

Heavy metal distribution at dump-field Ľubietová – Podlipa and possibilities of clay fraction natural sorbent utilisation

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The article present the results of the environmental study at the Ľubietová Podlipa dump-field. The distribution of the selected elements and heavy metals is unequal and depend on the geochemical behaviour of the elements (mainly on their migration ability). The present natural sorbents are predominantly the clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals are good sorbents of K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta a Th and at the hydrogoethite of Cu, Zn, Mo, Mn, Mg, P (\pm Fe, Cd, Co, Ca). In the case of the Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi, U was proved also the free sorption capacity.

Key words: dump-field, heavy metals, sediments, clay minerals, sorption

Introduction

The Ľubietová – Podlipa deposit belongs to the important deposits in the surrounding of Banská Bystrica. It is situated in the NE part of the Slovenské Stredohorie Mts. which include also the N part of the Poľana neovolcanic massive and the N part of the Vepor Mts. According to the archeological findings the copper was from the surface cementation zone in the surrounding of Ľubietová exploited already in the time of the Bronze Age (Koděra et al., 1990).

Ore bodies, formed mainly by ankerite – $\text{Ca}(\text{Fe}, \text{Mn}, \text{Mg})(\text{CO}_3)_2$ and siderite – FeCO_3 , are localised predominantly in acid crystalline rocks and in series of Permian age. The main ore minerals are chalcopyrite – CuFeS_2 , tetrahedrite – $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (often Ag-bearing) and pyrite – FeS_2 . Substantial part of the territory is built by Permian rocks and, as it is typical for Permian terraines, increased radioactivity of the rocks was described. At the locality it is possible find also numerous rare secondary minerals [libethenite – $\text{Cu}_2(\text{PO}_4)(\text{OH})$, brochantite – $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$, langite – $\text{Cu}_4(\text{OH})_6(\text{SO}_4) \cdot 2\text{H}_2\text{O}$, malachite – $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$, azurite – $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, etc.].

Weathering of the reactive minerals first of all under acid conditions mobilise the heavy metals and numerous next elements. This process cause the contamination of the landscape components. pH decrease in technogenous sediments of the Cu-deposit Ľubietová effect the heavy metals release (Cu, Fe, Cd, As, Sb, Pb, Zn, Mn, Ni, Co) from the solid phase, where are they present in form of less soluble minerals or in sorption complex to groundwater or to surface water. Resistance of the landscape components against heavy metal contamination is significantly conditioned by various natural sorbents (e.g. clay minerals and hydrogoethite). They form natural geochemical barrier, on which the precipitation of the metals to stable bondings is realised. Utilisation of the present natural sorbents could be a very good method of remediation.

As a very good sorbents for remediation is possible utilise clay minerals (and zeolites). These predominantly crystalline aluminosilicates with foliated texture, have usually negative surface charges (Kozáč, 1969) and therefore they are able to fixate $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$, $\text{K}(\text{I})$, $\text{Na}(\text{I})$, $\text{Al}(\text{III})$, $\text{Mn}(\text{II})$ cations and heavy metal cations on their surface. These cations could be substituted by other cations (Čurlík, 2003).

Also hydrogoethite - $\text{FeOOH} \cdot \text{H}_2\text{O}$ („limonite“), can be a very good sorbent. It is formed under weathering conditions by oxidation of Fe containing ores and of some mafic rock-forming minerals. Fe-hydroxide, which originate during the hydrolyze FeSO_4 hydrolysis, form well coagulating hydrosalt. The precipitated gel is partly dehydrated and results Fe-monohydrate. As hydrogoethite has negative surface charge and enormous reaction surface, it is predetermined to be a excellent natural heavy metal sorbent.

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Experimental

Sampling

The sampling was realised during summer months in 2007. 23 samples of technogenous sediment (samples marked by indexes HD and A), 1 sample of mud from the bottom of the terrain depression underneath of the dump of the Andreas adit (sample JP-1) were collected. Each of them represent 30 cm deep horizon and area of 50 x 50 m (fig. 1). The grain size of the samples was below 1 cm and their weight about 30 – 35 kg. The set was supplemented by 2 samples of hydrogoethite rich rocks: A-17 and VZ-A. Sample A-17 represents several homogenised samples from sampling localities A-2, A-3 a A-5 and sample VZ-A was obtained at the sampling locality A-15.

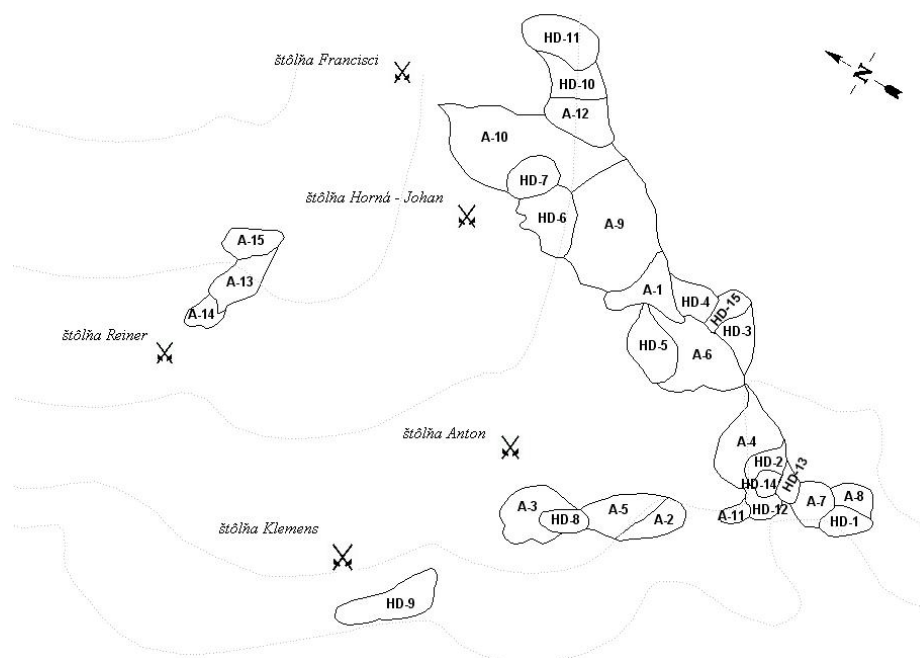


Fig. 1. Localisation of samples.

Elaboration and analysis of the samples

The monomineral fractions of clay minerals were prepared according to Šucha et. al. (1991). This proceeding consists of displacement of organic mater, of carbonates, of chlorides as well as of iron and manganese from the sample.

To remove carbonates from the sample pulverised to <0,16 mm grain size, is to the 10 g of sample added 100 cm³ of natrium acetate (SOTR) buffer. Reacted solution is after 2 days segregated from the solid phase and the solid phase is dispersed by SOTR addition in ultrasound device during 2 – 3 minutes. The sample is three times heated up to 90 °C with 100 cm³ SOTR addition and the suspension is decanted.

Organic mater was removed by reaction with 10 cm³ of concentrated hydrogen peroxide and 100 cm³ of SOTR. The mixture was heated at 70 °C 15 minutes. This proceeding was two times repeated and the reacted solution was removed.

The free Fe and Mn oxides are removed by addition of 90 cm³ citrate solution and by heating up to 75 – 85 °C. After 5 minutes double additions of 2 g of natrium hydrosulphite was realised and the solution was decanted. The rest of the sample was irrigated by distilled water.

After mentioned procedure is possible to realize the true separation of individual clay minerals (<2 μm fraction). The colloidal rest of the sample in 2 dm³ of distilled water is after 41 hours and 8 minutes (the time is calculated according to Stokes rule for gravitation sedimentation) decanted to beaks and saturated solution of NaCl is added. After treating is the solution fleeced. The solid rest is transposed to calciferous form using 1 mol.dm⁻³ CaCl₂ solution. This procedure regulate the replacable cations in clay minerals. Dialysis i used for chlorides removal and the presence of chlorides is verified by additament of AgNO₃ solution. After removing of chlorides is the rest of the sample drained at 30 °C.

To the 0,14 g of sample was added 3,5 cm³ of distilled water and using ultrasound was the sample dispersed. Suspension was applied using syringe on mount glass and was drained at laboratory temperature

to get oriented mount. These oriented mounts were saturated by ethylenglycol gasses in exicator during 8 hours on ceramic skid at 60 °C to optimise the conditions of the rtg-difraction analysis.

Rtg-difraction analysis of clay fraction was realised in laboratories of the Geological Institute of Slovak Academy of Sciences in Bratislava using rtg-difraktograph Philips.

The pH of the sediments was measured in H₂O and in 1M KCl lixivium according to the method described by Lintnerová and Majerčík (2005). To 10 g of sample was added 25 ml of distilled water or 1M KCl and after two hours mixing in the laboratory mixer were the pH and Eh measured by pH-meter.

In samples of the technogenous sediments (HD-1 to HD-15), sediment from terraine depression beneath the Mária-Empfängnis adit (JP-1), fractions of the clay minerals (A-1c to A-8c) as well as in the samples of hydrogoethite (A-17, VZ-A) was analysed set of 22 elements by ICP-MS analysis. The efficiency of the sorption was studied in the clay minerals and in the hydrogoethite. The samples for sorption efficiency on clay mineral fraction (mixture of clay minerals) study were prepared by separation of the clay fraction based on disperseion of the sediment sample using distilled H₂O in volumetric cylinder (of 2 dm³ volume). After 41 hours and 8 minutes sedimentation (calculated according to Stokes rule) was the clay minerals containing suspension (< 2 µm fraction) decanted. The clay fraction was drained at laboratory temperature.

The existence of clay mineral free sorption capacity was studied using heavy metals containing drainage water from terraine depression beneath the dump of the Maria-Empfängnis adit. To 20 g of clay sample (A-1c to A7c and A-17) was added 50 cm³ of 5-times concentrated drainage water. Analyses were realised from 1 g of sample (A-1c* až A7c* and A-17* after 14 days maceration in drainage water.

The samples for Ca, Na, K, Mg, Ti, Al, P, S, Cd, Bi, Co, Ni, As, Sb, Mn, Mo, Rb, Sr, Hf, V, Ba, Li, La, Cr, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, U and Th determination were melted using addition of Li-metraborate and Li-tetraborate mixture and solved in diluted nitric acid. The Au, Ag, Fe, Pb, Zn and Cu was determined from 0,5 g weight of sample after leaching by hot aqua regia. The samples were analysed using ICP – MS in ACME Analytical Laboratories Vancouver Ltd. Kanada.

Results

Heavy metal distribution in technogenous sediments components

Heavy metal distribution in technogenous sediments and ores of the dump-field Lúbietová – Podlipa is variable (tab. 1 – 3). The distribution of individual elements reflect the primary concentration in separate parts of the dump-field as well as their geochemical relations (fig. 2 – 4), first place their migration ability.

pH of the sediments, determined in water-lixivium range from 4.21 to 7.93. The pH interval of the sediments measured in 1M KCl lixivium range from 4.0 to 7.34.

The presented results show that the distribution of selected elements at the dump-field is non-uniform. Maximal concentration of teoretically extractable elements in the dump-field material range from 30 000 ppm (Fe) to 0,9 ppm (Cd). Also important concentrations of Cu (7000 ppm) and As (350 ppm) were described. Noticeable are also the high concentrations of Pb and Zn (Cd) at the reference area. We have no explanation of this evidence. (Both within the territory of reference area and of the all deposit there are no occurrences of sphalerite or other minerals which could explain the high Zn and Cd contents.) The source of the increased U and Th contents at the reference area are in the Permian rocks (rauwackes). In the dump range oriented in E – NE vs. W – NW direction (samples HD-6, A-2, A-3, A-5 a A-11) only low contents of Ag, Bi and Cd were described.

Tab. 1. ICP-MS analyses of technogenous sediments.

Element	Unit	Sample																
		HD-1	HD-2	HD-3	HD-4	HD-5	HD-6	HD-7	HD-8	HD-9	HD-10	HD-11	HD-12	HD-13	HD-14	HD-15	JP-1	VZ-A
Ca	%	0.08	0.19	0.04	0.19	0.47	0.13	0.04	0.14	0.25	0.14	0.27	0.11	0.17	0.12	0.07	1.35	8.93
Na		0.305	0.039	0.082	0.311	0.081	0.067	0.066	0.036	0.062	0.195	0.765	0.189	0.299	0.184	0.067	0.363	0.269
K		2.49	4.27	3.96	4.29	4.29	4.14	3.48	3.47	4.23	2.44	2.43	3.24	2.91	2.79	2.66	0.62	0.28
Fe		1.33	1.64	3.59	2.67	2.26	2.14	2.58	2.37	1.84	1.12	1.38	2.25	1.61	1.66	1.01	1.19	33.22
Mg		0.49	0.64	0.63	0.61	1.07	1.41	0.52	0.61	0.85	0.34	0.53	0.61	0.52	0.46	0.48	1.98	0.32
Ti		0.092	0.124	0.096	0.134	0.116	0.099	0.112	0.097	0.111	0.108	0.176	0.115	0.122	0.111	0.116	0.075	1.166
Al		4.44	6.45	7.12	7.97	7.11	8.03	6.65	5.68	6.89	4.27	4.99	5.63	5.15	4.91	4.45	9.31	4.18
P		0.041	0.049	0.098	0.081	0.076	0.081	0.112	0.055	0.079	0.039	0.032	0.075	0.058	0.066	0.034	0.009	0.419
S		0.1	0.2	0.3	0.1	0.5	0.1	0.1	0.1	0.2	0.3	<1	<1	0.2	0.1	0.1	0.1	0.1
Cu	ppm	4044	2956	2243	331	7486	1977	541	>10 000	5466	390	25	6766	1388	2402	29	5	>10 000
Pb		10.4	15.8	27.9	30.3	15.6	7.9	24.1	13.5	17.8	53.6	16.1	17.7	16.2	20.1	29.8	9.1	114.6
Zn		14	211	13	19	21	23	20	15	24	36	39	19	29	21	25	44	188
Cd		<1.0	0.9	0.1	0.1	<1.0	0.1	0.1	0.1	0.1	0.3	0.2	<1.0	0.3	0.1	0.2	0.1	1.3
Bi		3.5	3.1	102.7	0.4	3.8	2.2	9.2	2.6	8.1	1.7	0.2	7.1	3.8	5.1	0.5	0.5	38.8
Co		59.3	69.9	43.2	15.5	82.5	36.2	53.6	84.5	96.3	7.1	5.1	34.9	15.1	15.5	2.1	0.5	50.1
Ni		14.2	35.6	35.5	11.5	48.7	17.1	31.6	62.1	51.9	7.8	8.5	25.8	16.6	23.2	5.5	1.5	188.6
As		60	77	397	58	138	34	294	206	130	32	7	153	85	105	11	12	1144
Sb		15.5	25.6	98.2	12.1	5.2	15.6	39.2	36.3	27.7	17.5	10.4	26.4	17.7	18.3	13.4	14.2	62.6
Mn		657	500	598	2755	486	377	517	1258	391	486	559	372	416	231	47	392	821
Mo		0.2	0.1	0.4	0.4	0.2	0.1	0.6	0.7	0.2	0.3	0.3	0.3	0.2	0.2	0.3	0.2	4.8
Au		<1	<1	<1	<1	0.1	<1	0.1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0.2
Ag		0.4	0.3	3.4	0.1	0.9	0.3	1.6	0.3	0.6	0.3	0.1	0.7	0.6	0.8	0.1	<1	4.3

Tab. 1. (continuation) ICP-MS analyses of technogenous sediments

Element	Unit	Sample																
		HD-1	HD-2	HD-3	HD-4	HD-5	HD-6	HD-7	HD-8	HD-9	HD-10	HD-11	HD-12	HD-13	HD-14	HD-15	JP-1	VZ-A
Rb	ppm	93.9	149.3	148.6	166.2	147.3	134.2	131.8	119.2	151.4	103.3	88.4	123.9	108.5	103.2	119.4	12.5	12.5
Sr		23	44	57	32	33	18	35	16	23	37	40	25	33	27	21	137	218
Hf		0.5	0.8	0.8	0.7	0.7	0.9	0.9	0.6	0.7	0.6	1.4	0.9	0.9	0.7	0.7	3.2	11
V		22	33	46	26	32	43	51	29	32	22	31	36	31	30	19	5	400
Ba		349	390	350	531	315	216	410	343	269	346	391	375	370	314	377	608	74
Li		24.1	30.9	37.6	47.8	43.8	53.2	29.5	28.8	38.7	19.7	26.9	31.3	26.6	24.3	27.7	227.3	52.1
La		19.8	21.4	31.2	28.3	20.6	15.1	33.9	23.8	27.5	19.8	24.7	25.8	23.9	26.1	17.2	5.7	105.8
Cr		8.6	8.8	17.9	9.1	8.8	11.7	19.3	9.4	11.8	12.5	18.9	14.3	13.2	11.6	13.6	0.6	348.6
W		0.9	1.3	1.4	0.6	1.2	1.4	1.6	1.1	1.1	0.9	1.2	1.3	1.1	1.1	0.9	0.1	3.4
Zr		13.3	23.2	21.9	16	18.2	23.3	22.5	14.2	19.2	18.7	36.7	22.2	20.9	22.5	19.1	72.1	363.5
Ce		38	43	62	5	41	31	67	47	51	38	48	51	47	51	34	69	201
Sn		4.4	4.5	17.6	2.2	11.4	7.1	19.6	9.1	12.1	4.1	1.7	8.8	7.4	8.7	1.9	3.7	70.8
Y		4.4	5.6	6.2	9.1	4.8	4.4	7.1	5.1	5.6	3.4	6.6	6.5	5.2	5.1	3.1	16.2	74.2
Nb		2.5	2.5	2.1	2.6	2.4	1.9	2.6	1.9	2.2	2.9	4.1	2.9	2.9	2.5	3.1	45.5	38.7
Ta		0.3	0.3	0.2	0.2	0.3	0.2	0.2	2	0.2	0.3	0.4	0.3	0.3	0.3	0.3	5.2	2.9
Be		2	3	3	3	4	3	3	3	2	1	3	2	2	1	5	4	3
Sc		3	4	7	4	4	4	7	4	4	3	4	5	4	4	3	2	39
U		1.4	2.6	2.5	2.5	1.7	1.3	3.1	1.5	2.1	1.1	2.2	1.7	1.5	1.6	0.9	3.4	10.7
Th		7.2	6.9	10.9	8.4	7.3	5.7	10.1	7.1	8.8	6.4	7.7	8.3	7.5	7.4	5.9	35.9	30.9

Tab. 2. ICP-MS analyses of technogenous sediments and of clay fraction and clay fractions after 14 days maceration in drainage water containing heavy metals.

Element	Unit	Sample														
		A-1	A-1c	A-1c*	A-2	A-2c	A-2c*	A-3	A-3c	A-3c*	A-4	A-4c	A-4c*	A-5	A-5c	A-5c*
Ca	%	0,05	0,09	0,18	0,20	0,26	0,20	0,09	0,13	0,17	0,15	0,11	0,14	0,25	0,19	0,20
Na		0.053	0.042	0.403	0.217	0.171	0.462	0.147	0.171	0.654	0.054	0.070	0.365	0.150	0.087	0.373
K		2.86	3.42	4.80	2.40	3.59	4.36	2.22	3.66	4.33	2.06	3.60	4.74	2.25	3.58	4.82
Fe		1.31	1.45	2.98	1.42	1.46	2.17	1.94	2.14	2.90	2.64	2.47	3.65	1.71	1.66	1.83
Mg		0.51	0.47	0.99	1.01	0.93	1.50	0.81	0.77	1.16	0.70	0.67	1.26	0.71	0.73	1.35
Ti		0.090	0.075	0.148	0.127	0.107	0.174	0.127	0.138	0.200	0.117	0.092	0.159	0.102	0.089	0.169
Al		5.99	4.98	9.26	6.76	6.05	8.75	7.33	6.64	8.77	6.88	6.35	10.22	5.87	5.42	9.49
P		0.048	0.074	0.144	0.047	0.048	0.030	0.065	0.065	0.056	0.080	0.080	0.079	0.053	0.047	0.020
S		0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.02	<0.1	0.2	<0.1	<0.1
Cu		ppm	2829	1693	2345	199	574	472	828	624	857	4471	3324	3112	3150	3001
Pb	28.1		63.8	229.1	130	22.4	27.9	16.0	23.1	37.4	9.6	14.9	37.8	16.9	14.8	21.9
Zn	14		18	95	21	36	62	20	25	47	23	16	27	19	18	45
Cd	<0.1		<0.1	0.2	0.1	0.2	0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	2.8		4.5	14.6	0.2	1.4	1.5	8.5	7.2	12.1	23.7	39.2	90.9	1.7	2.1	3.2
Co	10.4		11.3	18.3	5.9	10.3	6.4	14.0	17.0	11.0	50.0	58.3	32.1	24.4	30.4	29.6
Ni	36.8		36.0	71.8	9.8	12.2	17.0	32.1	28.3	30.4	55.0	42.4	64.4	34.0	34.1	55.4
As	162		258	628	10	19	15	71	110	105	169	237	300	60	64	105
Sb	61.6		60.1	153.2	7.1	9.2	12.6	22.4	24.0	28.0	59.5	79.3	129.8	17.2	16.3	30.3
Mn	34		64	87	212	348	133	252	334	207	420	446	216	570	631	512
Mo	0.5		1.2	2.1	<0.1	0.2	0.2	<0.1	0.4	0.4	0.1	0.3	0.4	0.1	0.2	0.2
Au	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ag	0.7		0.8	1.7	<0.1	0.1	0.2	0.4	0.6	0.9	1.4	2.1	4.1	0.1	0.1	0.2

Explanations to the tabs. 2 and 3: A-1 to A-8 technogenous sediments; A-1c to A-8c clay fractions* clay fractions after 14 days maceration in drainage water; A-17 hydrogoethite

Tab. 2. (continuation) ICP-MS analyses of technogenous sediments and of clay fraction and clay fractions after 14 days maceration in drainage water containing heavy metals.

Element	Unit	Sample														
		A-1	A-1c	A-1c*	A-2	A-2c	A-2c*	A-3	A-3c	A-3c*	A-4	A-4c	A-4c*	A-5	A-5c	A-5c*
Rb	ppm	116.2	129.7	173.2	93.9	143.5	144.8	91.7	156.7	172.7	85.6	142.1	160.8	90.0	132.4	156.9
Sr		27	24	49	26	25	27	16	22	41	24	28	63	16	13	21
Hf		0.5	0.5	0.9	0.6	0.7	0.9	0.7	0.9	1.2	0.6	0.6	1.0	0.4	0.5	0.8
V		29	22	49	39	33	46	57	50	77	52	39	70	38	30	50
Ba		397	381	548	343	351	481	246	267	385	349	320	498	251	261	432
Li		29.4	25.0	54.3	50.0	34.4	67.5	43.4	36.0	68.8	35.6	25.3	64.1	34.1	28.7	60.9
La		20.6	18.2	15.4	22.9	18.6	2.9	30.2	28.2	9.8	27.5	26.0	5.9	20.8	19.8	5.3
Cr		38	9	24	36	17	26	34	21	37	38	15	30	30	10	22
W		0.9	1.0	1.9	1.5	1.0	1.5	1.2	1.3	1.8	1.2	1.1	1.8	0.9	0.9	2.0
Zr		14.7	15.1	30.9	21.8	23.5	30.4	19.9	32.8	41.8	19.2	19.9	31.8	12.6	15.6	28.4
Ce		38	39	35	43	38	7	56	61	22	52	54	14	38	42	12
Sn		10.9	11.1	29.4	3.5	2.7	4.4	9.8	7.2	9.5	17.3	12.8	22.7	4.9	3.3	8.1
Y		3.5	3.7	5.3	5.4	4.7	2.6	5.5	6.1	4.6	5.1	5.1	3.6	4.6	4.8	2.8
Nb		1.9	2.3	3.8	3.2	3.3	4.4	2.9	4.0	5.7	2.2	2.6	3.6	2.0	2.4	3.8
Ta		0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.3	0.1	0.1	0.2	0.2	0.2	0.2
Be		3	3	6	2	2	3	2	3	4	3	3	5	2	2	4
Sc		2	3	5	3	4	5	5	6	8	5	5	7	3	3	5
U		1.3	1.4	3.3	1.4	1.1	1.1	1.7	1.8	1.9	1.6	1.7	2.2	1.0	1.2	1.4
Th		5.8	6.0	9.5	7.6	5.9	2.2	9.1	9.2	5.2	8.3	7.8	5.0	5.9	5.8	4.0

Tab. 3. ICP-MS analyses of technogenous sediments and of clay fraction and clay fractions after 14 days maceration in drainage water containing heavy metals.

Element	Unit	Sample											
		A-6	A-6c	A-6c*	A-7	A-7c	A-7c*	A-8	A-8c	A-8c*	A-17	A-17c	A-17c*
Ca	%	0.17	0.09	0.12	4.74	1.99	1.35	0.08	0.71	0.11	0.02	>100	<0.10
Na		0.076	0.061	0.302	0.819	0.606	0.911	0.034	0.111	0.109	0.110	<0.10	>100
K		2.16	3.92	4.69	2.01	1.99	4.49	2.22	4.70	3.18	0.022	0.040	1.020
Fe		2.06	2.09	3.36	1.32	1.43	2.81	0.91	1.29	0.79	1.72	1.50	13.10
Mg		0.80	0.71	1.25	3.15	1.61	1.75	0.47	0.91	0.46	12.92	11.80	0.20
Ti		0.128	0.102	0.171	0.111	0.114	0.198	0.112	0.190	0.086	0.01	<0.10	0.02
Al		7.60	6.70	10.02	4.91	4.51	8.79	6.37	10.43	5.66	0.36	0.37	1.90
P		0.067	0.070	0.081	0.041	0.041	0.069	0.054	0.056	0.051	0.90	1.00	0.40
S		0.2	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu		ppm	4797	2503	2918	756	855	2026	716	836	837	>10 000	20 360
Pb	15.6		24.6	72.3	16.8	20.2	73.7	6.5	6.3	4.2	8.4	49.0	60.0
Zn	13		14	65	26	33	176	7	14	4	59	80	50
Cd	0.2		<0.1	0.3	<0.1	0.2	0.7	<0.1	<0.1	<0.1	0.2	0.2	0.2
Bi	25.4		24.4	51.7	0.9	1.2	3.6	0.5	0.7	0.8	7.2	6.0	5.0
Co	41.8		40.9	32.0	10.2	12.0	15.5	89.9	69.7	104.5	73.4	70.0	83.0
Ni	51.6		45.1	61.7	10.4	10.1	26.0	58.0	66.5	62.5	51.7	43.0	58.0
As	134		224	305	16	17	33	61	52	46	289	260	280
Sb	49.8		56.2	92.3	11.5	7.1	17.4	17.9	20.2	18.9	43.2	40.0	34.0
Mn	198		254	147	372	547	931	1190	905	1458	1074	960	1010
Mo	<0.1		0.3	0.4	0.2	0.3	0.6	<0.1	0.3	0.3	2.2	2.0	30.0
Au	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ag	1.0		1.6	3.0	0.2	0.2	0.4	<0.1	<0.1	0.1	0.8	1.0	1.0

Tab. 3. (continuation) ICP-MS analyses of technogenous sediments and of clay fraction and clay fractions after 14 days maceration in drainage water containing heavy metals.

Element	Unit	Sample											
		A-6	A-6c	A-6c*	A-7	A-7c	A-7c*	A-8	A-8c	A-8c*	A-17	A-17c	A-17c*
Rb	ppm	87.5	155.1	167.6	77.3	80.1	168.9	91.9	138.3	132.9	47.4	45.0	46.0
Sr		23	24	51	67	49	90	19	48	31	6	6	6
Hf		0.7	0.8	1.2	0.6	0.7	1.5	0.5	1.3	0.6	0.2	0.2	2.0
V		44	34	57	40	39	67	35	69	22	15	16	15
Ba		303	307	405	342	340	680	248	470	229	286	250	270
Li		40.5	32.0	73.4	20.7	14.4	67.0	35.8	65.3	31.9	5.6	6.0	11.0
La		24.9	20.9	4.4	17.3	17.6	21.3	40.6	15.0	34.2	24.8	21.0	23.0
Cr		31	11	23	28	11	35	23	21	7	7	8	8
W		1.2	1.4	2.0	1.5	0.7	1.5	1.4	2.2	1.5	0.4	0.4	0.5
Zr		20.2	23.5	37.1	18.3	22.1	48.9	14.7	43.9	23.1	7.7	9.0	9.0
Ce		46	47	10	31	35	43	77	41	68	49	40	50
Sn		14.9	12.9	19.6	4.0	2.6	6.8	3.9	7.1	3.0	8.8	4.0	9.0
Y		4.6	5.0	2.9	4.9	6.2	10.4	6.7	6.7	8.0	9.8	9.0	9.0
Nb		2.5	2.8	4.1	2.6	3.5	6.3	2.2	5.0	2.6	0.5	0.5	0.5
Ta		0.2	0.2	0.2	0.2	0.2	0.4	0.1	0.4	0.2	<0.1	<0.1	0.1
Be		3	4	5	1	1	4	3	5	2	2	2	3
Sc		4	4	6	3	4	7	4	6	3	4	5	5
U		1.4	1.6	2.2	1.1	1.1	2.3	2.6	2.5	2.1	2.3	2.0	1.0
Th		6.9	6.1	4.1	4.8	5.3	11.8	6.8	5.7	6.7	2.5	2.0	2.0

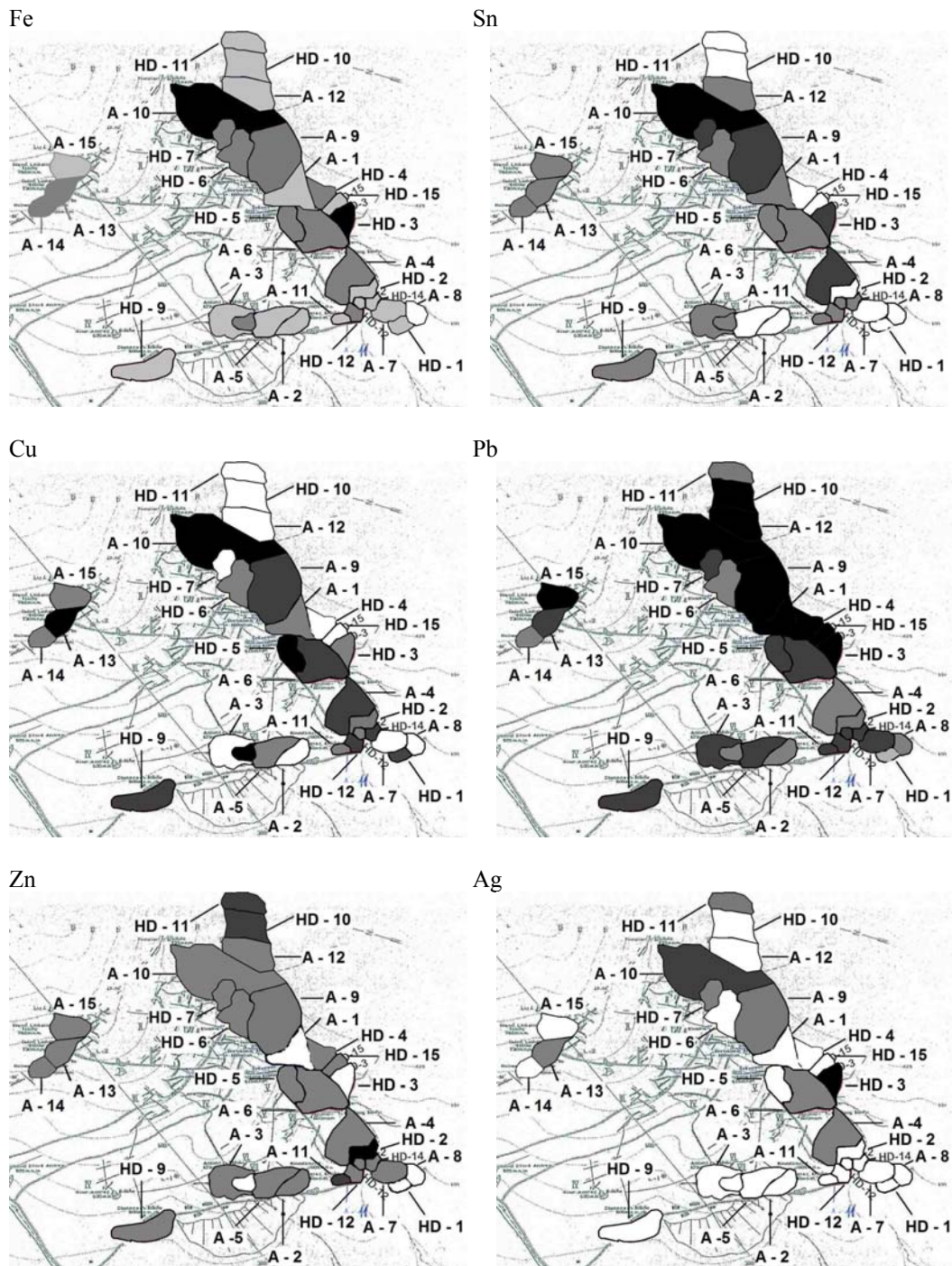
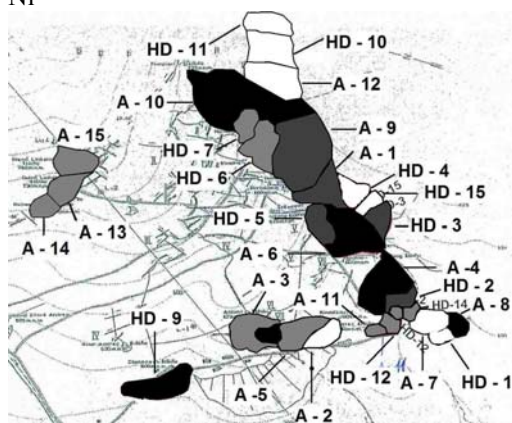


Fig. 2. Distribution of Fe, Sn, Cu, Pb, Zn and Ag at dump-field Lubietová – Podlipa.

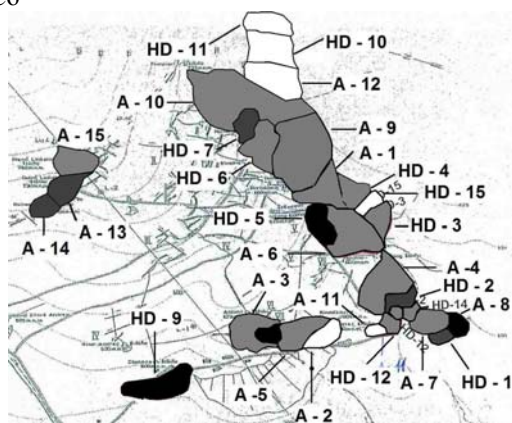
Tab.4. Explanations to fig. 2 (Fe, Sn, Cu, Pb, Zn and Ag content).

	Fe	Sn	Cu	Pb	Zn	Ag
	%			ppm		
	< 1	< 5	< 1000	< 5	< 15	< 1
	1 – 2	5-15	1000 -4000	5-15	15-35	1-2
	2 – 3	15-25	4000-7000	15-25	35-50	2-3
	> 3	> 25	> 7000	> 25	> 50	> 3

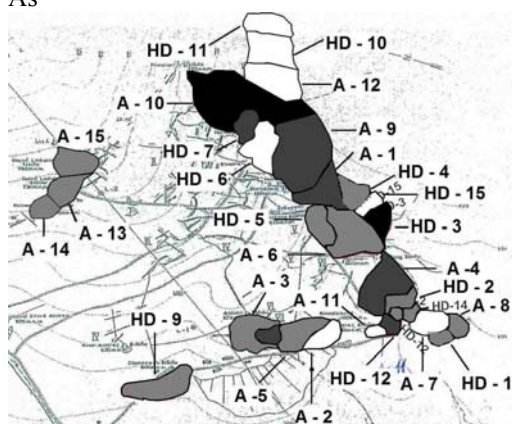
Ni



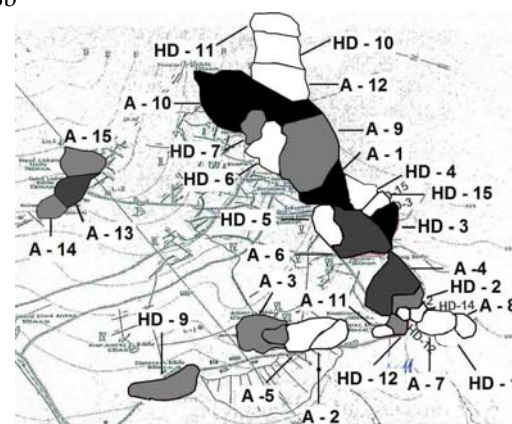
Co



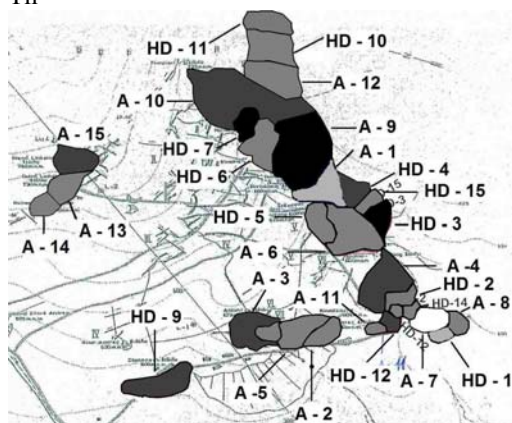
As



Sb



Th



U

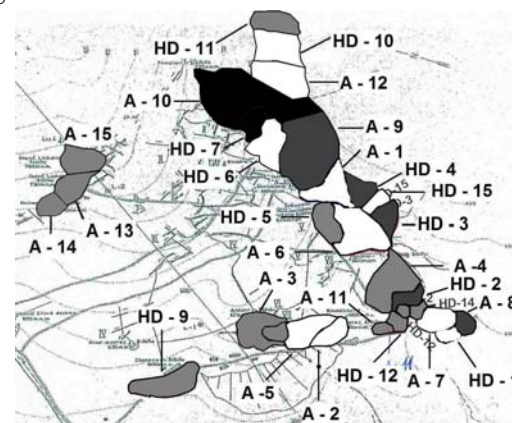


Fig. 3. Distribution of Ni, Co, As, Sb, Th and U at dump-field Eubietová – Podlipa.

Tab. 5. Explanations to fig. 3 (Ni, Co, As, Sb, Th and U content).

	Ni	Co	As	Sb	Th	U
	ppm					
	< 15	< 10	< 50	< 20	< 5	< 1,5
	15 – 35	10-50	50-150	20-40	5-8	1,5-2,5
	35 – 50	50-80	150-350	40-60	8-10	2,5-3
	> 50	> 80	> 350	> 60	> 10	> 3

Natural sorbents

Rtg.-diffraction analyse proved, that the most important potential natural sorbents in studied area are the clay minerals and hydrogoethite – $\text{FeO}(\text{OH})\cdot n\text{H}_2\text{O}$, which are formed during the weathering process of rock-material. The research confirmed, that the clay minerals are represented by illite – $(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$ and muscovite – $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$, caolinite – $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as well as smectite and chlorite mixture. Illite and muscovite are dominant in all samples. The next important mineral is smectite.

Heavy metals sorption on clay minerals and hydrogoethite

The heavy metal sorption study of clay minerals and hydrogoethite from technogenous dump sediments and the study of the free sorption capacity of these natural sorbents in individual samples is a relatively complex problem and the interpretation of these data is very confusing. Better reproducibility enable the complex interpretation of the results if the concentrations of the individual elements in technogenous sediment, in clay mineral mixture and in clay fraction after maceration in drainage water is presented in form of total values for each element (tab. 2 and 3). Such a total data enable better understand the studied processes and trends.

Preferential sorption of K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th on surface of clay minerals in comparison with hydrogoethite was described. On hydrogoethite surface are preferentially fixed Cu, Zn, Mo, Mn, Mg, P (\pm Fe, Cd, Co, Ca). The following elements: Sb, Bi, Ba, La, Ce, Sn, Y, Be, Sc, S, Pb, Ag, Ni, As and U show no legible trends of preferred sorption both on clay minerals and on hydrogoethite rich rock (tab. 2 and 3).

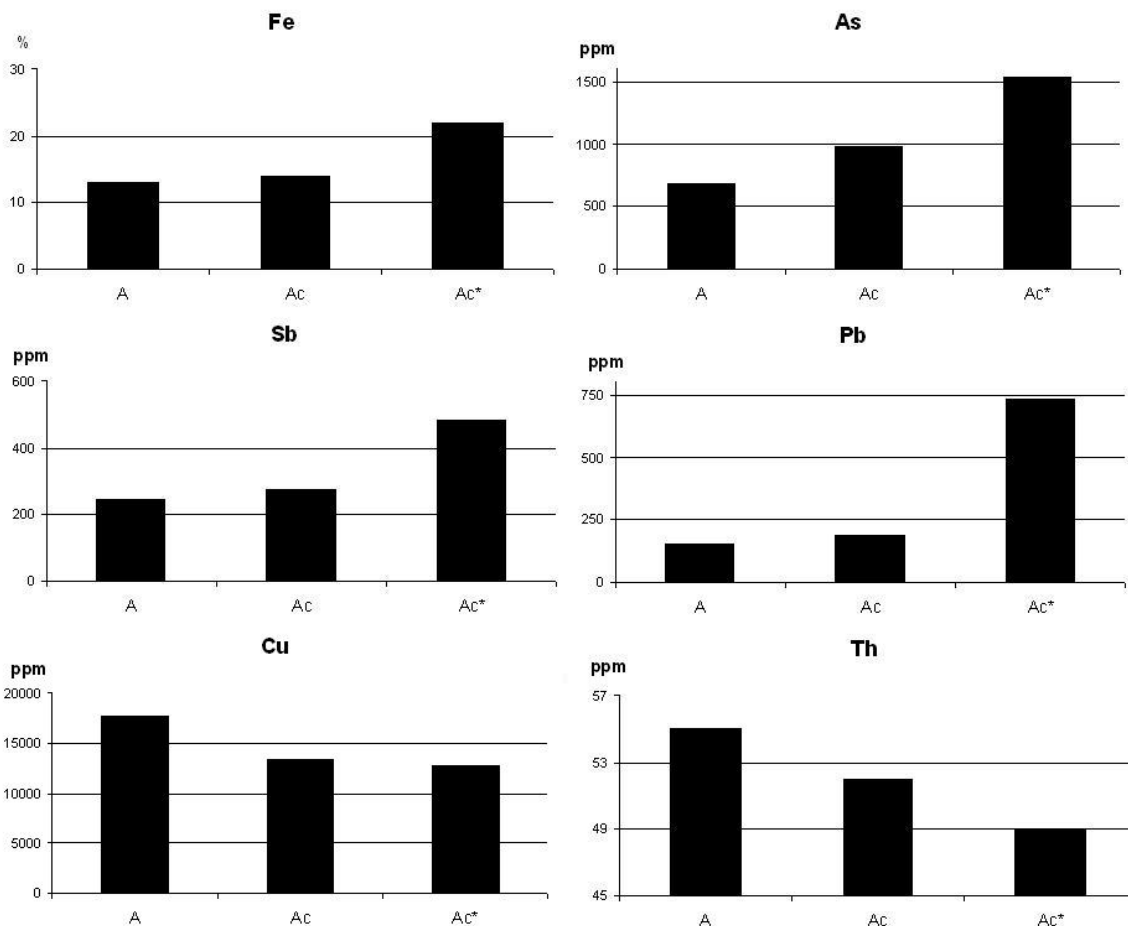


Fig. 5. Total content of Fe, As, Sb, Pb, Cu and Th in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (Ac*).

The following heavy metals: Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi and U show not only good sorption efficiency on clay minerals but also free sorption capacity of the clay fraction. Opposite trend – lower heavy metal content in clay component in comparison with the sediment and metal elements washing during

maceration was proved in case of Th and Cu (fig. 5). Co show moderate increase of content in clay minerals but no free sorption capacity was proved. The Cd, Ni, Co, V and Cr behaviour is very complex (fig. 6).

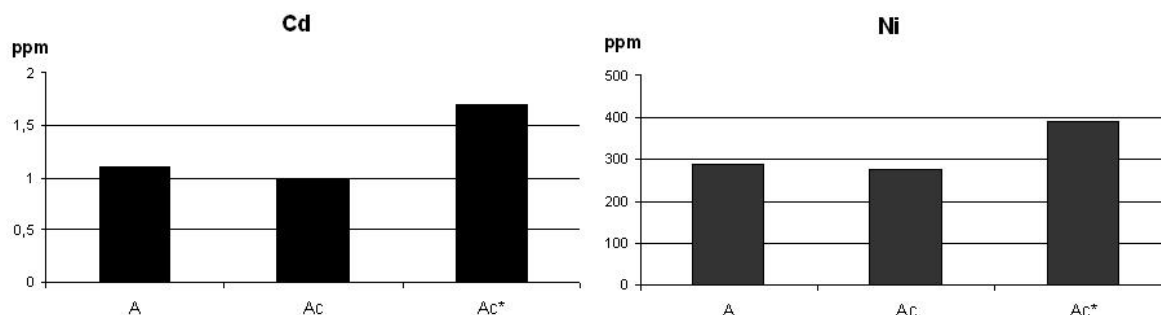


Fig. 6. Total content of Cd and Ni in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (Ac*).

Cd, Ni and V are preferentially fixed in sediments, lower Cd, Ni and V contents are in clay fraction but the clay mineral mixture proved a good ability to fix the mentioned heavy metals (Cd, Ni and V) on their surface (fig. 6). The probable reason of this behaviour is the fact, that the Cd, Ni and V majority is bound in the solid phase and only with difficulties create soluble forms, so in consequence of this behaviour in weathering process are the autochthonous clay minerals insufficiently saturated by V. The same trend was described for Cd, Ni, V and Co in case of hydrogoethite. The Cr behaviour is very similar, only with this difference that while V concentrations are in macerated clay higher as in the original sediment, the Cr concentrations are the highest in the original sediment.

The most complex relations were recognized in the case of Co.

The highest Th content was described in sediments and in soil. The Th contents in clay minerals are lower as in the sediment and after maceration is Th washed out from the clays. This trend is noticeable because in general is U considered to be more mobile as Th. The better mobility of U was described also at the Ľubietová deposit (Andráš et al., 2008), where the content of Th in soil is several times higher as the content of U, while in plants are the contents both of U and Th in consequence of better U mobility approximately identical. The Th/U rate is about 1 : 1.

Discussion

Mobility of the most heavy metals in nature is determined mostly by their solubility and sorption ability on natural sorbents, among which are the most important the clay minerals (Missanaet et al., 2008). According to the sorption mechanics it is possible distinguish several following types:

- mechanic sorption,
- physical adsorption conditioned by surface tension at the phase interface,
- physical-chemical replaceable sorption, which is realised by ion replacement,
- chemical adsorption, which make possible the anion fixation in form of coagulums,
- bioaccumulation – e.g. income of biogenic elements by root system of plants and by bacteria (Chmielewska and Lesný, 1995; Lischke and Frank, 1988).

In case of clay minerals the dominant process is represented by ionic replacement between solution and solid phase but partially also physical process of adsorption (Kozáč, 1969).

The caolinite is in general a very good sorbent of the majority of the heavy metals (Wahba and Zaghloul, 2007). Cu, Pb, Zn and Cd are fixed preferentially on smectite but Pb also on illite (Rybicka et al., 1995). Illite and smectite are very good sorbents of Pb and Cu. The sorption of Zn, Ni and Cd on illite and smectite is not so efficient. The sorption of Mg, Fe and Al on clay minerals is substantially more efficient at higher pH. It is caused by lack of free H⁺ ions and by increase of negative charge on surface of clay minerals (Kishk and Hassan, 1973). pH(H₂O) of technogenous sediments from the dump-field Podlipa (tab. 7) range from 4.21 to 7.93 (pH(KCl) 4.00 – 7.34), so it is possible to observe, that the sorption conditions of Cu, Pb, Zn and Cd on clay minerals are not the best but, on the other hand, they are not wholly ineffective.

From the viewpoint of the environmental risk are according to Andráš et al. (2008) at the studied locality the most important metals Cu, As and Sb.

The main sources of Cu at the dump-field are tetrahedrite, chalcopyrite and Cu-secondary minerals (libethenite, brochantite, langite, malachite, azurite and pseudomalachite). Cu released to the solutions during the weathering process contaminate the whole local water-net. Andráš et al. (2007) described at the locality

cementation process, which enable Cu precipitation on Fe oxides (hydrogoethite) and on the iron surface. In natural water are present the following forms of Cu: hydrated Cu(II) ion, complexes $\text{CuCO}_3(\text{aq})^0$, $[\text{Cu}(\text{CO}_3)_2]^{2-}$ and hydrocomplexes $[\text{CuOH}]$, $[\text{Cu}(\text{OH})_2(\text{aq})^0]$, $[\text{Cu}(\text{OH})_3]^-$ and $[\text{Cu}(\text{OH})_4]^{2-}$ (Pitter, 1990).

Cu sorption on clay minerals surface depend on pH. In case of carbonate lack (as it is at Ľubietová-Podlipa) are during the sorption process formed complex compounds $\equiv\text{SOCu}^+$, $\equiv\text{SOCuOH}$ and $\equiv\text{SOCu}_2(\text{OH})_2^+$, less also $\equiv\text{Cu}(\text{OH})_2$ and $\equiv\text{SOCu}_2(\text{OH})_3$ precipitates (Quinga et al., 1996).

Tab. 7. pH of technogenous sediments and their Eh measured in H_2O and 1M KCl lixivium.

Sample	H_2O		1M KCl	
	pH	Eh	pH	Eh
A-1	5.14	77	4.61	109
A-2	5.89	34	5.40	63
A-3	4.87	94	4.21	131
A-4	5.46	59	5.33	66
A-5	5.77	42	5.37	64
A-6	5.17	74	5.06	83
A-7	7.93	-84	7.34	-58
A-8	5.42	36	5.22	42
A-9	5.03	83	5.01	85
A-10	5.25	71	5.14	78
A-11	6.11	22	5.95	30
A-12	4.21	133	3.47	173
A-13	5.20	75	5.11	85
A-14	4.91	97	4.32	125
A-15	4.47	111	4.00	165

Notice: Eh (mV).

The most important As source at the Ľubietová is tetrahedrite. The weathering of the As-minerals (their oxidation) cause modification of native As and As(III) to As(V) containing compounds of arsenic acid (Lin and Puls, 2000). The arsenic acid is water soluble, but only rarely migrate on greater distances, because quickly react with heavy metals and As is fixed in form of various arsenates. As is in the water solutions most often present in following forms: H_2AsO_4^- , HAsO_4^{2-} and HAsO_2^0 (Greenwood and Earnshaw, 1990). As(III) is in the weathering zone much more mobile as As(V) (Manning and Goldberg, 1997).

In oxidation (weathering) conditions of the Ľubietová-Podlipa dump-field markedly prevail As(V) (Andraš et al., 2008). The sorption capacity of clay minerals, of hydrogoethite and Fe-oxyhydroxides related to As is very high (up to 76 mg As.g^{-1} in Fe oxyhydroxides at pH 5). As sorption depend on pH, time, As concentration in solution and on temperature (Mohapatra et al., 2007). The most efficient sorption was described at pH 4 (García-Sánchez et al., 2002; Lombi et al., 2000). According to Mohapatra et al. (2007) is from the natural sorbents described at Ľubietová dump-field the best As(V) sorbent caolinite. The sorption of the less toxic As(V) in comparison to As(III) on clay minerals is much more efficient and more quantitative. As(III) is during this process oxidized to As(V). The reductive process during the sorption of As was not confirmed (Lin and Puls, 2000).

The most important part of Sb descend from tetrahedrite. Both Sb(III) and Sb(V) exist in environmental conditions in following soluble compounds: Sb(V) in form $\text{Sb}(\text{OH})_6^-$ and Sb(III) in form of $\text{Sb}(\text{OH})_3$ (Filella et al., 2002). Hydrogoethite and Fe-hydroxides are the most important Sb sorbents. Sb(III) as well as Sb(V) form on the hydrogoethite and Fe-hydroxides surfaces complex compounds. The best Sb(III) sorption conditions are at pH 3 – 12, and the maximal Sb(V) sorption was described at pH <7. The Sb(III) on the hydrogoethite and Fe-hydroxides surface can be within pH range from 3 to 5.9 oxidised during several days. At pH ~ 9 start its mobilisation and dissolution, while at pH <7 is fixed on the Fe-oxides surface (Leuz et al., 2006).

The main soluble lead-compounds in the nature are mainly Pb(II) and $[\text{PbCO}_3(\text{aq})]^0$. The later one may be in wide pH range the dominant form of occurrence. In alkaline conditions substantial also concentrations of $[\text{Pb}(\text{CO}_3)_2]^{2-}$, $[\text{Pb}(\text{OH})_2(\text{aq})]^0$ and $[\text{PbOH}]^+$ complexes are formed (Pitter, 1990). The lead is in the solid matter present usually in form of PbCO_3 and PbSO_4 , and the ulmous substances effect its immobilisation Beneš and Pabianová (1987). Pb show affinity to formation of complexes with insoluble ulmous matters and in the consequence of the mentioned trend it is fixed in the upper part of the soil level (in the mould). Copper

and Pb are usually in comparison with Zn fixed on clay mineral surface much more strongly (Sipos et al., 2008). The increasing pH cause the increasing Cd sorption on clay minerals (Hayashi and Liu, 2008).

Soluble Cd is in the water present in the form of simple hydrated ion Cd(II), in form of inorganic complexes $[\text{CdOH}]^+$, $[\text{Cd}(\text{OH})_2(\text{aq})]^0$, $[\text{Cd}(\text{OH})_3]^-$, $[\text{CdCO}_3(\text{aq})]^0$, $[\text{Cd}(\text{CO}_3)_2]^{2-}$, $[\text{CdSO}_4]^0$ as well as in form of organic complexes with various organic ligands (Pitter, 1990). Proportion of sorbed Cd(II) on clay minerals show important increase at pH 6.5 – 9.0, while on illite is sorbed more intensively as on caolinite (Reid and McDuffie, 2005).

Conclusions

Heavy metal distribution in technogenous sediments and ores of the dump-field Ľubietová – Podlipa is variable and reflect the original concentration of metals in technogenous sediments as well as their migration abilities. Rtg-diffraction analyse proved, that the main natural sorbents prevail illite, muscovite and smectite, less caolinite and chlorites. Hydrogoethite is relatively rare. Results of the sorption properties of clay minerals and hydrogoethitised rocks show, that the studied dumps dispose by certain level of „self-cleaning ability.“ Substantial part of heavy metals and contaminants is catch in porous substances, in Fe-hydroxides (hydrogoethite) and in clay minerals (mainly K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th), which in case of Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi and U show important free sorption capacity. The mentioned data enable express the following result: The arrangement (opening) of the dumps could cause massive release of this way fixed heavy metals to the environment.

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