Carpth. J. of Earth and Environmental Sciences, 2008, Vol. 3, No. 2, p. 5 - 18

PODLIPA DUMP-FIELD AT ĽUBIETOVÁ – LAND CONTAMINATED BY HEAVY METALS (SLOVAKIA)

Peter ANDRÁŠ[1,2], Adam LICHÝ[3], Ivan KRIŽÁNI[2], Jana RUSKOVÁ[4], Juraj LADOMERSKÝ[5], Stanislav JELEŇ[2], Emília HRONCOVÁ[5] & Lenka MATUŠKOVÁ[1]

[1]Department of Ecology and Environmental Education, Matej Bel University, Tajovského 40,
974 01 Banská Bystrica, Slovakia
[2] Geological Institute, Slovak Academy of Sciences,
Severná 5, 974 01 Banská Bystrica, Slovakia, andras@savbb.sk
[3] Envigeo, Kynceľová 2, 974 11 Banská Bystrica, Slovakia, ; e-mail: lichy@envigeo.sk
[4] Regionál Office of Public Health verejného zdravotníctva, Cesta k nemocnici 1,
974 01 Banská Bystrica; e-mail: jana.ruskova@vzbb.sk
[5] Faculty of Environmental and Manufacturing Technology, T. G. Masaryka 24,
960 53 Zvolen, Slovakia; e-mail: ladomer@vsld.tuzvo.sk

Abstract: The dump-field Ľubietová – Podlipa is situated at the boundary of the village settlement. The heavy metal contamination of the technogenous sediments and soils at the investigated dump-field show irregular planar distribution. Also the heavy metal content in the surface water, drainage water and in the groundwater was studied both in the dry as well as during the rainy periods. The cementation process causes substitution of iron by copper. Natural installation and development of plant species was observed at the old mine waste dumps, specific to the local chemical conditions such as low content of essential nutrients and high content of heavy metals. The individual parts of the plant tissues (roots, branches/stems, leaves/needles, flowers/fruits) are contaminated by heavy metals and tissues are damaged differently, respectively. The technogenous sediments and the contaminated soil of the dump show only very limited acid potential.

Keywords: contamination, dump-field, heavy metals, sediment, soil, acid potential, neutralization potential

1. INTRODUCTION

The Ľubietová deposit was in the 15th and 16th centuries one of the most important and most extensively exploited Cu-mines of Europe. Although mining activities were stoped during the 19th century and only a few geological survey activities with negligible effect have been carried out here since (Ilavský et al. 1994), the area remains substantially affected.

The main dump-field Podlipa represents about 2 km^2 area. The deposit is situated in the Ľubietová crystalline complex of Permian age which consists of greywackes, arcose schists and conglomerates. The copper content in manually graded ore was about 4 – 10 wt. %. Copper content in dump waste material was 0.9 – 2.4 wt. % (Bergfest 1951; Koděra et al. 1990; Ilavský et al. 1994).

The heavy metals from the ore contaminated the technogenous sediments of the dumps, the soil and the surface water, drainage water as well as the groundwater (Andráš et al. 2007). The heavy metals can reach plants from the soils due to their higher content in the base rocks or from the sources of different anthropogenic activities. Heavy metals from the air pollutants can reach plants through pores/water or soil solution. Their penetration influences soil-ecological conditions such as soil types, soil pH, concentrations and bonds of heavy metals, humus content in soil, oxidative-reductive conditions around root system connecting with microbial decomposition of inorganic and organic substances, soil moisture, temperature, utilized fertilizes and preparations for the plant protection (Andráš et al. 2007).

Natural installation of mine waste dumps by plants is inhibited due to fine-grained soil flushing from the slopes and fast draining of rain water from the surface into the basal level of dumps or into the impermeable sub-soil by soil-forming substratum. Therefore only several large mine waste dumps provide the possibility to enroot to resistant plants in depressions or at local plains after centuries (Andráš et al. 2007).

2. EXPERIMENTAL

The samples (of about 10 kg weight) of sediments from the dumps and soils from the 15 – 20 cm depth (the sampling step was 25 m^2), surface water (stream water, drainage water, and groundwater) were collected for the characterization of components of landscape contamination. To the each water samples of 1 000 ml volume was added 10 ml of HCl.

The reference site was selected for comparison of territories loaded by heavy metals and non-contaminated natural environment (Fig. 1). It was situated outside of geochemical anomalies of heavy metals and represent graywakes of Permian age) similar to material at the dump-field. The samples of plant material were collected from the contaminated dumps.

Vegetation creates small isles and is enrooted in few depressions which have enabled limited soil-forming process. The selection of plant species was performed so that it could be possible to compare all identical plant species from the contaminated planes with plants from the reference sites. The samples of hardwood species (*Betula pendula, Quercus petraea, Salix fragilis*), coniferous species (*Pinus sylvestris, Abies alba, Picea abies*) and herbs (*Juncus articulatus, Mentha longifolia*) were studied. At everyone site were sampled 10 individuals of each plant species to get average sample Five coniferous individuals of approximately same age were sampled for branches (in case of *Picea abies* also needles) from the fourth or fifth spike with approximate length of segment from 10 to 15 cm. In the case of *Pinus sylvestris* were analysed two years old needles. Roots of the same length and with 2 - 3 cm diameter were obtained from the surface soil level. Similar mode of sampling was used at hardwood species: 3 – 4 years old branches were sampled from the lower limbs. The samples were dried at laboratory temperature and then homogenized.

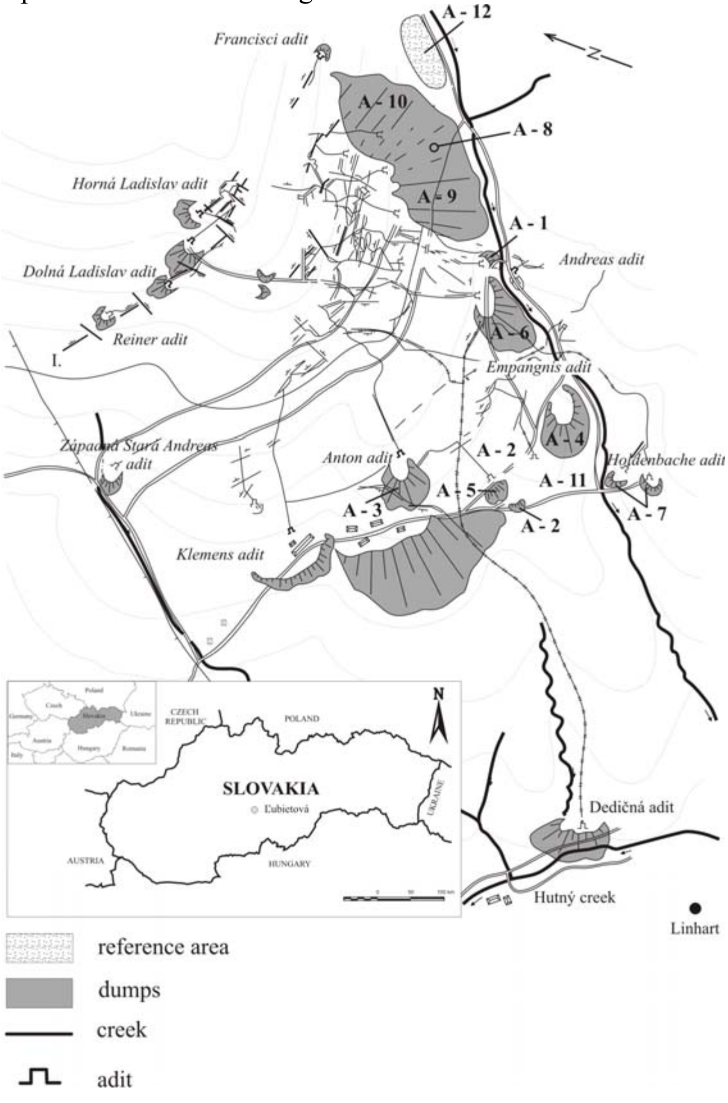

Figure 1. The dump-field Podlipa in Ľubietová

The samples of technogenous sediments from the dumps and soils were dried and 0.25 g of sample was heated in HNO_3-$HClO_4$-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 HNO_3 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 minerals of the clay fractions were determined by x-ray diffraction and the clay mineral samples were ICP-MS analysed, than macerated 14 days in natural drainage water from the studied locality containing heavy metals and again analysed. The pH of the sediments was determined from suspension both with distilled water and 1M KCl after 3 hours of maceration.

The sulphur, total carbon, organic carbon and inorganic carbon content in the sediments was IR analysed using furnace Ströhlein C-MAT 4000 in the laboratories of Geological Institute of Slovak Academy of Sciences. The static test of the total acid potential was realized according to Morin and Hutt (1997) and Sobek et al. (1978).

The water samples were analyzed using AAS in the National Water Reference Laboratory for Slovakia at the Water Research Institute in Bratislava. The speciation of As was performed on the basis of different reaction rate of As^{3+} and As^{5+} depending on pH. The experimental study of the Cu precipitation on the surface of iron particles was realized in the laboratory of the Comenius University in Bratislava by Dr. B. Lalínska.

Microscopical analyses of plant tissues were realized in the laboratories of the Department of Wood Science of the Technical University Zvolen.

3. RESULTS

3.1 Technogenous sediments and soil

The dump-field mining sediments are influenced by heavy metals from the hydrothermal Cu-mineralization. The main contaminants: Cu (up to 20 360 ppm), Fe (up to 2.58 %), As (up to 457 ppm), Sb (up to 79.3 ppm) and Zn (up to 80 ppm) are accompanied also by U (up to 10 ppm) and Th (up to 35 ppm). The distribution of the contamination is irregular (Fig. 2 – 4). In general it is possible distinguish according to the geochemical behaviour three main groups of elements: 1a): Fe, Sn, Ag, U, 1b): Cu, Ni, Co, As, Sb, Cr, V, Th 2): Zn, Bi and Cd, 3): Pb.

The weathering processes of reactive minerals in predominantly acid rock surrounding mobilize heavy metals and toxic elements (e.g. Cu, As) and contaminate the landscape components. The natural sorbents were studied to secure efficient landscape remediation. The most important possible natural sorbents at the studied locality are clay minerals and limonite. X-ray diffraction analyse of the clay fraction showed that it consists of illite and muscovite mixture, of caolinite, minerále of the smectite group and of chlorite group. Within the studied symplex the dominant clay minerále are illite and muscovite. The second most important clay minerál is the smectite.

The present study showed that the best sorbent is the limonite (tab. 1, sample A-17) but its occurrence at the dump-field is very limited. In most cases show good sorption property alsi clay minerals. These minerals form at the locality the natural geochemical barrier which enable precipitation of heavy metals and their fixation on clay minerals surface.

Important sorption was prowed predominantly in the case of Cu, Pb and Zn but in some cases also As, Sb, Bi, Mn show good sorption power (Tab. 1). This tendency was not prowed only in limited cases: in samples where was determined presence of not oxidized primary ore minerals (e.g. chalcopyrite in sample A-1), which case that the content of the individual heavy metal (in case of sample A-1 it is the Cu content) ins in the technogenous sediment or soil higher as in the fraction of the clay minerals (Tab. 1, Fig. 5).

Table. 1. ICP-MS analyses of technogenous sediments and soils from the dump-field

Sample	Cu	Pb	Zn	Ni	Co	As	Sb	Bi	U
	Ppm								
A-1	2829	28.1	14	36.8	10.4	162	61.6	2.8	1.3
A-1*c*	1693	63.8	18	36.0	11.3	258	60.1	4.5	1.4
A-1*c**	2345	229.1	95	71.8	18.3	628	153.2	14.6	3.3
A-2	198.8	13.0	21	9.8	5.9	10	7.1	0.2	1.4
A-2*c*	574.3	22.4	36	12.2	10.3	19	9.2	1.4	1.1
A-2*c**	472.4	27.9	62	17.0	6.4	15	12.6	1.5	1.1
A-3	827.5	16.0	20	32.1	14.0	71	22.4	8.5	1.7
A-3*c*	624.2	23.1	25	28.3	17.0	110	24.0	7.2	1.8
A-3*c**	857.4	37.4	47	30.4	11.0	105	28.0	12.1	1.9
A-4	4471	9.6	23	55.0	50.0	169	59.5	23.7	1.6
A-4*c*	3324	14.9	16	42.4	58.3	237	79.3	39.2	1.7
A-4*c**	3112	37.8	27	64.4	32.1	300	129.8	90.9	2.2
A-5	3150	16.9	19	34.0	24.4	60	17.2	1.7	1.0
A-5*c*	3001	14.8	18	34.1	30.4	64	16.3	2.1	1.2
A-5*c**	2078	21.9	45	55.4	29.6	105	30.3	3.2	1.4
A-6	4797	15.6	13	51.6	41.8	134	49.8	25.4	1.4
A-6*c*	2503	24.6	14	45.1	40.9	224	56.2	24.4	1.6
A-6*c**	2918	72.3	65	61.7	32.0	305	92.3	51.7	2.2
A-7	755.8	16.8	26	10.4	10.2	16	11.5	0.9	1.1
A-7*c*	855.1	20.2	33	10.1	12.0	17	7.1	1.2	1.1
A-7*c**	2026	73.7	176	26.0	15.5	33	17.4	3.6	2.3
A-8	716.0	6.5	7	58.0	89.9	61	17.9	0.5	2.6
A-8*c*	835.5	6.3	14	66.5	69.7	52	20.2	0.7	2.5
A-8*c**	836.7	4.2	4	62.5	104.5	46	18.9	0.8	2.1
A-9	5903	29.5	24	39.8	36.0	244	37.0	15.1	2.7
A-10	7699	30.2	19	52.2	48.0	457	62.7	25.1	4.0
A-11	1563	24.8	37	19.0	8.7	16	14.9	4.8	1.7
A-12	113.1	39.4	29	8.9	8.6	16	5.6	0.7	1.4
A-17	14 440	8.4	59	51.7	73.4	289	43.2	7.2	2.3
A-17c	20 360	49.0	80	43.0	70.0	260	40.0	6.0	2.0
A-17*c**	23 060	60.0	50	58.0	83.0	280	34.0	5.0	1.0

Explanations: A-1 to A-11 – technogenous sediments and soils from the dump-field, A-12 reference area, A-17 limonite, A-1c to A-17c clay fraction, A-1* to A-17* - clay fraction after 14 days maceration in drainage water, containing heavy metals**.**

In the very most cases were the heavy metals after 14 days maceration of the clay fraction in the drainage water sorpted on the clay minerals surface. This result prowed that the clay minerals dispose by free sorption capacity (fig. 5). For the not numerous exceptions as e.g. the decrease of the As content in samples A-2, A-3 or A-8, eventualy decrease of the Mn content in samples A-2 to A-6 we have in the present state of the investigation no relevant explanation.

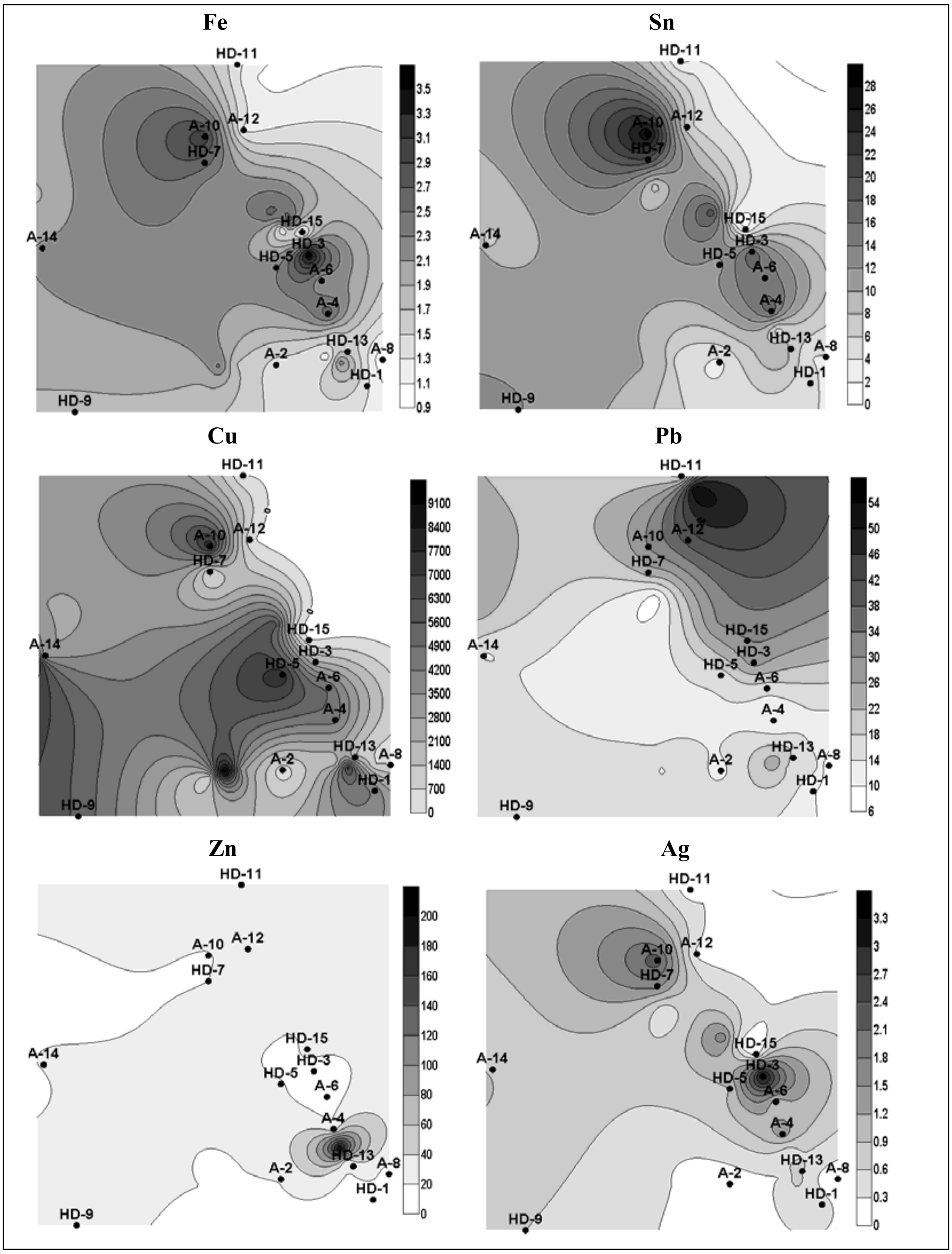

Figure 2. Distribution of the heavy metal contamination at the dump-field sediments at the Ľubietová deposit. The number indexes on the isolines represent the concentration in %.

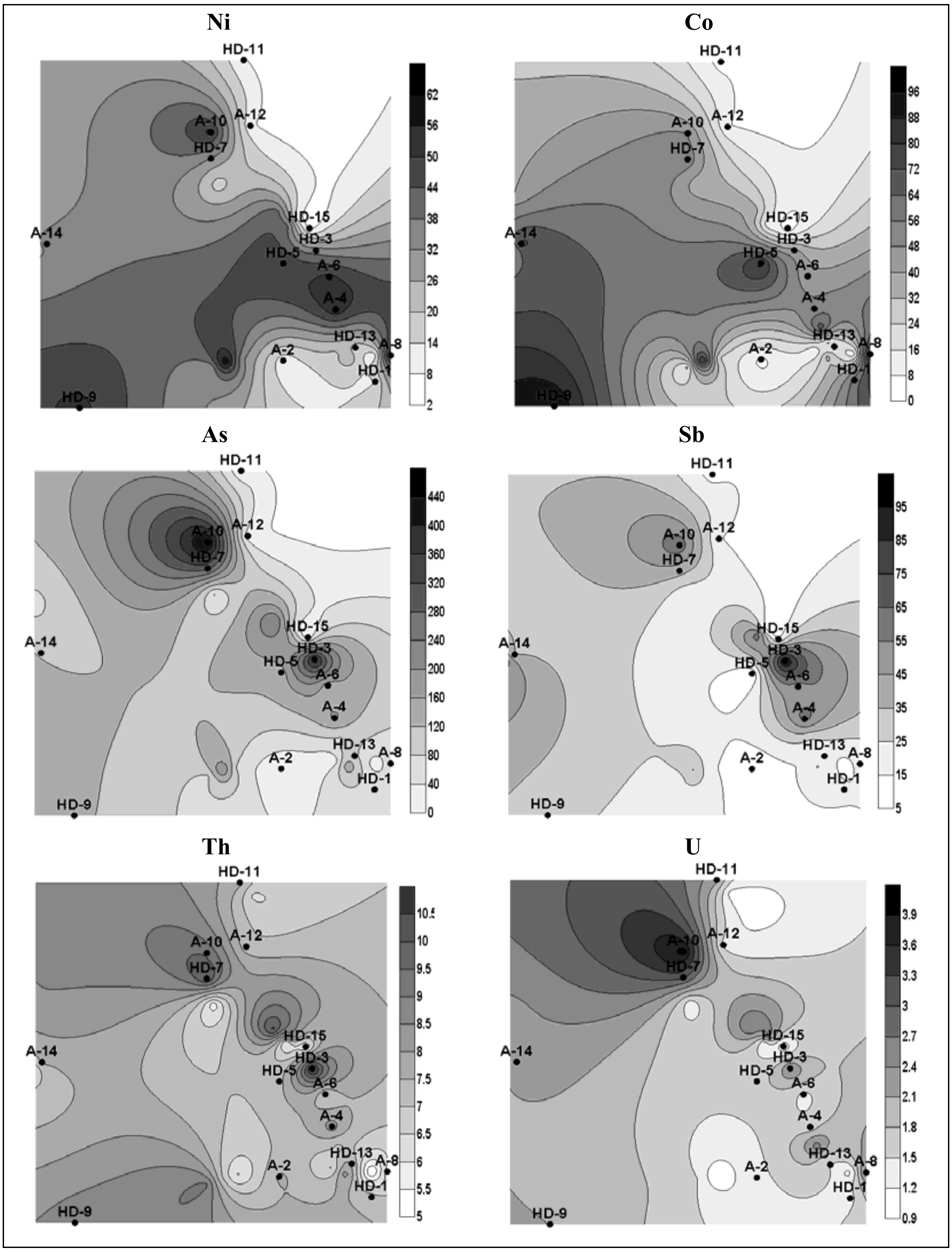

Figure 3. Distribution of the heavy metal contamination at the dump-field sediments at the Ľubietová deposit. The number indexes on the isolines represent the concentration in ppm.

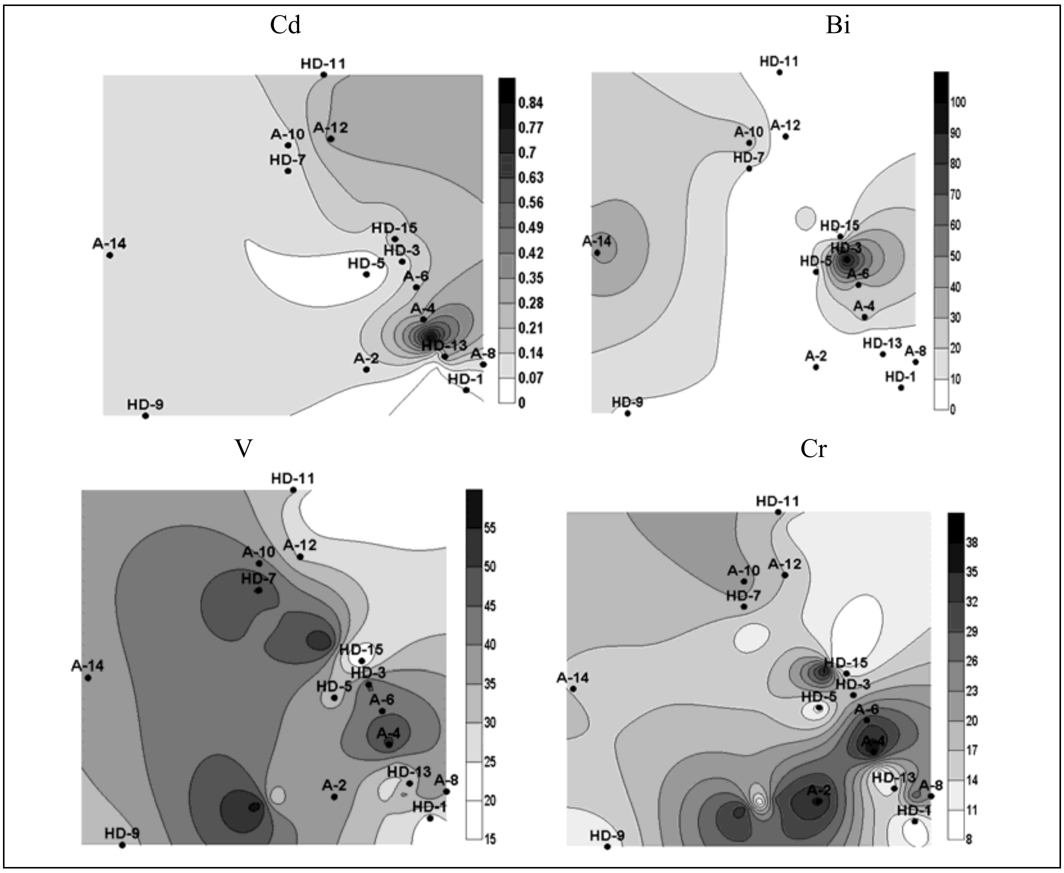

Figure 4. Distribution of the heavy metal contamination at the dump-field sediments at the Ľubietová deposit. The number indexes on the isolines represent the concentration in ppm.

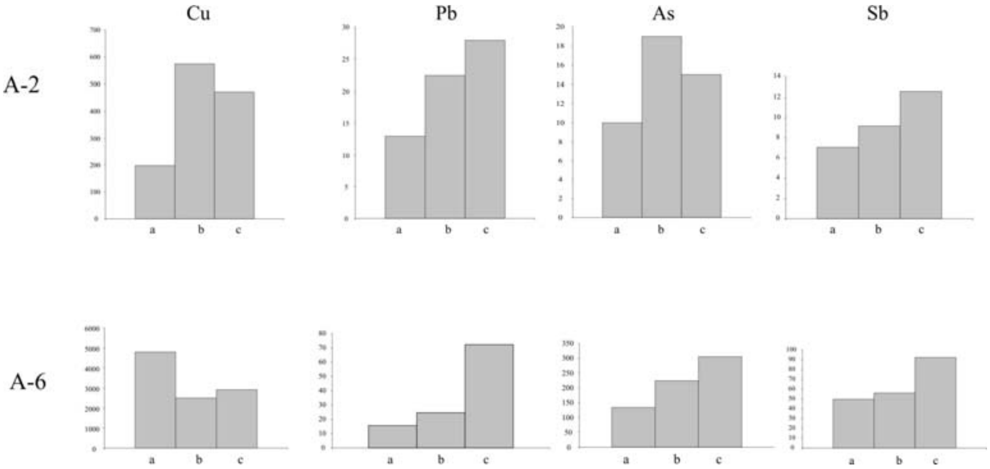

Figure 5. Histograms of Cu, Pb, As and Sb content in technogenous sediments (a), in fraction of clay minerals (b) and in clay minerals macerated 14 days in heavy metals containing drainage water

Differences of the sorption capacity among individual clay mineral mixtures were not prowed. It could be caused probably by the fact that the matrix of each clay fraction consists from the larger part of illite and muscovite. The variable quota of smectite, which has according to Kozáč (1996) higher sorption capacity as illite or muscovite, is not enough important to show substantially higher sorption efficiency.

3.2 Water

The surface water in the creek draining the valley along the dump-field is gradually contaminated by heavy metals from leached from the technogenous sediments of the mining dumps. The drainage water contains high Cu (up to 2060 ppm), Fe (up to 584 ppm), Zn (up to 35 ppm) and sometimes also Co (up to 10 ppm) and Pb (up to 5 ppm) concentrations. The highest As concentration is 0.6 ppm.

The heavy metal content in the water is probably in one third higher during the dry period in comparison with the rainy period. The As content is both in the surface (and drainage) as well as in the groundwater not high (0.061 ppm). The speciation of the As proved only the presence of the less toxic As^{5+}. The more toxic inorganic As^{3+} is not present (Fig. 6).

The presence of *Acidithiobacteria* or of sulphate reducing bacteria was not proved. The acidity both of the surface and groundwater is close to neutral pH (6.4 – 7.6) so the formation of acid mine drainage water is not probable.

It was found that the process of the cementation is present but not fast. In spite of the limited kinetics of the process the electron microprobe study proved that the cementation cause on the surface of iron gradual displacement of the Fe^{2+} ions and precipitation of Cu^{2+} ions, both in form of the Cu-oxides, Cu carbonates as well as in form of native copper (Fig. 7). The electron microprobe study show that the cementation copper is of a high fineness. The electron microprobe point analyses proved Cu-contents up to 96.07 $_{wt.}$%.

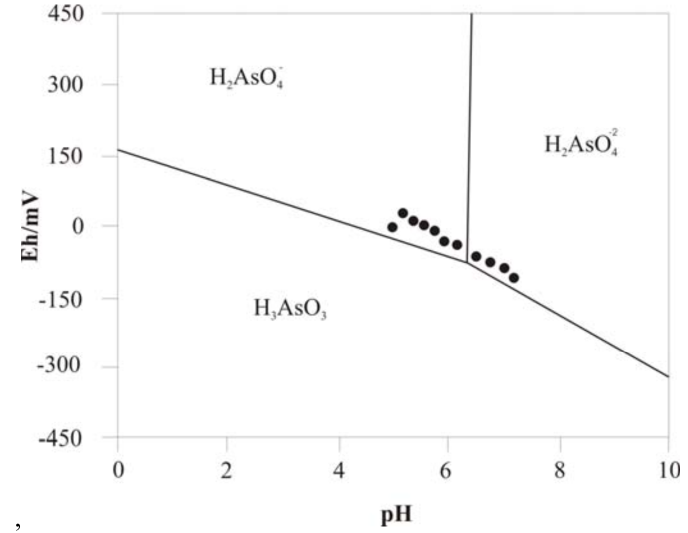

Figure 6. The pH vs. Eh plot show only the presence of the As^{5+} in the groundwater

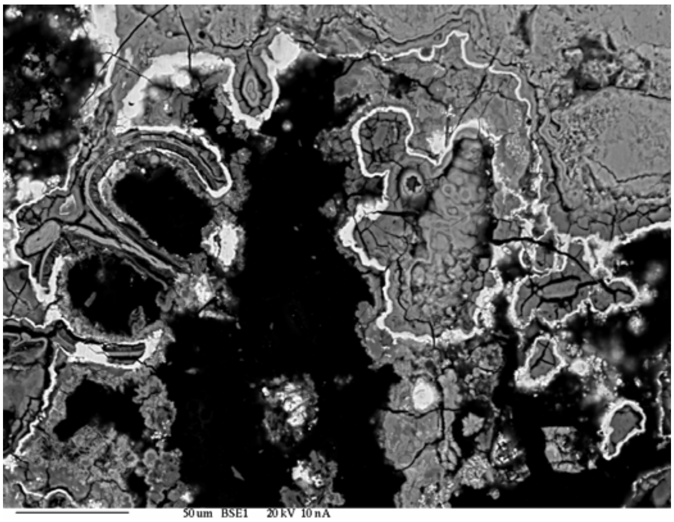

Figure 7. Native copper (white) of high fineness (up 91,68 % Cu) and the Cu-oxides and carbonates (grey) on the oxidized steel surface (dark) were precipitated after two months of maceration.

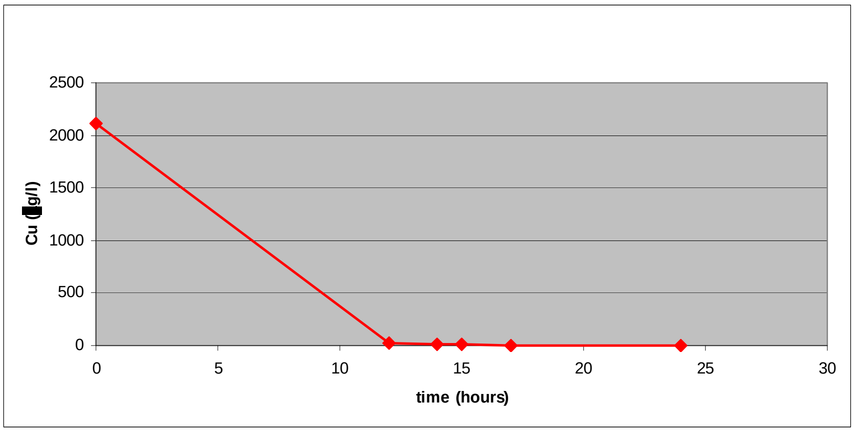

Figure 8. The experimental removing of Cu from the drainage water using Fe^0 –barrier

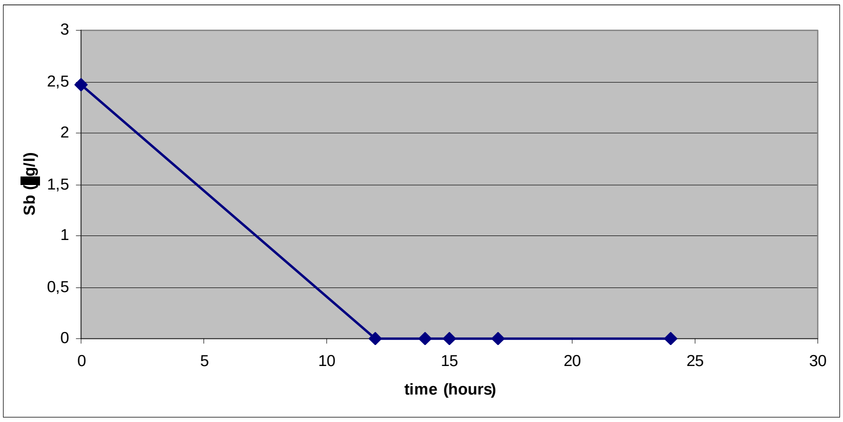

Figure 9. The experimental removing of Sb from the drainage water using Fe^0 -barrier

The ability of the drainage water precipitate cementation copper on the iron surface give possibility to realize Fe^0-barrier for elimination of heavy metals from the drainage water and contribute to the remediation of the mining country.

The most contaminated is the mineral water from the spring Linhart (Fig. 1). The average total radioactivity is 6,498 $Bq.l^{-1}$, the Fe (381 ppm) and Cu (80 ppm). These contents as well as contents of Pb (81 ppm) and Cd (476 ppm) in singular analysis substantionally exceed the Slovak decrees No. 296/2005 - No 354/2006 Coll.

The experimental test using the Fe^0-barrier (Laboratory evaluation of Fe^0 barriers to treat acid drainage water) according to Bartzas et al. (2006) showed that the Cu and Sb were from the acid drainage water removed the objective metals (Cu and Sb; figures 8 and 9) during 12 hours at pH 6 – 8.

3.3 Plants

The mineralogical composition of the mine waste dumps at Cu-deposit Ľubietová - Podlipa deposit influence the chemical composition of the products resulted from the specific weathering reactions of the ore and gangue minerals. The geochemistry characteristics of the mine waste dump sediments, soils, surface and drainage water influence the natural installation of the plant species. The chemical analysis of the dump sediments, soils, water and plants from the dump-field show that they are contaminated by heavy metals: Fe, Cu, As, Sb, Cd and others.

The plants adapted to the specific conditions of the different zones of the studied area show different level of the contamination in individual tissues (roots, twigs/stems, leafs/needles or in flowers/fruits). The article presents also results of the plant tissue degradation study in heavy metal contaminated conditions and compare them with those from reference sites.

The contents of the heavy metals in plant tissues decrease in the following rank: Fe, Zn, Pb a Cu. In most cases the highest contents of metals were described in roots, than in leaves and stems and less in flowers, semens and fruits. The plant tissues at the dump sites are considerably damaged. Growth of the annual rings are extraordinary tight. Anomalous coarsening of the cell walls, presence of the calluses and of resin canals, as well as of numerous hyfes in vessels indicate the defensive plant-reactions.

It was determined that at the Podlipa locality the concentrations of heavy metals decrease in plant tissues in the following order: Fe, Zn, Pb and Cu. The comparison of contamination of individual plant tissues showed that the highest concentrations of heavy metals have roots then leaves and stems. Flowers, seeds and fruits have the lowest concentrations of heavy metals. Plant tissues are considerably damaged at the dump-field and increments of year shoots are extremely narrow. Anomalous cell-wall exfoliation and coarsening, occurrence of calluses, resin canals and numerous hyphaes in vessels suggest defense mechanism of plants which are exposed to the stress factors at the dump-field such as contamination by heavy metals, soil and moisture deficiency, movement of incohesive material down to slope.

4. THE TOTAL ACID POTENTIAL OF THE DUMP-FIELD AND THE POSSIBILITY OF REMEDIATION

If distilled water is used in the measurment of paste or rinse pH of sediments or soils, its pH is usually around 5.3. The pH values less than 5.0 indicates that the Sample contain net acidity at the time of analyse (Sobek 1978). Values of paste pH between 5.0 and 10.0 can be considered near neutral at the time of the analysis. From viewpoint of this study only two samples (A-3 and A-12) account acid values (Tab. 2). It is interesting that one of this samples is the sample from treference area. The reason of such a behaviour is the lack of the carbonates (Tab. 2).

Table 2. Paste and rinze pH (H_2O and 1M KCl), sulphur and carbon contents in samples of technogenous sediments and soils

Sample	H_2O		1M KCl		%							
	pH	Eh	pH	Eh	$S_{tot.}$	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.

Table 3. Total acid potential of the sediment and soil samples

Sample	TAP ($kg.t^{-1}$)
A-1	7.813
A-2	0.625
A-3	3.125
A-4	10.313
A-5	1.563
A-6	13.125
A-7	0.938
A-8	0.313
A-9	0.938
A-10	1.250
A-11	3.438
A-12	0.625

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 total acid potential (TAP) was calculated according to Morin and Hutt (1997):

$$TAP = (\%\ S_{tot.}) \times 31.25,$$

where TAP is provided in any of three equivalent units: kg $CaCO_3$, equivalent/metric tone (t) of sample, t $CaCO_3$ equivalent/1000 t of sample, or parts per thousand (ppt) $CaCO_3$ equivalent.

The TAP values from the dump-field Podlipa vary in range from 0.625 in samples A-12 (reference area) and A-2 to 13.125 in sample A-6 (Tab. 3).

If we compare the highest TAP value for sample A-6 with the data about the sulphur kontent, we can demonstrate, that both the highest sulphide and sulphate sulphur content were described from this sample, which represents the sedimentary material from Empfängnis adit. The highest TAP value is also the consequence of the relatively low carbon content.

5. CONCLUSIONS

The results for the irregular contamination of sediments by selected heavy metals are shown at figure 2 - 4.

The surface water (and drainage water) as well as the groundwater water are substantially contamined predominantly by Cu, Fe and As. Both the As content and its speciation don't pose acute risk (the highest arsenic content is only 0.6 ppm and it is present only in the form of moderately toxic inorganic As^{5+}). The only risk poses the spring of the mineral water Linhart because of the high radioactivity and high Fe, Cu, Cd and Pb contents. For this reason was the spring closed and it is not used for drinking.

The concentrations of the heavy metals in plant tissues decrease seriately in rate: Fe, Zn, Pb and Cu. Comparison of individual types of plant tissues show that the highest concentrations of heavy metals are in roots, than in leafs and stems and the lowest concentrations are in flowers, seeds and in fruits. The plant tissues from the dump-field are heavily damaged and the growth of the current year shoots are extraordinary tight. The results of the research document the plant defense reactions under the influence of stress factors at the dump sites (absence of soil and water, the heavy metal contamination, mobility of the cohesionless slope material).

The ability of the drainage water precipitate cementation copper (as well as Sb and probably also other heavy metals as As) on the iron surface give possibility to realize Fe-barrier for elimination of heavy metals from the drainage water and contribute to the remediation of the mining country.

The Ľubietová – Podlipa dump-field dispose by certain degree of „self-cleaning ability.“ Great part of the heavy metals and contaminants is fixed in porous material, Fe-hydooxides and in clay minerals, which show still an important free sorption capacity. The possible developing of the dumps in the case of the remediation activities could relieve and mobilize the fixed heavy metals and contaminants to the landscape. From this reason we not advise to interfere with the dump material.

6. ACKNOWLEDGEMENTS

This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-51-015605, APVV-LPP-0362-06 and to Dr. Bronislava Lalínska for analytical works.

REFERENCES

Andráš, P., Mamoňová, M., Ladomerský, J., Turisová, I., Lichý, A. & Rusková, J., 2007, *Influence of the dump sites on development of selected plant tissues at the Ľubietová area (Slovakia)"* Acta Facultatis Ecologiae,16, 1, 147-158.

Bartzas, G., Komnitsas, K. & Paspaliaris, I., 2006, *Laboratory evaluation of* Fe^0 *barriers to treat acidic leachates,* Minerals Engineering, 19, 5, 505-514.

Ilavský, J., Vozárová, A.& Vozár, J., 1994, *Ľubietová – štruktúrno-vyhľadávacie vrty Lu-1, L-2 a Lu-3*." Geologický ústav Dionýza Štúra, Bratislava, 77 p.

Koděra, M. et al., 1990, *Topografická mineralógia 2.* Bratislava, Veda, vydavateľstvo SAV, 518 p.

Kozáč, J., 1996, *Nerastné suroviny ako sorbenty katiónov ťažkých a toxických kovov a základná zložka čistiacich prostriedkov*. Mineralia Slovaca, Geovestník, 28, 6, 5-7.

Morin, K. A. & Hutt, N. M., 1997, *Environmental geochemistry of minesite drainage: Practical Tudory and case studies.* MDAG Publishing, Vancouver, 246 p.

Bergfest, A., 1951, *Baníctvo v Ľubietovej na medenú rudu.* Banská Štiavnica, Ústredný banský archív pre Slovensko, 89 p.

Sobek, A. A., Schuller, W. A., Freeman, J. R., & Smith, R. M., 1978**,** *Field and laboratory methods applicable to overburden and minesoils,* EPA 600/2-78-054, 203p.

Received at 21. 08. 2008
Revised: 09. 10. 2008
Accepted for publication 15. 10. 2008