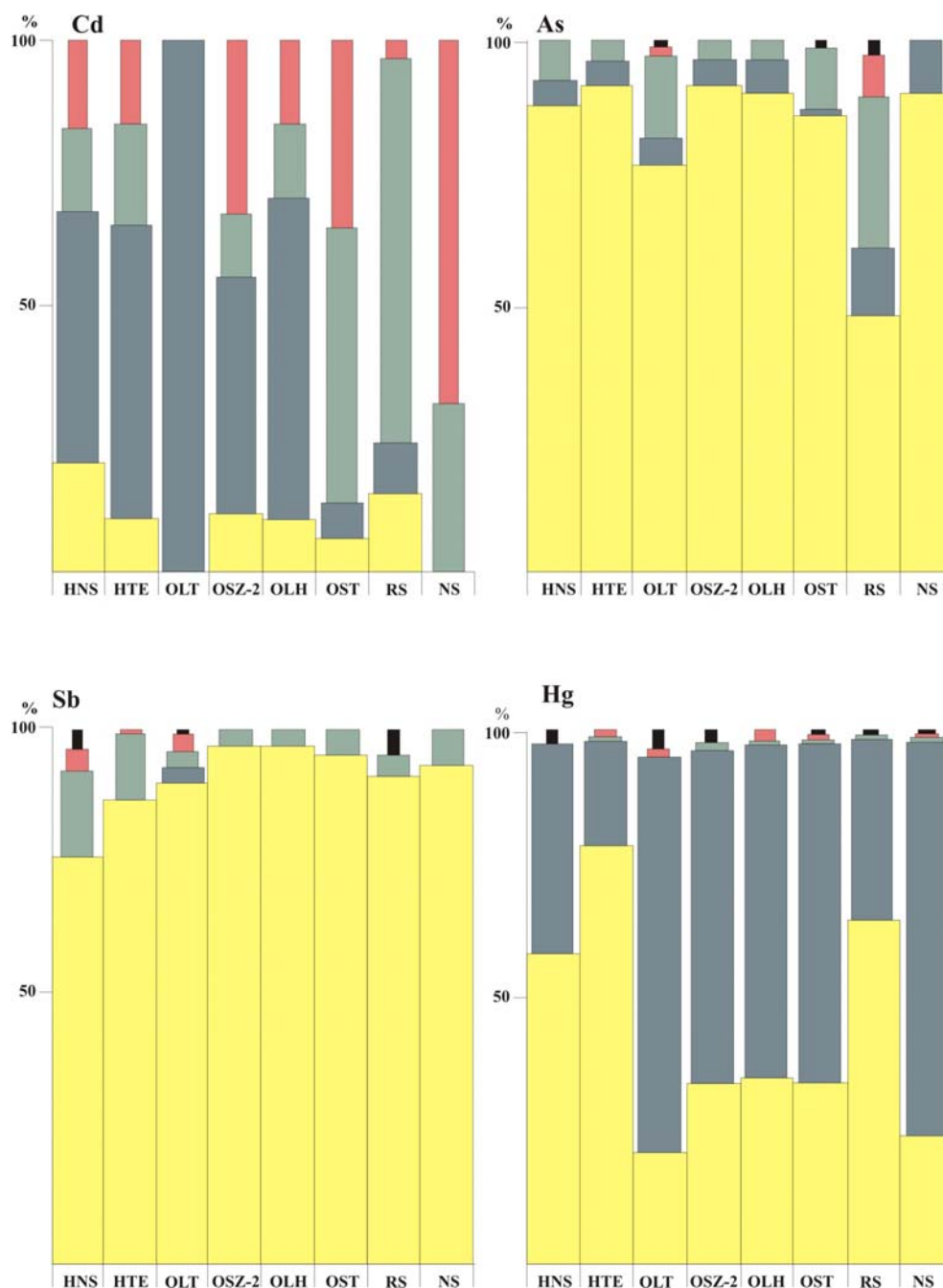
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Figure 2 a). Cumulative histograms of the ratio of selected elements
in fractions 1 – 5 of the sequence leaching
(black - by distilled water; pink – by 0.11 mol of acetic acid; blue – by hydroxylamine
hydrochloride solution, grey – by H_2O_2 and $C_2H_3O_2NH_4$; yellowish – by HF)

Figure 2 b). Cumulative histograms of the ratio of selected elements
in fractions 1 − 5 of the sequence leaching
(black - by distilled water; pink – by 0.11 mol of acetic acid; blue – by hydroxylamine
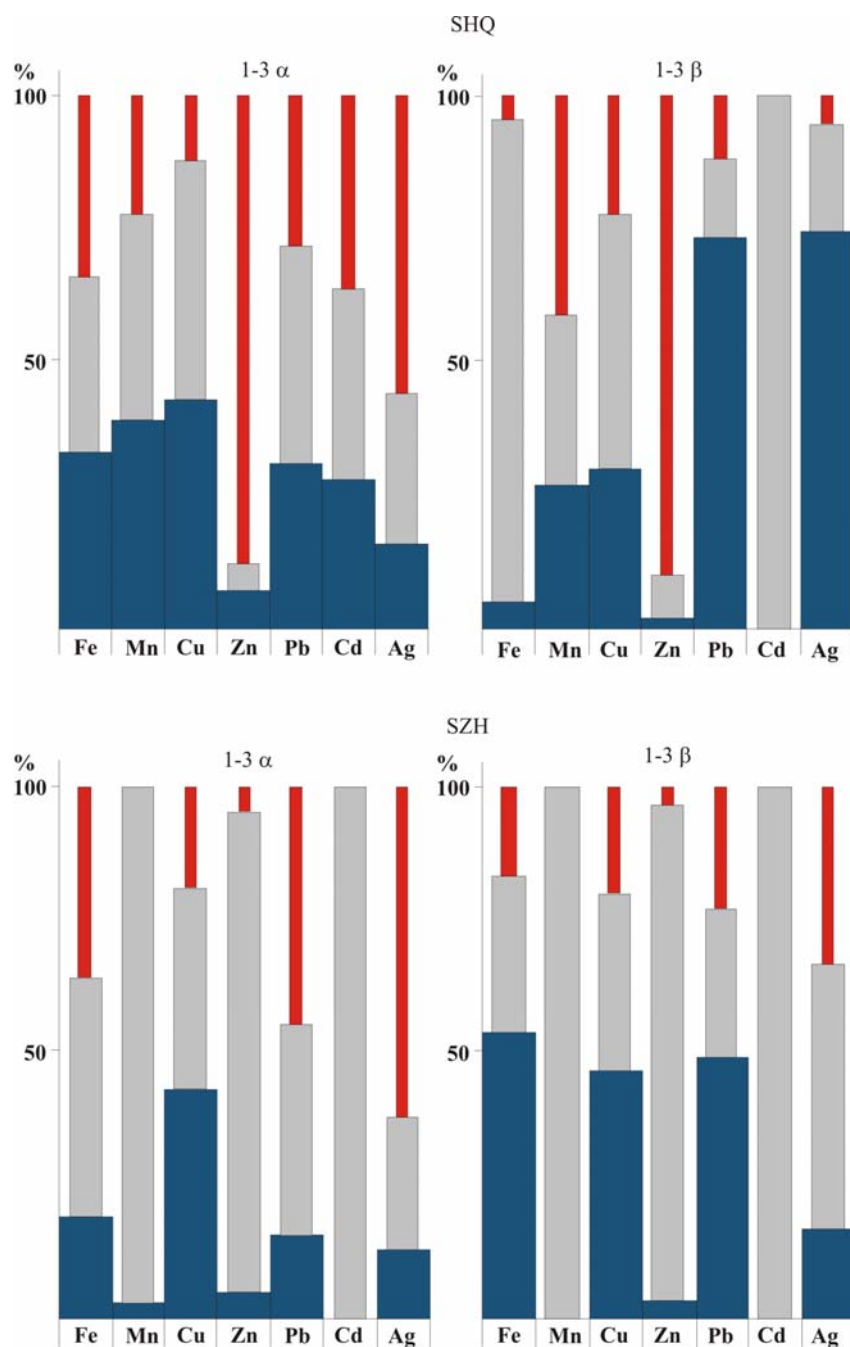hydrochloride solution, grey – by H_2O_2 and $C_2H_3O_2NH_4$; yellowish – by HF)

Figure 3. Cumulative histograms of the ratio of selected elements in percolation extracts using (1, red) - real rain water, (2, grey) - imitated rain water (3, blue) - distilled water from the average sample of hydroquartzite from Šobov (SHQ) and sediments from the aerated slope of the settling pit (SZH)

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Table 5. Content of the selected elements in percolating extracts

Sample	Set	Medium	Fe	Mn	Cu	Zn	Pb	Cd	Ag
			mg.l⁻¹						
SHQ	I α	1	675.0		1.1		0.0	0.0	0.0
		2	500.0		1.0		0.0	0.0	0.0
		3	700.0		1.01		0.0	0.0	0.0
	I β	1	3.3	0.1	0.1	0.1	21.5	0.0	0.0
		2	72.0	0.1	0.2	3.7	0.6	0.0	0.0
		3	2.4	0.1	0.1	25.2	0.2	0.0	0.0
	II α	1	665.0	2.6	1.3	1.3	0.1	0.1	0.0
		2	765.0	2.5	1.5	0.7	0.5	0.1	0.0
		3	750.0	1.3	2.6	22.5	0.3	0.1	0.1
	II β	1	0.0	0.2	0.0	0.1	0.0	0.0	0.0
		2	12.0	0.0	0.0	0.3	0.0	0.0	0.0
		3	0.0	0.0	0.0	30.0	0.0	0.0	0.0
	III α	1	575.0	0.9	0.0	0.5	0.5	0.0	0.2
		2	577.0	1.1	0.0	0.6	0.3	0.0	0.3
		3	583.0	0.9	0.0	1.0	0.3	0.0	0.6
	III β	1	0.4	0.0	0.2	0.9	4.0	0.0	0.0
		2	5.7	0.2	0.1	1.1	4.5	0.1	0.1
		3	0.4	1.7	0.1	1.7	3.8	0.0	0.0
SZH	I α	1	0.0		0.2		0.0	0.0	0.0
		2	2.5		0.1		0.1	0.2	0.0
		3	1.09		0.0		0.1	0.0	0.0
	I β	1	1.6	0.0	0.0	0.0	4.5	0.0	0.0
		2	0.0	70.0	0.5	21.0	0.1	0.3	0.0
		3	1.3	0.5	0.0	0.0	0.1	0.0	0.0
	II α	1	0.2	1.4	0.1	0.5	0.1	0.0	0.0
		2	0.4	46.0	0.1	10.3	0.3	0.1	0.0
		3	0.5	0.1	0.1	0.4	0.3	0.0	0.0
	II β	1	0.0	0.0	0.0	0.1	0.5	0.0	0.0
		2	0.0	110.0	0.0	11.0	0.6	0.2	0.0
		3	0.0	0.0	0.0	0.1	0.0	0.0	0.0
	III α	1	1.0	0.0	0.0	0.1	0.0	0.0	0.0
		2	0.0	0.1	0.0	0.2	0.0	0.0	0.1
		3	0.0	0.0	0.0	0.1	0.0	0.0	0.2
	III β	1	0.5	0.4	0.2	1.0	3.8	0.0	0.0
		2	0.4	1.6	0.1	2.9	4.2	0.0	0.0
		3	0.1	0.3	0.1	1.2	4.0	0.0	0.0

The portions fall used 3 media in percolation of SZH sample do not show symmetry in distribution; in ά and β phases 90 % of Zn is extracted by model rain water (2) and Cd is extracted by 100 % medium 2. In both phases Mn and Zn are extracted by medium 2 to approximately 90 – 97 %, Cd to 100 %. In ά-phase 62 % of Ag is extracted by real rain

water, only 33 % of Ag is extracted by real rain water in β-phase, 40 – 50 % of Cu in ά-phase, Cu and Pb are extracted by distilled water in β-phase.

Table 6. Average contents of the selected elements in percolation extracts

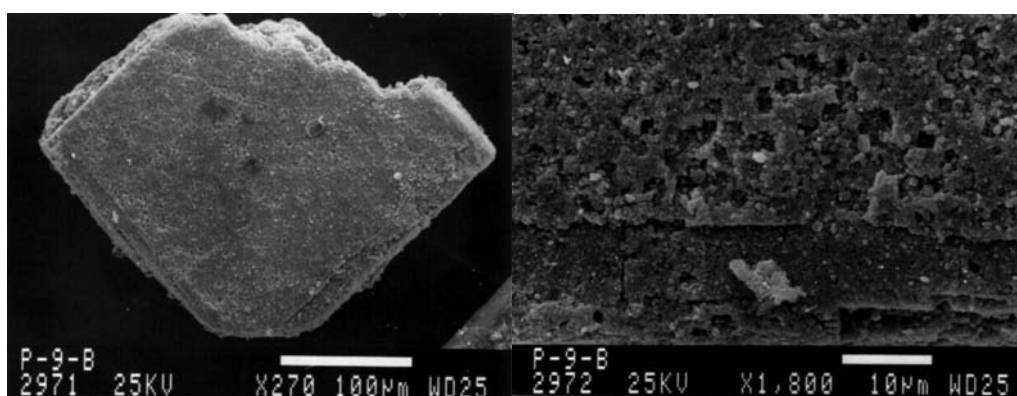| Sam-ple	Set	Me-dium	Fe	Mn	Cu	Zn	Pb	Cd	Ag
						mg.l^{-1}			
SHQ	I-III α	1	638.00	1.77	0.79	0.89	0.21	0.021	0.061
		2	614.00	1.78	0.82	0.64	0.27	0.027	0.103
		3	677.00	0.98	0.22	11.75	0.19	0.037	0.210
	I-III β	1	2.43	0.09	0.08	0.38	8.50	0.000	0.730
		2	46.93	0.11	0.13	1.69	1.70	0.031	0.197
		3	2.10	0.14	0.06	18.07	1.33	0.000	0.053
SZH	I-III α	1	0.41	0.68	0.09	0.29	0.05	0.000	0.015
		2	0.98	23.56	0.08	5.25	0.12	0.104	0.030
		3	0.80	0.04	0.04	0.26	0.14	0.000	0.073
	I-III β	1	2.23	0.23	0.07	0.36	2.90	0.000	0.017
		2	1.23	60.53	0.05	11.63	1.64	0.164	0.050
		3	0.70	0.12	0.03	0.44	1.37	0.000	0.033

Figure 4. a) Biodegradation of the galena surface by metal-rich sulphate water containing *Acidithiobacillus* bacteria; b) Detail of the etched surface.
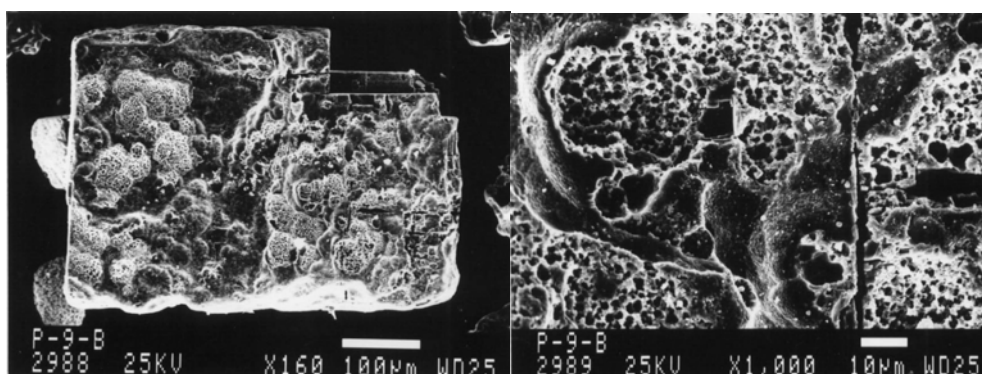

Figure 5.a) Galena surface etched by dissolved nitrate acid; b) Detail of the etched surface.

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The interaction effects among vitriol water, inoculated *Acidithiobacillus* bacteria from Šobov and selected sulphides from the Sedem žien tailings dam Križáni and Andráš (2006) documented. Etched edges and electro-corrodible effects are visible at the pyrite grains at the marcasite inclusions and mineral carrying interface. Abundant secondary minerals micro-granular jarosite and gypsum are in the striae. Sphalerite surface is markedly etched. The character of etchings is markedly different at the splitting galena plain after the maceration by vitriol water (Fig. 4) in comparison with the maceration by dilute nitric acid (Fig. 5).

Heavy metals from the dump material from the 14th and 16th Century at the study area Lúky pod Tanádom hint as evident microbial participation by their release from minerals-hosts, chemical liberation and surface etching as well (Križáni & Andráš 2006).

4. DISCUSSION

Forgáč et al. (1995) studied in laboratory conditions bleaching of andesites. They recognized that even very weak inorganic acids cause alteration of rock to clay minerals. This process release wide scale of heavy metals both from main and accessory minerals of primary rocks.

Table 7. Content of the selected elements in connected samples of solid residues after
I – III sets of percolation by media 1 - 3

Sample	Set	Fe	Mn	Cu	Zn	Pb	Cd	Ag
		ppm						
SHQ	I	2 247.0	1.6	0.2	5.7	9.6	0.013	0.75
	II	1 700.0	1.6	0.1	5.1	11.3	0.016	0.45
	III	1 340.0	1.4	0.1	6.6	14.5	0.038	0.53
SZH	I	11 060.0	1 420.0	59.2	653.7	193.4	4.140	1.40
	II	11 250.0	1 430.0	61.3	652.0	170.4	4.180	3.70
	III	11 630.0	14 400.0	65.8	651.0	193.7	4.130	1.40

Sequential analysis proved wide spectrum of bioavailable forms of monitored elements in all compared samples. As and Sb proved minimal bioavailability. Hg has surprisingly high bioavailability mainly in organic – sulphide fraction. This fact could hint as its portion in the form of methyl-mercury (along with cinnabar and vermilion) in the samples OST, RS, NS which contain more organic detritus.

It is remarkable that from the hydroquartzite containing less heavy metals than settling pit sediments at average about 1 – 3 order more observed metals were released into the solution as from the abundant settling pit sediments. Similar differences are listed in table 7 as well; in the connected samples of solid residues after the extraction. It is possible to explain this phenomenon by the fact that sulphidogenous metamorphose of rain water increased by *Acidithiobacillus* bacteria activity (Tab. 8) has pelted with hydroquartzite for thousand years, whereas bacterial transmission of sediments by material filling containing *Acidithiobacillus* bacteria has lasted only for 10 years. Meanwhile abrasion pH of sediments decreased from 12 – 12.5 to values less than 3 at the tailings dam air side (Líšková et al. 1998). Settling pit sediments were bacterial sterile during deposition and *Acidithiobacillus ferrooxidans* bacteria were isolated from the water extract later (Kušnierová et al. 1997).

Table 8. Synopsis of the *Acidithiobacillus* bacteria occurrence at the Šobov locality, Nová shaft dump and Sedem Žien settling pit

Locality	Medium	Number of samples	pH	Bacteria		
				ATF	*ATT*	*LF*
Šobov – quarry and dump	drainage water	6	2.0 – 2.4	+	+	+
Nová shaft – dump	drainage water	3	5.6 – 6.8	+	+	+
Sedem Žien – settling pit	lixivium from sand	1	5.7	+	-	-

Explanatory notes: *ATF – Acidithiobacillus ferrooxidans, ATT – Acidithiobacillus thiooxidans, LF – Leptospirillum ferrooxidans*; + presence of bacteria, - absence of bacteria

5. CONCLUSIONS

Sequential analysis indicated high portion of Mn, Cu, Zn, Pb, and Cd in the bioavailable forms and low portion of bioavailable bonds in As, Sb, Hg from the selected elements.

The slag fragments (OLT) in comparison with other samples of technogenous sediments show higher portions of Mn, Cu, Zn and Pb in insoluble rest, it means presumably in glass phase. This finding is positive from the environmental viewpoint.

The comparatory percolation by three liquid media showed that in the leachates from hydroquartzite, which contain lower contents of heavy metals as the flotation waste from the tailing dam are higher heavy metal contents. The explanation of this paradox is the different time of the activity of *Acidithiobacteria (ATB)*. In the acid background of the hydroquartzite are the *ATB* present several million years (at least from the time of the revelation of the hydroquartzite body by erosion). The flotation waste was originally alkaline (pH 12) and it was "infected" by *ATB* only during the period 1994 – 1997 when the tailing was covered by mining waste containing *ATB*. This intervention changed the acidity of the waste (pH = 4).

Experimental percolation model from the air side of the tailings dam Sedem Žien shows different portion distribution falls on individual medium as SHQ sample. The highest portions in ά-phase are in rain water leachates in case of Fe, Mn, Zn, Cd, by distilled water in case of Cu and real rain water in case of Ag. In β-phase the highest portions are in distilled water leachates in case of Fe and Cu, by model rain water in case of Mn, Zn, Cd, Ag, and by real rain water the extractable portions are abreast below 25 % in all investigated samples besides Ag which portion is 33 %.

The experiment of static maceration of heavy metals by acid metal-rich sulphate water from Šobov showed different surface degradation character of selected minerals (pyrite, marcasite, sphalerite, galena) and the formation of secondary minerals on their surface (mainly gypsum and jarosite) as well. Etchings at the galena surface have different character in relation to the leaching medium. The galena surface after biodegradation by acid metal-rich sulphate water inoculated with *Acidithiobacillus* bacteria is displayed in the figure 4 and the character of its etching with diluted nitric acid in the figure 5.

Those chemical changes modify mineral composition of sediments at the mine stock-piles, mainly settling pits. Bio-oxidation processes produce inorganic and organic acids that are decomposing silicate minerals as well. Clay minerals originate to

the prejudice of quartz and primary aluminosilicates whereas the physical characteristics of sediments change in time and the stability of dam system as well.

5. ACKNOWLEDGEMENTS

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