Testing of the Permeable Fe0-Barrier at Dump-Field Podlipa (Ľubietová Cu-Deposit, Slovakia)

Jiří KUPKA1), Peter ANDRÁŠ2), Jana DADOVÁ3), Peter ANDRÁŠ Jr.4), Dávid DEMETER5)

1) Ing., Ph.D.; VSB-Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, 708 33 Ostrava-Poruba, Czech Republic; email:jiri.kupka@vsb.cz, peter.andras@vsb.cz
2) RNDr., CSc.; VSB-Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, 708 33 Ostrava-Poruba, Czech Republic; email: peter.andras@vsb.cz, peter.andras@umb.sk
3) Ph.D.; VSB-Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, 708 33 Ostrava-Poruba, Czech Republic
4) Ing.; VSB-Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, 708 33 Ostrava-Poruba, Czech Republic
5) Matej Bel University, Bánská Bystrica, Faculty of Natural Sciences , Tajovského 40, 974 01 Banská Bystrica, Slovak Republic

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Abstract

The Podlipa dump-field material at Ľubietová abandoned Cu-deposit show high Cu, Fe, Cd, Co, Mn, Ni and Pb contents. In most cases higher metal contents were described in winter dry period as in the rainy periods. The oposite situation was very rare. The depression under the Empfängnis dump is saturated by several outflows of drainage water percolating through the dump material. For the most part it is a case of surface water of a mountain stream draining the area along the valley. In the area under the Podlipa dump field, the brook several times percolate the dump sediments. In the points of outflow of drainage water from the dumps on the surface, secondary minerals of copper (pseudomalachite?) deposit preferentially on dead plant residues. Moreover, on the bottom of the pool in the depression under the dump of Empfängnis gallery, a continuous green coat of Cu carbonates can be seen. The bottom sediment contains up to 2.15 wt.% of Fe, 15 402 ppm of Cu, 134 ppm of Pb and 220 ppm of As. The results show a significant contamination of water as a consequence of percolation through the dump sediments - above all contamination with Cu, Ni, Pb and Sb, and an increase in the contents of majority of the heavy metals in the dry season. Fe^0-barrier seems to be relatively efficient for Fe and As removal and vice versa removal of Zn and S is limited. Cd, Pb and P contents are very low so the results are not unambiguous. The relation between pH/Eh ratio and of the efficiency of Fe^0-barrier could not be with respect to the low values proved.

Keywords: dumpf-fields, heavy metals, contaminated water, Fe0-barrier, remediation

Intruduction

The Ľubietová deposit was exploited since the time of the Bronze Age and in the 16th and 17th centuries it was one of the most important and most extensively exploited Cu-mines of Europe. The Cu-ore was in the 18. century exported to more than 50 countries (Koděra et al., 1990).

The Cu mineralisation with Ag admixture is developed within 4–5 km long and 1.5 km wide range of N-S direction. There are three main ore-fields in the Ľubietová surrounding: Podlipa, Svätodušná and Kolba with admixture of Co/Ni-mineralisation. The Cu content in the ore ranged from 4–10% and the Ag content was about 70 $g.t^{-1}$ (Koděra et al., 1990). 25 thousand tons of Cu were exploited during last five centuries.

The main dump-field Podlipa represents about 2 km^2 area and was exploited by 18 adits (fig. 1).

The ore mineralisation is situated in the Ľubietová terrigene crystalline complex of Permian age which consists of greywackes, arcose schists and conglomerates. The main tectonic structures are of NE-SW direction, the main ore veins strike approximately E-W and N-S. Ore veins are 30–40 m thick. In the southern part of the ore-field was described also disseminated mineralisation.

The probably volcano-sedimentary mineralisation, genetically connected with the basic, intermediate and acid Permian volcanism, was mobilised by Hrončok granite intrusion during the Alpine (upper Cretaceous) orogene (Ebner et al., 2004). The vein mineralisation is characterised by a rather simple paragenesis which is represented by quartz, siderite, (± calcite and ankerite), chalcopyrite, Ag-bearing tetrahedrite, arsenopyrite, pyrite, barite and rare galena. In the well developed cementation zone the main Cu-minerals were cuprite and native copper. The deposit is famous also because of formation of wide range of rare secondary minerals as libethenite, langite, annabergite, aurichalcite, azurite, brochantite, cyanotrichite, erithrine, evansite, euchroite, farmacosiderite, hemimorphite, chrysocol, cuprite, limonite, malachite, olivenite, tirolite, pseudomalachite, copper etc. (Koděra et al. 1990).

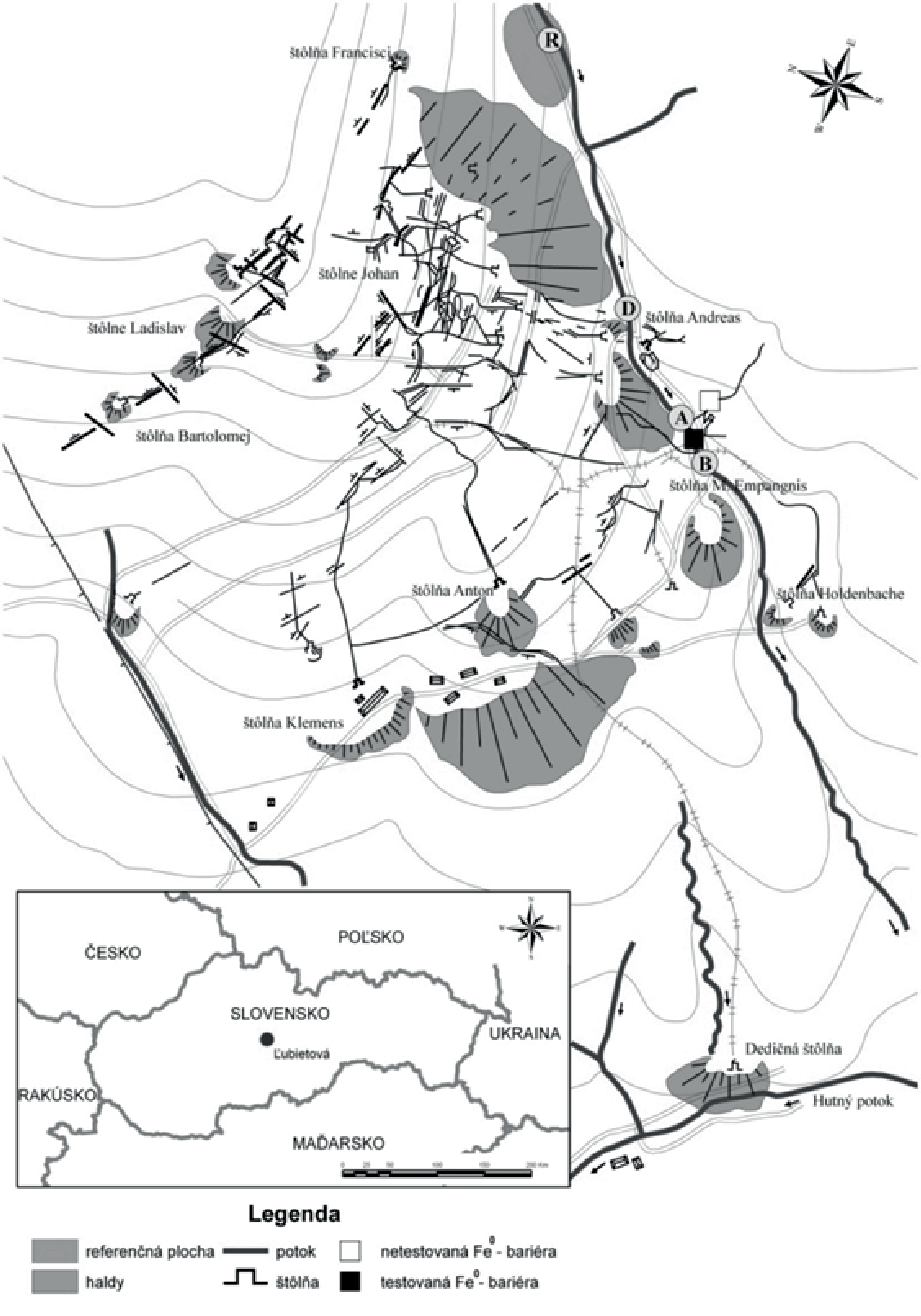

Fig. 1. Map of the Podlipa dump-field and localization of the Fe^0-barrier as well as of the water sampling points A-D; the water sample H-1 was obtained from the brook in the reference area (R) and the H-2 sample from the bottom of the dump of the Maria Empfängnis gallery

Rys. 1. Mapa osadnika Podlipa i lokalizacja bariery Fe^0 oraz miejsca pobierania próbek A–D, próbka wody H-1 pobrana z potoku w obszarze pomiędzy obszarem bazowym (R) a próbką H-2 od dna zrzutu Maria Empfangnis

From the 15th to the 17th century, copper from Slovak deposits became a sought article on the world market. It created the basis for minting at Kremnica and was imported to 52 countries; not only to the whole of Europe but also to North and South America, India and China. By the end of the 15th century, mostly crude copper was produced and merely copper rich ores containing silver were treated.

At the deposits of Smolník and Špania Dolina, copper was also obtained from copper-bearing – cementation water for centuries. As for the area of Smolník, records on the use of cementation already at the end of the 13th century have been preserved. Copper was precipitated from water by means of metallic iron (Magula & Čiško, 1993; Sombathy, 2005). Somewhat later, in the year 1605, copper was discovered and recovered from cementation water at Špania Dolina too (Vozár, 2000; Sombathy, 2005). Also at present, dendritic aggregates of native copper, precipitating from ascending solutions in the vicinity of iron objects on rock fissures can be found in the Ivan gallery. By the alteration of sulphides (chalcopyrite and tetrahedrite), sulphates (mainly copper sulphate solution - $CuSO_4.5H_2O$) were formed according to an equation given below:

$$CuFeS_2 + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + CuSO_4 + FeS_2$$

During two to three weeks, copper sludge - cementation copper was formed on iron (scrap iron). Because cementation was more efficient in the open air, water was taken to the surface and began to be retained in shallow ponds and pools, into which iron was placed (later, in the 19th century, concrete cementation ponds were built in the vicinity of the František shaft). The eliminated copper replaced iron in the form of brown pulp, washed away each week from it to keep intensive contact with the non-corroded metal. The sludge was collected, dried in the open air and once a year transported in bags to the Staré Hory and Banská Bystrica smelting plants where so-called "royal copper" was smelted from it (Žuffa-Ellek, 2003).

In the years 1736–1745, in the locality of Špania Dolina 21 quintals of cementation copper were produced annually. For the longest time, till the year 1963, cementation copper was obtained at Piesky. At present, malachite precipitates from water here (Hrmo & Longauer, 1989; Paulínyová & Žuffa-Ellek, 2002; Andráš et al., 2009; Lichý et al., 2010).

Already in the distant past, numerous specialists were interested in the process of cementation at Špania Dolina, namely Georgius Agricola, German mineralogist, Isaac Newton, great physicist, Theophrastus Bombastus von Hohenheim (called Paracelsus), Swiss alchemist and physician, Montesquieu, and others. Some of them even visited Špania Dolina (Koděra et al. 1990).

Cementation is an electrochemical process („internal electrolysis") of displacement of metals from solution, based on the electrochemical reaction between a metal – cementator and ions of the precipitating metal (Annamalai et al., 1978; Karavasteva, 1996), or on the reaction of displacement of a nobler metal from solution by a metal less noble. Cementation is used in the purification of a solution containing a base metal (e.g. $CuSO_4$) from admixtures (Zn, Cd) or in the precipitation of a base metal from a solution, e.g. extraction of Cu^{2+} by cementation to Fe^{2+}, of gold to Zn^{3+}, etc. (Brown & Thirsk, 1965; Sulka & Jaskula, 2004; Karavasteva, 2005).

Recently, much attention has been paid to the study of the mechanism of precipitation of Cu^{2+} ions on iron, zinc and aluminium (Brown & Thirsk, 1965; Annamalai & Murr, 1978; 1979, Annamalai et al., 1978, Fisher, 1986; Karavasteva, 1996, 2005). In the process of cementation, there are two basic stages, namely a) supply of ions to the cathode surface and removal of ions from the anode surface by diffusion, b) electrochemical reaction, i.e. discharge of ions on the cathode faces and ionization on the anode faces.

Materials and methods

The Fe^0-barrier consists of iron granulas mixed with pieces of dolomite to enable Fe precipitation. Its testing of Fe^0-barrier was realised under laboratory conditions using Fe chips and granules (Aldrich) in mixture with dolomite (to avoid colmatage) in rate 9:1.

Water sample H-1 was taken from the little brook in the reference area. The H-2 sample for laboratory testing of the Fe^0-barrier were obtained from little lake in depresion beneath the dump oft he Empfängnis gallery. The drainage water in the lake is contamined by dump sediments.

Water for Fe^0-barrier testing was sampled in two dry periods: on 9th and 25th September 2013 and two times in rainy period: on 8th and 26th November 2013. The first sampling place was at the bottom of the dumps (sample D). The second sampling place was direct above the Fe^0-barrier (sample A), the third under the Fe^0-barrier (sam-

Tab. 1. Atom absorption spectrometric analysis of surface water from reference area and of drainage water from the pool under the Empfängnis gallery

Tab. 1. Analiza ASA wody powierzchniowej z powierzchni referencyjnej i odcieku z rejonu Empfängnis

Sample	$\mu g.L^{-1}$								
	Zn	Cd	Co	Cu	Fe	Ni	Pb	Sb	As
H-1a	<10	0.04	3.2	20	260	4.1	4.2	1.74	2,60
H-1b	<10	0.05	4.1	13	173	1.9	4.3	1.75	2.17
H-1c	10	0.06	3.9	21	235	5.2	5.3	1.80	2.98
H-2a	30	0.04	7.0	1 810	160	8.2	8.2	2.12	2.70
H-2b	40	0.03	7.0	2 060	301	9.9	10.8	1.90	3.40
H-2c	40	0.04	9.0	2 059	311	7.7	9.8	2.15	3.38

Explanations:
H1 – brook water from the reference area (Zelená Valley)
H2 – drainage water from the pool under the Empfängnis gallery
Samples with index „a“ were sampled after rain on June 2006
Samples with index „b“ were sampled during dry season on February 2007
Samples with index „c“ were sampled during dry season on May 2007

Tab. 2. Microprobe analyses of steel and cementation copper

Tab. 2. Analiza mikropróbek stali i miedzi

Sample	Ag	S	Cu	Sb	As	Au	Fe	Total
	% (wt.)							
ST-1*	-	0.02	0.19	0.00	0.00	-	98.95	99.16
CEM-1	0.00	0.07	75.78	0.00	0.45	0.00	7.39	83.69
CEM-1	0.00	0.07	75.78	0.00	0.45	0.00	7.39	83.69
CEM-2	0.00	0.12	64.06	0.05	0.22	0.06	7.60	72.11
CEM-3	0.01	0.04	91.68	0.00	0.15	0.05	4.88	96.81
CEM-4	0.00	0.05	90.74	0.00	0.41	0.03	4.50	95.73
CEM-5	-	0.02	96.07	0.05	0.11	-	4.40	100.65
CEM-6	-	0.07	81.03	0.07	0.00	-	5.11	86.28
CEM-7	-	0.06	80.99	0.02	0.00	-	4.01	85.08
CEM-8	0.00	0.07	75.78	0.00	0.45	0.00	7.39	83.69
CEM-9	0.00	0.12	64.06	0.05	0.22	0.06	7.60	72.11
CEM-10	0.01	0.04	91.68	0.00	0.15	0.05	4.88	96.81
CEM-11	0.00	0.05	90.74	0.00	0.41	0.03	4.50	95.73

Explanations: ST – steel, CEM – cementation copper;
* 0,16 wt.% Co, 0,03 % wt.% Bi, 0,03 wt.% Zn and 0,01 wt.% Ni.

ple B) and the fourth within the reference area (sample R).

The samples were stabilized with 10 $ml.L^{-1}$ HCl and analysed in the Water Research Institute in Bratislava using atomic absorption spectrometry in air/acetylene flame on a double-beam atomic absorption spectrophotometer from the company PerkinElmer from HCl medium.

The values of pH and Eh were determined in the groundwater and surface waters of the dump fields wider surroundings and in draining waters percolating through dump sediments „in situ“ directly in the process of sampling.

Hg and As contents were determined using hydride generation atomic absorption analyse. Flame atomic absorption spectroscopy was used for quantitative determination of Cu, Fe, Cd, Co, Mn, Ni, Pb, Sb and Zn in laboratory of Water Research Institute in Bratislava (Ing. Adriana Shearman, PhD.). Resulting values of determination of individual metals represent mean values from two checking parallel determinations.

Results and discussion

The depression under the Empfängnis dump is fed by several outflows of drainage water percolating through the dump material. For the most part it is a case of surface water of a mountain stream draining the area along the Green Valley. In

Tab. 3. pH, Eh and AES-ICP and HG-AAS water analyses of water samples D, A, B and R from Podlipa dump-field

Tab. 3. pH, Eh analizy AES - ICP próbek wody D,A,B i R z rejonu stawu Podlipa

Sample	pH	Eh		Cu	Fe	Zn	As	Sb	P	S
				mg,L^{-1}						
Dry period										
September 3rd										
1D	6,87	-37		2,360	0,064	0,015	0,003	0,002	<0,050	12,540
1A	6,38	-10		3,551	0,360	0,020	0,010	0,002	<0,050	12,500
1B	6,03	12		3,240	0,028	0,021	0,004	0,001	<0,050	12,000
1R	6,16	5		0,115	0,175	0,007	0,002	<0,001	0,050	7,170
September 25th										
2D	6,66	-24		1,960	0,053	0,011	0,002	0,001	<0,050	12,000
2A	6,22	1		3,570	0,163	0,020	0,005	<0,001	0,050	12,800
2B	5,95	16		3,330	0,200	0,019	0,003	<0,001	<0,050	12,300
2R	6,49	-20		0,161	0,468	0,006	0,001	<0,001	0,060	7,970
Rainy period										
October 19th										
3D	6,25	-3		1,889	0,028	0,012	0,002	0,002	<0,050	11,870
3A	5,84	23		3,612	0,296	0,041	0,003	0,006	<0,050	12,140
3B	5,88	20		3,415	0,200	0,012	0,004	0,003	<0,050	11,780
3R	6,32	-6		0,142	0,545	<0,005	0,003	0,004	<0,050	7,420
November 26th										
4D	6,89	8		1,506	0,098	0,022	0,002	0,010	<0,050	11,840
4A	5,85	23		2,776	0,118	0,017	0,003	0,005	<0,050	10,240
4B	5,87	21		2,733	0,130	0,014	0,003	0,005	<0,050	10,080
4R	6,91	-43		0,340	1,840	0,009	0,007	0,003	0,010	6,930

Explanations:

D – water samples from the bottom oft he dump-field
A – water samples from creek above the Fe^0-barrier
B – water samples from creek under the Fe^0-barrier
R – water samples from creek sampled within the reference area
Cd contents are <0.002 $mg.L^{-1}$ and Pb contents <0,010 $mg.L^{-}$

the area under the Podlipa dump field, it plunges several times below the dump sediments. There is variation in the mobility of heavy metals carried upwards into surface recipients by groundwater, mine water and leachate; considerable water contamination is indicated by the abundant occurrence of secondary minerals, considerable part of which are metastable, both in the subsurface parts of ore bodies and in dumps of waste products of extraction of copper ores. In the points of outflow of drainage water from the dumps on the surface, secondary minerals of copper (pseudomalachite?) deposit preferentially on dead plant residues. Moreover, on the bottom of the pool in the depression under the dump of Empfängnis gallery, a continuous green coat of Cu carbonates can be seen. The bottom sediment contains up to 2.15 wt. % of Fe, 15 402 ppm of Cu, 134 ppm of Pb and 220 ppm of As. Analyses of water taken from the stream in the reference area and that from the pool are stated in tab. 1. They show a significant contamination of water as a consequence of percolation through the dump sediments – above all contamination with Cu, Ni, Pb and Sb, and an increase in the contents of majority of the heavy metals in the dry season.

The iron (steel), immersed in the cementation water of the pool under the dump of Empfängnis gallery, were, after one-month maceration, significantly oxidized and the surface of them was locally covered with a layer of green coats of Cu oxides and cementation copper. Also the study of polished specimens from the nail cross sections using the electron microanalyser has confirmed that on the surface of iron, gradual copper precipitation takes place.

The X-ray point microanalyses of iron (steel) and cementation copper are given in tab. 2. They show a relatively high purity of copper (up to 96.07 wt % of Cu). Rather significant admixtures are merely Fe (as a maximum, 7.60 wt %) and As (0.45 wt. %). Relatively small number of analyses were affected by the porous (sponge-like) surface of precipitates and the small size of grains of cementation copper being analysed.

The testing of Fe^0-barrier was realised under laboratory conditions using iron (steel) chips and granules in mixture with dolomite. The water containing heavy metals percolated hrough the agents 5 hours. Content of all studied metals decreased most intensively during the first two hours of the experiment when the pH ranged from 6.3 to 8.11. During the next hours was described already only sorption of Cd and Zn. The most effective was the As sorption (99,97%). Also the Cu sorption (98,98%) and Zn sorption (98,13%) was satisfactory. The effectivity of Cd sorption (99,64%) is with respect to the relatively low primary Cd content in the drainage water also acceptable. The experiment proved the possibility to remove from the water (using dolomite as calcination agent) together with Cu, As, Cd and Zn also Fe (which is during the cementation released to solution).

Fe^0-barrier efficiency is with respect to the Cu after 3 years of use weak (tab. 3). Under both conditions: in dry as well as in rainy period is the Cu from water not substantially removed. In spite of the above mentioned situation the efficiency of the barrier is nevertheless in the dry period a little bit better (from 3.551 $mg.L^{-1}$ to 3.240 $mg.L^{-1}$ and from 3.570 to 3.330 $mg.L^{-1}$). This finding is in conflict with change of the water in retention reservoir from green (in the time before the Fe^0-barrier installation) to brownish. It is possible explain only by exhaust of the reagents in the barrier (iron and dolomite) after three years of activity.

Fe^0-barrier seems to be relatively efficient for Fe and As removal and vice versa removal of Zn and S is limited. Cd, Pb and P contents are very low so the results are not unambiguous. The relation between pH/Eh ratio and of the efficiency of Fe^0-barrier could not be with respect to the low values proved.

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Testy sprawdzające przepuszczalną barierę Fe^0 w miejscu zrzutu wód z kopalni Podlipa (złoże Cu w Ľubietová, Słowacja)

Materiał pochodzący z miejsca zrzutu wód kopalni Podlipa w opuszczonym złożu Cu w Lubietovie wykazuje dużą zawartość Cu, Fe, Cd, Co, Mn, Ni oraz Pb. W większości przypadków wyższe zawartości metalu odnotowywano w suchym okresie zimy, niż w okresach deszczowych. Bardzo rzadko było odwrotnie. Wgłębienie pod wysypem Empfängnis jest podmywane kilkoma odpływami wody drenażowej, która przesącza się przez materiał zrzutu. W większości są to wody powierzchniowe z górskiego strumienia drenującego obszar wzdłuż doliny. Strumień kilkukrotnie przepływa przez osady kopalniane pod miejscem zrzutu wody kopalni Podlipa. W miejscach odpływu wody drenażowej na powierzchni obszaru zrzutu, na pozostałościach martwych roślin, osadzają się wtórne minerały miedzi (pseudomalachitu). Ponadto, na dnie wgłębienia pod miejscem zrzutu wody Empfängnis można zauważyć nieprzerwaną zieloną warstwę węglanów Cu. Osad denny zwiera do 2,15% żelaza, 15 402 ppm ołowiu oraz 220 ppm arsenu. Wyniki wskazują na poważne zanieczyszczenie wody spowodowane przenikaniem przez osady wody – przede wszystkim miedzią, niklem, ołowiem i antymonem – oraz na podwyższenie zawartości większości metali ciężkich w sezonie suchym. Choć bariera Fe^0 jest relatywnie skuteczna w usuwaniu Fe oraz As, to w przypadku Zn oraz S jest ograniczona. Zawartości Cd, Pb oraz P są bardzo niskie, zatem wyniki nie są jednoznaczne. Związek między proporcją pH/Eh, a skutecznością bariery Fe^0 nie może być udowodniony ze względu na zbyt niskie wartości.

Słowa kluczowe: osadniki, metale ciężkie, ścieki, bariera FeO, rekultywacja