

Toxicity of arsenic and antimony in the area of Cu-Ag deposit Ľubietová

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Abstract

In the surroundings of the Ľubietová deposit the As and Sb contamination of the landscape components, i.e. sediments (both technogenous sediments and soils) and as well groundwater and surface water was described. As(V) and Sb(V) species are predominant species in the sediments while in the water As(III) and Sb(III) are dominant. The utilization of Eh-pH stability diagrams is complemented by the classic determination of As and Sb species by means of HG AAS method.

The presence of very toxic As(III) and Sb(III) species encourages the increased aspect during the estimation of the environmental risk within the studied area.

Key words: arsenic, antimony, speciation, toxicity, technogenous sediments, groundwater, surface water

Introduction

The decrease of pH and changes of oxidation–reduction potential (Eh) in sediments of the dump fields at the Ľubietová Cu-Ag deposit induces the release of toxic metal elements (mainly Cu, Fe, Cd, As, Sb, Pb, Zn, Mn, Ni, Co) from the solid phase where they are presented in the form of the less soluble minerals or in sorption complex into the groundwater and surface water. Concerning the environmental risk, toxic metals As and Sb represent the highest risk at the studied locality (according to Andráš et al., 2008).

Arsenic belongs among nerve poisons with cumulative character (Pitter, 1990). Elementary As⁰ is insoluble in the water and is not considered as toxic. In a matter of fact, after its consummation its transition to various toxic compounds occurs. Arsenic begins to be toxic (arsenious oxide – As₂O₃) in the dose above 10 mg (1 to 2 mg per 1 kg of weight). Average fatal dose is 180 mg for grown-up man. Generally, 99 % of As is imported into the human organism by the water and food consummation. The as compounds have mutagenic, cancerous and teratogenic effects. Arsenic penetrates through the placenta into the breast milk. It binds on erythrocytes, deposits in the liver, kidney, skin, hair, nails, and cerebrum. It acts as capillary and cytostatic poison (Kafka and Punčochářová, 2002). It inhibits or blocks SH-group in enzymes by biochemical effect on human organism. It causes change of their effects, disconnects oxidation phosphorylations running in mitochondria whereby causing the destruction of respiration

function of tissues. Arsenic replaces very often phosphorus and inhibits corresponding enzymes. It has an impact on capillary epithelium, causes destruction of blood vessels and increases their fragility. It accumulates in liver, bones, nails and hairs where it is mainly bound to S-S bridging of keratin (Benbrahim-Talla and Waalkes, 2008).

As toxicity increases in the order: organic compounds As(V) – arsenate, inorganic compounds containing As(V), organic compounds As(III) – arsenate, inorganic compounds As(III) – arsan. As(III) compounds are about 5 or 10 times more toxic than As(V) compounds (Lin and Puls, 2000) but As(V) has stronger cancerous effects. As(III) and As(V) can create methyl compounds (mono – di – trimethylarsenic) whereby causing the transition to less toxic forms (Matschullat, 2000). Majority of mammals methyl inorganic arsenic to dimethylarsenic acid. This substance is causing organ-specified toxicity and is promoting the formation of tumors in many organs (Benbrahim-Talla and Waalkes, 2008).

Acute poisoning by As is evident as gastro-intestinal disease accompanied by vomiting and diarrhea. As(III) inorganic compounds cause cancer of prostate, skin, blood vessels and kidney (Benbrahim-Talla and Waalkes, 2008). Chronic poisoning causes neurological difficulties, faint paralysis of hands and legs whereas gastro-intestinal symptoms are weaker. There can be observed formation of stains on the skin, decrease of potency, salivation, weight loss, central damage of visual and acoustic analyzer, painful peripheral polyneuritis, anemia, damage of bone

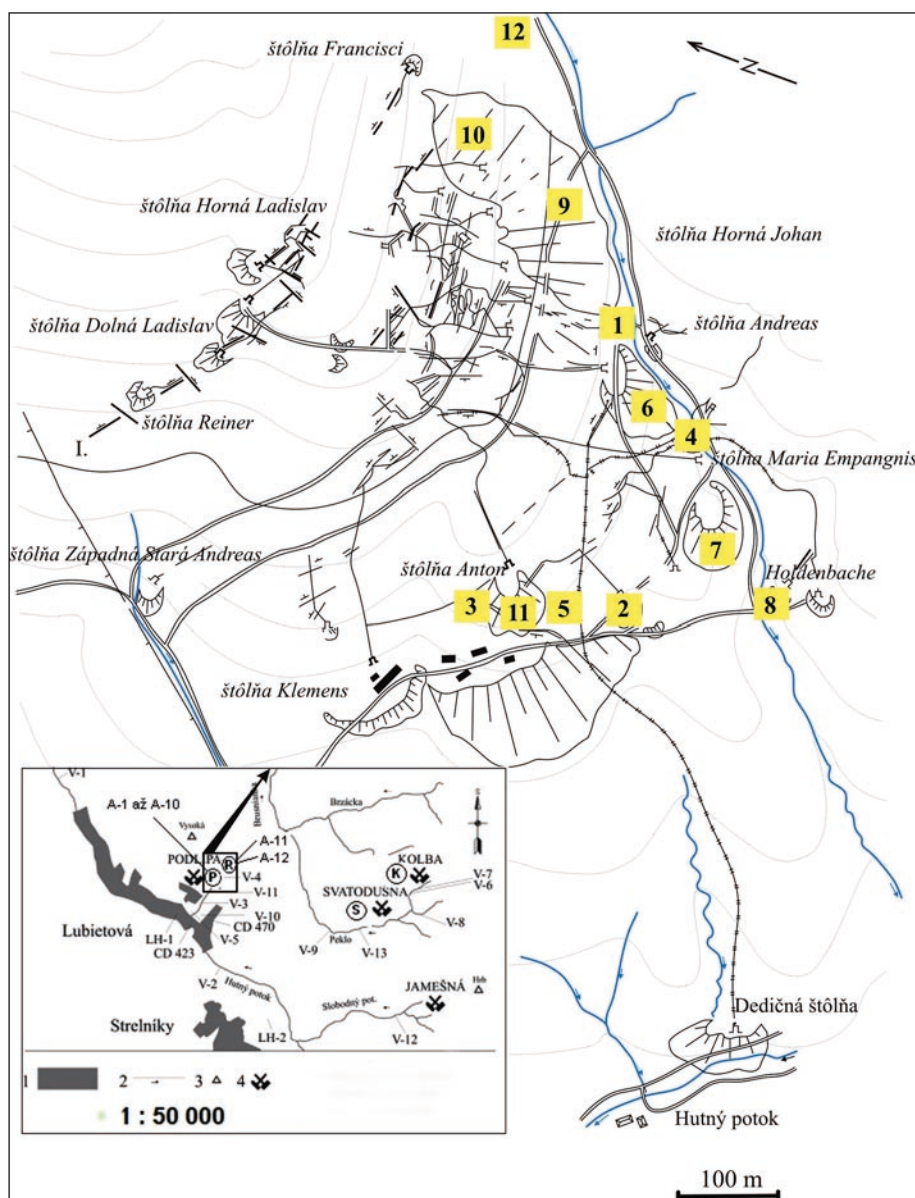


Fig. 1. Localization of the sampling points. a – samples of technogenous sediments; b – water samples.

marrow and spleen and neurological and hematological changes (Melicherčík and Melicherčíková, 1997). The most serious chronic effect is cancer of skin and lungs. Poisoning by As can be identified by horny skin with characteristic glaucous chromatosis, white stripes on nails and garlic-smelling breath (Kafka and Punčochářová, 2002).

In the fields treated by pesticides, arsenic is built into the soil and causes drop in productivity of arable crops and damage of trees (Kafka and Punčochářová, 2002).

The main source of As at the locality of Lubietová is tetrahedrite, less important and more rare is arsenopyrite. During weathering, arsenic ore minerals are easily oxidized and As is transformed from forms with lower oxidation number to As(V) creating compounds of arsenic acid (Lin and Puls, 2000). It is soluble in the water but rarely can migrate to greater distances due to the fast reaction with metal cations and As and is bounded in the form of various arsenates.

Antimony compounds are less toxic than arsenic compounds. It is similar to arsenic with its impacts but poisoning by antimony is easier due to slower adsorption of its compounds. Soluble compounds in digestive tract hydrolyze, insoluble are less toxic. The most toxic compound of Sb is antimony potassium tartrate which is equally toxic as arsenious oxide and has similar disease effects.

Antimony causes temporary state reminding heart-attack. It inhibits some enzymes, influences metabolism of proteins and sugars, prevents the formation of glycogen in liver, and raises hypoglycemic states (Cejpek, 2000). Acute poisoning is evident as irritation of digestive tract, capillary dilatation, bloody diarrhea, persistent vomiting causing dehydration. There is observed the blood pressure drop causing collapse. There can be also observed bronchial spasma and persistent cough. Blood sugar level is decreasing and acute poisoning can be followed by symptoms of the liver damage.

During the long-term exposition the formation of stains on the skin on uncovered parts of the body can be observed as well as the degenerative changes on nails, formation of abscesses on nose septum, early loss teeth, chronic bagassosis, dyspepsia, vertigo, weight loss, cardiac-vessel diseases, failure of menstruation cycle and a retardation of the children's growth up to 1 year. Sb can enter into the human organism by inhalation or by direct skin contact. Toxic dose is 150 mg (Marhold, 1980).

Elementary Sb is more toxic than its salts. Sb(III) compounds are 10 times more toxic than Sb(V) compounds (Smichowskia, 2008) and methyl forms of Sb are less toxic than its inorganic salts. Sb(III) is markedly carcinogenic. Antimony in waters is usually presented as Sb(III), Sb(V), $\text{CH}_3\text{SbO}(\text{OH})_2$ and $(\text{CH}_3)_2\text{Sb}(\text{OH})$.

Antimony is presented in nature mainly in the form of sulphides or oxides of Sb(III) and Sb(V), most frequently as antimonious oxide Sb_2O_3 , antimonite sulphide Sb_2S_3 and antimony chloride SbCl_3 (Bencko et al., 1995). Oxidation mechanism of Sb(III) to Sb(V) is controlled by pH. This process is slower than by oxidation of many other metals (for instance Mn, Fe, etc.). Sb(III) can be stabilized by the formation of complex compounds (Leus and Johnson, 2005). It can bind very strongly on particles containing Fe, Mn or Al in the soils. From soils it gets into the food web (Smichowskia, 2008).

Knowledge on various levels of toxic effects and on quality of different impacts of individual compounds of toxic metals on living organisms led to the efforts to specify the forms of toxic metals. From the point of environment, As and Sb present serious danger due to highly toxic character of their compounds.

Methodology

For characterization of contamination of the landscape components there were collected samples of technogenous sediments (dump material, Fig. 1) and samples of the groundwater and surface water (water from wells, mine water and mineral water from the Linhart Spring). Reference site A-12 (Fig. 1) is situated outside of geochemical anomalies of heavy metals to represent similar rock environment (Permian greywacke) as on dump field. It enables the comparison with territories polluted with toxic metals due to the mine activities.

pH of sediments was determined in the water and 1 M KCL leachate according to guidelines described by Lintnerová and Majerčík (2005). Samples of the groundwater and surface water were collected 3 times: in December (drought period), on 31 March 2008 (rain period) and on 27 May 2008 (drought period).

Samples of technogenous sediments were analyzed in the ACME Analytical Laboratories in Vancouver (Canada) by the ICP/MS analysis. Fe content was in the water samples determined by AAS and As and Sb contents by means of hydride method (HG AAS) at the Water Research Institute in Bratislava. Determination of As speciation in the water was realized by the connection of hydride generator Labtech HG-2 and electrothermic automizer Perkin-

-Elmer HGA-500 with the aim to overconcentrate arsenic volatile compounds on modified surface of graphite cuvette (analysed by Ing. Adriana Shearman, CSc.).

Results

As and Sb distribution in the landscape components in the surroundings of the Ľubietová deposit

Distribution of toxic metals on the dump field is unequal and reflects their primary concentration in individual parts of dump field and geochemical relations of which migration capabilities are very important (Andraš et al., 2009).

Maximum concentrations of theoretical extractable As (7 – 289 ppm) and Sb (7.1 – 61.6 ppm) can be considered as relatively high (Tab. 1).

It is possible to divide samples of the groundwater (Tab. 2) into 2 classes: a) crude waters, b) drinking waters. It is possible to assign samples T-1, LH-8 and LH-9 to crude waters and water samples from the wells of the houses No. 423 and No. 470 (under the dump field Podlipa) to drinking waters where as well sample LH-1 of the mineral water from the Linhart Spring belongs. First group of samples was compared with the Regulation of the Ministry of Environment of the Slovak Republic No. 636/2004 Coll. – The public water-supply systems – where individual categories of standard methods of crude water treatment to drinking water are established. Second group of samples was compared with the Resolution of the Government of the Slovak Republic No. 354/2006 Coll., establishing requirements on water intended for human consumption (drinking water) and on monitoring of drinking water.

Crude water: Except As content in the samples LH-8 and LH-9 (limit value established by the Regulation No. 636/2004 Coll. is $< 0.05 \text{ mg} \cdot \text{l}^{-1}$) all samples were in accordance with requirements of the Regulation No. 636/2004 Coll.

Drinking water: Water samples from the wells of the houses No. 423 and No. 470 did not exceed limit values for indicators of heavy metals established by the Resolution

Tab. 1
pH and Eh values, Fe, As and Sb content in technogenous sediments from the Reiner and Podlipa dump fields

Sample	H ₂ O		1M KCl		%	mg · kg ⁻¹ (ppm)		
	pH	Eh (mV)	pH	Eh (mV)	Fe	As	Sb	
A-1	5.14	77	4.61	109	1.31	162	62	
A-2	5.89	34	5.40	63	1.42	10	7	
A-3	4.87	94	4.21	131	1.94	71	22	
A-4	5.46	59	5.33	66	2.64	169	59	
A-5	5.77	42	5.37	64	1.71	60	17	
A-6	5.17	74	5.06	83	2.06	134	49	
A-7	7.93	-84	7.34	-58	1.32	16	12	
A-8	5.42	36	5.22	42	0.91	61	18	
A-9	5.03	83	5.01	85	1.84	130	28	
A-10	5.25	71	5.14	78	1.12	32	17	
A-11	6.11	22	5.95	30	2.37	206	36	
A-12	4.21	133	3.47	173	1.38	7	10	

Tab. 2
ICP-MS analyses of groundwater

Sample	pH	Eh (mV)	$\mu\text{g} \cdot \text{l}^{-1}$		
			Fe	As	Sb
T-1	6.55	-4	11	< 1	< 1
T-1c	6.63	-10	17	< 1	< 1
LH-8	6.40	+1	200	58	< 1
LH-9	6.95	-27	120	61	< 1
ČD 423	6.72	-14	366	< 1	< 1
ČD 423c	6.71	-14	210	< 1	< 1
ČD 470	6.85	-21	146	5	1.42
ČD 470c	6.84	-20	120	1.52	1.21
LH-1a	6.40	+4	380		< 1
LH-1	6.51	-3	381		< 1
LH-1b	6.48	-2	2 260	2.52	< 1

Explanatory notes to tables 2 and 3:

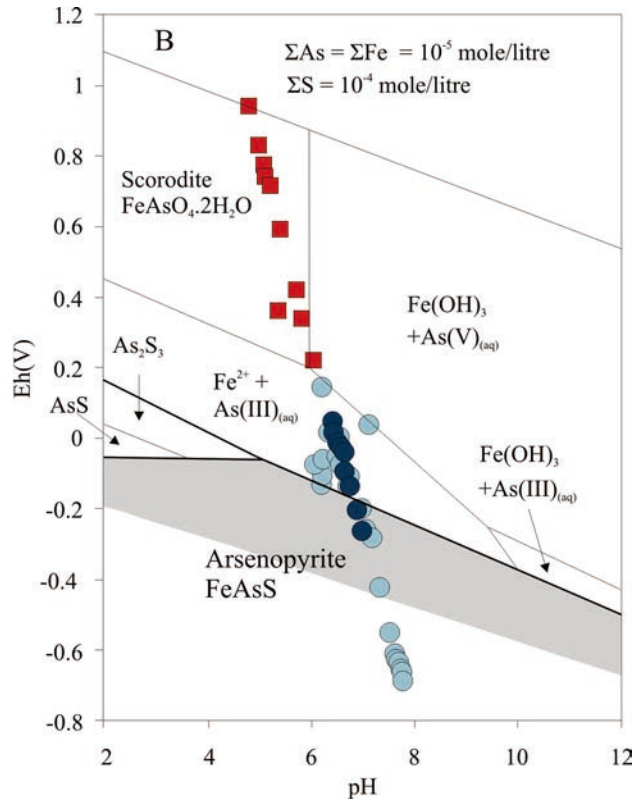
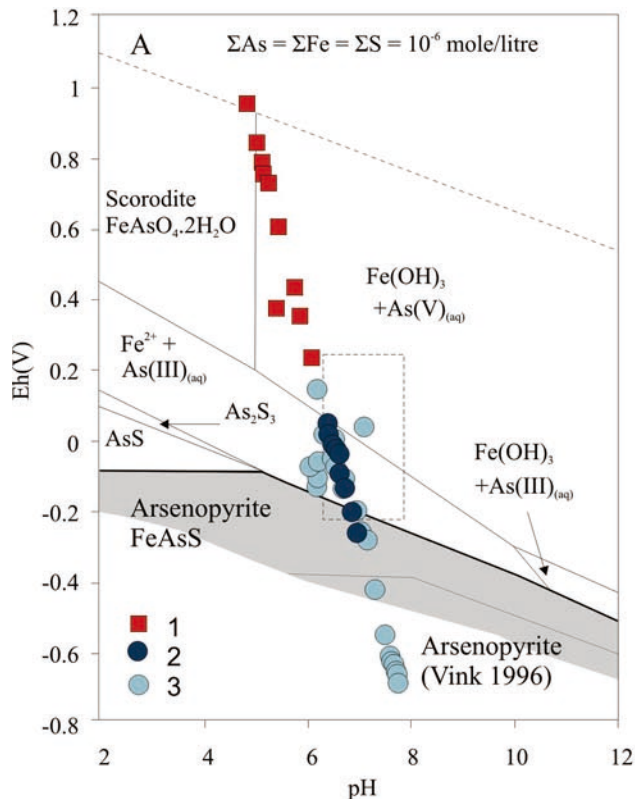
Sampling: a) December 2007, b) March 31, 2008, c) May 27, 2008

No. 354/2006 Coll., only water sample from the well of the house No. 470 exceeded limit values for Zn ($3 \text{ mg} \cdot \text{l}^{-1}$) and has high content of Cu ($41.1 \text{ mg} \cdot \text{l}^{-1}$, limit value is $30 \text{ mg} \cdot \text{l}^{-1}$). The most polluted was the water sample from the mineral spring Linhart. It exceeded limit values for Mn ($55 \mu\text{g} \cdot \text{l}^{-1}$, limit value is $0.05 \text{ mg} \cdot \text{l}^{-1}$) and Cd ($6 \mu\text{g} \cdot \text{l}^{-1}$, limit value is $0.003 \text{ mg} \cdot \text{l}^{-1}$).

Surface water (including drainage water) had generally moderately acid character at the Podlipa Locality (pH 6.1

Tab. 3
ICP-MS analyses of surface water

Sample	pH	Eh (mV)	$\mu\text{g} \cdot \text{l}^{-1}$		
			Fe	Sb	As
V-1a	7.7	-69	390	2.10	7.05
V-1c	7.7	-66	215	< 1.00	< 1.00
V-2a	7.6	-62	270	2.00	6.02
V-3a	6.7	-12	86	1.12	< 1.00
V-3b	6.2	14	101	1.88	3.41
V-3c	6.5	0	45	2.35	1.14
V-4a	6.5	-6	26	0.74	< 1.0
V-4b	7.5	-58	73	< 1.00	< 1.0
V-4c	6.54	-8	94	1.03	< 1.0
V-5*	6.2	-7	160	2.00	1.08
V-5a	6.2	-11	170	1.66	2.79
V5b	6.1	-8	210	2.21	3.21
V-6a	6.4	1	200	3.38	58.5
V-6d	7.1	3	57	3.25	37.9
V-7a	7.0	-27	120	3.44	61.5
V-7b	7.1	-29	8	4.38	38.5
V-8a	7.7	-66	540	1.13	5.03
V-8b	7.3	-43	466	1.20	38.5
V-9a	7.6	-64	260	5.10	52.0
V-9a	7.7	-67	250	4.98	48.4
V-10a	6.7	-14	263	1.72	< 1.0
V-10b	6.2	14	274	1.57	1.21
V-11b	6.7	-14	584	< 1.00	1.69
V-11c	6.9	-21			
V-12a	7.6	-63	140	1.10	5.0
V-13a	7.6	-64	260	5.10	49.0



Figs. 2 – 3. Eh-pH stability diagrams of the As-Fe-O-S system. A – Vink (1996); B – Pokrovski et al. (1996, 2000).

to 7.5) whereas water from the areas Kolba and Svätodušná had neutral or moderately alkalic character with pH values within the range of 7.0 (only in one case 6.4) to 7.7 (Tab. 3). Water pH was not influenced by the seasonal changer (summer vs. winter) at any from the studied localities.

With utilization of comparison of the concentration values of toxic metals in the surface water from the studied localities with the recommended limit values pursuant to the Resolution of the Government of the Slovak Republic No. 296/2005 Coll. it is possible to state that recommended limit values were exceeded in the case of Cu (recommended limit value is $20 \mu\text{g} \cdot \text{l}^{-1}$) and As (recommended limit value is $30 \mu\text{g} \cdot \text{l}^{-1}$). Concentrations of individual studied metals were in the drought period generally about 3 times higher than in the rain period (Tabs. 2 and 3).

As and Sb speciation

Application of results of thermodynamic studies of various authors enabled to determine Fe, As and Sb speciation in the samples.

The Eh-pH stability diagrams of the As-Fe-O-S system (Figs. 2 and 3) displaying stability fields of arsenic calculated according to thermodynamic data published by Vink (1996) and Pokrovski et al. (1996, 2000) were adjusted by Lalínska (2009). Arsenic data of analysed samples of the technogenous sediments from Ľubietová falling within these diagrams mainly into the stability fields of complexes $\text{Fe}(\text{OH})_3$ and $\text{As}(\text{V})_{(\text{aq})}$ or to mineral scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Probably, most of As occurs in solution in the less toxic oxidation level as $\text{As}(\text{V})$.

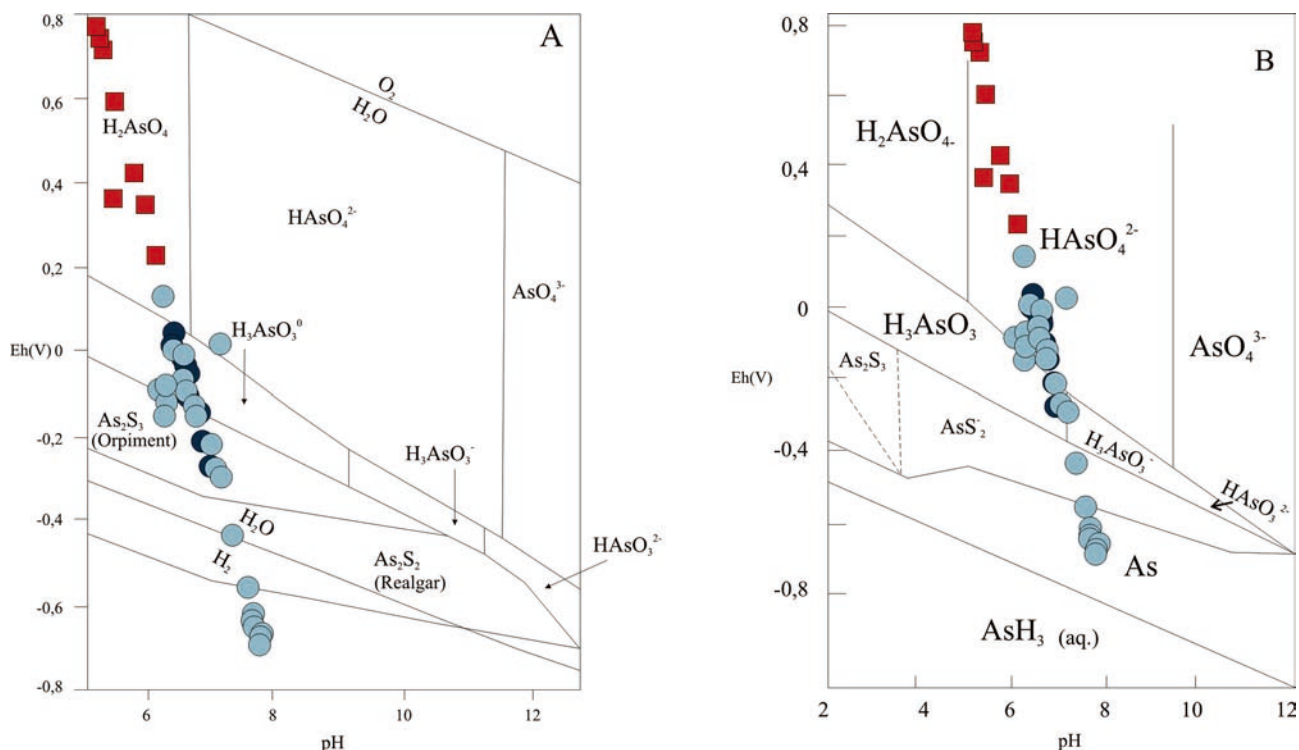
Similarly as in the previous paragraph, Eh-pH stability diagrams of the As- H_2O -S system (Figs. 4 and 5) published by Ryu et al. (2002) and Ferguson and Gavis (1972) point at As occurrence in the oxidation level (V) in the technogeneous sediments of the dump field and soil. Most of As occurs mobile in the solution in the form of complex H_2AsO_4^- .

The study of As speciation in the groundwater with utilization of Eh-pH stability diagrams points out that within the stability diagrams by Vink (1996) and Pokrovski et al. (1996, 2000) most of samples fall within the stability fields of $\text{As}(\text{III})$ (Figs. 2 and 3). According to stability diagrams of Ryu et al. (2002) and Ferguson and Gavis (1972) As occurs in the form of complex H_3AsO_3 (Figs. 4 and 5) or in the form of mineral orpiment As_2S_3 (Fig. 4) and complex HASO_4^{2-} (Fig. 5).

Arsenic in the surface water is presented as $\text{As}(\text{III})_{(\text{aq})}$ (Figs. 2 – 5), in the form of finely dispersed arsenopyrite (FeAsS ; Figs. 2 and 3) or in the form of H_3AsO_3 , As_2S_3 , HASO_4^{2-} , AsS^{2-} or in the elementary form (Figs. 4 and 5).

Antimony is according to Vink (1996) in the supergene oxidation conditions mobile and behaves as arsenic. Eh-pH stability diagram by Brookins (1988) and Vink (1996) enables to specify Sb speciation (Fig. 6). Samples of technogenous sediments from Ľubietová are falling within the stability field of complex SbO_3^- . Similar Sb form in the water with nearly neutral pH was described as well by Ashley et al. (2003).

In the groundwater antimony occurs mainly in the form of oxides Sb_4O_6 . In one sample antimony occurs in the elementary form and in the other sample occurs on the



Figs. 4 – 5. Eh-pH stability diagrams of the As- H_2O -S system. A – Ryu et al. (2002); B – Ferguson and Gavis (1972).

is the best sorbent of As(V) from clay minerals presented in the dump field Lubietová-Podlipa. Less toxic As(V) sorbs on clay minerals more easier and quantitative than more toxic As(III). During this process As(III) is oxidized on As(V) (Lin and Puls, 2000). Low oxidation–reduction potential causes arsenic precipitation and therefore clay shale with content of organic matter or sulphides are richer in arsenic.

The greatest portion of As(III) was determined in the samples of the groundwater and the surface water with high negative values of Eh. Sb speciation was not verified by the hydride method HG AAS. Sb(III) and Sb(V) exist in natural conditions in soluble forms: Sb(V) as $\text{Sb}(\text{OH})_6^-$ and Sb(III) in the form of $\text{Sb}(\text{OH})_3$ (Filella et al., 2002). Hydrogoethite and Fe oxyhydroxides are important sorbents of Sb. Sb(III) and Sb(V) create on the surface of hydrogoethite and Fe oxyhydroxides complex compounds. Sb(III) can best sorb under pH 3 – 12 while maximum sorption of Sb(V) occurs under pH < 7. On the surface of hydrogoethite and Fe oxyhydroxides can occur during several days Sb(III) oxidation mainly under pH 3 – 5.9. Under pH ~ 9 its mobilization and release into the solution occurs while under pH < 7 it remains bounded on the surface of Fe oxides (Leus et al., 2006).

As Sb sorbs relative well on the surface of Fe oxides and oxyhydroxides it is possible to assume that part of Sb occurs in the water solution in the form of Sb_4O_6 and SbO_3^- particles < 0.4 μm (Lalínska, 2009). It is suggested from relatively high level of Fe : Sb correlation (Tabs. 1 – 3).

Andráš et al. (2008) found out that cementation process known at the Špania Dolina deposit occurs as well as at the Lubietová deposit. It would be possible to use this process for construction of the Fe^0 – barrier to remove heavy metals (mostly Cu, As, Sb and Cd) from the drainage water.

Conclusions

Technogenous sediments and water at the locality of Lubietová are contaminated by arsenic and antimony. In the sediments (and soils) there is predominant arsenic in the less toxic oxidation level as As(V) and occurs in the form of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ or in the forms of H_2AsO_4 and HAsO_4^{2-} . The study of antimony speciation pointed out at the occurrence of SbO_3^- species corresponding to minerals senarmontite and triphuyite.

In the groundwater there is predominant As(III) in various forms as H_3AsO_3^0 , HAsO_4^{2-} and As_2S_3 . Antimony is predominant as Sb_4O_6 which is identical with the valentinite. In the surface water As was determined in both oxidation levels as As(III) and As (V). There are predominant forms of H_3AsO_3^0 and As_2S_2 .

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