

THE HEAVY METAL SORPTION ON CLAY MINERALS AND RISK OF THE AMD FORMATION AT THE REINER AND PODLIPA DUMP-FIELDS AT ĽUBIETOVÁ DEPOSIT (SLOVAKIA)

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Abstract: The study realised at the Reiner and Podlipa dump-fields at the Ľubietová deposit present the results of the heavy metal distribution, which depend on the geochemical behaviour of the elements (mainly on their migration ability). Weathering of the reactive minerals mobilise the heavy metals and numerous next elements. This process causes the contamination of the landscape components. The present natural sorbents are predominantly the clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals are good sorbents of V, Cr, Ti, W, Zr, Nb, Ta, Th and at the hydrogoethite of Cu, Zn, Mo, Mn, Mg, (\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. Calculation of the AMD formation potential (neutralisation potential, total acidity production, net neutralisation potential) is discussed. The result suggest that at the localities Reiner and Podlipa is the assumption of AMD production very limited and the environmental risk is negligible.

Keywords: dump-fields, heavy metals, natural sorbents, acid potential, neutralisation potential

1. INTRODUCTION

The Ľubietová deposit 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; Andráš et al., 2007, 2008).

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 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.].



Figure 1. Lúbieťová: Podlipa dump-field.

Weathering of the reactive minerals first of all under acid conditions mobilise the heavy metals and numerous elements. This process cause the contamination of the landscape components. pH decrease in technogenous sediments of the Cu-deposit Lúbieťová 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 fix $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$, $\text{K}(\text{I})$, $\text{Na}(\text{I})$, $\text{Al}(\text{III})$, $\text{Mn}(\text{II})$ cations and heavy metal cations on their

surface. These cations could be substituted by other cations (Čurlík, 2003).

Also hydrogoethite („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 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.

Two dump-fields of the mining area were studied: Reiner and Podlipa (Fig. 1).

2. EXPERIMENTAL

The samples (of about 30 kg weight) of sediments from the dumps and soil from the 30 – 50 cm depth (the sampling step was 25 m²) were collected. The reference site was selected for comparison of territories loaded by heavy metals and non-contaminated natural environment (Fig. 2). It was situated outside of geochemical anomalies of heavy metals and represents graywakes of Permian age, similar to material at the dump-field. The samples of plant material were collected both from the reference area and from the contaminated dumps.

The dump-sediments are represented by two sets of samples: the first one consists of 15 samples (samples HD-1 to HD-15) and the second one of 15 samples (A-1 to A-15). Samples HD-10, HD-11 and A-12 are from the reference area. The sample set is completed by sample of limonitised rock (A-17), which represents mixture of three samples from localities A-2, A-3 and A-5.

The clay mineral fractions from 8 samples (A-1c to A-11c and A-17c) of technogenous sediments were prepared according to the method described by Šucha et al., (1991). 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 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 realise the true separation of 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 the replacable cations in clay minerals. Dialysis is sused 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.

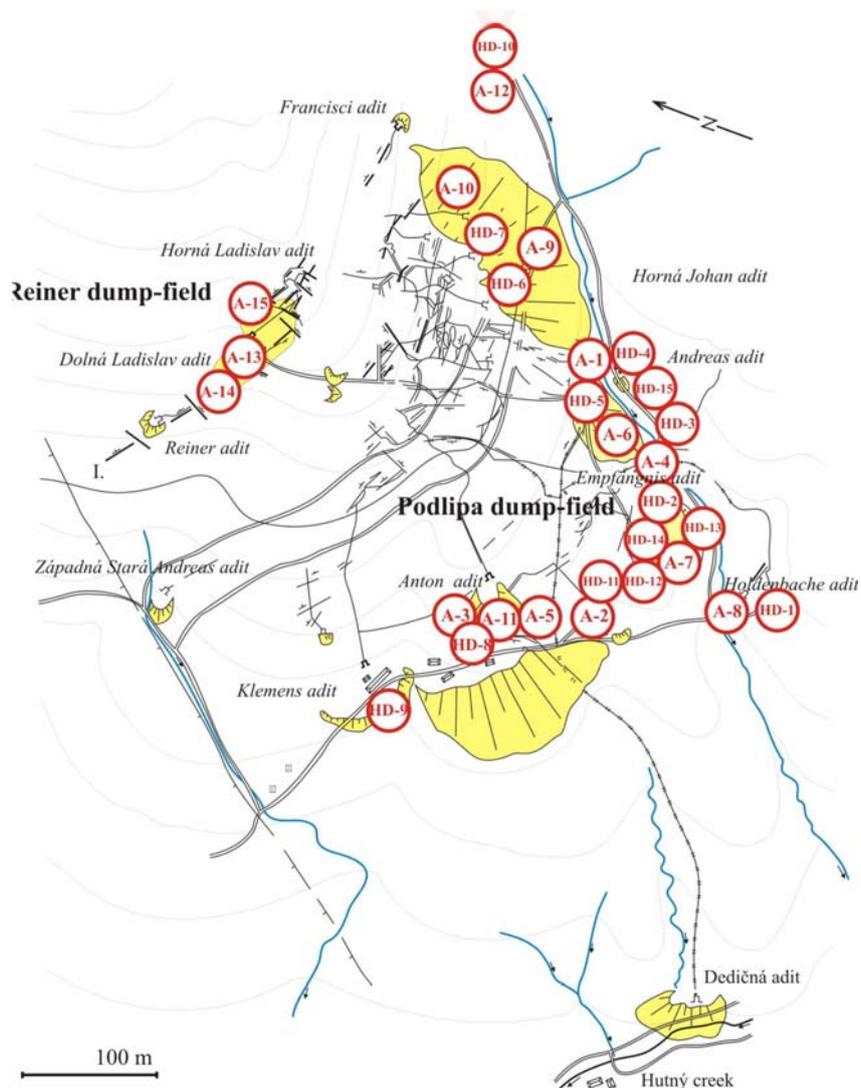


Figure 2. The Reiner and Podlipa dump-fields: localisation of the technogenous sediment samples.

To the 0.14 g of sample was added 3.5 cm³ of distilled water and using ultrasound was the sample dispergated. 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-diffraction analysis.

Rtg-diffraction analyses of clay minerals was realised in the laboratories of the Geological Institute of the Slovak Academy of Sciences using X-ray diffractograph PW 1710 Philips.

The existence of clay mineral free sorption capacity was studied using heavy metals containing drainage water from terraine depression beneath the dump of the

Empfängnis adit. To 20g 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-1* to A7* and A-17* after 14 days maceration in drainage water.

Rinse pH of the sediments was measured in the mixture of distilled water and unpulverised sample (Sobek et al., 1978). The pH of the sediments was determined also from mixture of unpulverised sediment and 1M KCl according to Sobek et al. (1978). In both eventualities to 10 g of sediment sample 25 ml of distilled water or 1M KCl was added and after two hours of mixing in laboratory mixer the pH and Eh was measured.

The samples of technogenous sediments from the dumps and soils were dried and 0.25 g of sample was heated in HNO₃-HClO₄-HF to fuming and taken to dryness. The residue was dissolved in HCl. Solutions were analysed by ICP-MS analyse in the ACME Analytical Laboratories (Vancouver, Canada). Plant samples were divided into roots, branchess/stems, leaves/needles and flowers/fruits. 0.5 g of vegetation sample was after split digestion in HNO₃ and then in Aqua Regia analysed by ICP-MS for ultralow detection limits. The contamination of live and dead parts was compared in several plants. Plants were analyzed in the same laboratory as sediments.

The carbon content (total carbon – C_{tot.}, organic carbon - C_{org.} and inorganic carbon C_{inorg.}) was determined in the laboratories of the Geological Institute of the Slovak Academy of Sciences by IR spectroscopy using device Ströhlein C-MAT 5500.

3. RESULTS

3.1 Heavy metal contamination of the technogenous sediments

The dump-field sediments are influenced by heavy metals from the hydrothermal Cu-mineralisation. The main contaminants: Fe (up to 2.64 %), Cu (25 ppm - >10 %), Mn (34 - 1258 ppm), As (7 - 289 ppm), Pb (8 - 130 ppm), Co (5.1 – 96.3 ppm), Sb (7 – 62 ppm) and Ni (7.8 – 62.1 ppm) are accompanied also by U (up to 10 ppm) and Th (up to 35 ppm).

The heavy metal distribution in technogenous sediments of the dump-fields is variable (Tabs. 1 – 3). The distribution of individual elements reflect the primary concentration in separate parts of the dump-fields as well as their geochemical relations, first place their migration ability.

The oxidation of sulphide minerals is indicated by coating of secondary oxides and Cu-carbonates. The less oxidised is the fine grained pelitic material. The direct indicator of oxidation processes is the pH.

To determine the Total Acid Production (TAP) and the Neutralisation Potential (NP) is necessary to know the Eh and pH values of the sediments (in distilled water and in 1M KCl lixivium) as well as the carbon and sulphur content. If distilled water is used in the measurment of paste or rinse pH, its pH is typically around 5.3. Consequently, any pH measurment less than 5.0 indicates the sample contained net acidity. Carbonate minerals show pH values around 8 – 10 and thus values above 10 are usually alkaline. Values of paste pH between 5 and 10 can be considered near neutral (Sobek et al., 1978).

Table 1. ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water

Explanation to tabs. 1 to 3: A-1 to A-12 technogenous sediments, A-1c to A-10c clay fraction; A-1* to A-10* clay fraction after 14 days maceration in drainage water; A-17 hydrogoethite rich rock

Element	Unit	Sample											
		A-1	A-1c	A-1*	A-2	A-2c	A-2*	A-3	A-3c	A-3*	A-4	A-4c	A-4*
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
Cu	ppm	2829	1693	2345	199	574	472	828	624	857	4471	3324	3112
Pb		28	64	229	130	22	28	16	23	37	10	15	38
Zn		14	18	95	21	36	62	20	25	47	23	16	27
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
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
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
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
As		162	258	628	10	19	15	71	110	105	169	237	300
Sb		62	60	153	7	9	13	22	24	28	59	79	130
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
Cr		38	9	24	36	17	26	34	21	37	38	15	30
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
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
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

Table 2. ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water

El.	Unit	Sample											
		A-5	A-5c	A-5*	A-6	A-6c	A-6*	A-7	A-7c	A-7*	A-8	A-8c	A-8*
Fe	%	1.71	1.66	1,83	2.06	2,09	3.36	1,32	1.43	2,81	0.91	1.29	0.79
Cu	ppm	3150	3001	2078	4797	2503	2918	756	855	2026	716	836	837
Pb		17	15	22	16	25	72	17	20	74	7	6	4
Zn		19	18	45	13	14	65	26	33	176	7	14	4
Cd		<0.1	<0.1	<0.1	0.2	<0.1	0.3	<0.1	0.2	0.7	<0.1	<0.1	<0.1
Bi		1.7	2.1	3.2	25.4	24.4	51.7	0.9	1.2	3.6	0.5	0.7	0.8
Co		24.4	30.4	29.6	41.8	40.9	32.0	10.2	12.0	15.5	89.9	69.7	104
Ni		34.0	34.1	55.4	51.6	45.1	61.7	10.4	10.1	26.0	58.0	66.5	62.5
As		60	64	105	134	224	305	16	17	33	61	52	46
Sb		17	16	30	50	56	92	12	7	17	18	20	19
Ag		0.1	0.1	0.2	1.0	1.6	3.0	0.2	0.2	0.4	<0.1	<0.1	0.1
Cr		30	10	22	31	11	23	28	11	35	23	21	7
Sn		4.9	3.3	8.1	14.9	12.9	19.6	4.0	2.6	6.8	3.9	7.1	3.0
U		1.0	1.2	1.4	1.4	1.6	2.2	1.1	1.1	2.3	2.6	2.5	2.1
Th		5.9	5.8	4.0	6.9	6.1	4.1	4.8	5.3	11.8	6.8	5.7	6.7

Table 3. ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water

Element	Unit	A-11	A-11c	A-11*	A-12	A-17	A-17c	A-17*
Fe	%	2.37	3.02	4.44	1.38	1.72	1.50	13.10
Cu	ppm	>10 000	8 756	7654	25	>10 000	20 360	23 060
Pb		14	24	33	16	8	49	60
Zn		15	17	21	39	59	80	50
Cd		0.1	0.1	0.2	0.2	0.2	0.2	0.2
Bi		2.6	3.2	4.7	0.2	7.2	6.0	5.0
Co		84.5	77.5	85.1	5.1	73.4	70.0	83.0
Ni		62.1	59.8	64.1	8.5	51.7	43.0	58.0
As		206	211	243	7	289	260	280
Sb		36	38	40	10	43	40	34
Ag		1 258	1 322	1 452	559	1 074	960	1 010
Cr		0.7	0.8	1.7	0.3	2.2	2.0	30.0
Sn		<1	<0.1	<0.1	<1	<0.1	<0.1	<0.1
U		0.3	0.4	0.6	0.1	0.8	1.0	1.0
Th		29	25	31	31	15	16	15

To determine the Total Acid Production (TAP) and the Neutralisation Potential (NP) is necessary to know the Eh and pH values of the sediments (in distilled water and in 1M KCl lixivium) as well as the carbon and sulphur content. If distilled water is used in the measurement of paste or rinse pH, its pH is typically around 5.3. Consequently, any pH measurement less than 5.0 indicates the sample contained net acidity. Carbonate minerals show pH values around 8 – 10 and thus values above 10 are usually alkaline. Values of paste pH between 5 and 10 can be considered near neutral (Sobek et al., 1978). ICP-MS analyses of technogenous sediments, clay fraction and of clay fraction after 14 days maceration in drainage water (Tabs. 1 – 3).

The pH values in sediments measured at the dump-field in the distilled water lixivium range from 4.21 to 7.93 (Tab. 4). It is interesting, that the lowest pH value was determined in the samples from reference area. It is caused probably by the fact, that in spite of absence of sulphides there are no carbonates; the carbon content is very low (C_{tot} 0.40 %, C_{org} 0.37 % and concentration of the inorganic carbon C_{org} is below the detection limite (Tab. 4). The highest carbon content is in sample A-7 (C_{tot} 1.63 %; re-counted for $CaCO_3$ even 12.71 %).

The samples contain 0.01 – 0.42 % of total sulphur (Tab. 4). The highest content of total sulphur is in the sample A-6 from the Empfängnis adit, where the sulphidic sulphur (S_S 0.27 %) prevalence on sulphate sulphur (S_{SO_4} 0.15 %) was recognised. At the dump-field Ľubietová in the majority of the samples is dominant the S_{SO_4} vs. S_S thus in the dump material still contain a great portion of not oxidised sulphidic minerals. According to Sobek et al. (1978) the calculation of the TAP value is possible by multiplication of the S_{tot} (or S_S) content by coefficient 31.25, which is derived from the neutralisation equation:



Table 4. Characteristic of the samples of technogenous sediments from dump-field

Sample	H ₂ O		1M KCl		%							
	pH	Eh (mV)	pH	Eh (mV)	S _{tot.}	S _{SO4}	S _s	C _{tot.}	C _{org.}	C _{inorg.}	CO ₂	CaCO ₃
A-1	5.14	77	4.61	109	0.25	0.10	0.15	0.74	0.20	0.54	1.97	4.48
A-2	5.89	34	5.40	63	0.02	0.01	0.01	0.86	0.38	0.48	1.75	3.99
A-3	4.87	94	4.21	131	0.10	0.03	0.07	0.62	0.34	0.28	1.02	2.32
A-4	5.46	59	5.33	66	0.33	0.13	0.01	0.34	0.26	0.08	0.29	0.66
A-5	5.77	42	5.37	64	0.05	0.01	0.05	0.78	0.35	0.43	1.57	3.57
A-6	5.17	74	5.06	83	0.42	0.15	0.27	0.40	0.27	0.13	0.47	1.08
A-7	7.93	-84	7.34	-58	0.03	0.02	0.01	1.63	0.10	1.53	5.61	12.71
A-8	5.42	36	5.22	42	0.01	0.01	0.01	0.45	0.13	0.32	1.17	2.66
A-9	5.03	83	5.01	85	0.03	0.03	0.01	0.40	0.37	tr.	tr.	tr.
A-10	5.25	71	5.14	78	0.04	0.02	0.02	0.48	0.46	tr.	tr.	tr.
A-11	6.11	22	5.95	30	0.11	0.04	0.07	4.31	4.18	0.13	0.47	1.08
A-12	4.21	133	3.47	173	0.02	0.01	0.02	4.05	4.03	tr.	tr.	tr.

This datum is equal to quantity of acid which could be potentially produced by the dump material. At Lubietová – Podlipa dump-field range the TAP value from 0.31 to 13.12 (in average 3.7; Tab. 5). The highest TAP values are at the dump of the Empfängnis adit and the lowest at the little dump of Holdenbachen adit beneath the wooded slope of the valley (Fig. 2).

Table 5. Values of Total Acidity Production (TAP). Neutralisation Potential (NP) and net neutralisation potential (NNP)

Sample	TAP	NP	NNP	NP:TAP
A-1	7.81	44.8	37.0	5.7
A-2	0.62	39.9	39.3	63.8
A-3	3.12	23.2	20.1	7.4
A-4	10.31	6.6	-3.7	0.6
A-5	1.56	35.7	34.1	22.8
A-6	13.12	10.8	-2.3	0.8
A-7	0.93	127.1	126.2	135.6
A-8	0.31	26.6	26.3	85.1
A-9	0.93	0	-0.9	0.0
A-10	1.25	0	-1.3	0.0
A-11	3.43	10.8	7.4	3.1
A-12	0.62	0	-0.6	0.0
Mean	3.7	27.1	23.5	7.4

To define the risk of the acidity production it is necessary to know also the neutralisation potential (NP), which define the content of the neutralisation matter in the dump-field able to neutralise the dump produced acidity. The distribution of NP values within the individual parts of the Podlipa dump-field show substantial differences (from 0 to -127.1, in average 27.1; Tab. 5) and it is more or less in

negative correlation to the Total Acid Potential (TAP). For example to the TAP 13.125 value (in sample A-6 where the highest S_{tot} 0.42 % and S_S 0.27 % contents were described; Tab. 4) rises value NP 10.8, while to the lowest TAP value 0.3125 (sample A-8) rises NP 26.6. Higher NP – 127.1 is only in the sample A-7 (Tab. 5), where the highest C_{tot} was appointed (equal to $12.71 \text{ kg.t}^{-1} \text{ CaCO}_3$; Tab. 4).

The Net Neutralisation Potential (NNP) is equal to the quantity of neutralisation matter (usually n.kg CaCO_3 per 1 ton of material), necessary for neutralisation of dump-field matter produced acidity ($\text{NNP} = \text{NP} - \text{TAP}$). NNP values at the Podlipa dump-field are presented in table 5. The results show that to neutralise the dump material it would be necessary use such a quantity of neutralisation reagent which is in average equal to $23.5 \text{ kg CaCO}_3 / 1 \text{ ton of dump matter}$. The risk of the Acid Mine Drainage water (AMD) formation is best expressed by NP:TAP ratio. If it is close to 1, the risk of the AMD formation is highly feasible, while when ratio is equal to 3 or >3, the risk of the AMD formation is negligible (Sobek et al., 1978).

If we consider the average NP:TAP ratio at the Podlipa dump-field (7.4; Tab. 5), the risk of the AMD formation is beyond possibility. Such a high average NP:TAP ratio is caused only by value from the dump of the Empfängnis adit (NP:TAP = 135.6). If this only extreme value will be excluded, the NP:TAP ratio will change to 1.72 and it correspond to the low risk of AMD creation.

3.2 Heavy metal sorption on clay minerals and hydrogoethite

Rtg.-diffraction analyse proved, that the most important potential natural sorbents in studied area are the clay minerals and hydrogoethite – $\text{FeO(OH).nH}_2\text{O}$, which are formed during the weathering process of rock-material. The research confirmed that the clay minerals are represented by illite and muscovite, caolinite as well as smectite and chlorite mixture. Illite and muscovite are dominant in all samples. The next important mineral is smectite.

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 (Tab. 6) is presented in form of toatal values for each element (Tabs. 1 - 3). Such a toatal data enable better understand the studied processes and trends.

Table 6. ICP-MS analyse of drainage water used for 14 days maceration of clay fraction

Sam- ple	Fe	Cu	Pb	Zn	Cd	Bi	Co	Ni	As	Sb	Mn	Mo	Ag	Cr
	$\mu\text{g.l}^{-1}$													
V-1	486	9864	12.4	189	0.25	2.11	44.2	23.1	14.8	8.43	52	0.2	0.1	8.2

Notice: Sn $0.2 \mu\text{g.l}^{-1}$; the Au, Ag, V, W, Zr, Sn, U and Th concentrations were below the detection limit

Preferential sorption of Cr and Th on surface of clay minerals in comparison with hydrogoethite was described. On hydrogoethite surface are preferentially fixed Cu, Zn (\pm Fe, Cd, Co). The following elements: Sb, Sn, Pb, Ag, Ni, As and U show no

legible trends of preferred sorption both on clay minerals and on hydrogoethite rich rock (Tabs. 1 - 3).

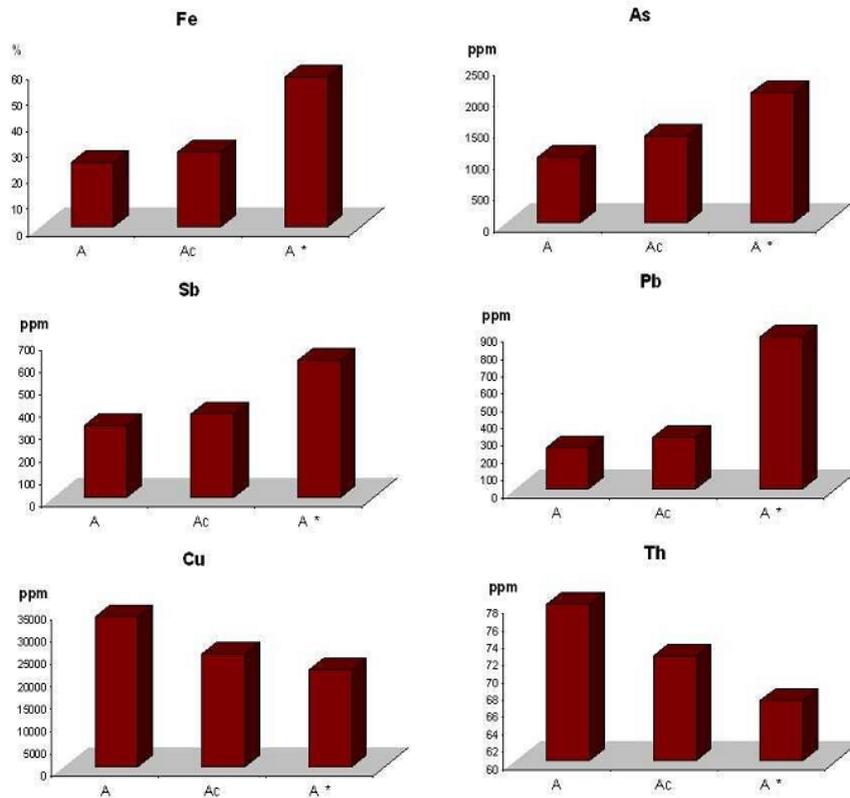


Figure 3. Total content of Fe, As, Sb, Pb, Cu and Th in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (A*).

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. 4). 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 following heavy metals: Fe, As, Sb, Ag, Pb, Zn, 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. 3). Co show moderate content in clay minerals but no free sorption capacity was proved. The Cd, Ni, Co, V and Cr behaviour is very complex (Fig. 4).

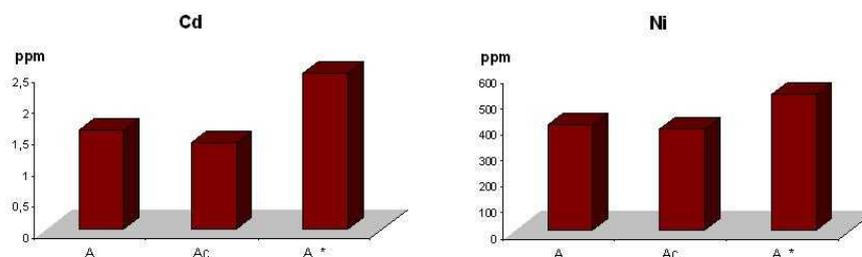


Figure 4. Total content of Cd and Ni in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (A*).

3. DISCUSSION

Heavy metal distribution at the dump-fields reflect the geochemical behaviour of the elements, depend on their content, solubility, migration potential and sorption properties. Lack of carbonates cause, that in 5 samples from 12 studied samples are the NNP values negative (neutralisation matter is entirely absent) and two values (samples A-3 and A-11) are very low (7.4 and 20.1; Tab. 4). NNP values from -20 to 20 ($\text{kg CaCO}_3 \cdot \text{t}^{-1}$ od dump material) is possible to account as a „scale of uncertainty“ sensu US EPA methodics (in Lintnerová and Majerčík, 2005) from viewpoint of the acidity production, because there is no unambiguous forecast if the AMD will be produced. In spite of this fact the result of our study suggest that at the localities Reiner and Podlipa is the assumption of AMD production very limited.

Mobility of the majority of the heavy metals is in the nature determined mostly by their sorption ability on natural sorbents, which are represented predominantly by clay minerals (Missanaet et al., 2008). Sorption of metals by clay minerals is a complex process controlled by a number of environmental variables.

Caolinite have been used as a good sorbent for most heavy metals (Wahba & Zaghoul, 2007). Cu, Pb, Zn and Cd show favourable sorption on smectite and Pb also on illite surface (Rybicka et al., 1995). The uptake of Pb and Cu on illite and smectite is usually very fast. The kinetics of Zn, Ni and Cd sorption on illite and smectite is not so efficient. Mg, Fe and Al sorption on clay minerals is more efficient at higher pH. It is caused by absence of free H^+ ions and by increase of negative charge on clay minerals surface (Kishk and Hassan, 1973). $\text{pH}_{(\text{H}_2\text{O})}$ of the technogenous sediments at the Reiner and Podlipa dump-fields range from 4.21 to 7.93 ($\text{pH}_{(\text{KCl})}$ 4.00 – 7.34), so the conditions for Cu, Pb, Zn and Cd adsorption on clay minerals are not the best but also not inefficient.

From the viewpoint on the environmental risk the most important heavy metals are Cu, As and Sb.

The main Cu source at the dump-fields are tetrahedrite, chalcopyrite and secondary Cu-minerals (libethenite, brochantite, langite, malachite, azurite and pseudomalachite). Cu released during the weathering to the solution contaminate the

whole aqueous medium. In natural water are present the following soluble Cu compounds: hydrated Cu^{2+} ion, complexes $[\text{CuCO}_3(\text{aq})]^0$, $[\text{Cu}(\text{CO}_3)_2]^{2-}$ and hydrocomplexes $[\text{CuOH}]$, $[\text{Cu}(\text{OH})_2(\text{aq})]^0$, $[\text{Cu}(\text{OH})_3]^{3-}$ and $[\text{Cu}(\text{OH})_4]^{2-}$ (Pitter, 1990).

The sorption of Cu on clay minerals surface depend on the pH. If there is a lack of carbonates (as it is at the Reiner and Podlipa dump-fields) during the sorption process are formed complex compounds $\equiv\text{SOCu}^+$, $\equiv\text{SOCuOH}$ a $\equiv\text{SOCu}_2(\text{OH})_2^+$, less also $\equiv\text{Cu}(\text{OH})_2$ and $\equiv\text{SOCu}_2(\text{OH})_3$ precipitates (Sun et al., 1997).

The main source of As at the studied dump-fields Reiner and Podlipa is tetrahedrite. The weathering of the As containing ore minerals cause transformation of As^{3+} to As^{5+} (Lin and Puls, 2000). As^{5+} is water-soluble but only rarely migrate for greater distances, while easily react with heavy metal cations and form various arsenates. As is in the aqueous conditions present most often in following forms: H_2AsO_4^- , HAsO_4^{2-} and HAsO_2^0 (Greenwood & Earnshaw, 1990). As^{3+} is in the oxidation zone better mobile than As^{5+} (Manning & Goldberg, 1997).

The sorption capacity of clay minerals, hydrogoethite and Fe-oxyhydroxides for As is very high (up to 76 mg As.g^{-1} in Fe oxyhydroxides at pH 5). The As sorption depend on pH, time, concentration of As in solution and on temperature (Mohapatra et al., 2007). The most intensive sorption was described at pH 4 (García-Sánchez et al. 2002; Lombi et al., 2000). In comparison with results of Mohapatra et al. (2007) would have been the best As^{5+} sorbent at the Reiner and Podlipa dump-fields caolinite. The sorption of the less toxic As^{5+} on clay minerals is in comparison with more toxic As^{3+} much more efficient and quantitative. As^{3+} is during this process oxidised to As^{5+} . Reduction during the As sorption process was not proved (Lin & Puls, 2000).

The greatest part of Sb is derived from tetrahedrite. Sb^{3+} as well as Sb^{5+} are present under natural conditions in soluble compounds: Sb^{5+} in form $\text{Sb}(\text{OH})_6^-$ and Sb^{3+} in form $\text{Sb}(\text{OH})_3$ (Filella et al., 2002). Hydrogoethite and Fe-hydroxides are important Sb-sorbents. Sb^{3+} as well as Sb^{5+} create on the hydrogoethite and Fe-hydroxide surfaces complex compounds. The most efficient sorption of Sb^{3+} was described at pH 3–12, while the maximum Sb^{5+} sorption was determined at pH < 7. Sb^{3+} is on hydrogoethite and Fe-hydroxide surface at pH 3–5.9 during several few days oxidised. Sb^{3+} is at pH ~ 9 released to solution and mobilised and at pH < 7 is fixed on surface of Fe-oxides (Leuz et al., 2006).

In the nature prevail from the soluble forms of lead $[\text{PbCO}_3(\text{aq})]^0$, which could be in wide range of pH the most dominant form. In alkaline conditions were at higher Pb-concentrations described also complexes $[\text{Pb}(\text{CO}_3)_2]^{2-}$, $[\text{Pb}(\text{OH})_2(\text{aq})]^0$ and $[\text{PbOH}]^+$ (Pitter 1990). In soils is the Pb most often in solid forms of PbCO_3 and PbSO_4 and the ulmous matters cause its mobilisation (Beneš & Pabianová, 1987). Affinity of Pb to form complexes with insoluble ulmous matters cause that it is fixed in the upper ulmous level of the soil. Cu and Pb are in comparison with Zn usually sorbed on clay minerals surface much more stronger (Sipos et al., 2008). Cd sorption on clay minerals become generally more efficient with increasing pH (Hayashi a Liu, 2008).

Cd is in aqueous conditions soluble in form of simple hydrated ion Cd^{2+} : $[\text{CdOH}]^+$, $[\text{Cd}(\text{OH})_2(\text{aq})]^0$, $[\text{Cd}(\text{OH})_3]$, $[\text{CdCO}_3(\text{aq})]^0$, $[\text{Cd}(\text{CO}_3)_2]^{2-}$, $[\text{CdSO}_4]^0$ and in form of organic complexes with various organic ligands (Pitter 1990). The quantity of the sorbed Cd^{2+} on clay minerals increase at pH 6.5 – 9.0, while on illite is the sorption process much more efficient as on the caolinite surface (Reid & McDuffie, 2005).

5. CONCLUSIONS

The dump-field mining sediments are influenced by heavy metals from the hydrothermal Cu-mineralisation. The main contaminants: Cu (up to 20 360 ppm), Fe (up to 2.58 %), As (up to 457 ppm), Sb (up to 80 ppm) and Zn (up to 80 ppm) are accompanied also by U (up to 10 ppm) and Th (up to 35 ppm). The present natural sorbents are predominantly the clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals are good sorbents of V, Cr, Ti, W, Zr, Nb, Ta a Th and at the hydrogoethite of Cu, Zn, Mo, Mn, Mg, (\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.

The paste or rinse pH of sediments measured in distilled H₂O is around 5.3 and only very few samples account acid values (< 5.0). The measuring of the pH paste in the samples using solution of 1M KCl give similar values. It means that only several few samples show markedly acid reaction. The acidity production (AP) vary from 0.625 to 10.31 (in average 3,7) and the neutralisation potential (NP CaCO₃) from 0.66 to 12.71 kg.t⁻¹ (in average cca 27.1 kg.t⁻¹ CaCO₃). The value of the net neutralisation potential (NNP) and the NP : AP ratio show that the potential of the acid mine drainage water formation is very limited (NNP = 1.42; NP : AP = 1.72) and the environmental risk is negligible.

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